



Full Length Article

Influence of the temperature in the yield and composition of the bio-oil from the pyrolysis of spent coffee grounds: Characterization by comprehensive two dimensional gas chromatography



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ABSTRACT

Coffee is an important agricultural product being one of the most consumed beverages in the world. The goal of this work is to apply the pyrolysis to this residue for the production of bio-oil. The pyrolysis of the biomass (SCG) was done in a fixed bed reactor and varying the final temperature (400, 450, 500, 550 and 600 °C). The higher crude bio-oil yield was obtained at 500 °C with a flow of N₂ in 100 mL/min (mass yield = 30.51%). The bio-oil produced by pyrolysis of SCG had its chemical composition analyzed by comprehensive two-dimensional gas chromatography coupled to mass spectrometry detector (GC × GC/TOF-MS) and associated with LTPRI. This bio-oil showed potential for the production of chemical and liquid fuels, evidencing to be a good option for the destination of this waste. Its composition showed high amount of phenols, fatty acids and nitrogen compounds. The major compounds in the bio-oil sample were n-hexadecanoic acid (palmitic acid) (19%), 9-octadecenoic acid (oleic acid) (11%), octadecanoic acid (stearic acid) (10%).

1. Introduction

The combination of increased energy demand and depletion of fossil fuel sources, coupled with growing evidence of environmental problems [1] have motivated several researches to solve these problems through alternative forms of renewable and environmentally correct energies [2,3]. In this way, an interest in unconventional sources such as wind, solar, hydropower and biomass has grown [4].

Biomass derives from material that has a living, organic origin, and can be animal, vegetable and microorganisms. More specifically, it is related to a variety of organic materials, which can take various forms, such as wood, sawdust, agricultural and industrial waste, paper waste, household waste, sewage, among others [5]. The agro industrial waste, as stalk and straw of rape plant [6], cotton seed cake [7], banana leaves [8], hazelnut hull [9], apricot seed [10], sweet sorghum [11], has a great prominence due to its lignocellulosic composition, which is equivalent to a high energy content.

Biomass can be used as a source of energy, either directly or indirectly. Directly, heat is produced as an immediate energy product, through its combustion [12]. The indirect form is the combustion after

passing through a process, which can be: physical, thermodynamic (pyrolysis, gasification and liquefaction) or biological (anaerobic digestion and fermentation), resulting in a second energy source. Examples of secondary energy sources of biomass are biofuels, firewood, charcoal and gas [13–16].

Pyrolysis can be defined as a physicochemical process of thermal decomposition of organic substances, occurring under inert atmosphere (nitrogen) and at high temperatures (generally between 500 and 1000 °C). The main products are solid (ash and coal), liquid (bio-oil and water phase) and gaseous (light hydrocarbons and other gases) [17,18]. Bio-oil can be considered as an alternative to petroleum, both in energy aspect or for petrochemical industry. The conversion of solid biomass into a higher energy content product (bio-oil) for using as biofuels or chemicals, is one of the main aspects of the pyrolysis [17], facilitating handling and transport if compared to solid and gaseous fuels [18].

The crude bio-oil comprises a large amount of water, some solid particles and hundreds of organic compounds that belong to hydrocarbons, oxygenated and multifunctional compounds [19]. These compounds represent a wide range of chemicals compounds with recognized industrial importance [20–23] besides a variety of

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hydrocarbons potentially applicable as alternative fuels.

The use of residues plays an important role in the application of non-food biomasses to produce bio-oils [2]. One example of residual biomass with high impact in the environment and in the economy is the spent coffee ground (SCG), that is the residue obtained during the preparation of the beverage and was produced in large quantities, as in commercial establishments or in homes and does not have any important use. Coffee (*Coffea arabica L./Coffea canephora*) is the most important food commodity in the world and ranks second, after petroleum, among all commodities [23–25].

The amount of this residue is very high (around of 90% of the mass of coffee used) and it is normally disposed in landfills causing environmental problems due to the presence of complex organic substances (e.g.; caffeine, tannins and polyphenols) [26].

The pyrolysis of SCG has been discussed in previous studies [27–29]. some of them for producing bio-oil and bio-char [27]; for determining the influence of the temperature in the quality of the bio-oil [28]; or for developing a technique to characterize the bio-oil produced from the fast pyrolysis [29].

Currently, comprehensive two dimensional gas chromatography (GC × GC) have gained much attention for the analysis of bio-oils [30–32]. GC × GC provides the separation of the components of sample in two dimension using orthogonal columns in the first and second dimension. These independent mechanisms produce excellent results. In addition, the combination of GC × GC with a fast scanning time-of-flight mass spectrometer (TOFMS) increases the separation capacity, resolution, sensitivity and identification quality of complex mixtures.

Our research group has been published many studies in the characterization of bio-oils by GC × GC, using different biomasses (softwood and hardwood forest industry residues, sugar cane straw and bagasse, coconut fibers, among others) and using different equipments (GC × GC/qMS and GC × GC/TOFMS) [33–38].

Another important tool that assists in the identification of compounds is the retention index (RI), initially proposed by Kovatz and later modified by Van den Dool and Kratz [39] and adapted to GC × GC according von Muhlen et al. [40] The LPTRI (Linear Programmed Temperature Retention Indexes) can be calculated using a homologue series of linear alkanes and compared to libraries, aiding the identification of a great amount of compounds [37,38].

The purpose of this paper is to produce bio-oils from domestic SCG and characterize them by Fourier Transform Infrared Spectroscopy (FT-IR), GC × GC/TOFMS using LPTRI indexes, determining their chemical composition and indicating possible uses for this biomass.

2. Experimental

2.1. Materials and samples

Dichloromethane (DCM), acetone, ethanol, hexane, ethyl acetate, CO₂, anhydrous Na₂SO₄, and Silica Gel 60, (0.063 mm (+ 230 mesh) were purchased from Merck (Darmstadt, Germany). Reference standards and linear alkanes, were purchased from Sigma–Aldrich (Saint Louis, MO, USA). The snack bar of the Federal University of Rio Grande do Sul (Campus do Vale, Porto Alegre, Brazil) supplied the SCG. The biomasses was dried in an oven at 105 °C for 2 h without any pre-treatment.

2.2. Initial biomass characterization

The determination of moisture, volatile compounds, and ashes of the SCG were performed according to the ASTM standard methods E1756-01, E872-82 and E1755-01, the fixed carbon was determined by difference.

TGA (Thermal gravimetric analysis) was employed to evaluate the temperature at which high mass loss occurs for the SCG. The analysis was performed on a TGA equipment Q5000 coupled to an infrared

spectrometer (Thermo Scientific – Nicolet 6700) under an inert atmosphere (ultra-pure N₂ at 25 mL min⁻¹), heating from 25 °C to 1000 °C at 10 °C min⁻¹.

2.3. Pyrolysis

For the fast pyrolysis, a tubular furnace and a quartz reactor, built at the Institute of Physics of UFRGS, were used. The pyrolysis process was based on our group's previous work and the complete detailing of the equipments can be viewed in the literature [34–36,41]. Ten grams of biomass were used for each experiment, with a gas flow (N₂) of 150 mL min⁻¹. The vapors, together with the bio-oil, are charged by the passage of the nitrogen gas through a condenser (with circulation of ice water: T ~ -5 °C) in order to provide the condensation of the gases, which are collected in the collection flask.

The heating rate was 100 °C min⁻¹, until reaching the final temperature. It was tested four temperatures (400, 450, 500, 550, 600 °C) and the process was maintained at this final temperature for 15 min. The mass yield (w/w%, for triplicate analysis) was determined by weighing the liquid phase (crude bio-oil) and solid products (bio-char) with reference to the initial weight of solid biomass. The non-condensable products (gases) plus losses in the system was determined by difference. The efficiency of the process was defined as the condition that produces the higher amount of bio-oil. The crude bio-oils were separated into aqueous and organic phases by liquid–liquid extraction (LLE), using five portions of 5 mL of DCM for aiding the phase separation.

2.4. Bio oil characterization

2.4.1. Analysis by FT-IR

The samples of the organic fraction of bio-oil (without dissolution or any pre-treatment) from SCG was analyzed by FT-IR being inserted directly into the reading cell of the equipment. The spectra was obtained in a Bruker spectrometer, model ALPHA FT-IR from 4000 cm⁻¹ to 400 cm⁻¹, using 24 scans for each spectra.

2.4.2. Analysis by GC × GC/TOFMS

For analysis of the samples and fractions of bio oil, was utilized a GC × GC (Agilent Technologies, Palo Alto, CA, EUA) with a Pegasus IV (Leco, St. Joseph, MI, USA) time-of-flight mass spectrometric system, equipped with a secondary oven, cryogenic quad-jet modulator refrigerated with liquid nitrogen and a CTC-CombiPal (Analytix AG, Zwingen, Switzerland) auto sampler. The column set used was formed by a DB-5 (95% dimethylpolysiloxane and 5% phenyl groups) with 60 m in length, 250 μm of i.d. and 0,25 μm of thickness phase in the first dimension and a DB-17-ms (50% phenyl and 50% dimethylpolysiloxane) with 2,5 m in length, 180 μm of i.d. and 0,18 μm of film thickness in the second dimension. Both columns were purchased from J & W Scientific (Folsom, CA, USA).

The parameters used for these analyzes, after a previous step of optimization were as follows: injector temperature and ion source of 280 °C; splitless injection volume of 1 μL and samples concentration equal to 10,000 μg mL⁻¹. The oven heating program started at 60 °C for 1 min, heating rate at 3 °C/min until 280 °C. Second oven was maintained at 5 °C above the first one. The carrier gas was helium at flow rate of 1 mL/min. Modulation period was 8 s with hot pulse of 0.6 s. Mass spectrometer operated in a mass range of 45–400 Da and using 100 scans per second (100 Hz) [34–36,41].

2.5. Data acquisition for qualitative and semi-quantitative analysis

From the injections of bio-oils and fractions in the GC × GC/TOFMS, the data were processed using the ChromaTOF software version 3.32. After processing, solvent peaks, column bleed peaks, peaks of low intensity and low area very (less than 0.02%) and compounds with

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