Waste and Biomass Valorization (2019) 10:2863–2878
https://doi.org/10.1007/s12649-018-0291-0

ORIGINAL PAPER

Availability and Suitability of Agroindustrial Residues as Feedstock for Cellulose-Based Materials: Brazil Case Study

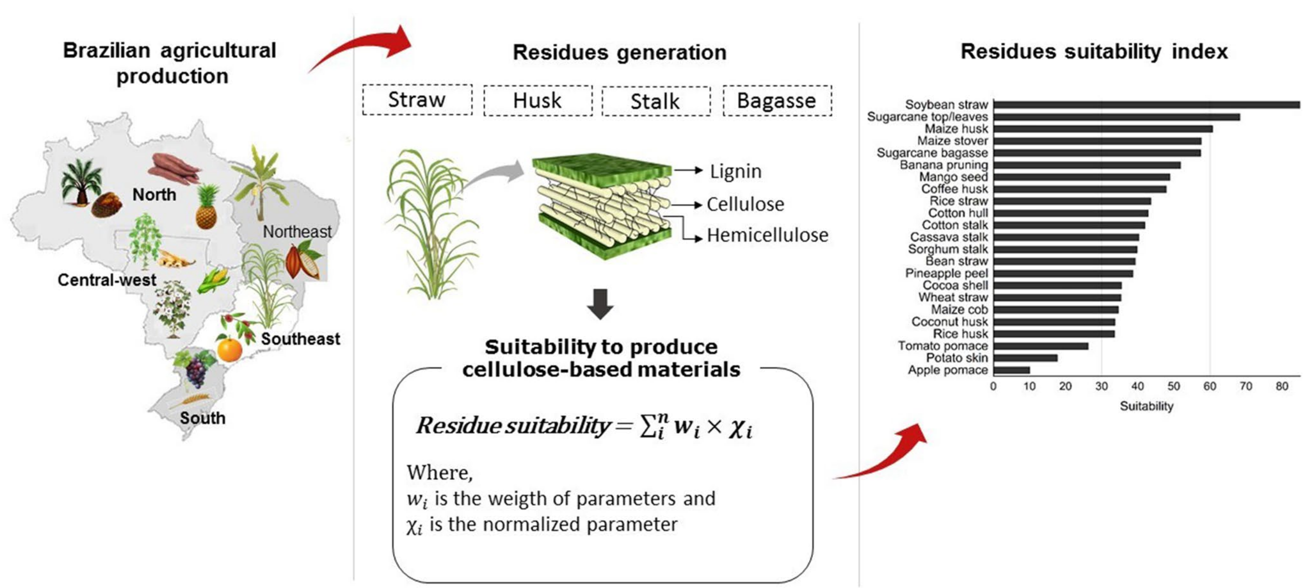
David Jefferson Cardoso Araújo[1] · Ana Vera Machado[2] · Maria Cândida Lobo Guerra Vilarinho[3]

Received: 15 October 2017 / Accepted: 2 April 2018 / Published online: 16 April 2018
© Springer Science+Business Media B.V., part of Springer Nature 2018

Abstract

Bio-based polymers have emerged as a feasible alternative to petrochemical polymers mainly due to their biodegradability and renewable feedstock. Brazil is considered one of the largest producers of agricultural commodities. Hence, the country is also distinguished by the large generation of this residue type, which can be potentially used as a source to obtain biopolymers, such as cellulose. Based on the Brazil agriculture market, the study aims to analyze the suitability of agroindustrial residues as raw material for cellulose-based materials. A methodology for the selection of the most suitable residues is proposed, which takes into account the chemical composition of residues, namely the cellulose content and the cellulose-to-lignin ratio, as well as, their availability. In order to meet conservation issues, the availability of residues is calculated as a function of sustainable removal rates and competitive uses. Taking as reference the main crops identified, the average amount of agroindustrial residues available in Brazil was estimated at 108 million tons/year. Among the most suitable residues to be used as cellulose feedstock are soybean straw, sugarcane top/leaves, maize husk and stover and sugarcane bagasse.

Graphical Abstract



Keywords Cellulose · Lignocellulosic biomass · Bio-based materials · Availability of residues

✉ David Jefferson Cardoso Araújo
david_bct@hotmail.com

Extended author information available on the last page of the article

Introduction

In the last decades, the industrial segment of polymeric products has shaped the humankind life. Increasing demand for versatile products for several applications has been a major factor responsible for the growth of this segment. Nowadays, polymers are found throughout many sectors and industries including packaging, build and construction, automotive, electric and electronics, agriculture and consumer goods [1].

Currently, its improper disposal, persistence and fossil-based raw material represent factors with negative environmental and economic effects, namely greenhouse gas emission and land and marine pollution [2, 3]. In terms of disposal for example, only in Brazil, plastic represents around 13.5% of the total solid waste collectible [4]. Nonetheless, in 2015, from 72.5 million tons of solid waste collected, almost 30 million tons were sent to unsuitable destinations such as dumps [4]. Depending on the kind of plastic, it will take a very long time to degrade when released into the environment, enhancing its accumulation [5]. Even in the controlled environment of landfills plastics hardly degrade [6]. In the marine environment, common plastics used in packaging degrade at a very slow rate [2, 7]. According to Eriksen et al. [8], a minimum of 5.25 trillion plastic particles weighing 268,940 tons is estimated to be floating in the world's oceans.

In this sense, the search for renewable raw materials suitable for the production of biodegradable polymeric products is imperative, especially considering the depletion of fossil resources, fluctuation in oil price and the negative environmental impacts. Indeed, bioplastics have been mentioned as a lead market by the European Commission, with global production capacity set to grow 350% by 2019 [1]. In recent years, the group of bioplastics derived from renewable and biodegradable resources has received greater interest. They can be manufactured by different techniques using biopolymers as feedstock, such as cellulose, lignin and starch.

Among the available sources of renewable feedstock, lignocellulosic biomass stands out in the global scenario. Currently, this category of biomass assumes relevant importance for the generation of renewable energy, fuels and several other products (composites, dispersants, flocculants, textile fibers and activated carbon), mainly due to its chemical constitution. Lignocellulosic biomass consists mainly of three natural organic polymers—cellulose, hemicellulose and lignin—and small amounts of proteins, pectin and extractives [9, 10]. Among the aforementioned components, cellulose is the most abundant organic polymer on earth, and owing to its mechanical and thermal properties, renewability, widely availability, non-toxic, low cost, biodegradability and derivatizability, cellulose is considered a promising feedstock for the development of sustainable materials [11–14].

Cellulose is a high molecular weight homopolymer assembled from the repetition of cellobiose units (β 1–4 glucosidic covalent bonds between D-glucopyranose subunits) [15, 16]. Each cellobiose unit has hydroxyl groups that promote strong interactions by intra and intermolecular hydrogen bonds. This spatial structure allows the molecules to crystallize in a horizontal plane and in parallel chains, forming microfiber packages [17]. In the plant cell walls, the cellulose is embedded in a matrix of hemicellulose and lignin, bound together by covalent cross-links, which results in the recalcitrant property of the lignocellulosic biomass. Hence, the performance of physical or chemical pretreatments aiming the fractionation of lignocellulosic biomass is essential to convert cellulose into polymeric materials [10, 18]. After extraction, cellulose can be processed in the form of nanocellulose, derivatized cellulose, composites fillers or matrix and regenerated materials, such as films and gels [13, 19].

In general, lignocellulosic biomass may result from agricultural waste, forest waste, energy crops and municipal and industrial wastes [10, 20]. The set of activities associated with the vegetable agribusiness sector stands out as one of the main residues generators. Framed worldwide as one of the leading agricultural producers, Brazil also excels due to the large waste generation originated from this type of activity. It is estimated that the production of agricultural residues in Brazil exceeds 200 million tons per year [21, 22]. Despite some of these residues are currently applied to a range of valorization processing, a large portion is still directed to sanitarium landfills and incineration plants, or burned in the harvest field.

The first step in the sense of analyze the valorization feasibility of agroindustrial residues, regarding its application to produce cellulose-based products, consists in the identification of residues types that besides to have high content of cellulose, are also generated and available in significant quantities. In general, the availability of agroindustrial residues is estimated based on the annual production of crops and its respective residue-generation-rate. In Brazil, studies aiming this type of estimation have already been performed by [22–25]. However, besides the time lag and lack of properly environmental constraints and competitive uses assumptions, these studies are focused on the assessment of residues as an energy resource and, in many cases, potentials and limitations are exclusively based on the residues availability.

The present study aims to estimate the amount of agroindustrial residues available in Brazil and to identify the most suitable residues that can be used as raw material in the production of cellulose-based materials. The required estimates were carried out based on the agroindustrial market of Brazil and the availability of residues was calculated as a function of the average crop production and conservative assumptions, such as sustainable removal rates and competitive uses. Furthermore, the availability and chemical composition of residues were taken into account in order to assess their suitability to produce for the development of cellulose-based materials.

Methodology

Crop Residues Production and Chemical Composition

Spatiotemporal characterization of agricultural crops production was performed with statistical data of Brazilian Institute of Geography and Statistics (IBGE) [26], extending from 2004 to 2014. In order to complement this previous assessment and support the selection of main crops, information about residues types and their respective cellulose, hemicellulose and lignin contents were obtained from associated literature.

The crop residues production can be calculated in terms of the average annual production of crops (AAP) and the residue generation rate (RGR). The AAP of crops intended to processing industries was set as the portion of production allocated for this purpose. For all other residues, the AAP values resulted directly from IBGE database. RGR values were obtained directly as default values from natural resource module (NRM), as well as from other published documents. The NRM consist of a data processing and handling digital module, applied to assess the availability of bioenergy feedstock originating from crop production, agricultural residues and forestry [27].

Residue Generation Rate

The RGR can be understood as the ratio, on a dry basis, of the weight of residue produced to the total weight of the main crop product (e.g. the ratio of straw to wheat grain). RGR values may vary temporally and spatially according to several aspects, depending on the cultivation techniques, soil fertility and weather conditions [22]. Considering that RGR data used come from other studies targeted to different geographic areas, including those belonging to NRM database, it is expected that these values encompass a technical, environmental and cultural variability, so that their application meet only a rough estimate. The diversity and variability of residues generation rates can be seen in Table 1.

Table 1 Residues generation rates of agroindustrial residues

Crop	Residue	Residues generation rate				
Cotton	Hull	0.26 [27]	2.95 [22]			
	Stalk	3.4 [27]		3.0 [28]		
Rice	Husk	0.25 [27]	1.49 [22]		1.0 [29]	0.26 [30]
	Straw	1.33 [27]		1.0 [28]		1.55 [30]
Banana	Tree pruning	0.8 [31]				
Potato	Skin	0.04 [32, 33]				
Cocoa	Pod	1.5 [27]				
Coffee	Husk	1.32 [27]				
Sugarcane	Top/leaves	0.20 [27]	0.22 [22]	0.1 [28]		
	Bagasse	0.26 [27]				
Coconut	Husk	0.49 [27]				
	Shell	0.39 [27]				
Beam	Straw	1.7 [28]				
Apple	Pomace	0.30 [34]				
Cassava	Stalk	0.13 [27]	0.20 [22]			
Maize	Cob	0.30 [27]	1.42 [22]		0.7 [29]	1.96 [30]
	Husk	0.22 [27]				
	Stover	1.96 [27]		2.0 [28]		
Soybeam	Straw	1.53 [27]	2.05 [22]	2.12 [30]		
	Pod	1.09 [27]				
Tomato	Pomace	0.01 [35, 36]				
Wheat	Straw	1.28 [27]	1.42 [22]	1.1 [28]	1.0 [29]	1.5 [30]
Mango	Seed	0.07 [37, 38]				
Pineapple	Peel	0.12 [37, 39]				

Availability of Agricultural Residues

After identifying the main crops produced in Brazil, the availability of crop residues (AR_{CR}) (Eq. 1) was calculated as a function of the AAP, RGR, sustainable removal rate (SSR) and other competitive uses, while the availability of industry-driven crops residues (AR_{IDC}) (Eq. 2) took into consideration the AAP, the portion of production allocated to industrial processing (IP), RGR and other competitive uses (CU).

$$AR_{CR} = (AAP)(RGR)(SRR)(1 - CU) \tag{1}$$

$$AR_{IDC} = (AAP)(IP)(RGR)(1 - CU) \tag{2}$$

Sustainable Removal Rate

SRR of crop residues are required to meet environmental and economic sustainability associated with the agricultural activity. The main objectives of sustainable crop residues removal consist in maintaining the natural soil fertility via incorporation of nutrients, promoting stability of upper soil layers and increase the organic matter content [40]. The percentage of crop residues that must be kept in the field depends on factors, such as the soil structure and type, planting techniques (e.g. fertilizers usage, crop rotation and till or no-till farming) and conservation practices.

In the literature is commonly suggested that a residue removal up to 30% does not imply damage to the soil [41–44]. However, estimates for sustainable residue removal may vary greatly from crop to crop, and it depends on another series of factors, such as geographical, climatic and technical/technological. For example, according to SoCo project team [45], regardless the cultivation method, it is indicated a maximum removal rate of straw around 70%. Karkee et al. [46] found that depending on soil characteristics, topography and farming practices (tillage, conventional and no-till), the percentage of available biomass to be removed may vary from 0 to 98%, without negative effects on the soil. In this study we adopted the sustainable removal rates of 40% for wheat straw, maize residues, rice straw and husk, bean straw and cotton stalk [24], and 30% for sugarcane top/leaves [41], cassava stalk and soybean straw and pods [24].

Competitive Use of Residues

Besides SRR, agroindustrial residues may be used in a range of applications, including energetic valorization, animal feed and bedding, application in the construction sector, as well as starting materials for activated carbon production [45, 47–49]. These applications represent competitive use with direct influence over the availability of residues and must be taken into account. It is worth mentioning that Brazil, besides being one of the main producers/generators of lignocellulosic fibers, also stands out for the development of projects and research related to the valorization of this sort of material/residue [50]. Considerable attention has been given to the application of some lignocellulosic residues as reinforcing agents/fillers in composite materials [50–54]. While recognizing such applications, the use of some residues is still restricted to research activities, and therefore they were not handled as a competitive use since they still do not have commercial or large-scale application.

Generally, very little information is available on industrial processing residues used for recycling/reuse purposes. Notwithstanding, in order to proceed with conservative estimates, for those crops with no information on the percentage of residues destined for other valorization routes it is assumed that only 50% is available. For residues that no other valorization route was identified, such as cassava stalk, rice straw, cotton stalk, soybean straw and sugarcane top/leaves, is estimated that 75% of the total generated is available (Table 2). It was also assumed that 35% of coconut [55], 10% of mango [56, 57], 40% of tomato [58], 10% of potato [59] and 15% of apple national production [60] are allocated to industries processing. Besides, it is verified that practically all the production of cocoa and coffee goes to processing industries [61, 62].

Suitability of Agroindustrial Residues to Develop Cellulose-Based Products

The assessment of residues suitability has been carried out based on methodology reported by Araújo et al. [80], where the suitability scale of residues is measured (Eq. 3) taking into account the normalized values of three main parameters (χ_i'): Availability of residues (AR), cellulose content (CC) and cellulose to lignin ratio ($R_{C/L}$). The presence of lignin in lignocellulosic biomass can be considered as one of the major obstacle in biomass pretreatment processes [81, 82]. Therefore, the influence of lignin over the selection of residues was accounted by including the cellulose-to-lignin ratio. The greater the ratio, the greater is the cellulose percentage compared to the lignin content, and thus more efficient is the biomass treatment.

$$S_{ij}' = \sum_{i}^{n} w_i \times \chi_{ij}'; \quad \text{Lignin content} > 0 \tag{3}$$

where,

$$\chi_{ij}' = a + \left[\frac{(\chi_j - \chi_{\min})(b - a)}{(\chi_{\max} - \chi_{\min})} \right]; \tag{4}$$

The constants a and b in Eq. 4 correspond to arbitrary points, equivalent to 0.1 and 1, respectively, used to restrict the range of suitability values. Besides, w_i correspond to

Table 2 Competitive uses of agroresidues

Residue	Availability (%)	Competitive uses	Reference
Sugarcane bagasse	10	Fired in stem boilers in the own mill to produce electricity	[63, 64]
Sugarcane top/leaves	75	Not identified	–
Maize husk, cob and stover	40	Animal feed	[63]
Rice husk	25	Drying, power generation at rice mills and chicken bedding production	[63]
Rice straw	75	Usually burned in the harvest field	[64]
Bean straw	50	Used to produce activated carbon and as a substrate for the production of other crops	[65, 66]
Cassava stalk	75	Used as animal feed, but its toxic principle limits this kind of application	[23, 64]
Orange residues	0	Aromatizing and animal feed	[67]
Grape residues	0	Used in food, pharmaceutical and cosmetics industries	[21, 68]
Coconut residues	90	Biomass, composites, agricultural fertilizer, activated carbon and filler for automotive banks	[69–71]
Mango stone and husk	50	Animal feed	[72, 73]
Tomato pomace	50	Fractionation of components, carotenoids extraction and biofuels	[74–76]
Potato skin	50	Cattle feed	[77]
Appla pomace	50	Organic fertilizer and animal feed	[78]
Cocoa shell	50	Energetic valorization	[79]
Coffee husk	50	Animal bedding	[63]
Cotton stalk	75	Not identified	–
Soybean straw	75	Not identified	–

weights of parameters AR, CC and $R_{C/L}$, which are equivalent to 35, 45 and 20, respectively, and the subscript index *j* represents the residue under evaluation. In the same equations, the parameters designated by maximum and minimum subscripts are related to residues that present the highest and lowest values, respectively, of the parameter concerned. Thus, for each residue, the suitability index (S_{ij}') may vary from 10 (lowest suitability) to 100 (highest suitability), expressed as dimensionless (Eq. 3).

Results and Discussion

Agricultural Production and Harvested Area

The crop production can be divided into two categories: (i) permanent and (ii) temporary. The permanent category includes the long-term crops that do not require replanting after harvesting, while the temporary one generally require replanting after harvesting. Within the period from 2004 to 2014, among all permanent crops, excel the high production of orange, banana, coffee and coconut (Fig. 1). In fact, Brazil is among the world's leading producers of these crops. Only the Southeast region is responsible for more than 80% of national orange production and 55% of the total permanent crops production. Northeast region accounts the largest production of coconut and banana and 23% of permanent crops production (Fig. 2a, b).

Southeast and Northeast regions accounted about 5,224,000 ha (43.43 and 39.68%, respectively), on average, of the total area used for the cultivation of permanent crops in Brazil. Around 80% of coffee plantation and 74% of orange plantation are located in the Southeast region. In the Northeast predominates plantation areas for banana, cocoa, cashew nut, coconut and sisal. In other regions, crops with lower percentage of area for cultivation prevails.

Regarding the temporary crops, over the last 11 years of data, it was possible to verify that the production has almost doubled, reaching 972.2 megatons in 2014. Among all the temporary crops, sugarcane production is by far the most relevant. In 2014 were produced 737.2 Mt of sugarcane, 86.7 Mt of soybean, and 79.8 Mt of maize (Fig. 2). These figures place Brazil among the world's largest producers of these crops. The other crops, which account for a total of 28 different types, contributed with 68.5 Mt (about 7% of the total production) (Fig. 2). About 52% of the national temporary crops production takes place in the Southeast region. The Centre-West region presents the second higher percentage contribution, mainly due to its leadership as maize and soybean producer.

It could also be noticed that 43% of the total harvesting area was used for soybean crop, 22.5% was used for maize plantation and 14.8% for sugarcane growing. It is worth highlighting that, in 2014, two Brazilians regions accounted for about 45% of all harvested areas, namely Centre-west

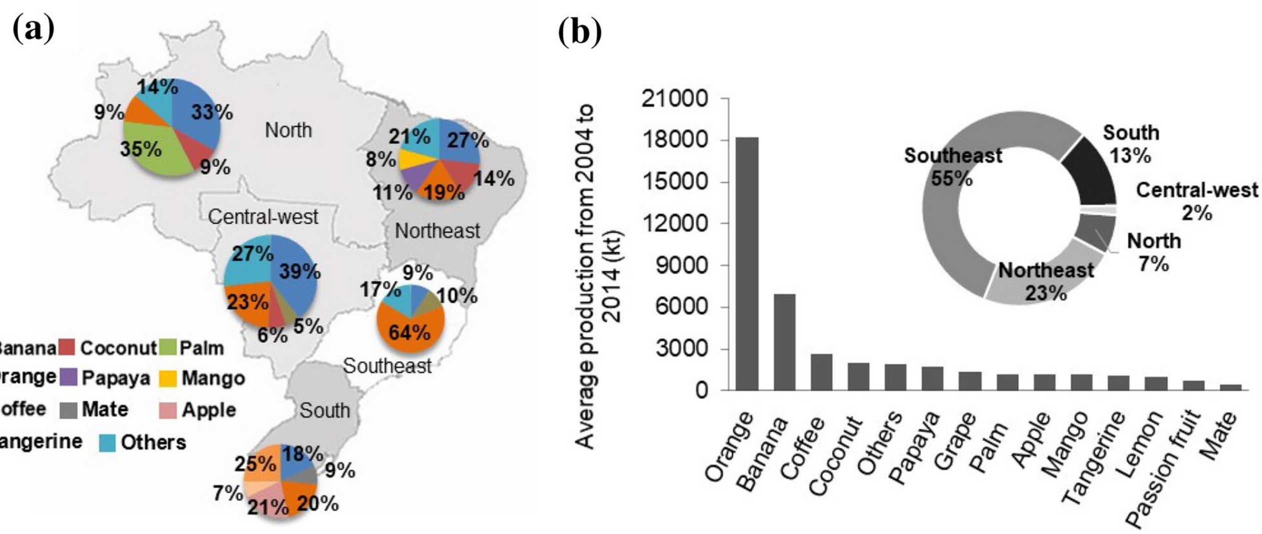


Fig. 1 Average production of permanent crops in Brazil. **a** Average percentage of the main crops produced by each macroregion. **b** Average production of permanent crops from 2004 to 2014 and average percentage of permanent crop production by macroregions

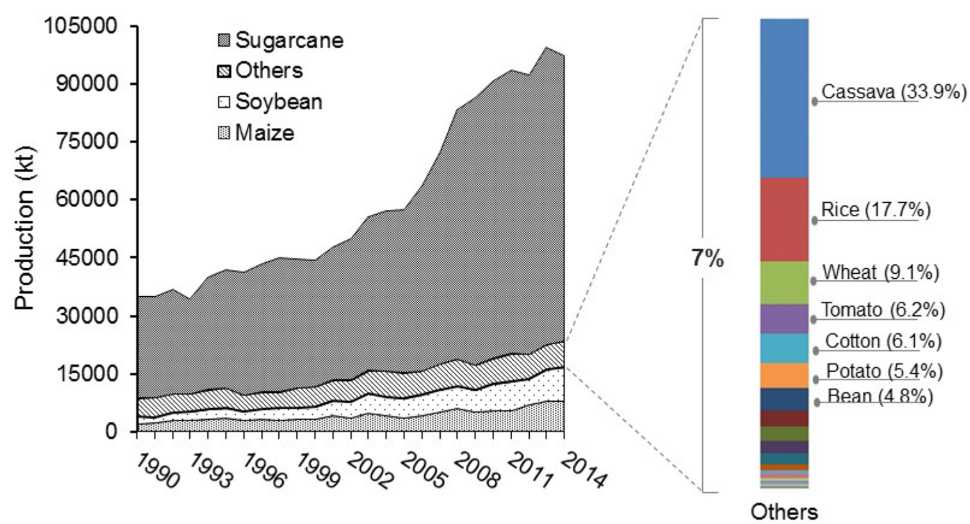


Fig. 2 Annual evolution of temporary agricultural crops production from 1990 to 2014

(with 24.3 million hectares) and South (with 21 million hectares).

Chemical Composition of Agroindustrial Residues

Depending on the morphological structure of crops and the processing levels to which they are subject, different types of residues with specific cellulose, hemicellulose and lignin contents can be obtained (Fig. 3; Tables 3, 4). Cereals and oilseed crops may be mentioned as crops capable of generating residues still in the harvesting phase. On the other hand, crops such as grape, orange, apple, potato, coconut, coffee, mango and cocoa, particularly interesting to obtain processed products, may result in the generation of residues at different stages of industrial processing. Figure 3 presents different agroindustrial residues provided by local farmers and processing industries. Tables 3 and 4 present cellulose, hemicellulose and lignin values for a range of lignocellulosic residues derived from temporary and permanent agricultural crops, respectively. These tables highlight several agroindustrial residues with high cellulose content and potentially interesting to be used as sustainable resources to produce cellulose-based materials.

Availability of Agroindustrial Residues

The availability of residues related to the main crops identified in previous assessment took into consideration: (i)

Table 3 Chemical composition of lignocellulosic biomass derived from temporary crops

Biomass		Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Pineapple	Peel	21.98	74.96	2.68	[83]
Cotton	Hull	44.35	11.2	16.15	[84]
	Stalk	40.4	–	20.9	[85]
Garlic	Skin	41.7 ± 2.1	20.8 ± 1.6	34.5 ± 2.4	[86]
Peanut	Shell	49.4 ± 1.4	8.1 ± 0.6	33.1 ± 1.5	[87]
Rice	Straw	39.5–41	24.4–31	15.9–24	[88, 89]
	Husk	35	33	23	[90]
Oat	Stalk	31–48	27–38	16–19	[91]
Potato	Skin	10.5	–	4.0	[92]
Sugarcane	Top/leaves	39.8	28.6	22.5	[93]
	Bagasse	43.10	22.82	24.09	[12]
Onion	Skin	41.1 ± 1.1	16.2 ± 0.6	38.9 ± 1.3	[94]
Rye (stalk)	Stalk	33–50	27–30	16–19	[91]
Barley	Straw	33–40	20–35	8–17	[10]
Pea	Hull	62.3	8.2	–	[95]
Bean	Straw	40.2	19.32	18.13	[96]
Sunflower	Straw	40.41	31.44	19.45	[96]
Jute	Stem	61–71.5	13.6–20.4	12–13	[97]
Flax	Stem	75.4 ± 0.2	13.4 ± 2.8	3.4 ± 0.9	[98]
Cassava	Stalk	38.8	7.2	11.8	[99]
Maize	Husk	62.07 ± 0.86	17.93 ± 0.86	14.6 ± 0.6	[100]
	Stover	40.8	34	22	[89]
	Cob	31.2–45	35–43.1	15–16.5	[10, 101]
Ramie	Fiber	69–91	5–17	< 1	[102, 103]
Soybean	Straw	44–83	24.3 ± 3.0	5.0–14	[104]
Sorghum	Stalk	41.7	23	18.2	[105]
Tomato	Plant	39.1	28.8	12.1	[106]
	Pomace	29.1	13.5	57.4	[107]
Wheat	Straw	30–40.8	38.32–50	15–22.45	[10, 96]
Triticale	Straw	32.20	–	15.02	[108]

Table 4 Chemical composition of lignocellulosic biomass derived from permanent crops

Biomass		Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Olive	Pomace	24.1–14.45	11.0–6.63	14.1–8.54	[109]
Banana	Raquis	48.7	16.1	12.2	[110]
	Pseudostem	48.19–59.22	12.09–15.91	14.39–21.56	[111]
	Peduncle	48.31–60.41	10.20–13.99	17.56–20.66	
Cocoa	Shell	35.4	14.0	37	[79]
Coffee	Husk	43.0 ± 8.0	7.0 ± 3.0	9.0 ± 1.6	[112]
Coconut	Husk	37.0	–	32.5	[113]
Orange	Pell	14.4–37.08	10.9–11.04	1.33–7.52	[114]
Lemon	Pell	23.06 ± 2.11	8.09 ± 0.81	7.56 ± 0.54	[114]
Apple	Pomace	7.2	–	23.5	[115]
Mango	Seed	55.0 ± 1.0	20.6 ± 0.3	23.85 ± 0.21	[116]
Nut	Shell	53.9	15.4	30.7	[107]
Oil palm	Empty fruit brunch	40–50	20–30	20–30	[117]
Pear	Pomace	32.9 ± 0.3	22.1 ± 0.2	17.0 ± 0.4	[118]
Sisal	Fiber	64.9–78	10–25.4	8–11.7	[119, 120]
Grape	Pomace	27.9	9.1	63.0	[107]

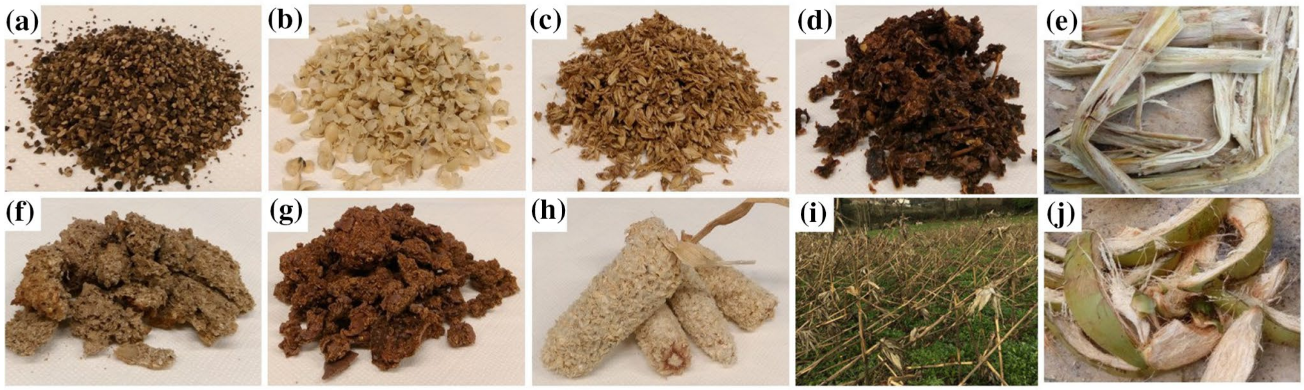


Fig. 3 Agroindustrial residues: **a** olive pomace, **b** soybean husk, **c** barley (brewing by-product), **d** apple pomace, **e** sugarcane bagasse, **f** potato skin, **g** pear pomace, **h** corncob, **i** maize stover, **j** coconut husk

average annual production of crops; (ii) residue generation rate; (iii) sustainable removal rates; and (iv) other competitive uses. Table 5 shows the values of variables encompassed in Eqs. 1 and 2, as well as the annual RP and the availability of residues. Exclusively for the industry-driven crops, the AAP is equivalent to the portion of production allocated for industrial processing. Residues classified in this approach are highlighted in Table 6.

Taking into account only the main residues identified, the total amount of agroindustrial residues produced in Brazil is estimated at over 589 million tons/year on average. However, in response to the conservation assumptions, the availability of residues is estimated at about 108 million tons/year (Table 6). The analysis of these results along with the data provided in Tables 2 and 3,

Table 5 Availability of residues, cellulose content and cellulose-to-lignin ratio normalized values

Residue	Normalized available residue (AR_i')	Normalized cellulose content (CC_i')	Normalized cellulose-to-lignin ratio ($R_{C/Li}'$)
Cocoa shell	0.105	0.551	0.353
Coconut husk	0.110	0.576	0.195
Coffee husk	0.156	0.672	0.610
Maize cob	0.196	0.484	0.302
Maize husk	0.164	0.977	0.550
Maize stover	0.668	0.637	0.277
Sugarcane bagasse	0.620	0.674	0.269
Cassava stalk	0.123	0.605	0.440
Rice husk	0.124	0.544	0.239
Rice straw	0.255	0.616	0.348
Bean straw	0.135	0.628	0.318
Cotton hull	0.116	0.694	0.378
Cotton stalk	0.224	0.631	0.285
Banana pruning	0.188	0.816	0.426
Mango seed	0.100	0.864	0.328
Apple pomace	0.101	0.100	0.100
Soybean straw	0.807	1.000	0.827
Sorghum stalk	0.112	0.652	0.326
Sugarcane top/leaves	1.000	0.621	0.267
Wheat straw	0.142	0.551	0.281
Pineapple peel	0.101	0.336	1.000
Tomato pomace	0.100	0.450	0.123
Potato skin	0.100	0.153	0.364

Table 6 Average availability of agricultural residues

Residues	AAP (kt/year)	RGR ($t_{resíduo}/t_{crop}$)	RP (kt/year)	SRR (%)	CU (%)	AR (kt/year)
Cocoa	227.83					
Shell		1.5	314.75	–	50	170.87
Coconut	694.86[a]					
Husk		0.49	340.48	–	10	306.43
Shell		0.39	270.99	–	10	243.90
Coffee	2643.6					
Husk		1.32	3489.60	–	50	1744.8
Banana	6923.9					
Pruning		0.8	5539.12	–	50	2769.6
Mango	115.50[a]					
Seed		0.07	8.09	–	50	4.05
Apple	173.5[a]					
Pomace		0.30	52.05	–	50	26.03
Maize	56,688.7					
Cob		0.33	18,707.3	40	60	2993.2
Husk		0.22	12,471.5	40	60	1995.4
Stover		1.96	111,109.9	40	60	17,777.6
Soybean	64,194.4					
Straw		1.53	98,217.4	30	25	22,098.9
Sorghum	1861.00					
Stalk		1.4	2,605.4	30	50	390.80
Sugarcane	625,452.7					
Top/leaves		0.20	125,090.5	30	25	28,145.4
Bagasse		0.26	162,617.7		90	16,261.8
Cassava	24,743.0					
Stalk		0.13	3,216.6	30	25	723.73
Wheat	5130.8					
Straw		1.28	6567.5	40	50	1313.5
Rice	12,181.0					
Husk		0.25	3045.2		75	761.3
Straw		1.33	16,200.7	40	25	4860.2
Bean	3194.5					
Straw		1.7	5430.7	40	50	1086.1
Cotton	3818.0					
Hull		0.26	992.7		50	496.3
Stalk		3.4	12.981.4	40	25	3894.4
Pineapple	648.9[a]					
Peel		0.12	77.9	–	50	38.9
Tomato	1265.4[a]					
Pomace		0.01	12.7	–	50	6.3
Potato	349.5[a]					
Skin		0.04	13.98	–	50	6.99

AAP average annual production of crops, *RGR* residue generation rate, *RP* annual residue production, *SRR* sustainable removal rate, *AR* availability of residues, *CU* competitive uses

[a]Production intended to industry processing

emphasize the potential of the accounted residues as a cellulosic feedstock for valorization options.

Figure 4 summarizes the information discussed so far about the availability of residues and the average percentage of cellulose. Evaluating only these two parameters, it can be observed the greater relevance of sugarcane top/leaves, soybean straw, maize stover, sugarcane bagasse and rice straw, which accounted for about 82% of the total generation of available residues. It is worth highlight the relevance of sugarcane crop, which contributes alone with 41% of the total available residues. The remaining residues, despite having reasonably high percentages of cellulose, are generated and available in smaller quantities.

By comparison, the estimates obtained in this study are similar to others identified in literature, especially when taken into consideration the total production of residues and not only the portion available [22–24]. For instance, Forster-Carneiro et al. [22] also highlight the sugarcane as the crop with the largest production of residues (estimated at 157 million tons), and stressed a possible increase in the generation of agroindustrial residues around 25.2% by 2020.

Assessing the annual variability of AR for the whole historical series (Fig. 5) it is possible to notice a marked increase of residues generation throughout the years. For instance, from 2005 to 2014 the availability of residues increased 40%. It is estimated that 134 million tons of residues were available in Brazil in 2014. These estimates are consistent with current developments in the global agricultural sector. Only in the last three decades the Brazilian agricultural production has more than doubled in volume. The sector has contributed significantly to the country's trade balance, mainly as a foreign currency collector due to export business. Driven by continuous productivity improvements, and the implementation of stimulus and investment policies in research and development as well, the outlook for 2024 is that the sector will continue to grow [121].

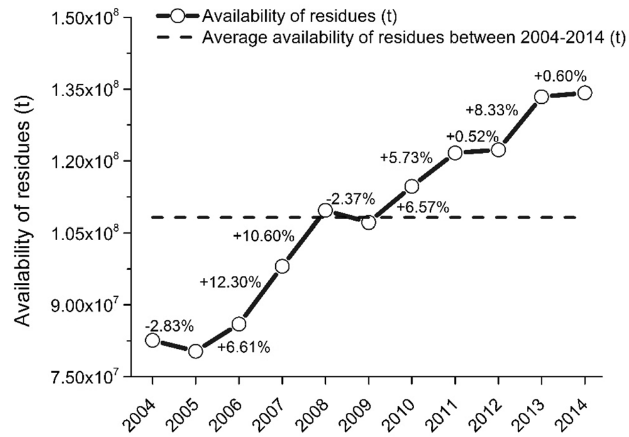


Fig. 5 Annual evolution of availability of residues in Brazil

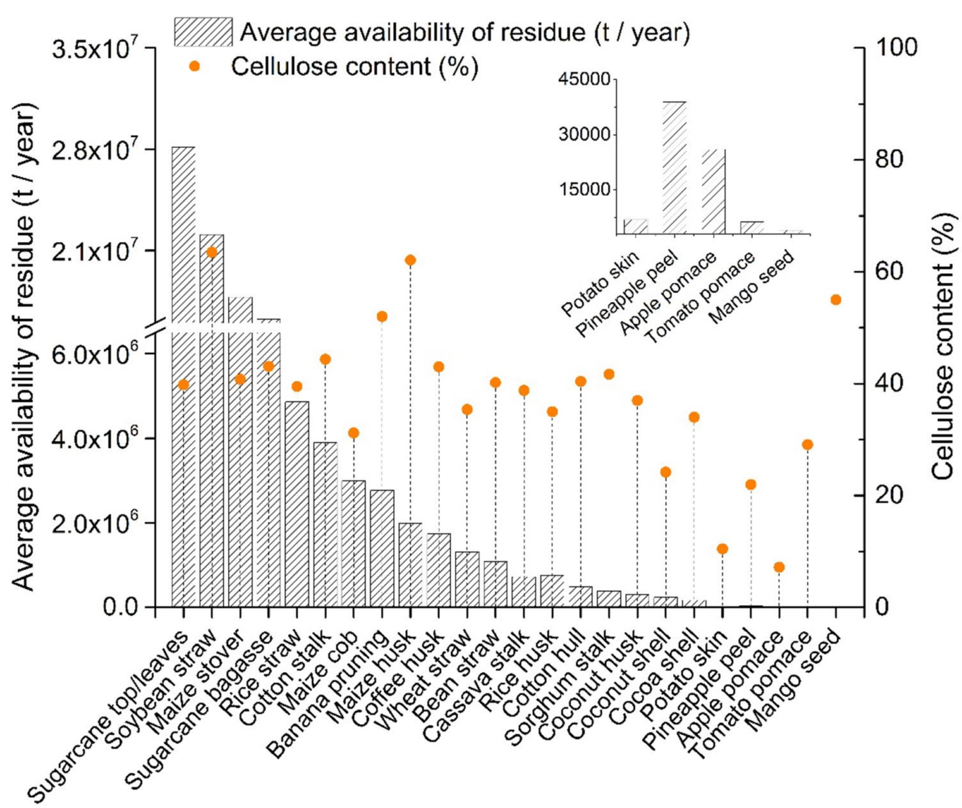


Fig. 4 Availability and cellulose content of the major agroindustrial residues identified

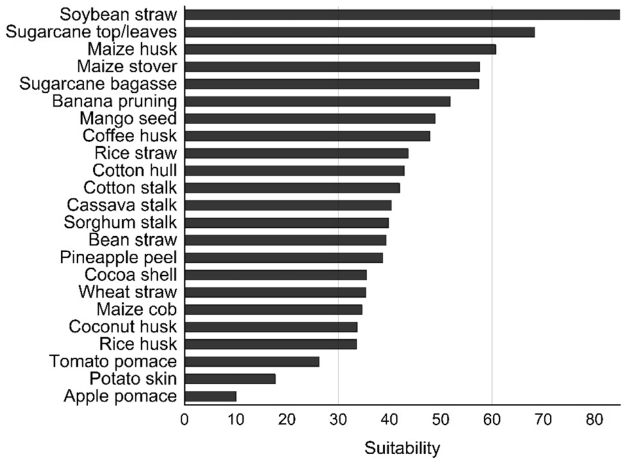


Fig. 6 Suitability of agroresidues for cellulose-based materials production

In Brazil, the massive generation of agroindustrial residues (Fig. 6), which still have marginal economical use [22], has kept pace with the high agricultural productivity. Taking as reference the average availability of residues from 2004 to 2014, positive and negative variations of availability ranging from −25.7 to +24.04% were found. Moreover, it is possible to predict an increase of agroindustrial residues generation, considering that, since 2005, the availability of residues has shown positive growth rate, with average annual fluctuation of about +5.43%.

Suitability of Agroindustrial Residues

The ranking of residues with greater potential to be used as raw material (Fig. 6) was obtained by applying AR_i', CC_i' e $R_{C/Li}'$ (previously calculated and shown in Table 5) as input parameters in Eq. 3. From the results obtained, it could be noticed that the parameters AR e $R_{C/L}$ play an important role in the final ranking of suitability. The low lignin content associated with pineapple peel resulted in a normalized cellulose-to-lignin ratio much higher than the others' (Tables 3, 5), which contributed significantly to the final value of suitability. The same is true for sugarcane top/leaves and soybean straw, in response to their great availability.

Among the main agroindustrial residues identified, those with greater potential to be used as raw material are soybean straw, sugarcane top/leaves, maize husk, maize stover and sugarcane bagasse. The lowest suitability values were assigned to apple pomace, potato skin and tomato pomace (Fig. 6). A close relationship between the suitability of residues and the productivity of crops was identified, since the most suitable residues are originated from the most productivity crops. Additionally, in the production and manufacturing cycle of agricultural products, the largest parcel of residues is generated during the harvest phase. However, some residues coming from processing industries excel as potential feedstock for cellulose-based materials manufacturing, namely sugarcane bagasse, mango seed, coffee husk and pineapple peel.

Residues with intermediate or low value of suitability may also be applied to the application concerned. However, in such situations, the feasibility of using these residues should be assessed, since the improvement and optimizing of treatments or pretreatments techniques must be carried out. For instance, besides to affect the efficiency of pretreatment steps, the presence of substantial amounts of non-cellulosic components may negatively influence their biodegradability, crystallinity, density, tensile strength, modulus and moisture of fibers and end products [11, 122, 123].

It is worth mentioning that the use of agricultural residues as a polymeric feedstock requires to encompass, besides availability and good chemical composition, a number of issues, including the temporal variability of generation, technological alternatives affordable, perception and social impact on different farmers' category and logistical issues. For instance, in Brazil, about 63% of sugarcane production takes place in the southeast region, hence, the largest share of sugarcane residues will be available in that region.

Several agroindustrial residues highlighted herein have already been reported as source for nanocellulose production, namely mango seed [116], soy hulls [124], cotton stalk [125], sugarcane bagasse [126], oil palm empty fruit bunch pulp [127], corncob [128] and wheat straw [129]. Ongoing studies in this field are focused mainly on the use of nanocrystalline cellulose (NCC) and microfibrillated cellulose (MFC) as fillers to nanocomposites, aiming the improvement of packaging and films properties [130–132].

Other newly applications and trends on cellulose-based materials are focused on the functionalization of natural lignocellulosic fibers, to produce polymeric composites [133–135] and biosorbents [136, 137], and NCC and MFC for assembling well-defined nanomaterials with unique properties [14, 125, 132, 138]. Additionally, is worth mentioning the development of regenerated cellulose, which is manufactured through the dissolution of cellulose, followed by its shaping and subsequent regeneration [13], as well as the conversion of lignocellulosic biomass into chemical building blocks through the biorefinery concept approach [139, 140].

Conclusion

In this study, a methodology to select agroindustrial residues suitable for cellulose-based materials production has been conducted based on the agricultural sector of Brazil. Besides the availability of residues, the chemical composition was also taken into account. The results indicated a large amount of residues available (108 million tons/year, on average) that could be recovered. Furthermore, since 2005 the availability of residues has shown positive growth rate, and it is likely that the generation of residues will continue to increase in the coming years along with the expected increase in agricultural productivity. Based on the methodology applied, the results indicate that the soybean straw is the most suitable residue to be used as feedstock to produce cellulose-based materials, followed by sugarcane top/leaves, maize husk and stover and sugarcane bagasse. This clearly reveals that the most suitable residues are derived from the main agricultural crops produced in the country. Moreover, over the next decades these residues tend to increase and be used as a potential resource.

As future works and improvements, should be mention that spatial and temporal variability related to residues generation should also be considered when planning valorizations routes. Besides acceptable physical performance, the viability of using the new developed products will be defined by environmental and economic aspects associated with their production, use and post use destination chains, which must be assessed by life and cost cycle analysis.

Acknowledgements This work was supported by the Brazilian National Council for Scientific and Technological Development (Grant Number 201940/2015-9).

Compliance with ethical standards

Conflict of interest The authors have declared no conflict of interest.

References

1. European Bioplastics: Biopalstics facts and figures. Institute for Bioplastics and Biocomposites, 1–6 (2016). http://twixar.me/43T3
2. Avio, C.G., Gorbi, S., Regoli, F.: Plastics and microplastics in the oceans: from emerging pollutants to emerged threat. Mar. Environ. Res. **128**, 2–11 (2017). https://doi.org/10.1016/j.marenvres.2016.05.012
3. Hervy, M., Evangelisti, S., Lettieri, P., Lee, K.Y.: Life cycle assessment of nanocellulose-reinforced advanced fibre composites. Compos. Sci. Technol. **118**, 154–162 (2015). https://doi.org/10.1016/j.compscitech.2015.08.024
4. ABRELPE: Panorama of solid waste in Brazil 2015. Panor. dos Resíduos Sólidos no Bras. 2015. 92 (2015). ISSN 2179-8303 9
5. Shah, A.A., Hasan, F., Hameed, A., Ahmed, S.: Biological degradation of plastics: a comprehensive review. Biotechnol. Adv. **26**, 246–265 (2008). https://doi.org/10.1016/j.biotechadv.2007.12.005
6. Webb, H.K., Arnott, J., Crawford, R.J., Ivanova, E.P.: Plastic degradation and its environmental implications with special reference to poly(ethylene terephthalate). Polymers (Basel). **5**, 1–18 (2013). https://doi.org/10.3390/polym5010001
7. Andrady, A.L.: Persistence of plastic litter in the oceans. In: Bergmann, M., Gutow, L., Klages, M. (eds.) Marine Anthropogenic Litter, pp. 57–72. Springer, Berlin (2015)
8. Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J.: Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PLoS ONE. **9**, 1–15 (2014). https://doi.org/10.1371/journal.pone.0111913
9. Singh, M., Kaushik, A., Ahuja, D.: Surface functionalization of nanofibrillated cellulose extracted from wheat straw: effect of process parameters. Carbohydr. Polym. **150**, 48–56 (2016). https://doi.org/10.1016/j.carbpol.2016.04.109
10. Lee, H.V., Hamid, S.B., Zain, S.K.: Conversion of lignocellulosic biomass to nanocellulose: structure and chemical process conversion of lignocellulosic biomass to nanocellulose. Sci. World J. (2014). https://doi.org/10.1155/2014/631013
11. Reddy, N., Yang, Y.: Biofibers from agricultural byproducts for industrial applications. Trends Biotechnol. **23**, 22–27 (2005). https://doi.org/10.1016/j.tibtech.2004.11.002
12. Yue, Y., Han, J., Han, G., Aita, G.M., Wu, Q.: Cellulose fibers isolated from energycane bagasse using alkaline and sodium chlorite treatments: structural, chemical and thermal properties. Ind. Crops Prod. **76**, 355–363 (2015). https://doi.org/10.1016/j.indcrop.2015.07.006
13. Wang, S., Lu, A., Zhang, L.: Recent advances in regenerated cellulose materials. Prog. Polym. Sci. **53**, 169–206 (2016). https://doi.org/10.1016/j.progpolymsci.2015.07.003
14. Grishkewich, N., Mohammed, N., Tang, J., Tam, K.C.: Recent advances in the application of cellulose nanocrystals. Curr. Opin. Colloid Interface Sci. **29**, 32–45 (2017). https://doi.org/10.1016/j.cocis.2017.01.005
15. Klemm, D., Heublein, B., Fink, H.P., Bohn, A.: Cellulose: fascinating biopolymer and sustainable raw material. Angew. Chem. Int. Ed. **44**, 3358–3393 (2005). https://doi.org/10.1002/anie.200460587
16. Habibi, Y., Lucia, L.A., Rojas, O.J.: Cellulose nanocrystals: chemistry, self-assembly, and applications. Chem. Rev. **110**, 3479–3500 (2010). https://doi.org/10.1021/cr900339w
17. Ojeda, T.: Polymers and the environment. Polym. Sci. (2013). https://doi.org/10.5772/51057
18. Li, Q., Jiang, X., He, Y., Li, L., Xian, M., Yang, J.: Evaluation of the biocompatibile ionic liquid 1-methyl-3-methylimidazolium dimethylphosphite pretreatment of corn cob for improved saccharification. Appl. Microbiol. Biotechnol. **87**, 117–126 (2010). https://doi.org/10.1007/s00253-010-2484-8
19. Mondal, S.: Preparation, properties and applications of nanocellulosic materials. Carbohydr. Polym. **163**, 301–316 (2017). https://doi.org/10.1016/j.carbpol.2016.12.050
20. Ullah, K., Sharma, V.K., Dhingra, S., Braccio, G., Ahmad, M., Sofia, S.: Assessing the lignocellulosic biomass resources potential in developing countries: a critical review. Renew. Sustain. Energy Rev. **51**, 682–698 (2015). https://doi.org/10.1016/j.rser.2015.06.044
21. Schneider, V.E., Peresin, D., Trentin, A.C., Bortolin, T.A., Sambuichi, R.H.R.: Caderno de diagnósticos: Resíduos Agrosilvopastoris I. (2011)
22. Forster-Carneiro, T., Berni, M.D., Dorileo, I.L., Rostagno, M.A.: Biorefinery study of availability of agriculture residues and wastes for integrated biorefineries in Brazil. Resour. Conserv. Recycl. **77**, 78–88 (2013). https://doi.org/10.1016/j.resconrec.2013.05.007
23. Carvalho, F.C., De: Disponibilidade De Resíduos Agroindustriais E Do Beneficiamento De Produtos Agrícolas. Inf. Econ. **22**, 31–46 (1992)
24. Tolmasquim, M.T., et al.: Inventário Energético de Resíduos Rurais. EPE, Resur. tesnológicos. 1–47 (2014)
25. Schneider, V.E., Peresin, D., Trentin, A.C., Bortolin, T.A., Sambuichi, R.H.R.: Resíduos Agrosilvopastoris I. Cad. Diagnóstico. 1–269 (2011)

26. IBGE - Brazilian institute of geography and statistics: No Title, https://sidra.ibge.gov.br/pesquisa/lspa/tabelas
27. FAO - Food and Agricultural Organization: natural resources module - biomass potential assessement, http://www.fao.org/energy/bioenergy/befs/assessment/befs-ra/natural-resources/en/
28. Jiang, D., Zhuang, D., Fu, J., Huang, Y., Wen, K.: Bioenergy potential from crop residues in China: availability and distribution. Renew. Sustain. Energy Rev. **16**, 1377–1382 (2012). https://doi.org/10.1016/j.rser.2011.12.012
29. Panoutsou, C., Labalette, F.: Cereals straw for bioenergy and competitive uses. In: Proceedings of the Cereals Straw Resources for Bioenergy in the Europian Union, Pamplona, pp. 18–19. Pamplona (2006)
30. Koopmans, A., Koppejan, J.: Agricultural and forest residues—generation, utilization and availability. Reg. Consult. Mod. Appl. Biomass Energy (1997). https://doi.org/10.1016/S0251-1088(83)90310-8
31. Rosal, A., Rodriguez, A., Gonzalez, Z., Jimenez, L.: Use of banana tree residues as pulp for paper and combustible. Int. J. Phys. Sci. **7**, 2406–2413 (2012). https://doi.org/10.5897/IJPS11.1661
32. Schieber, A., Stintzing, F., Carle, R.: By-products of plant food processing as a source of functional compounds—recent developments. Trends Food Sci. Technol. **12**, 401–413 (2001). https://doi.org/10.1016/S0924-2244(02)00012-2
33. Arapoglou, D., Varzakas, T., Vlyssides, A., Israilides, C.: Ethanol production from potato peel waste (PPW). Waste Manag. **30**, 1898–1902 (2010). https://doi.org/10.1016/j.wasman.2010.04.017
34. Dhillon, G.S., Kaur, S., Brar, S.K.: Perspective of apple processing wastes as low-cost substrates for bioproduction of high value products: a review. Renew. Sustain. Energy Rev. **27**, 789–805 (2013). https://doi.org/10.1016/j.rser.2013.06.046
35. Jiang, F., Hsieh, Y.L.: Cellulose nanocrystal isolation from tomato peels and assembled nanofibers. Carbohydr. Polym. **122**, 60–68 (2015). https://doi.org/10.1016/j.carbpol.2014.12.064
36. del Campo, I., Alegría, I., Zazpe, M., Echeverría, M., Echeverría, I.: Diluted acid hydrolysis pretreatment of agri-food wastes for bioethanol production. Ind. Crops Prod. **24**, 214–221 (2006). https://doi.org/10.1016/j.indcrop.2006.06.014
37. Ayala-Zavala, J.F., Rosas-Domínguez, C., Vega-Vega, V., González-Aguilar, G.A.: Antioxidant enrichment and antimicrobial protection of fresh-cut fruits using their own byproducts: looking for integral exploitation. J. Food Sci. (2010). https://doi.org/10.1111/j.1750-3841.2010.01792.x
38. Okpala, L.C., Gibson-Umeh, G.I.: Physicochemical properties of mango seed flour. Niger. Food J. **31**, 23–27 (2013). https://doi.org/10.1016/S0189-7241(15)30052-7
39. Kareem, S., Akpan, I., Alebiowu, O.: Production of citric acid by *Aspergillus niger* using pineapple waste. Malays. J Microbiol. **6**, 161–165 (2010)
40. Scarlat, N., Martinov, M., Dallemand, J.F.: Assessment of the availability of agricultural crop residues in the European Union: potential and limitations for bioenergy use. Waste Manag. **30**, 1889–1897 (2010). https://doi.org/10.1016/j.wasman.2010.04.016
41. Lindstrom, M.J.: Effects of residue harvesting on water runoff, soil erosion and nutrient loss. Agric. Ecosyst. Environ. **16**, 103–112 (1986). https://doi.org/10.1016/0167-8809(86)90097-6
42. Nikolaou, A., Remrova, M., Jeliazkov, I.: Biomass availability in Europe. Lot 5 Appendix to EC report on Bio-energy's Role in the EU Energy Market, 1–80 (2003)
43. Wilhelm, W.W., Johnson, J.M.F., Hatfield, J.L., Voorhees, W.B., Linden, D.R.: Crop and soil productivity response to corn residue removal: a literature review. Agron. J. **96**, 1–17 (2004). https://doi.org/10.2134/agronj2004.0001
44. Kludze, H., Deen, B., Weersink, A., van Acker, R., Janovicek, K., De Laporte, A., McDonald, I.: Estimating sustainable crop residue removal rates and costs based on soil organic matter dynamics and rotational complexity. Biomass Bioenergy **56**, 607–618 (2013). https://doi.org/10.1016/j.biombioe.2013.05.036
45. SoCo Project Team, SoCo, P.T.: Addressing soil degradation in EU agriculture: relevant processes, practices and policies. (2009)
46. Karkee, M., McNaull, R.P., Birrell, S.J., Steward, B.L.: Estimation of optimal biomass removal rate based on tolerable soil erosion for single-pass crop grain and biomass harvesting system. Trans. Asabe. **55**, 107–115 (2012)
47. Koubaissy, B., Toufaily, J., Cheikh, S., Hassan, M., Hamieh, T.: Valorization of agricultural waste into activated carbons and its adsorption characteristics for heavy metals. Cent. Eur. J. Eng. (2014). https://doi.org/10.2478/s13531-013-0148-z
48. Zhang, P., Dong, S.J., Ma, H.H., Zhang, B.X., Wang, Y.F., Hu, X.M.: Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids. Ind. Crops Prod. **76**, 688–696 (2015). https://doi.org/10.1016/j.indcrop.2015.07.037
49. Mtui, G.Y.S.: Recent advances in pretreatment of lignocellulosic wastes and production of value added products. Afr. J. Biotechnol. **8**, 1398–1415 (2009). https://doi.org/10.1073/pnas.1014862107/-/DCSupplemental.www.pnas.org/cgi/
50. Satyanarayana, K.G., Guimarães, J.L., Wypych, F.: Studies on lignocellulosic fibers of Brazil. Part I: source, production, morphology, properties and applications. Compos. A **38**, 1694–1709 (2007). https://doi.org/10.1016/j.compositesa.2007.02.006
51. Faulstich de Paiva, J.M., Frollini, E.: Unmodified and modified surface sisal fibers as reinforcement of phenolic and lignophenolic matrices composites: thermal analyses of fibers and composites. Macromol. Mater. Eng. **291**, 405–417 (2006). https://doi.org/10.1002/mame.200500334
52. Guimarães, J.L., Frollini, E., da Silva, C.G., Wypych, F., Satyanarayana, K.G.: Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil. Ind. Crop. Prod. **30**, 407–415 (2009)
53. Miléo, P.C., Leão, R.M., Luz, S.M., Rocha, G.J.M., Gonçalves, A.R.: Typical Brazilian lignocellulosic natural fibers as reinforcement of thermosetting and thermoplastics matrices. In: Thakur, V.K. (ed.) Lignocellulosic Polymer Composites, pp. 103–124. Wiley, Hoboken (2014)
54. Satyanarayana, K.G., Flores-Sahagun, T.H., Bowman, P.: Lignocellulosic materials of Brazil—their characterization and applications in polymer composites and art works. In: Kalia S. (ed.) Lignocellulosic Composite Materials. Springer Series on Polymer and Composite Materials (2018)
55. Cuenca, M.A.G., Resende, J.M., Saggin Júnior, O.J., et al.: Mercado brasileiro do coco: situação atual e perspectivas. In: Aragão, W.M. (ed.) Coco: pós póscolheita, pp. 11–18. Embrapa Informação Tecnológica, Brasília (2002)
56. Ferraz, M.S.: Perspectivas de mercado - Produção e Consumo de manga. I Simpósio manga do Val. do São Fr. 12 (2005)
57. Treichel Michelle, et al.: Anuário Brasileiro da Fruticultura. Editora Gazeta Santa Cruz, Santa Cruz do Sul (2016)
58. Treichel Michelle, et al.: Brazilian tomato Yearbook 2016. Editora Gazeta Santa Cruz, Santa Cruz do Sul (2016)
59. Brasil, H.F.: Procuram-se agroindústrias, http://migre.me/wKQ8N, (2011)
60. Bernardo, B.K., et al.: Brazilian Apple Yearbook 2016. Editora Gazeta Santa Cruz, Santa Cruz do Sul (2016)
61. Müller, I., et al.: Brazilian Cocoa yearbook 2012. Santa Cruz do Sul (2012)
62. Kist, B.B., dos Santos, C.E., Carvalho, C., Reetz, E.G., Müller, I., Beling, R.R.: Brazilian Coffee Yearbook 2015. Editora Gazeta Santa Cruz (2015)

63. Roozen, A.: Availability of sustainable lignocellulosic biomass residues in Brazil for export to the EU. 92 (2015)
64. Ferreira-Leitao, V., Gottschalk, L.M.F., Ferrara, M.A., Nepomuceno, A.L., Molinari, H.B.C., Bon, E.P.S.: Biomass residues in Brazil: availability and potential uses. Waste Biomass Valor. **1**, 65–76 (2010). https://doi.org/10.1007/s12649-010-9008-8
65. Torres, G.A., Renato, L., Tarifa, M.: Aproveitamento de Resíduos Agrícolas. p. 27 (2012)
66. Brum, S.S., Oliveira, L.C.a., De Bianchi, M.L., Guerreiro, M.C., Oliveira, L.K., De Carvalho, K.T.G.: Síntese de acetato de celulose a partir da palha de feijão utilizando N-bromossuccinimida (NBS) como catalisador. Polímeros. **22**, 0–0 (2012). https://doi.org/10.1590/S0104-14282012005000061
67. CitrusBR: Brazilian orange juice: en route to sustainability. p. 9 (2012)
68. Mello, L.M.R., Silva, G.A.: Disponibilidade e Características de Resíduos Provenientes da Agroindústria de Processamento de Uva do Rio Grande do Sul. Embrapa Comun. Técnico 155. Fevereiro, pp. 1–6 (2014)
69. Mattos, A.L.A., Rosa, M.D.F., Crisóstomo, L.A., Bezerra, F.C., Correia, D.: Beneficiamento da casca de coco verde. Embrapa Agroindústria Trop. Fortaleza. 37 (2011)
70. Fontenele, R.E.S.: Cultura do coco no Brasil: Caracterização do mercado atual e perspectivas futuras. XII Congr. da SOBER. pp. 1–20 (2005)
71. Idoeta, P.A.: Indústria do coco cresce, mas alto desperdício gera desafio tecnológico, http://www.bbc.com/portuguese/noticias/2014/02/140207_coco_reciclagem_abre_pai
72. Azevêdo, J.A.V., Filho, S.C.V., Pina, D.S., Detmann, E., Valadares, F.R.D., Pereira, L.G.R., Souza, N.K.P., Silva, L.F.C.: Intake, total digestibility, microbial protein production and the nitrogen balance in diets with fruit by-products for ruminants. Rev. Bras. Zootec. **40**, 1052–1060 (2011)
73. Pereira, L.G.R., Aragão, A.L.S., Santos, R.D., Azevêdo, J.A.G., Neves, A.L.A., Ferreira, A.L., Chizzotti, M.L.: Com Farelo De Manga. Arq. Bras. Med. Veterinária e Zootec. **65**, 675–680 (2013)
74. García Herrera, P., Sánchez-Mata, M.C., Cámara, M.: Nutritional characterization of tomato fiber as a useful ingredient for food industry. Innov. Food Sci. Emerg. Technol. **11**, 707–711 (2010). https://doi.org/10.1016/j.ifset.2010.07.005
75. Mirabella, N., Castellani, V., Sala, S.: Current options for the valorization of food manufacturing waste: a review. J. Clean. Prod. **65**, 28–41 (2014). https://doi.org/10.1016/j.jclepro.2013.10.051
76. Kehili, M., Schmidt, L.M., Reynolds, W., Zammel, A., Zetzl, C., Smirnova, I., Allouche, N., Sayadi, S.: Biorefinery cascade processing for creating added value on tomato industrial by-products from Tunisia. Biotechnol. Biofuels **9**, 261 (2016). https://doi.org/10.1186/s13068-016-0676-x
77. Nelson, M.L.: Utilization and application of wet potato processing coproducts for finishing cattle. J. Anim. Sci. (2010). https://doi.org/10.2527/jas.2009-2502
78. Paganini, C., Nogueira, A., Silva, N.C., Wosiacki, G.: Utilization of apple pomace for ethanol production and food fiber obtainment. Ciênc Agrotecnol **29**, 1231–1238 (2005)
79. Daud, Z., Kassim, A.S.M., Aripin, A.M., Awang, H., Hatta, M.Z.M.: Chemical composition and morphological of cocoa pod husks and cassava peels for pulp and paper production. Aust. J. Basic Appl. Sci. **7**, 406–411 (2013)
80. Araújo, D.J.C., Machado, A.V., Vilarinho, M.C.L.G.: Suitability of agroindustrial residues for cellulose-based materials production. In: Vilarinho, C., Castro, F., Russo, M. (eds.) Wastes: Solutions, Treatments and Opportunities, p. 452. CRC Press, Boca Raton (2017)
81. Kumar, P., Barrett, D.M., Delwiche, M.J., Stroeve, P.: Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind. Eng. Chem. Res. **48**, 3713–3729 (2009)
82. Brandt, A., Gräsvik, J., Hallett, J.P., Welton, T.: Deconstruction of lignocellulosic biomass with ionic liquids. Green Chem. **15**, 550 (2013). https://doi.org/10.1039/c2gc36364j
83. Choonut, A., Saejong, M., Sangkharak, K.: The production of ethanol and hydrogen from pineapple peel by *Saccharomyces cerevisiae* and *Enterobacter aerogenes*. Energy Procedia **52**, 242–249 (2014). https://doi.org/10.1016/j.egypro.2014.07.075
84. Silanikove, N., Levanon, D.: Cotton straw: composition, variability and effect of anaerobic preservation. Biomass **9**, 101–112 (1986). https://doi.org/10.1016/0144-4565(86)90114-9
85. Balasubramanya, R.H., Shaikh, A.J.: Utilization of cottonseed by-products. Model training course on Cultivation of long staple cotton. Central Institute for Cotton Research, pp. 130–138 (2007)
86. Prasad Reddy, J., Rhim, J.W.: Isolation and characterization of cellulose nanocrystals from garlic skin. Mater. Lett. **129**, 20–23 (2014). https://doi.org/10.1016/j.matlet.2014.05.019
87. Wang, B., Li, D.: Strong and optically transparent biocomposites reinforced with cellulose nanofibers isolated from peanut shell. Compos. Part A **79**, 1–7 (2015). https://doi.org/10.1016/j.compositesa.2015.08.029
88. Kim, J.W., Kim, K.S., Lee, J.S., Park, S.M., Cho, H.Y., Park, J.C., Kim, J.S.: Two-stage pretreatment of rice straw using aqueous ammonia and dilute acid. Bioresour. Technol. **102**, 8992–8999 (2011). https://doi.org/10.1016/j.biortech.2011.06.068
89. Chaker, A., Mutjé, P., Vilar, M.R., Boufi, S.: Agriculture crop residues as a source for the production of nanofibrillated cellulose with low energy demand. Cellulose **21**, 4247–4259 (2014). https://doi.org/10.1007/s10570-014-0454-5
90. Johar, N., Ahmad, I., Dufresne, A.: Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk. Ind. Crops Prod. **37**, 93–99 (2012). https://doi.org/10.1016/j.indcrop.2011.12.016
91. Rowell, R.M., Han, J.S., Rowell, J.S.: Characterization and factors effecting fiber properties. Nat. Polym. Agrofibers Compos. **2000**, 115–134 (2000)
92. Önal, E.P., Uzun, B.B., Pütün, A.E.: Steam pyrolysis of an industrial waste for bio-oil production. Fuel Process. Technol. **92**, 879–885 (2011). https://doi.org/10.1016/j.fuproc.2010.12.006
93. Szczerbowski, D., Pitarelo, A.P., Zandoná Filho, A., Ramos, L.P.: Sugarcane biomass for biorefineries: comparative composition of carbohydrate and non-carbohydrate components of bagasse and straw. Carbohydr. Polym. **114**, 95–101 (2014). https://doi.org/10.1016/j.carbpol.2014.07.052
94. Rhim, J.W., Reddy, J.P., Luo, X.: Isolation of cellulose nanocrystals from onion skin and their utilization for the preparation of agar-based bio-nanocomposites films. Cellulose. **22**, 407–420 (2015). https://doi.org/10.1007/s10570-014-0517-7
95. Sosulski, F.W., Wu, K.K.: High-fiber breads containing field pea hulls, wheat, corn, and wild oat brans. Cereal Chem. **65**, 186–191 (1988)
96. Kopania, E., Wietecha, J., Ciechańska, D.: Studies on isolation of cellulose fibres from waste plant biomass. Fibres Text. East. Eur. **96**, 167–172 (2012)
97. Abraham, E., Deepa, B., Pothan, L.A., Jacob, M., Thomas, S., Cvelbar, U., Anandjiwala, R.: Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. Carbohydr. Polym. **86**, 1468–1475 (2011). https://doi.org/10.1016/j.carbpol.2011.06.034
98. Chen, W., Yu, H., Liu, Y., Hai, Y., Zhang, M., Chen, P.: Isolation and characterization of cellulose nanofibers from four plant

cellulose fibers using a chemical-ultrasonic process. Cellulose **18**, 433–442 (2011). https://doi.org/10.1007/s10570-011-9497-z
99. Castaño, P.H., Reales, A.J.G., Zapata, M.J.: Enzymatic hydrolysis of cassava stalk pretreated with the alkaline method. Agron. Colomb. **33**, 238–243 (2015). https://doi.org/10.15446/agron.colomb.v33n2.50115
100. Ma, Z., Pan, G., Xu, H., Huang, Y., Yang, Y.: Cellulosic fibers with high aspect ratio from cornhusks via controlled swelling and alkaline penetration. Carbohydr. Polym. **124**, 50–56 (2015). https://doi.org/10.1016/j.carbpol.2015.02.008
101. Silvério, H.A., Neto, W.P.F., Dantas, N.O., Pasquini, D.: Extraction and characterization of cellulose nanocrystals from corncob for application as reinforcing agent in nanocomposites. Ind. Crops Prod. **44**, 427–436 (2013). https://doi.org/10.1016/j.indcrop.2012.10.014
102. Mohanty, A.K., Mishra M, Drzal, L.T.: Natural Fibres, Biopolymers and Biocomposites, p. 855. CRC Press, Boca Raton (2005)
103. Saha, P., Chowdhury, S., Roy, D., Adhikari, B., Kim, J.K., Thomas, S.: A brief review on the chemical modifications of lignocellulosic fibers for durable engineering composites. Polym. Bull. **73**, 587–620 (2016). https://doi.org/10.1007/s00289-015-1489-y
104. Reddy, N., Yang, Y.: Natural cellulose fibers from soybean straw. Bioresour. Technol. **100**, 3593–3598 (2009). https://doi.org/10.1016/j.biortech.2008.09.063
105. Theerarattananoon, K., Xu, F., Wilson, J., Staggenborg, S., Mckinney, L., Vadlani, P., Pei, Z., Wang, D.: Effects of the pelleting conditions on chemical composition and sugar yield of corn stover, big bluestem, wheat straw, and sorghum stalk pellets. Bioprocess. Biosyst. Eng. **35**, 615–623 (2012). https://doi.org/10.1007/s00449-011-0642-8
106. Font, R., Moltó, J., Gálvez, A., Rey, M.D.: Kinetic study of the pyrolysis and combustion of tomato plant. J. Anal. Appl. Pyrolysis **85**, 268–275 (2009). https://doi.org/10.1016/j.jaap.2008.11.026
107. Chiou, B.S., Valenzuela-Medina, D., Bilbao-Sainz, C., Klamczynski, A.K., Avena-Bustillos, R.J., Milczarek, R.R., Du, W.X., Glenn, G.M., Orts, W.J.: Torrefaction of pomaces and nut shells. Bioresour. Technol. **177**, 58–65 (2015). https://doi.org/10.1016/j.biortech.2014.11.071
108. Fu, D., Mazza, G., Tamaki, Y.: Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues. J. Agric. Food Chem. **58**, 2915–2922 (2010). https://doi.org/10.1021/jf903616y
109. Vlyssides, A.G., Loizides, M., Karlis, P.K.: Integrated strategic approach for reusing olive oil extraction by-products. J. Clean. Prod. **12**, 603–611 (2004). https://doi.org/10.1016/S0959-6526(03)00078-7
110. Zuluaga, R., Putaux, J.L., Cruz, J., Vélez, J., Mondragon, I., Gañán, P.: Cellulose microfibrils from banana rachis: effect of alkaline treatments on structural and morphological features. Carbohydr. Polym. **76**, 51–59 (2009). https://doi.org/10.1016/j.carbpol.2008.09.024
111. Preethi, P., Balakrishna Murthy, G.: Physical and chemical properties of banana fibre extracted from commercial banana cultivars grown in Tamilnadu state. Agrotechnology 1, 8–11 (2013). https://doi.org/10.4172/2168-9881.S11-008
112. Murthy, P.S., Madhava Naidu, M.: Sustainable management of coffee industry by-products and value addition—a review. Resour. Conserv. Recycl. **66**, 45–58 (2012). https://doi.org/10.1016/j.resconrec.2012.06.005
113. Rosa, M.F., Medeiros, E.S., Malmonge, J.A., Gregorski, K.S., Wood, D.F., Mattoso, L.H.C., Glenn, G., Orts, W.J., Imam, S.H.: Cellulose nanowhiskers from coconut husk fibers: effect of preparation conditions on their thermal and morphological behavior. Carbohydr. Polym. **81**, 83–92 (2010). https://doi.org/10.1016/j.carbpol.2010.01.059
114. Marín, F.R., Soler-Rivas, C., Benavente-García, O., Castillo, J., Pérez-Alvarez, J.A.: By-products from different citrus processes as a source of customized functional fibres. Food Chem. **100**, 736–741 (2007). https://doi.org/10.1016/j.foodchem.2005.04.040
115. Dhillon, G.S., Kaur, S., Brar, S.K., Verma, M.: Potential of apple pomace as a solid substrate for fungal cellulase and hemicellulase bioproduction through solid-state fermentation. Ind. Crops Prod. **38**, 6–13 (2012). https://doi.org/10.1016/j.indcrop.2011.12.036
116. Henrique, M.A., Silvério, H.A., Flauzino Neto, W.P., Pasquini, D.: Valorization of an agro-industrial waste, mango seed, by the extraction and characterization of its cellulose nanocrystals. J. Environ. Manag. **121**, 202–209 (2013). https://doi.org/10.1016/j.jenvman.2013.02.054
117. Li, Q., Ng, W.T., Wu, J.C.: Isolation, characterization and application of a cellulose-degrading strain *Neurospora crassa* S1 from oil palm empty fruit bunch. Microb. Cell Fact. **13**, 1–8 (2014). https://doi.org/10.1155/2014/702538
118. Aguedo, M., Kohnen, S., Rabetafika, N., Bossche, S.V., Sterckx, J., Blecker, C., Beauve, C., Paquot, M.: Composition of by-products from cooked fruit processing and potential use in food products. J. Food Compos. Anal. **27**, 61–69 (2012). https://doi.org/10.1016/j.jfca.2012.04.005
119. Rahman, M.M., Khan, M.A.: Surface treatment of coir (*Cocos nucifera*) fibers and its influence on the fibers' physico-mechanical properties. Compos. Sci. Technol. **67**, 2369–2376 (2007). https://doi.org/10.1016/j.compscitech.2007.01.009
120. Rodrigues, B.V.M., Ramires, E.C., Santos, R.P.O., Frollini, E.: Ultrathin and nanofibers via room temperature electrospinning from trifluoroacetic acid solutions of untreated lignocellulosic sisal fiber or sisal pulp. J. Appl. Polym. Sci. **132**, 1–8 (2015). https://doi.org/10.1002/app.41826
121. OCDE/FAO: Brazilian agriculture: prospects and challenges. OECD-FAO Agric. Outlook 2015. 61–108 (2015). https://doi.org/10.1787/agr_outlook-2015-en
122. Sánchez, C.: Lignocellulosic residues: biodegradation and bioconversion by fungi. Biotechnol. Adv. **27**, 185–194 (2009). https://doi.org/10.1016/j.biotechadv.2008.11.001
123. Abdulkhani, A., Marvast, E.H., Ashori, A., Karimi, A.N.: Effects of dissolution of some lignocellulosic materials with ionic liquids as green solvents on mechanical and physical properties of composite films. Carbohydr. Polym. **95**, 57–63 (2013). https://doi.org/10.1016/j.carbpol.2013.02.040
124. Flauzino Neto, W.P., Silvério, H.A., Dantas, N.O., Pasquini, D.: Extraction and characterization of cellulose nanocrystals from agro-industrial residue—Soy hulls. Ind. Crops Prod. **42**, 480–488 (2013). https://doi.org/10.1016/j.indcrop.2012.06.041
125. Rahbar Shamskar, K., Heidari, H., Rashidi, A.: Preparation and evaluation of nanocrystalline cellulose aerogels from raw cotton and cotton stalk. Ind. Crops Prod. **93**, 203–211 (2016). https://doi.org/10.1016/j.indcrop.2016.01.044
126. Wulandari, W.T., Rochliadi, A., Arcana, I.M.: Nanocellulose prepared by acid hydrolysis of isolated cellulose from sugarcane bagasse. IOP Conf. Ser. Mater. Sci. Eng. 107, (2016). https://doi.org/10.1088/1757-899X/107/1/012045
127. Zianor Azrina, Z.A., Beg, M.D.H., Rosli, M.Y., Ramli, R., Junadi, N., Alam, A.K.M.M.: Spherical nanocrystalline cellulose (NCC) from oil palm empty fruit bunch pulp via ultrasound assisted hydrolysis. Carbohydr. Polym. **162**, 115–120 (2017). https://doi.org/10.1016/j.carbpol.2017.01.035
128. Ditzel, F.I., Prestes, E., Carvalho, B.M., Demiate, I.M., Pinheiro, L.A.: Nanocrystalline cellulose extracted from pine wood and corncob. Carbohydr. Polym. **157**, 1577–1585 (2017). https://doi.org/10.1016/j.carbpol.2016.11.036

129. Barbash, V.A., Yaschenko, O.V., Shniruk, O.M.: Preparation and properties of nanocellulose from organosolv straw pulp. Nanoscale Res. Lett. **12**, 241 (2017). https://doi.org/10.1186/s11671-017-2001-4
130. Brinchi, L., Cotana, F., Fortunati, E., Kenny, J.M.: Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. Carbohydr. Polym. **94**, 154–169 (2013). https://doi.org/10.1016/j.carbpol.2013.01.033
131. Dufresne, A.: Nanocellulose: a new ageless bionanomaterial. Mater. Today **16**, 220–227 (2013). https://doi.org/10.1016/j.mattod.2013.06.004
132. Julkapli, N.M., Bagheri, S.: Progress on nanocrystalline cellulose biocomposites. React. Funct. Polym. **112**, 9–21 (2017). https://doi.org/10.1016/j.reactfunctpolym.2016.12.013
133. Asgher, M., Ahmad, Z., Iqbal, H.M.N.: Bacterial cellulose-assisted de-lignified wheat straw-PVA based bio-composites with novel characteristics. Carbohydr. Polym. **161**, 244–252 (2017). https://doi.org/10.1016/j.carbpol.2017.01.032
134. Yan, L., Kasal, B., Huang, L.: A review of recent research on the use of cellulosic fibres, their fibre fabric reinforced cementitious, geo-polymer and polymer composites in civil engineering. Compos. B **92**, 94–132 (2016). https://doi.org/10.1016/j.compositesb.2016.02.002
135. Gurunathan, T., Mohanty, S., Nayak, S.K.: A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Compos. A **77**, 1–25 (2015). https://doi.org/10.1016/j.compositesa.2015.06.007
136. Kumar, R., Sharma, R.K., Singh, A.P.: Cellulose based grafted biosorbents - Journey from lignocellulose biomass to toxic metal ions sorption applications—a review. J. Mol. Liq. **232**, 62–93 (2017). https://doi.org/10.1016/j.molliq.2017.02.050
137. Hokkanen, S., Bhatnagar, A., Sillanpää, M.: A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. Water Res. **91**, 156–173 (2016). https://doi.org/10.1016/j.watres.2016.01.008
138. Sazali, N., Salleh, W.N.W., Ismail, A.F.: Carbon tubular membranes from nanocrystalline cellulose blended with P84 co-polyimide for H_2 and He separation. Int. J. Hydrogen Energy **42**, 9952–9957 (2017). https://doi.org/10.1016/j.ijhydene.2017.01.128
139. Harmsen, P.F., Hackmann, M.M., Bos, H.L.: Green building blocks for bio-based plastics. Biofuels Bioprod. Biorefining. **8**, 306–324 (2014). https://doi.org/10.1002/bbb
140. Özdenkçi, K., De Blasio, C., Muddassar, H.R., Melin, K., Oinas, P., Koskinen, J., Sarwar, G., Järvinen, M.: A novel biorefinery integration concept for lignocellulosic biomass. Energy Convers. Manag. **149**, 974–987 (2017). https://doi.org/10.1016/j.enconman.2017.04.034

Affiliations

David Jefferson Cardoso Araújo[1] · Ana Vera Machado[2] · Maria Cândida Lobo Guerra Vilarinho[3]

[1] Institute for Polymers and Composites/I3N and Centre for Waste Valorization, University of Minho, Guimarães, Portugal

[2] Institute for Polymers and Composites/i3N, University of Minho, Guimarães, Portugal

[3] Mechanical Engineering and Resources Sustainability Centre, University of Minho, Guimarães, Portugal