CHEMICAL ENGINEERING TRANSACTIONS
VOL. 65, 2018

A publication of
AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Mario Costa

ISBN 978-88-95608- 62-4; **ISSN** 2283-9216

Biomass from Colombian agroindustrial activities: characterization and potential for oligosaccharides production

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Lignocellulosic materials from forest or agroindustrial activities are sources for obtaining different natural fibres and biopolymers, which may have low density and biodegradability and excellent mechanical and physical properties. These materials constitute a new source of a huge variety of different biochemical compounds, between them, oligosaccharides having prebiotic properties. Colombia is an agricultural country, having a great potential for developing the lignocellulosic biomass processing which can lead to a variety of products and reach the zero residue in the different agricultural production chain. In this work, different agricultural residues typical from the Santander region, such as panela cane bagasse, empty fruit bunch from oil palm, cocoa shells, coffee husks, among others, were selected and characterized to determine the cellulose, hemicellulose, lignin and other fractions content. Depending to the lignocellulosic materials analysed, the hemicellulose and cellulose fractions varied between 5.4 – 37.0 wt.% and 7.9 – 41.4 wt.% of the dry biomass, respectively. Avocado seeds have a higher glucose content (41.4 wt.%) but a poor xylose fraction (4.5 wt.%), while biomass as panela cane bagasse has a homogeneous distribution having 32 wt.% glucose and 35 wt.% xylose, respectively. Additionally, the biomass production in Colombia and its composition were used to evaluate the potential of producing different oligomers, such as Xylooligosaccharides, Arabinooligosaccharides, Mannanoligosaccharides and Glucooligosaccharides, as well as the potential for energy generation for the biomass selected. The distribution of these fractions evidences the possibility of obtaining high added value compounds from biomass that can be used for both energy recovery and food industry.

1. Introduction

Colombia is an agricultural country having around 5.6 MHa cultivated and where 36.2% of its territory has agricultural potential (Junguito, Perfetti and Becerra, 2014). The waste generated by the agricultural activities and/or agroindustry is mostly used to generate energy in traditional and non-efficient ways or discarded directly to the environment. These wastes from agroindustry are known as lignocellulosic residual biomass (LRB) constituted mainly by husks, branches, bagasse and stubble. LRB are more reactive and have a higher volatility than coals. However, all biomass differs greatly in volatile matter concentration, and even the same type of biomass can change in composition based on the climatic conditions and seasonal variation. The characterization of the chemical composition profile of biomass is very important to determine future uses and conversion processes. The 75 – 85 wt.% of LRB is constituted by cellulose, hemicellulose and lignin, which can be decomposed into simple sugars or monosaccharides through physical, chemical or biological processes. In addition, it has low concentration of acids, salts, and minerals and also minimal concentration of proteins (Ruiz *et al.*, 2013). Cellulose is a crystalline polysaccharide component consisting of a linear chain of several β-(1,4) linked D-glucose units. Structurally, the chains are shaped by glucose units linked by hydrogen bonds between multiple hydroxyl groups and oxygen molecules on the same or neighbouring chain (Otieno and Ahring, 2012). On the other hand, hemicellulose fraction is an heterogeneous polymer highly branched of 5-carbon (C-5) sugars such as xylose and arabinose as well as 6-carbon (C-6) sugars such as galactose, glucose, fructose, and mannose (Mosier *et al.*, 2005). Due to its amorphous nature, hemicelluloses are non-crystalline, therefore is more easily hydrolysed compared to cellulose. Finally, lignin is a three-dimensional polymer made of phenylpropane units linked randomly through alkyl-aryl ether bonds. It acts as a protecting agent and binder in the cell-wall structure of lignocellulosic materials (Montane *et al.*, 2006). Considering its relative abundance in the biomass, cellulose has been the target compound because allows to obtain glucose, which can be fermented or pyrolyzed to obtain biofuels. Beside this, the lignin component has also been exploited for its degradation fragments including derivatives of phenolic acids, aldehydes, and alcohols (Otieno and Ahring, 2012). On the other side, hemicellulose fraction of biomass has been less used but has the potential to produce oligosaccharides. The most well-known oligosaccharides are fructooligosaccharides (FOS), galactooligosaccharides (GOS), isomaltooligosaccharides (IMO), inulin, polydextrose, lactulose, glucooligosaccharides and resistant starch (Mussatto and Mancilha, 2007). However, a new novel non-digestible oligosaccharide (NDO) having prebiotic effect are xylooligosaccharides (XOS). There is a growing interest in the production of XOS based on their beneficial health effects including prebiotic effects for gastroenteritis treatment, functional properties as a soluble fibre and ability to lower cholesterol blood levels (Chen *et al.*, 2014). The focus of this study is to analyse the biomass composition coming from different agricultural chains in Colombia and establish the potential to obtain oligosaccharides as a high added value product.

2. Methodology

2.1 Raw material

Lignocellulosic residual biomass (LRB) was collected in the region of Santander, Colombia. The biomass used in the present study were the avocado seed (AS), cocoa shell (CS), mango seed (MS), coffee husks (CH), bean stubble (BS), tobacco stems (TS), panela cane bagasse (PCB), spent coffee (SC) and empty fruit bunch from oil palm (EFBOP). The selection of LRB was carried out considering the following aspects: contribution of culture to the gross domestic product of the region, amount of biomass generated, cultivated area and access for collection. All LRBs were sun dried, milled (<0.5 mm) and hermetically stored for further analysis.

2.2 Analytical Methods

In order to determine its composition, the different LRB were analyzed using the following standard methods (in triplicate): moisture and ash content (ASTM D7582-10), water and ethanol/toluene extractives (ASTM D1110-56), α-cellulose (NaOH extraction according to ASTM D1103-60), holocellulose (TAPPI Standard T9m-40), and Klason lignin (ASTM D1106-56). A liquid sample from klason lignin procedure was analyzed by high-performance liquid chromatography (HPLC) in order to quantify acetic acid and monosaccharides. The analysis was done using a Bio-Rad HPX 87H column at 65°C, using a H_2SO_4 0.005 M mobile phase and flow 0.6 ml min^{-1}. RI detector was used to determine the carbohydrates composition, calibrating the system with glucose, xylose, arabinose, mannose, galactose and acetic acid standards (Alfa Aesar >98%). The high calorific value (HCV) determination was done using a calorimetric pump (Parr 6200) following the ASTM D-5865 standard.

3. Results and Discussion

After a revision of the agroindustry sector in the region of Santander considering the contribution of culture to the gross domestic product of the region, the amount of biomass generated, the cultivated area and access for collection, the by-products described in Table 1 were selected for this study.

Table 1: Main agricultural products in Colombia and its lignocellulosic residues.

Culture	Production (Tons $year^{-1}$)	Residue selected	Generation (Tons $year^{-1}$)	Reference	HCV (MJ Kg^{-1})
Coffee	776,522	Coffee husks	458,166	(Escalante *et al.*, 2010)	16.48 ± 0.11
		Spent coffee	338,261	(Puerta-Quintero, 2010; Suarez, 2012)	22.92 ± 0.05
Panela cane	1,438,623	Bagasse	3,639,716	(Escalante *et al.*, 2010)	17.21 ± 0.14
Bean	149,112	Bean stubble	46,225	(Montoya-Rosales, 2016)	15.60 ± 0.09
Oil palm	1,017,046	Empty fruit bunches	1,078,069	(Escalante *et al.*, 2010)	16.16 ± 0.07
Tobacco	43,748	Stems	131,244	(Barla and Kumar, 2016)	15.60 ± 0.03
Cocoa	87,632	Shell	350,528	(Martínez-Ángel, Villamizar-Gallardo and Ortíz-Rodríguez, 2015)	15.62 ± 0.07
Avocado	288,739	Seed	72,185	(Sánchez, Agudín and San Mıguel, 2017)	16.88 ± 0.01
Mango	273,112	Seed	32,773	(Henrique *et al.*, 2013)	17.04 ± 0.06

Table 1 presents the amount of the crop produced per year (DANE, 2014), the lignocellulosic residues and the amount generated, and also the potential HCV (measured in this study). As it can be observed, the most cultivated crops in Colombia are panela cane, oil palm and coffee, generating more than 6 million tons of agroindustrial residues, representing a great opportunity for valorization and use towards obtaining novel products. Selected LRB present similar HCV around 16.50 MJ kg^{-1} except the spent coffee (SC), which has the highest calculated heat capacity (22.92 MJ kg^{-1}).

3.1 Moisture, ash and extractives fractions of lignocellulosic residual biomass

Figure 1 shows the moisture, water and ethanol/toluene extractives, and ash contents of the selected biomasses. Moisture is presented as reference of initial conditions of biomass, however, the other fractions are presented on a dry basis. The moisture contents of LRB are relatively low (less than 10%), except for the cocoa husks, which present a moisture content of around 12%. According to Escalante et al. (2010), these biomasses can be used to generate energy by direct combustion, pyrolysis or gasification in different sub processes of harvest due to its low moisture content. On the other side, the ash content plays an important role for this application due to biomasses having an ash content higher to 5 wt.% are not recommended for energy production by thermal ways, since ashes reduce its calorific power (Escalante *et al.*, 2010). Therefore, LRB such as cocoa shell (CS), coffee husk (CH), bean stubble (BS) and empty fruit bunch from oil palm (EFBOP) are not recommended for the generation of energy by combustion.

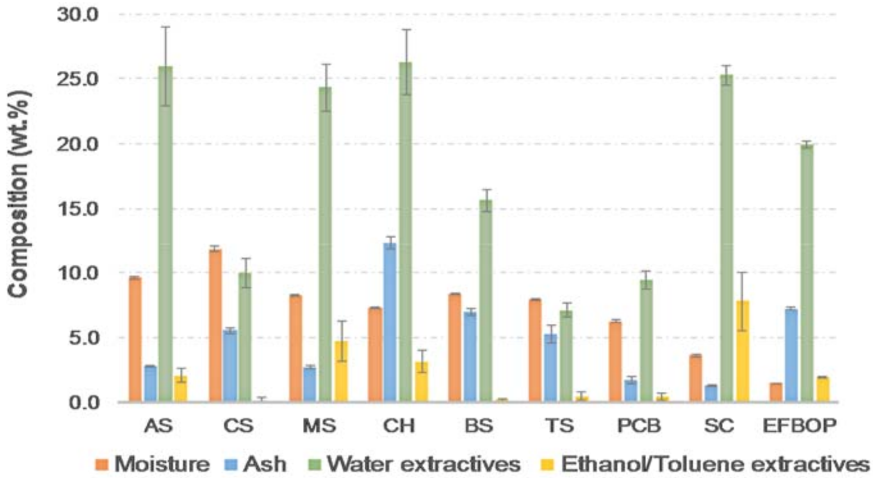

Figure 1. Composition of biomasses analysed in their moisture, ash and extractive fraction. Avocado seed (AS), cocoa shell (CS), mango seed (MS), coffee husks (CH), bean stubble (BS), tobacco stems (TS), panela cane bagasse (PCB), spent coffee (SC) and empty fruit bunch from oil palm (EFBOP).

The LRB analysed contained a higher fraction of water extractives (mineral salts, starch silicates, etc) than ethanol/toluene extractives (fatty acids, resins, tannins, etc.). The extractive fractions include non-structural components of material (non-chemically bound components) which depend on the nature of the residual biomass. Because these biomasses are mostly husks, branches and bagasse, do not contain a significant amount of organic extractive matter (Abril and Abril, 2009). According to Demirbas (2005), the HCV is affected by the proportion of combustible organic components (called as extractives) that are present on it.

3.2. Holocellulose and lignin contents

Figure 2 presents the holocellulose, α-cellulose and lignin fractions of LRB. Holocellulose corresponds to the total polysaccharide fraction of biomass and is made up of cellulose and hemicellulose, this fraction is obtained by removing the extractives and the lignin from the original natural material. The hemicellulose and cellulose (α-cellulose) contents define the future application of biomasses for obtaining oligomers. Holocellulose fraction in the analysed samples varies between 41 to 71 wt.% being the higher values for panela cane bagasse (PCB) and tobacco stems (TS). On the other side, the higher fractions of hemicellulose were obtained for TS, PCB and AS, 36 wt.%, 35 wt.% and 41 wt.%, respectively. The cellulose is a highly uniform 1-4-β-linked poly-glucan, while the hemicelluloses are constituted by polysaccharides of different structure containing glucose, xylose, mannose, galactose, arabinose, fucose, glucuronic acid, and galacturonic acid in various amounts or traces dependent on the natural source (Ebringerová and Heinze, 2000). The content of hemicellulose and its composition are essential for the production of oligosaccharides having prebiotic activity.

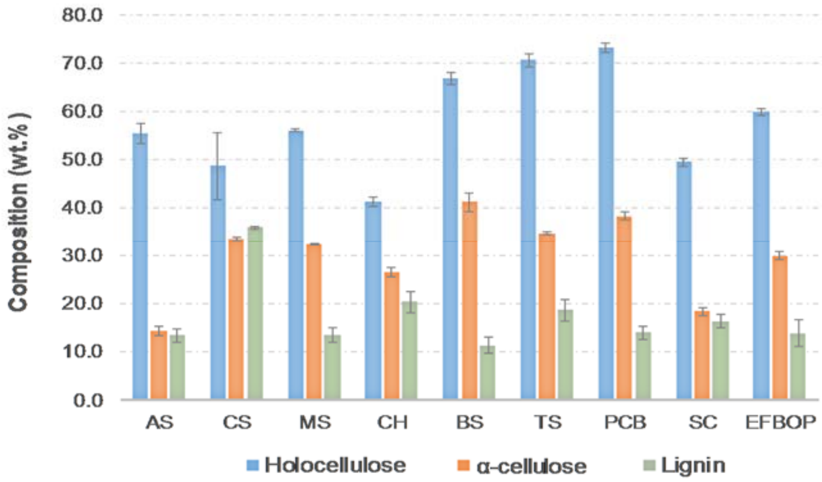

Figure 2. Chemical composition of selected lignocellulosic materials. Avocado seed (AS), cocoa shell (CS), mango seed (MS), coffee husks (CH), bean stubble (BS), tobacco stems (TS), panela cane bagasse (PCB), spent coffee (SC) and empty fruit bunch from oil palm (EFBOP).

According to Farinas (2015), the plant cell wall consists primarily of cellulose (20–50% on a dry weight basis), hemicellulose (15–35%) and lignin (10–30%), similar values to those obtained for the LRB analysed. The cocoa shell presented the highest lignin content between the analysed biomasses. While cellulose and hemicellulose are constituted mainly by carbohydrates, lignin is a highly complex polymer molecule having aliphatic and aromatic portions, that can be used for the production of animal feeds, coatings, agricultural chemicals, micronutrients and lignosulfonates. The composition of the structural carbohydrates and lignin obtained from biomass may vary, even within the same species, according to the climate conditions, the fertilizer used during culture, mineral contents of the soil, among others (Álvarez *et al.*, 2017).

3.3 Compositional analysis of simple sugars by HPLC

Figure 3 shows the carbohydrate profile of the different biomass determined by HPLC analysis of the liquor obtained after klason lignin procedure. As it can be observed, the predominant simple sugar is glucose, except in SC and EFBOP. The residual biomass obtained from coffee agroindustry presented the lowest cellulose contents (as glucan), 7.9 wt.% and 10.0 wt.% for SC and CH, respectively.

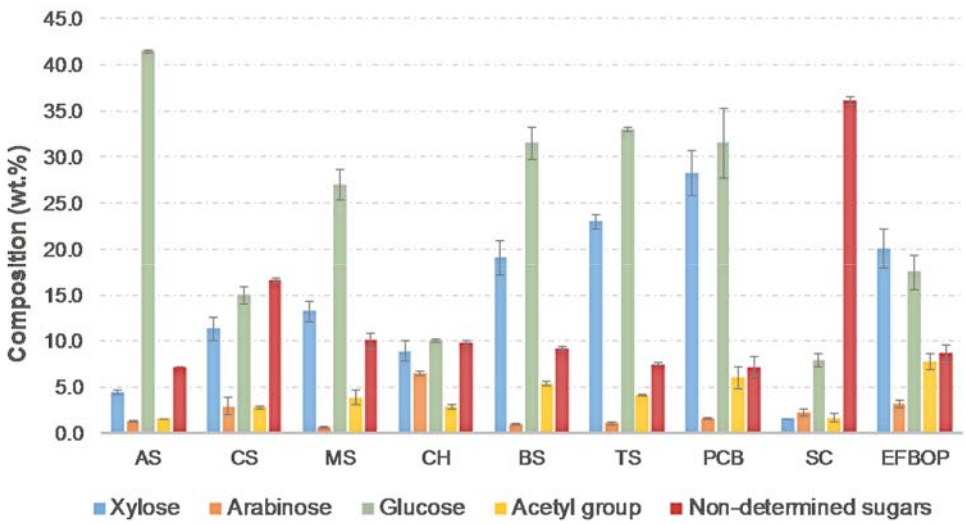

Figure 3. Carbohydrate composition of selected lignocellulosic materials. Avocado seed (AS), cocoa shell (CS), mango seed (MS), coffee husks (CH), bean stubble (BS), tobacco stems (TS), panela cane bagasse (PCB), spent coffee (SC) and empty fruit bunch from oil palm (EFBOP).

LRB with higher contents of glucose can be used as raw material in fermentation processes for fuel and/or energy generation (García-Acero, Velásquez and Brandão, 2017). However, biomass such as TS, PCB, CS and EFBOP have a xylose/glucose ratio greater than 0.7 and have a hemicellulose content (expressed as the sum of xylose, arabinose and acetyl groups) higher than 17 wt.%, representing an alternative source for the extraction of xylan. Xylans are the most common hemicelluloses and they are considered to be the second most abundant biopolymer in the plant kingdom, while its derivatives are gaining increasing importance as new biopolymer-based materials and functional polymers, pharmaceutical precursors and production of XOs or AOs. Xylan also contains variable amounts of glucuronic acid and some phenolic acids, besides other simple sugars (e.g mannose, galactose) were not quantified by the HPLC analytical procedure. The non-determined sugars, in this case, were quantified by weight difference in dry basis, representing a considerable amount for SC (higher than 36%), confirming that extracted hemicellulose can have a different structure depending on the biomass used.

3.4 Potential production of oligomers from LRB analyzed

Considering the annual generation of residual biomass (Table 1), the carbohydrate composition determined by HPLC, and assuming that the extraction of sugars as oligomers is possible (Nabarlatz, Ebringerová and Montané, 2007), a theoretical yield for oligosaccharides extraction from each LRB was quantified. Figure 4 presents the potential production of oligosaccharides (tones year^{-1}) from Colombian residual biomass. CH, PCB and EFBOP presented the highest availability for the production of oligosaccharides such as XOS and AOS, exceeding 1 million and 117,000 tons year^{-1}, respectively. Although biomasses such as BS and TS had a xylose content of more than 19 wt.%, the amount of residues generated is very low compared with the previous ones. In addition, the disperse location of the generated biomass and the difficulties in its collection may present a drawback for this application.

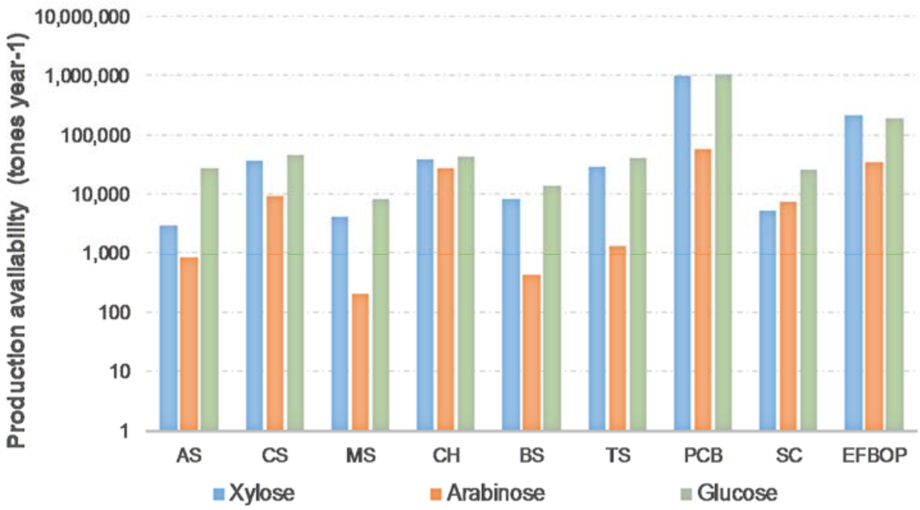

Figure 4. Potential production of oligosaccharides from Colombian lignocellulosic residual biomass. Avocado seed (AS), cocoa shell (CS), mango seed (MS), coffee husks (CH), bean stubble (BS), tobacco stems (TS), panela cane bagasse (PCB), spent coffee (SC) and empty fruit bunch from oil palm (EFBOP).

4. Conclusions

The biomasses analysed in this work represent part of the Colombian agricultural potential and can be used in different applications depending on their composition, from energy recovery to applications in the food and pharmaceutical industry. The composition of the LRB was determined and based on this information, its theoretical potential to produce oligomers was evaluated. CH, EFBOP and specially PCB are the agroindustrial residues that presented the greatest potential for oligosaccharide extraction. This analysis opens the expectation for future studies in the extraction of hemicellulose through hydrolysis processes and the utilization of byproducts rich in lignin and cellulose. Despite the generation of residual biomass such as CS, BS and TS is low, these can be used for medium and small-scale applications. Avocado seed (AS) and mango seed (MS) have a xylose/glucose ratio of 0.1 and 0.5, respectively, favoring applications such as the production of second generation fuels due to its glucose content.

Acknowledgments

The authors are indebted to VIE from Universidad Industrial de Santander for financial support (Internal financed project cod. 1881). R. Acosta is grateful to Colciencias for the PhD scholarship.

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