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Research Paper

Classification of biomass through their pyrolytic bio-oil composition using FTIR and PCA analysis

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ABSTRACT

Fourier transform infrared (FTIR) spectroscopy, combined to principal components analysis (PCA), was applied in the classification of biomasses through the composition of their bio-oil. Bio-oils were produced through pyrolysis in a bed fixed reactor, using fifteen biomass sources available in Brazil and its characterization was made using gas chromatography coupled to mass spectrometric detector (GC/qMS). Around two hundred compounds were tentatively identified in the fifteen bio-oil samples. As expected, the chemical compositions in each bio-oil were distinct. Through the chromatographic information and PCA of the FTIR spectra it was possible observed the similarity and dissimilarity of biomasses according their bio-oil compositions. PCA revealed that FTIR spectra of biomasses fell into three different groups representing distinct bio-oil chemical compositions. The biomasses that belong to group 1 showed bio-oil compositions rich in carboxylic acids, the group 2 showed bio-oil compositions consisting predominantly of phenols and group 3 showed bio-oils with a significant amount of nitrogen compounds. Such clustering information allow exploring bio-oil quality prior to pyrolysis process.

1. Introduction

The use of biomass as a renewable source of energy can reduce the dependency on fossil sources (Jahirul et al., 2012). In Brazil and in the world, the agro-industrial wastes are an interesting biomass source due to the large amount generated per year and to the environmental problems associated with them. In the year 2015, only for sugarcane, cassava and coconut crops Brazil was responsible for more than 750, 22, and 5 million tons, respectively (IBGE, 2017; Rambo et al., 2015). For every ton of sugarcane, rice and coconut produced, approximately 250 kg of waste is generated and for cassava 490 kg of waste is generated (Rambo et al., 2015; Pattiya and Suttibak, 2012). Brazil also is known as one of the largest producers of rice, with an annual production of approximately 12 million tons. Agro-industrial wastes from rice processing are equivalent to 3 million tons annually (Rambo et al., 2015; IBGE, 2017). Some of other agro-industrial wastes generated in high amount in Brazil are coffee husk, peanut shell, mango waste, pineapple leaves, cottonseed, peach pit, peanut shell and wood.

Pyrolysis is a promising way to convert these biomasses into high-value products. The process of pyrolysis consists of the thermal decomposition of biomass at high temperatures and in the complete absence of oxygen to obtain gas, solid (bio-char) and liquid (bio-oil) products (Bridgwater, 2012). In recent years, bio-oil has received a lot of attention due to its potential uses as biofuel (after upgrading process) or as a starting material for producing chemicals (Czernik and Bridgwater, 2004).

Bio-oil is a complex mixture of water and a hundred of organic compounds that can be classified into the following categories: phenols, ketones, acids, esters, aldehydes, alcohols, furans, anhydrous-sugars, nitrogen containing compound, hydrocarbons, carboxylic acids (Jahirul et al., 2012). The distribution of these compounds in the bio-oil depends mainly on the variability of different proportions of lignin,

Abbreviations: AB, aquatic biomass; AMS, almond of mango seed; CF, coconut fibers; CP, cassava peel; CS, crambe seed; CSK, coffee silverskin; CTS, cotton seed; DCM, dichloromethane; ES, eucalyptus sawdust; ETS, energetic tobacco seeds; FTIR, Fourier transform infrared spectroscopy; GC/qMS, gas chromatography coupled to mass spectrometric detector; LTPRI, linear temperature programmed retention indexes; PC, peach cores; PCA, principal components analysis; PL, pineapple leaves; PLS, partial least squares; PS, peanut shell; RH, rice husk; SCB, sugarcane bagasse; SCG, spent coffee grounds

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Table 1
Details of the investigated biomasses.

Biomasses	Samples ID	Provided by local/industry[a]
Almond of Mango Seeds	AMS	Food industry, Dourados, MS, Brazil.
Coconut Fibers	CF	Embrapa, Aracaju, SE, Brazil
Pineapple Leaves	PL	Local market, Porto Alegre, RS, Brazil.
Sugarcane Bagasse	SCB	Food industry, Porto Alegre, RS, Brazil.
Cotton Seeds	CTS	Planalto Farm, Costa Rica, MS, Brazil.
Coffee Silverskin	CSK	Marata Industry, Itaporanga D'Ajuda, SE, Brazil.
Rice Husk	RH	Food industry, Pelotas, RS, Brazil.
Eucalyptus Sawdust	ES	CMPC Cellulose Industry, Guaíba, RS, Brazil.
Peach Cores	PC	Schrann Food Industry, Pelotas, RS, Brazil.
Spent Coffee Grounds	SCG	Local market, Porto Alegre, RS, Brazil.
Peanut Shell	PS	Local market, Porto Alegre, RS, Brazil.
Cassava Peel	CP	Food industry, Dourados, MS, Brazil.
Aquatic Biomass (duckweed)	AB	Pelotas, RS, Brazil
Crambe Seeds	CS	UERGS, Porto Alegre, RS, Brazil.
Residual Cake from Energetic Tobacco Seeds[b]	ETS	UNISC, Vale do Rio Pardo, RS, Brazil.

[a] Different Brazilian regions which show high biomass production.

[b] Residual cake was obtained by extraction of seeds of energetic tobacco.

polysaccharides (cellulose and hemicellulose), protein, triglycerides etc., in the biomass (Jahirul et al., 2012; Sharma et al., 2015).

Bio-oil applications are strongly influenced by their chemical composition and by the type of upgrade used to improve the quality of this bio-oil (Bridgwater, 2012; Czernik and Bridgwater, 2004). As its composition depends largely on the composition of the original biomass, it is necessary to know it and to associate it with the characterization of the bio-oil produced. Many authors demonstrated the production of bio-oil by pyrolysis and characterization their chemical composition using chromatographic techniques (Muradov et al., 2010; Lazzari et al., 2016; Almeida et al., 2013; Bispo et al., 2016; Faccini et al., 2013; Moraes et al., 2012). However, the biomass-to-bio-oil conversion process can be optimized using rapid methods for biomass characterization that allow pre-defining bio-oil quality prior to pyrolysis process.

In this context, FTIR is a non-destructive, simple, fast and cheap instrumental technique that has been used successfully in the analysis of the chemical composition of several biomass sources (Xu et al., 2013; Chadwick et al., 2014). It is likely that FTIR spectra might contain small differences between two biomasses that could not be distinguished visually, thus, multivariate data tool as PCA, are necessary for spectra analysis (Liu et al., 2015, 2016). PCA is an effective variable reduction technique for spectroscopic data (Liu et al., 2015). In the PCA their scores on new principal components (PCs) evidence the correlations among spectra (or samples). Similar samples appear as clusters in the score plot, while different samples appear segregate from each other (Liu et al., 2015, 2016). In a number of studies, spectroscopic data were associated with multivariate techniques for the rapid characterization of biomass samples for energy purposes. Everard et al. (2012) reported the use of online vis-NIR spectral sensing techniques in conjunction with partial least squares (PLS) and PCA for the rapid analysis of ash, carbon content and moisture of Miscanthus and two varieties of willow. In the results obtained, the PCA allow distinguished the different biomass types and the PLS gave strong prediction for the carbon content and moisture of the samples. Chen et al. (2010) reported satisfactory results for the prediction of lignin, cellulose and hemicellulose contents in wood samples using the FTIR spectral data in conjunction with PLS. Through the FTIR and PCA, the wood samples were discriminated into hardwoods and softwoods, in addition, wood samples with and without chemical treatments could also be differentiated. More recently, Liu et al. (2016) described the application of the FTIR associated with PCA to discriminate cotton plant biomass fractions. The results allowed evaluating the differences in the accumulation of carbohydrates among the samples.

The aims of the present study were to obtain and characterized by GC/qMS bio-oils from the pyrolysis of fifteen biomass sources available in Brazil and to use for the first time the FTIR data and PCA analysis to classify the biomass through their bio-oil composition.

2. Materials and methods

2.1. Biomass samples

Fifteen biomasses were investigated in this study. Among the biomasses evaluated twelve are agro-industrial waste: almond of mango seed (AMS); coconut fibers (CF); pineapple leaves (PL); sugarcane bagasse (SCB); cotton seed (CTS); coffee silverskin (CSK); rice husk (RH); eucalyptus sawdust (ES); peach cores (PC); spent coffee grounds (SCG); peanut shell (PS) and cassava peel (CP). These wastes represent a considerable environmental problem in Brazil, due to the large amounts produced per year.

Other biomasses evaluated were: aquatic biomass (AB) (commonly known as duckweed), crambe seed (CS) and residual cake from energetic tobacco seeds (ETS). Aquatic biomass does not compete with agriculture for land usage (Muradov et al., 2010), crambe is an interesting non-food source of seed oil (Onorevoli et al., 2014) and energetic tobacco seeds are a new biodiesel source available.

The great diversity of assessed biomass allows the representation of different biomass sources available in Brazil, which show distinct chemical composition, and exhibit potential for the production of bio-oil via pyrolysis.

Some of these biomasses have already been studied in our research group through pyrolysis as AMS (Lazzari et al., 2016), CS (Onorevoli et al., 2014), CF (Almeida et al., 2013; Bispo et al., 2016), SCG (Bispo et al., 2016), PC (Moraes et al., 2012), RH (Moraes et al., 2012) and ES (Faccini et al., 2013; Schneider et al., 2014).

Details of the biomasses investigated in this study are described in Table 1.

All the biomasses were ground in an industrial blender to produce a sub-sample at 28–60 mesh and dried in an oven at 110 °C during 24 h to remove moisture.

2.2. Pyrolysis process

All the fifteen biomasses were subjected to intermediate pyrolysis in a homemade vertical furnace containing a tubular fixed-bed quartz glass reactor. Schematic diagram of the reactor and furnace system was illustrated elsewhere (Faccini et al., 2013). An electrical furnace heated the reactor and nitrogen was used as carrier gas. The pyrolysis vapors were cooled through condenser at −10 °C, using a mixture of ethylene glycol and water (1:1).