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Novel method for holocellulose analysis of non-woody biomass wastes

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ABSTRACT

Compositional analysis of non-woody biomass is quite important to determine its possible applications. However, current standard methods developed for woody biomass compositional analysis have been revealed to be unsuitable when applied to non-woody biomass. Therefore, a novel and less-time consuming modified method which enables for a proper isolation of holocellulose in non-woody biomass samples while increasing lignin degradation has been developed. The novel method mainly consists in a treatment with sodium chlorite and glacial acetic acid at boiling point, which precludes changes in the holocellulose crystallinity degree or losses of carbohydrates, as shown by DSC, XRPD, and HPLC analysis. It was successfully applied to the determination of the structural components of 10 different non-woody biomass samples. Also, its use revealed that non-woody biomass belongs to LHC and LCH groups in the biomass structural composition ternary diagram, which are completely different than the ones the woody biomass belongs to.

1. Introduction

Olive oil extraction, as well as table olive and fruits production, represent highly relevant economic activities in wide areas of Europe -such as the Mediterranean countries- and in the rest of the world, as well (Rodríguez et al., 2008). Taking into account the input and output mass balance of the olive oil industry, the crops' yield and the cultivated area, only the amounts of olive stone and olive pomace in Europe are estimated to be of 2,012,211 t/year and 4,724,322 t/year, respectively (Agencia Andaluza de la Energía, 2016; elEconomista.es, 2017; Eurostat, 2015; Rosúa & Pasadas, 2012; Secretaría General Técnica and Subdirección General de Estadística, 2016).

Olive non-woody wastes like those aforementioned, as well as non-woody grapevine and fruit production wastes, could find several applications, such as eco-friendly adsorbents (Vecino, Devesa-Rey, Cruz, & Moldes, 2015), cosmetic and therapeutic products (Moudache, Colon, Nerín, & Zaidi, 2016), and energy production. Also, their upgrading would enable the increase of the profitability of olive and fruit producers as well as wineries; the reduction of fossil fuels dependence for different agricultural and industrial activities, as well as the reduction of carbon footprint.

In spite of the aforementioned potential applications and advantages, non-woody wastes remain underused. This is due to the lack of knowledge about the composition of the different non-woody wastes of several species, which is, for instance, quite important for the evaluation of conversion yields in biofuels production industry (Sluiter, Ruiz, Scarlata, Sluiter, & Templeton, 2010). Also, in order to determine the possible uses of a specific type of biomass is important to classify it in the ternary diagram. The ternary diagram divides biomass into six different organic structural types: CHL, CLH, HCL, LCH, HLC, and LHC. The classification of a biomass in the ternary diagram requires an accurate determination of its composition (Vassilev, Vassileva, & Vassilev, 2015) and is a key step for establishing a normalized biomass classification and to determining the possible use of biomass wastes, too.

Previous compositional analysis results for woody biomass have shown that this kind of biomass belongs to the groups which have higher quantities of cellulose such as CLH and CHL (Álvarez et al., 2015). The main compositional analysis method to determine the content of the structural components in a biomass sample is the summative mass closure, which consists in the determination of lignin and holocellulose by means of an acid hydrolysis with sulphuric acid according to NREL TP-510-42618 method (Sluiter et al., 2008). The solid residue is the acid-insoluble lignin and ashes, while the hydrolysates are the monomers and dimers of holocellulose and a minor part of the lignin called acid soluble lignin. Thus, this method gives information about the amount of holocellulose in the sample through the hydrolysates. However, if it is needed to isolate holocellulose as a solid fraction, the method proposed in this paper enables an appropriate one-

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List of Acronyms

Cel70	Cellulose obtained from hollocellulose 70 (Holo70)
Cel96	Cellulose obtained from hollocellulose 70 (Holo96)
CHL	Biomass group whose cellulose content > hemicellulose content > lignin content
CLH	Biomass group whose cellulose content > lignin content > hemicellulose content
DSC	Differential scanning calorimetry
HCL	Biomass group whose hemicellulose content > cellulose content > lignin content
HLC	Biomass group whose hemicellulose content > lignin content > cellulose content
Holo70	Holocellulose obtained by following the ASTM standard
Holo96	Holocellulose obtained by following the novel method proposed
HPLC	High-performance liquid chromatography
IC	Crystallinity index
LCH	Biomass group whose lignin content > cellulose content > hemicellulose content
LHC	Biomass group whose lignin content > hemicellulose content > cellulose content
MCC	Commercial microcrystaline cellulose
SEM	Scanning electron microscopy
XRPD	X-ray powder diffraction

step quantification and isolation of the holocellulose fraction. This is really important in order to study the properties of this fraction in some applications such as the holocellulose use as filler in composite materials, whose mechanical properties may be affected by the lignin presence in holocellulose (Angelini, Cerruti, Immirzi, Scarinzi, & Malinconico, 2016; Šimkovic et al., 2017). In addition, holocellulose is the starting-point of most work in carbohydrates study of biomass (Rabemanolontsoa & Saka, 2012). The most common methods used to isolate holocellulose are the Wise method (Wise, 1946) and the ASTM D1104 standard method based on the Wise's one (ASTM International, 1978). These methods consist in subjecting biomass samples to a specific number of acid chlorination stages in order to remove the lignin using a sodium chlorite and glacial acetic acid mixture.

Previous research works on non-woody biomass give an extremely high total summative or data of the structural composition normalised to 100%, because of the inability of the standard methods to achieve a proper separation of the lignin and holocellulose fractions of non-woody biomass samples (Álvarez et al., 2015; Demirbaş, 2001; Müller-Hagedorn, Bockhorn, Krebs, & Müller, 2002; Rabemanolontsoa, Ayada, & Saka, 2011). Although lignin and ash corrections could be done, in some cases there is a need for holocellulose isolation as mentioned above. To this end, a work of Rabemanolontsoa modified the Wise method for holocellulose determination in bamboo and sargasso. To prevent carbohydrate loss from the samples, they reduced the number of chlorination stages and made lignin, ash and protein corrections on crude holocellulose (Rabemanolontsoa & Saka, 2012). Other authors (Yeh, Chang, & Kadla, 2004) modified the reaction temperature and time as well as the amounts of reactants in order to isolate the holocellulose fraction of loblolly pine.

Also, current standard procedures (ASTM International, 1978; Sluiter et al., 2008; Wise, 1946) have been developed for woody and herbaceous biomass; however these procedures could be unsuitable for other lignocellulosic non-woody biomass, such as stones, shells or kernels, if it is necessary to isolate holocellulose as a solid fraction. A paper of Sluiter et al. highlighted the need for improved methods to characterize the components of biomass as well as the validation of the existing methods on a wider variety of biomass types (Sluiter et al., 2010). In this paper, it is shown that the standard method is unsuitable for the extraction of holocellulose from stones or shells, as the holocellulose fractions obtained following this method were brownish instead of whitish, due to the poor delignification of the samples. Therefore, this paper is devoted to a novel method for holocellulose determination for non-woody biomass. The novel method developed in this paper is based on the ASTM's one (ASTM International, 1978, but it

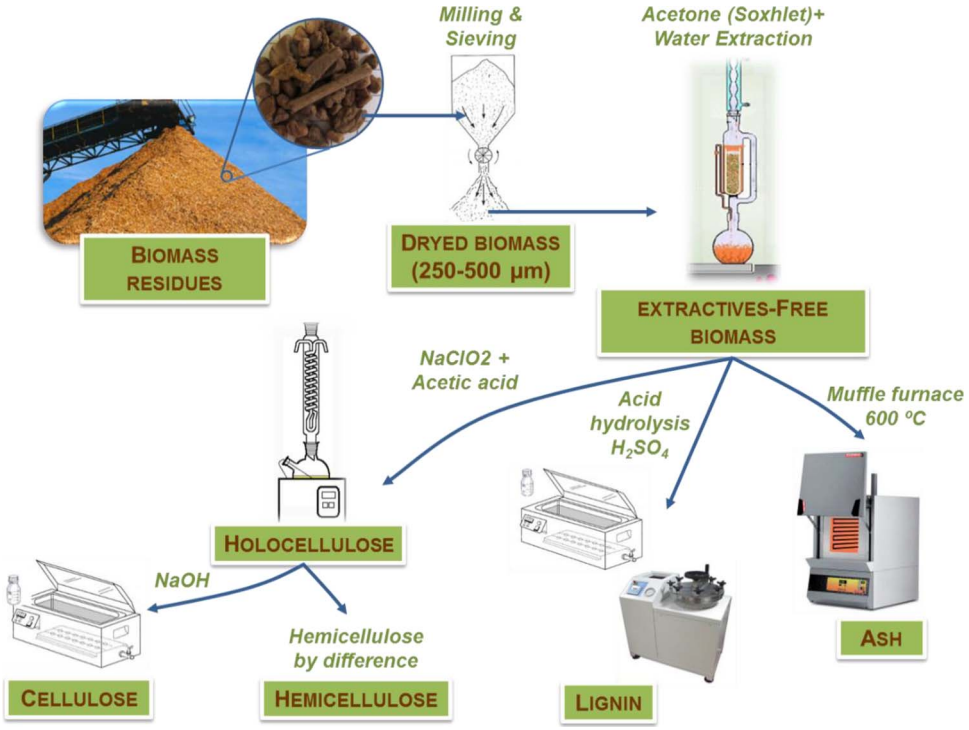

Fig. 1. Chemical extraction procedure to determine the structural composition of biomass.