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Valorization of coffee silverskin industrial waste by pyrolysis: From optimization of bio-oil production to chemical characterization by GC × GC/qMS

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ABSTRACT

Coffee bean tegument (silverskin) is a by-product derived from the coffee roasting process. This residue has been discarded, which constitutes a serious environmental problem. The depletion of oil reserves and environmental issues promoted by the combustion of fossil fuels has generated interest in the use of biomass to obtain fuel and chemicals products. The liquid product obtained by biomass pyrolysis is commonly called bio-oil. Bio-oil is a complex mixture of compounds, and its detailed chemical characterization is necessary to prospect its potential uses. Therefore, this study optimized the final temperature of pyrolysis and N_2 flow rate parameters for the pyrolysis of silverskin in a fixed bed reactor, by using a central composite design and response surface. The bio-oil chemical composition was evaluated by comprehensive two-dimensional gas chromatography coupled to rapid-scanning quadrupole mass spectrometry (GC × GC/qMS), combined with the use of standards and linear temperature-programmed retention indices (LTPRI). The optimal values calculated were 560 °C for the final pyrolysis temperature and 49 mL min^{-1} for the N_2 flow rate. The organic phase yield was 15.2% under these conditions. At the optimal conditions, 228 compounds were identified (90.1% of the sample chromatographic volume) in the organic phase. The major chemical class, in terms of volume percentage, were the phenols (26.70%), followed by nitrogen compounds (18.51%). In addition, it is worth mentioning the high representability of the saturated hydrocarbons (8.28%), unsaturated aliphatic (6.69%), and aromatics (7.77%), which together account for 22.74% of the sample chromatographic volume. These results showed that the silverskin bio-oil may have the potential use as a source of chemical inputs.

1. Introduction

Coffee is one of the most valuable primary products in world trade since it is one of the most consumed popular beverages worldwide and the second largest traded commodity after crude oil [1]. Approximately 151.6 million bags of coffee were produced globally in 2016 [2]. Due to its great production, large amounts of by-products are generated during the industrial processing of coffee beans since more than 50% of the coffee fruit is discarded during its processing [3]. However, few studies have been addressed to the reuse of the residues and the disposal of these by-products remains an environmental concern [1].

Coffee silverskin (CS) is a thin tegument of the outer layer of coffee beans and represents about 4.2% (w/w) of coffee beans, being the only by-product generated during the coffee roasting process. The CS chemical composition is mainly composed by cellulose and hemicelluloses; besides, proteins and extractives are present in significant amounts [4,5]. Because of its chemical composition, some studies have been recently developed suggesting the use of CS as a source of dietary fiber and antioxidants [4–12], prebiotics [4,13], and bioactive compounds [6,14,15]. However, currently, this material has no commercial value, being mostly disposed of as industrial waste, since the definitive reuse of CS has not yet been developed. This practice represents serious environmental problems due to the toxicity of this waste to plants and microorganisms present in the soil, as a result of the high content of caffeine, polyphenols, and tannins present in this residue. Therefore, CS can be regarded as biomass which is expected to be utilized [16–19].

Increasing attention has been focused on biomass, since it can be

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converted into various forms of energy and fuels by different processes (e. g. biological, mechanical and thermochemical processes) according to the types of raw materials and products desired [20–22]. Among the biomass valorization processes, its thermochemical conversion has attracted interest, being a promising substitution for fossil materials in many applications. Currently, the most common thermochemical processes are gasification, pyrolysis, and combustion. Pyrolysis process is a clean and renewable source of energy, fuels and chemicals, and consists of the thermochemical decomposition of biomass, in the absence of oxygen, to obtain gaseous, liquid (bio-oil), and solid (biochar) products [20,23,24]. In recent years, liquid products obtained from the pyrolytic processing of biomass have received considerable attention. Bio-oil consists of a dark brown organic liquid, that approximates biomass in elemental composition and thus may exhibit varying properties, depending on the feedstock, presenting potential uses such as second-generation biofuel or as a starting material for numerous chemicals [20,25–27]. This liquid product has a high chemical complexity, consisting of a wide variety of polar and non-polar organic compounds with different molecular-weight distributions, that can be classified according to their water solubility into high-polarity compounds (aqueous phase) and low-polarity compounds (organic phase) [28,29]. Therefore, in order to get improved insight into the chemical composition of bio-oils, as well to better assess their potential uses, detailed chemical analysis techniques are necessary.

GC/MS is the standard tool for characterization of the organic phase from bio-oils. However, this technique often does not provide satisfactory analytical results in samples of high chemical complexity, due to the insufficient resolution power of a single separation column [30]. In this case, a higher peak capacity is required to achieve a satisfactory resolution. Comprehensive two-dimensional gas chromatography (GC × GC) [31], besides producing high peak capacities, increases both resolution, and detectability, allowing the detection of compounds at trace levels and separation of related compounds in the second column [32]. However, only its coupling with a mass spectrometer (MS) provides structural information about the analytes. Therefore, an MS fragmentation pattern is indispensable for many identification purposes [33].

The MS coupling with a GC × GC instrument is an important consideration since it produces very small base-width chromatographic bands (generally 50–300 ms), which may be 5–1000 times narrower than those obtained in the conventional GC/MS, which requires detectors with a high data acquisition. Time-of-flight mass spectrometer (TOF-MS) are the main mass analyzer applied for GC × GC since it easily reaches the required acquisition parameters (50–100 Hz) for reliable GC × GC peak assignment [34]. However, its high cost is a significant limitation in laboratory use. Fortunately, the enhancement of the less expensive and more user-friendly quadrupole mass spectrometry (qMS) to achieve the high acquisition rates requirements of two-dimensional systems have allowed its consolidation in the GC × GC field. However, to the best of our knowledge, there are only two reports in the scientific literature data about the use of GC × GC/qMS for the chemical characterization of bio-oils [35,36]. Cunha et al. (2013) described the application of GC × GC/qMS for the chemical characterization of bio-oil from the pyrolysis of sugar cane straw and its fractions, tentatively identifying with LTPRI 166 compounds in the crude oil [36]. Schneider et al. (2014) also described the successful application of GC × GC/qMS for the chemical characterization of a sawdust bio-oil extract, tentatively identifying 130 compounds [35]. Therefore, the aim of the present study was to optimize some of the main parameters involved in the coffee silverskin pyrolysis by response surface methodology (RSM) and to evaluate the chemical composition of its organic fraction by GC × GC/qMS. Linear temperature-programmed retention indices were used to achieve a more reliable peak assignment.

2. Material and methods

2.1. Raw material

Coffee Silverskin was used in the pyrolysis experiments. The biomass was a residue from the coffee roasting process, provided by Café Maratá industrial complex, located in Sergipe, northeast of Brazil. The CS sample was dried at approximately 110 °C for 24 h, triturated in a mill (Wiley Mill Model no. 2, Arthur H. Thomas, Philadelphia, USA), and sieved to produce a sub-sample with a particle size between 2.38 and 1.19 mm.

2.2. Reagents and standards

All standard compounds and reagents used in the present study were of chromatographic grade and were obtained from Sigma–Aldrich (Saint. Louis, MO, USA). A standard mix containing the following 12 compounds (1 ppm) was prepared for the GC × GC/qMS analyses: furfural (99%), phenol (≥ 99.5%), 3-methyl-1,2-cyclopentanodione (99%), *p*-cresol (99%), *o*-guaiacol (≥ 99%), *p*-xylenol (≥ 99%), 3,4-xylenol (98%), *o*-benzenediol (≥ 99%), hydroquinone (≥ 99.5%), resorcinol (≥ 99%), syringol (99%), and caffeine. A linear C_6-C_{30} *n*-alkane mixture (100 ppm) was prepared to calculate the LTPRIs [37]. Standard mix and C_6-C_{30} *n*-alkane mixture were prepared by weighing appropriate amounts of standard, and diluting in dichloromethane (DCM) and stored at −4 °C.

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of CS was performed in order to investigate the temperature range for the effective pyrolysis of the biomass. The analysis was performed on a TGA Q5000 coupled to an infrared spectrometer (TA Instruments, New Castle, DE, USA). The CS sample, weighing 2,79 mg, was kept under an ultra-pure N_2 flow rate of 25 mL min^{-1} (99.999%, Linde Gases, Canoas, RS, Brazil), and heated from 25 °C to 1000 °C at a constant heating rate of 10 °C min^{-1} [38].

2.4. Pyrolysis process

CS samples pyrolysis were performed in a homemade vertical electrical heating furnace containing a tubular fixed-bed quartz reactor. The reactor was externally heated by an electrical furnace with 1.7 kW power. The quartz reactor had two openings: one used for N_2 gas supply, and the other one to exit the vapors generated during the pyrolysis process. Before each experiment, a weighed sample of CS (about 6.00 g) was introduced into the quartz reactor in the pyrolysis oven and the apparatus was fluxed with a nitrogen stream for 5 min. Then, the sample was heated from 25 °C to the set temperature at approximately 100 °C min^{-1} and remained at this temperature for about 10 min (till no more vapors are formed). The reactor was attached to two glass gas condensers: the first one with 30 cm length and 5 cm diameter, and the second one with 10 cm length and 2 cm diameter. In this condensers, a mixture of ethylene glycol and water (1:1) at about −10 °C was circulated to cool and condense the vapors resulting from the pyrolytic process. The condensed liquid products (crude bio-oil) and the residue left inside the reactor as solid char were collected and weighted for mass yield calculation (w/w%). Gaseous product yield was estimated by material balance as a difference between the total amount of biomass used, and the sum of liquid and solid pyrolytic products yield. After each pyrolysis, the system was cleaned with DCM and completely dried with a hot air stream prior to the next process [39].

Crude CS bio-oils were separated into aqueous and organic phases by liquid–liquid extraction (LLE) at pH 2.5. In the LLE process, the crude bio-oils were extracted with five portions of 5 mL of DCM in a separation funnel. Dichloromethane aliquots were mixed and its

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