Suitability of agroindustrial residues for cellulose-based materials production

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Abstract

The depletion of fossil resources and negative environmental impact related to conventional polymeric materials life cycle have fostered the search for renewable raw materials suitable for their manufacturing. This work aims to present a methodology for the selection of agroindustrial residues with potential to be used as feedstock in cellulose-based materials production. The suitability of main residues identified was calculated taking into consideration their intrinsic characteristics, namely the cellulose content, cellulose-to-lignin ratio and availability. The selection and generation estimates of residues were based on the reality of Portugal's agriculture sector. The results indicate a range of residues with potential to be used as raw materials. In addition to residues generated in harvest fields, the processing industries can also be considered a potential source of byproducts suitable for the application concerned.

INTRODUCTION

Over the last few decades, environmental pressures and concerns about the limited availability of fossil resources have fostered the search for technological alternatives and feedstocks less harmful to the environment. The fast growing of the polymeric industry in the last 30 years has significantly boosted the development of society, but it has also triggered many environmental problems (Barnes et al 2009). Only in 2014, the world plastic production reached a value close to 311 million tons (Statista 2016). From this total, a main portion is derived from fossil resources and has the characteristic of being non-biodegradable (Tokiwa et al. 2009), which makes its accumulation potentially adverse to terrestrial and aquatic ecosystems.

Therefore, the search of renewable raw materials suitable to produce biodegradable polymeric and bio-based materials is imperative. Biodegradable polymers are a specific type of polymer that can be naturally degraded by the action of weathering agents and microorganisms (Pillai 2014). Depending on environmental conditions and type of biopolymer high degradation rates can be reached (Song et al. 2009). In recent years, the group of bioplastics derived from renewable and biodegradable resources, such as cellulose, lignin and starch, has received greater interest. Indeed, bioplastics have been mentioned as a lead market by the European Commission, with global production capacity set to grow 350 % by 2019 (European bioplastic, 2016).

Among available sources of renewable feedstock, the lignocellulosic biomass stands out in the global scenario. Lignocellulosic biomass is mainly composed of three natural organic polymers, cellulose, hemicellulose and lignin, and smaller amounts of proteins, pectin and extractives (Monlau et al. 2013). Cellulose is labeled as the most abundant organic polymer in the earth, and due to some of its properties, such as mechanical, thermal, biodegradable, renewable and low cost, its application to the development of new bio-based products is increasingly being explored (Wang et al 2016, Chaker et al. 2014). In general, lignocellulosic feedstock may result from agriculture, forestry activities, energy crops and municipal and industrial wastes (Lee et al. 2014). The set of activities associated with the vegetable agribusiness sector excels as the one of the main residues generators. It is estimated that the production of agricultural and forestry residues in the Europe Union exceed 200 million tons/year (Searle & Malins 2013, Scarlat et al 2010).

Taking into account the growing interest of this research topic, as well as the wide variety of residues available, this paper proposes the development of an evaluation methodology to support the selection of agroindustrial waste suitable to be used as raw material in the production of cellulose-based materials. The developed methodology was applied based on the agroindustrial market of Portugal continental and insular.

METHODOLOGY

Suitability of agroindustrial residues for bioplastic production

The first step to analyze the feasibility of agroindustrial waste valorization (S), regarding its application to produce polymeric products, consists in the identification of waste types that besides to have high or low content of cellulose and lignin, respectively, are also generated in significant quantities. Thus, three main parameters were taken into account in order to obtain an output that reflects the suitability of different agroindustrial residues, namely availability of residues (AR), cellulose content (CC) and cellulose to lignin ratio ($R_{C/L}$) (Equation 1).

$$S=f\left(AR;CC;R_{C/L}\right) \quad (1)$$

The parameters included in equation 1 are positively correlated to the final value of S , and the importance of each one on the final selection criteria is also considered. This can be accomplished by weighting each parameter as presented in equation 2 . The constant β (45), of greater influence, is associated with CC, while $\gamma(35)$ and $\alpha(20)$ are related to AR e $R_{C/L}$, respectively. Greater importance was given to CC as it deals with the raw material required to produce bio-based materials. Less importance has been devoted to AR and $R_{C/L}$, since limitations attributed to these parameters can be circumvented. Since the range of values of raw data varies widely and the parameters included in the formulation (1) encompass different measuring units, it was necessary to adjust values to a notionally common scale by applying normalization. Thus, equation 1 was rewritten as shown in equation 2.

$$S_i' = \gamma\, AR_i' + \beta\, CC_i' + \alpha\, R_{C/Li}' ; \text{ Lignin content} > 0 \quad (2)$$

where,

$$AR_i' = a + \left[\frac{(AR_i - AR_{min})(b-a)}{(AR_{max} - AR_{min})} \right]; \quad (3)$$

$$CC_i' = a + \left[\frac{(CC_i - CC_{min})(b-a)}{(CC_{max} - CC_{min})} \right]; \quad (4)$$

$$R_{C/Li}' = a + \left[\frac{(R_{C/Li} - R_{C/Lmin})(b-a)}{(R_{C/Lmax} - R_{C/Lmin})} \right] \quad (5)$$

In equations 3, 4 and 5 the constants a and b correspond to arbitrary points, equivalent to 0.1 and 1, respectively, used to restrict the range of values in the dataset. In the same equations, the parameters designated by maximum and minimum subscripts are associated to residues that present the highest and lowest values of the parameter concerned, respectively.

Thus, for each residue, the S_i (suitability index) might vary from 10 to 100 and will be expressed as dimensionless.

Agroindustrial residues availability

The assessments of agroindustrial residues availability took into account the average annual production of crops (AAP), residue generation rate (RGR), sustainable removal rate (SSR) and other competitive uses. Average annual production of crops, as well as the selection of main crops, were obtained from FAO database with a temporal coverage from 2004 to 2013 (FAOSTAT, 2014). The sustainable removal rates of 40 % for wheat straw, maize residues and rice straw and husk was adopted (EPE 2014). Besides, based on studies conducted by Scarlat et al (2010) and Searle and Marlins (2013), it was assumed that 30 % of residues can have other use (Competitive uses-CU), such as consumption for livestock (animal bedding and feeding), cosmetics industries and mushroom production. It should be noticed that cellulose and lignin content were established based on data available in literature.

Exclusively for those industry-driven crops, residues generation took into consideration the portion of production directed to industrial processing (IP). According to data from Statistics Portugal (2014), approximately 97.3% of olive production are intended for olive oil production; 97.9 % of grape production are intended for wine production; and

91.8% of tomatoes production are intended for industrial processing. Besides, it was assumed that 23% of apple (USDA 2011), 7% of orange (Euromedcitrusnet 2007) and 10% of potato (Commission of the European Communities 2007) national production are allocated to industries processing. By applying these information, as well as the average annual production of crops and the residues generation rates (Table 1), it is possible to obtain the average availability of crop residues (AR_{CR}) (equation 6) and industry-driven crops (AR_{IDC}) (equation 7).

$$AR_{CR} = (AAP)(RGR)(SRR)(1-CU) \quad (6)$$

$$AR_{IDC} = (AAP)(IP)(RGR)(1-CU) \quad (7)$$

RESULTS

Table 1 provides the main information necessary to identify relevant residues to be used as feedstock for the production of cellulose-based materials. Although it is possible to identify

Table 1. Chemical characterization of lignocellulosic biomass and residues availability. RGR—residue generation rate; AR-availability of residue; $R_{C/L}$ - Cellulose-to-lignin ratio.

Residue	Cellulose (%)	Lignin (%)	RGR ($t_{residue}/t_{crop}$)	AR (kt)
Olive pomace	19.27 [1]	11.32 [1]	0.35 [2]	91.69
Orange bagasse	24.52 [3]	7.51 [3]	0.50 [4]	5.17
Apple pomace	7.2 [5]	23.5 [5]	0.30 [6]	12.07
Grape pomace	27.9 [7]	63 [7]	0.25 [8]	149.90
Maize cob	31.2 [9]	15 [9]	0.33 [10]	63.63
Maize husk	62.07 [11]	14.6 [11]	0.22 [10]	42.42
Maize straw	40.8 [12]	22 [12]	1.96 [10]	377.90
Tomato pomace	29.1 [7]	57.4 [7]	0.04 [13]	32.86
Potato skin	10.5 [14]	4.0 [14]	0.27 [15]	10.21
Wheat straw	35.4 [16] [17]	18.75 [16] [17]	1.28 [10]	49.30
Rice husk	35 [18]	23 [18]	0.25 [10]	11.41
Rice straw	39.5 [19]	15.9 [19]	1.33 [10]	59.27

[1] Vlyssides et al 2004; [2] Brscic et al 2009; [3] Bicu & Mustafa 2011; [4] Foster-Carneiro et al 2013; [5] Dhillon et al 2012; [6] Dhillon et al 2013; [7] Chiou et al 2015; [8] Dwyer et al 2014; [9] Silvério et al 2013; [10] FAO 2014; [11] Ma et al 2015; [12] Chaker et al 2014; [13] Jiang et al 2015; [14] Rommi et al 2015; [15] Schieber et al 2001; [16] Kopania et al 2012; [17] Lee et al 2014; [18] Johar et al 2012; [19] Kim et al 2011.
the relevance of some residues by looking at the results showed in this table, the decisionmaking to select the most suitable is not an easy task.

Besides to cellulose content and residues availability, lignin amount should also be taken into account. The presence of lignin in lignocellulosic biomass can be considered as one of the major obstacles in pretreatment processes (Monlau et al 2013). Moreover, the presence of substantial amounts of non-cellulosic components in lignocellulosic fibers may negatively influence their biodegradability, crystallinity, density, tensile strength, modulus and moisture (Monlau et al 2013, Reddy & Yang 2005). Therefore, in this study, the influence of lignin over the selection of residues was taken into account by including the cellulose-to-lignin ratio in the formulation of suitability. The greater the ratio, the greater is the cellulose percentage compared to the lignin content, and thus more efficient would be the biomass treatment.

The ranking of residues with greater potential to be used as raw material (Figure 1) was obtained from the substitution of the calculated parameters $AR_i^{'}, CC_i^{'}$ e $R_{C/Li}^{'}$ (Table 2) in equation 2 . It can be noticed that mainly the parameters AR and $R_{C/L}$ have a significant influence on the residues ranking. The high cellulose content associated with maize husk resulted in a normalized cellulose-to-lignin ratio and cellulose content much higher than of other residues (Tables 1 and 2), which contributed significantly to the final value of suitability index. Among residues with the highest cellulose contents are maize husk, maize straw, rice straw and wheat straw (Tables 1 and 2). Considering only the individual contribution of residues available, the maize straw, grape pomace and olive pomace (Tables 1 and 2) account about $70\%\left(619.5\,kt\right)$ of the total available residues generation.

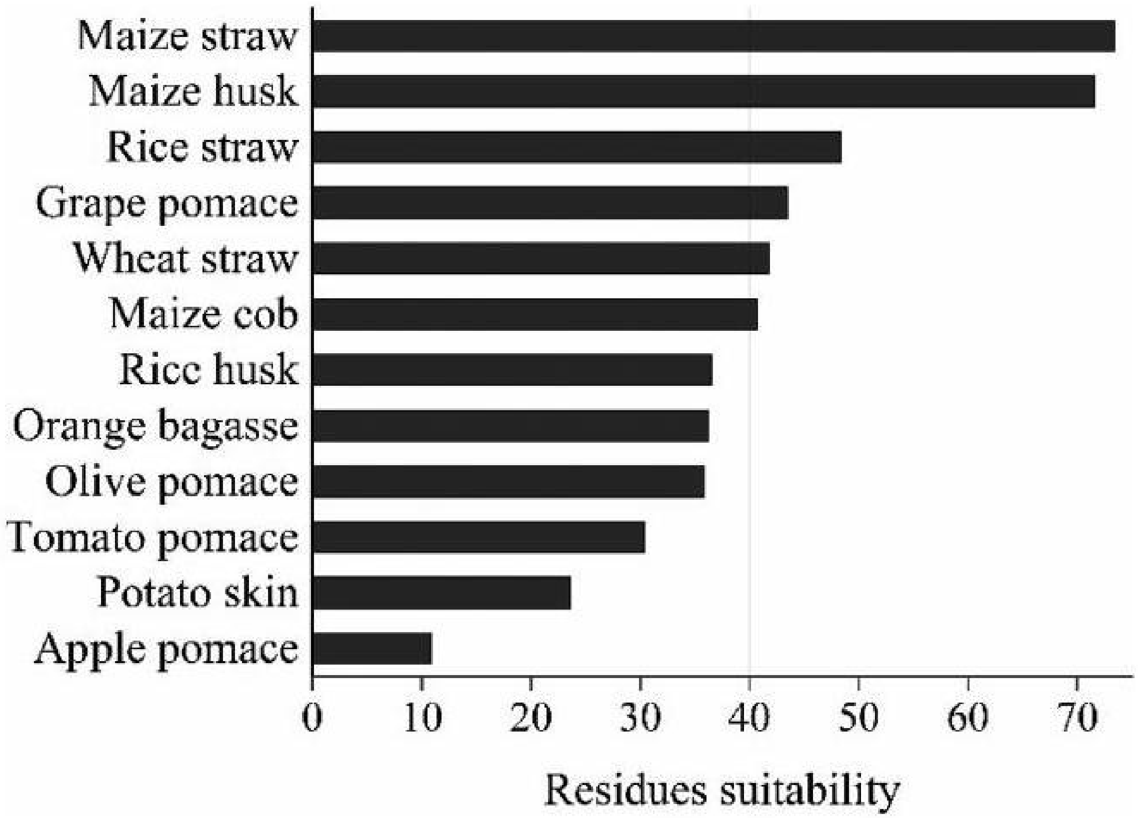

Figure 1. Cellulose-based materials production suitability of agroindustrial residues.

Table 2. RGA, $R_{C/L}$ and CC normalized values for each residue.

Residue	Normalized availability of residue (AR_i)	Normalized cellulose content (CC_i)	Normalized celulose-tolignin ratio ($R_{C/Li}$)
Olive pomace	0.40	0.298	0.418
Orange bagasse	0.1	0.384	0.775
Apple pomace	0.124	0.1	0.1
Grape pomace	0.602	0.439	0.131
Maize cob	0.241	0.493	0.504
Maize husk	0.190	1	1

Maize straw	1	0.651	0.453
Tomato pomace	0.196	0.459	0.145
Potato skin	0.117	0.154	0.629
Wheat straw	0.206	0.562	0.460
Rice husk	0.114	0.556	0.377
Rice straw	0.230	0.629	0.597

Among the major agroindustrial residues identified in Portugal, those with greater potential to be used as raw material are maize straw, maize husk, rice straw, grape pomace and wheat straw. On the other hand, lower suitability values were assigned to apple pomace and potato skin (Figure 1). It is important to emphasize that variables involved in the proposed methodology are directly influenced by climatic and soil conditions, as well as by agricultural business and farming practices. Consequently, the values assumed in this work tried to be as representative as possible of the reality of Portugal, thus the results obtained can only be applied to that country. Attempts to apply this methodology in other countries or regions should make use of a specific and reliable database.

According to the results, in the production and manufacturing cycle of agricultural products, the processing industries are also a potential source of suitable residues. About 40 % of the total amount of waste available come from them. The parameters used to obtain the suitability index are also relevant for other bio-based applications, such as biofuels and bioenergy (Scarlet et al 2010). Hence, some residues identified in this work have already been used in other valorization routes (Arevalo-Gallegos et al 2017) besides cellulose-based materials production (Wang et al 2016), which supports and validates the obtained results. It should be noted that the results obtained do not neglect the possibility of using the other residues not highlighted in Figure 1. However, in such situations, the improvement and optimizing of treatments or pretreatments techniques must be carried out.

Additionally, the use of agricultural residues to the application concerned still need to encompass a number of issues besides the availability and chemical composition of residues, among which include: temporal variability of generation, technological alternatives available for valorization, perception and social impact on different farmers' category, in addition to logistical issues mainly influenced by the spatial variability of residues generation. For instance, in Portugal, the maize production takes place mainly in the Alentejo region, hence, the largest share of maize residues would be available in that region.

CONCLUSIONS

In this study, a methodology to select agroindustrial residues suitable for cellulose-based materials production has been conducted based on the agricultural sector of Portugal. The chemical composition and availability of residues were taken into account. Besides to residues generated during the crops harvesting, the processing industries are also a potential source of byproducts. Among the most suitable residues to the application concerned are maize straw, maize husk, rice straw and grape pomace. Mainly due to its easy application and wide availability of needed input data, this methodology can be used as an efficient management tool in aid for decision-making. However, seeing that residues generation is closely related to crops production, in order to improve this methodology, in-depth studies on economic issues and spatial and temporal variability of residues should be performed and taken into account over the proposed formulation.

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