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Proceeding Paper

Thermal Characterization of Biochars Produced in Slow Co-Pyrolysis of Spent Coffee Ground and Concentrated Landfill Leachate Residue †

Ronei de Almeida [1],*, Francesco Lanero [2], Maria Cristina Lavagnolo [3], Paolo Sgarbossa [2], Roberta Bertani [2], Marcelo Mendes Vianna [1] and Juacyara Carbonelli Campos [1]

[1] School of Chemistry, Inorganic Processes Department, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil; email1@email.com (M.M.V.); email2@email.com (J.C.C.)
[2] Department of Industrial Engineering, University of Padova, Padova, Italy; email3@email.com (F.L.); email4@email.com (P.S.); email5@email.com (R.B.)
[3] Department of Civil, Environmental and Architectural Engineering, University of Padova, Padova, Italy; email6@email.com
* Correspondence: ronei@eq.ufrj.br

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Abstract: Resource depletion and climate change have fostered sustainable initiatives in the waste management sector. Pyrolysis (Py) has emerged as an option for valorizing spent coffee grounds (SCG). In addition, inorganic compounds can play catalytic effects in the pyrolytic reaction of organic materials, increasing the char yield and porosity of biochar. This study investigates the slow pyrolysis of SCG using concentrated landfill leachate residue (CLLR) (1:1 %wt) as a pyrolitic additive due to its high salinity. Biochars were characterized in terms of their thermal behaviour to discuss environmental benefits and potential application. Slow-py experiments were conducted using a lab-scale pyrolizer and Thermal characterization was performed using *TA Instruments,* SDTQ600 model. Biochars were characterized by higher water content and heating rate than their feedstocks. It is suggested that the high metal content of CLLR could change the biochar's thermal stability, decreasing the decomposition temperature. Values were 9.18 %wt and 18.11 MJ kg^{-1} and 23.25 %wt and 22.05 MJ kg^{-1} for biochars produced from SCG and SCG + CLLR (1:1 %wt), respectively. Future studies will include biochar ecotoxicity analyses and carbon-energy balance.

Keywords: biochar; landfill Leachate; pyrolysis; spent coffee ground; waste management

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1. Introduction

Membrane systems remove organic and inorganic compounds and provide high-level of leachate purification [1,2]. However, closing the leachate treatment loop and finding a final destination for the landfill leachate membrane concentrate (LLMC)—residual stream of membrane systems—is challenging [3]. Generally, LLMCs are high-saline streams (16,130–98,000 µS cm^{-1}) and, depending on the leachate composition and its treatment layout, refractory organic pollutants such as lignins-like, lipids/proteins-like and unsaturated hydrocarbons are presented on it in high-level [4]. LLMC recirculation onto the landfill body is typical, but contaminants can accumulate in the leachate, making this approach critical. Indeed, this practice is prohibited in developed nations like Germany [5]. On the other hand, treatment techniques (e.g., coagulation-flocculation, adsorption, ozonation, and incineration) can be costly and/or ineffective in handling highly polluted streams [2,6].

Considering the current global resource depletion and climate change scenario, material extraction and carbon sequestration strategies are increasingly in demand.

Pyrolysis (Py) has emerged as an option for valorisation and sustainable management of different kinds of biomasses (e.g., sewage sludge, agroindustrial residues, and urban/industrial wastes) and, therefore, could play a key role in this sense [7]. Py is defined as the thermochemical decomposition of carbon-based feedstock in an absence/low oxygen environment at a temperature > 400 °C. Solid carbonaceous material named biochar (BC) and py-gasses, including volatile organic substances, which can be condensed to liquid phase (bio-oil), and mixed non-condensable gasses (CO, CO_2, CH_4, and H_2) (syngas) are produced in this process [8]. Py-technology can be categorised as fast, intermediate, and slow depending on heating rate, peak temperature, and residence time. Slow pyrolysis is the most employed method for BC production because it offers the highest recovery of solid carbonaceous product [9]. Due to its physicochemical proprieties (e.g., porous structure and water retention capacity), BC can be used as a soil amendment for agronomic benefits. Besides, soil application of this stable carbon-rich material can imply a net carbon removal from the atmosphere since the organic waste conversion to long-term stabilized soil carbon acts as a C-sink [7].

Recently, co-pyrolysis of LLMC and sewage sludge for recovery of liquid and gas products was tested as an advanced technology for recycling organics in biofuels, which could be exported and/or used as an energy source for the thermochemical process itself [10]. In this sense, we attempted to expand the use of Py-technology, focusing on biochar production using RO leachate concentrate (ca. 5 g L^{-1} of total organic carbon). However, our preliminary findings showed that obtained pyrolysed material had low porosity and was mainly composed of salts (e.g., Na+, K+, and Cl^-) arranged in clusters with irregular shapes. Therefore, applying leachate concentrate in mono-Py may not be the most sustainable way to recycle organics as biochars. On the other hand, literature shows that inorganic compounds can play catalytic effects in the pyrolytic reaction of biomasses, increasing char yield and porosity of the produced carbonaceous material [11]. In that direction, we hypothesized that leachate concentrate residues could be used as an additive to boost the yield and/or improve the quality of the BC produced in the thermochemical conversion of biomasses.

This research focuses on the slow pyrolysis of spent coffee ground (SCG) using leachate concentrate residue as Py-additive. Brazil is currently the world's foremost coffee producer and exporter and the second major consumer of this product. Such a scenario promotes a considerable production of spent coffee grounds (SCG), generated either by manufacturing soluble coffee or homemade and commercial consumption, creating a residue generally constituted by small particles (20 μm) of an organic material composed of fibers (>50%) and complex lignin structures with high specific surface area [12,13].

Biochars were characterized in terms of their thermal behaviour to discuss environmental benefits and potential application. SCG is a solid waste by-product from the coffee processing industry. It is usually landfilled, open-burned with other coffee residues and/or mixed with animal fodder. Therefore, the carbon footprint and environmental burdens associated with the existing management solutions are very concerning [14]. Thus, our study aims to provide insights into alternative approaches for managing solid wastes within a circular bioeconomy context.

2. Materials and Methods

2.1. Biomass and Additive

The SLC was prepared following the procedure proposed by [15]. Hereafter, the sample was oven-dried at 105 °C for 24 h. The oven-dried SLC presented water content and VS/TS (volatile solids/ total solids) ratio of 2% and 51%, respectively. This residue was powdered and used in the subsequent pyrolytic tests. For practical applications, the LLMC could be evaporated using the heat from the Py-process. The SCG (100% Arabica blend) was provided by an Italian company. The sample was oven-dried overnight at 110 °C and stored in glass bottles.

It should be noted that thermal technologies such as submerged combustion evaporation and mechanical vapour recompression have been used to handle leachate concentrate streams [16]. In these systems, a dried residue is generated and commonly landfilled. Likewise, evaporation pounds used in warm regions for concentrate volume reduction generate sludges that must be properly managed [3]. In that way, this research could help expand the options to valorize waste streams from available options used to manage the membrane concentrate.

2.2. Py-Process

Slow pyrolysis experiments were conducted using a lab-scale pyrolizer at a heating rate of 45 °C min^{-1}. The lab pyrolizer was operated at atmospheric pressure and room temperature. Py conditions were a temperature of 600 °C, an inert gas flow of 100 cm^3 N_2 min^{-1}, and a residence time of 1 h. Below 500 °C, pyrolysis of biomass may produce biochar with low structural stability, while at temperature > 800 °C the quantity of carbon left on char is minimum [17]. Our tests showed a solid material production of 37%, 33%, 7%, and <3%wt at 500, 600, 700, and 800 °C, respectively.

Biochar produced around 600 °C had a stable coked carbonaceous fraction compared to those obtained at lower temperatures. Pyrolysis at higher temperatures decomposes the material, reducing its carbonaceous fraction and its surface area [17]. The biochar yields were, on average, higher than 30%wt at 600 °C of pyrolytic conversion of 1.0 g of feedstocks. Obtained chars were washed with deionized water on a paper filter and left to dry at ambient temperature (20 °C). BCs were stored for morphological and thermal characterisation.

2.3. Characterisation

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) micrographs of biomass, blending, and BCs were portrayed by an FEI-QUANTA200 instrument (Milan, Italy). Thermogravimetric (TG) analysis and decomposition profile of feedstocks, i.e., SCG, CLLR, SCG + CLLR (1:1%wt) (blend), and the produced biochars were carried out using a TA Instruments equipment, model SDTQ600. The samples were weighed to around 5 mg. Then, they were heated from 20 to 1000 °C (in an alumina pan) at a rate of 20 °C min^{-1} under an air gas flow rate of 100 mL min^{-1}.

3. Results and Discussion

3.1. Thermal Analysis

Figure 1 shows the TG, derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) analyses for SCG and the produced biochar.

Thermal analysis for SCG showed that free water loss occurred from 20 to 150 °C, followed by combustion of organics at around 580 °C. The first DTG peak and its respective endothermic DSC at 150 °C are linked to the free water vaporization. DTG and exothermic DSC peaks from 150 °C to 580 °C are connected to the combustion of SCG organic compounds. Similar behaviour was observed for the produced biochar from that biomass. However, a DSC peak from 150 to 390°C is not presented for biochar, which can be explained by VM loss during the biomass pyrolysis. From TG analysis, water content is estimated at 3.9 and 9.2 wt% for SCG and biochar, respectively.

TG, DTG, and DSC analyses of biomass and additive (SCG + CLLR, 1:1 wt%) and the produced biochar from that blending is illustrated in Figure 2.

For SCG + CLLR blend, water loss occurred from 20 to 160 °C. Organics were combusted from 160 to 650 °C. Inorganic salts, mostly present in the oven-dried SLC, melt and vaporise above 650 °C. From thermal analysis, the water content in the produced biochar is estimated at 23.25 wt%.

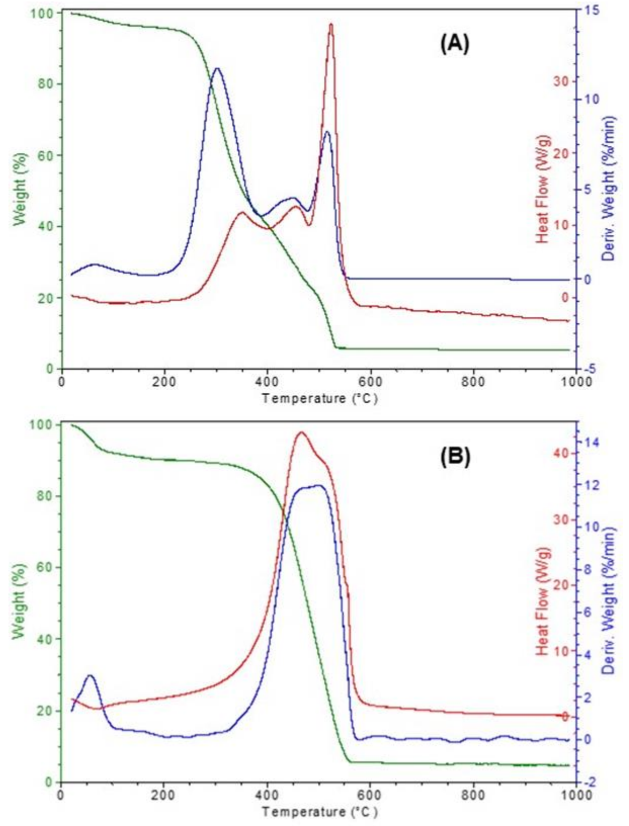


Figure 1. TG, DTG, and DSC analyses for SCG (**A**) and the produced biochar (**B**).

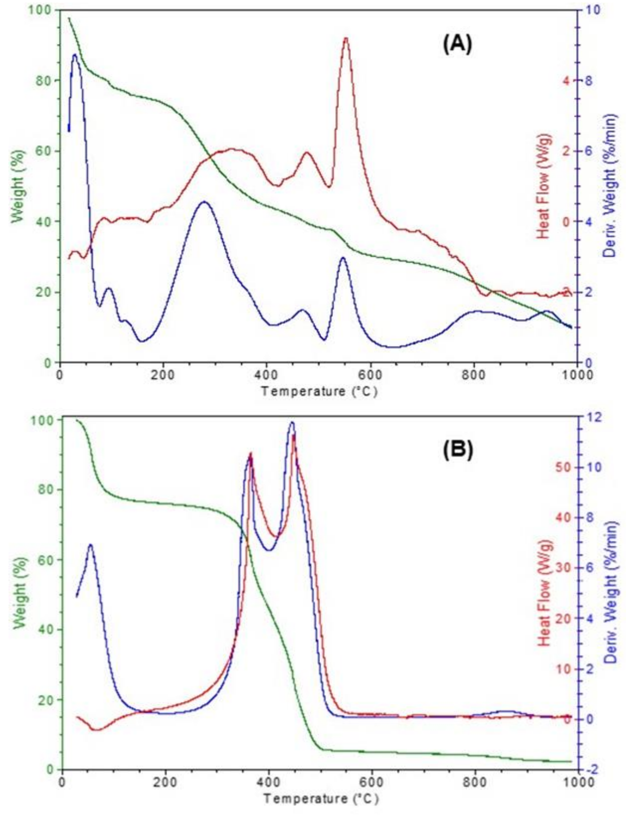


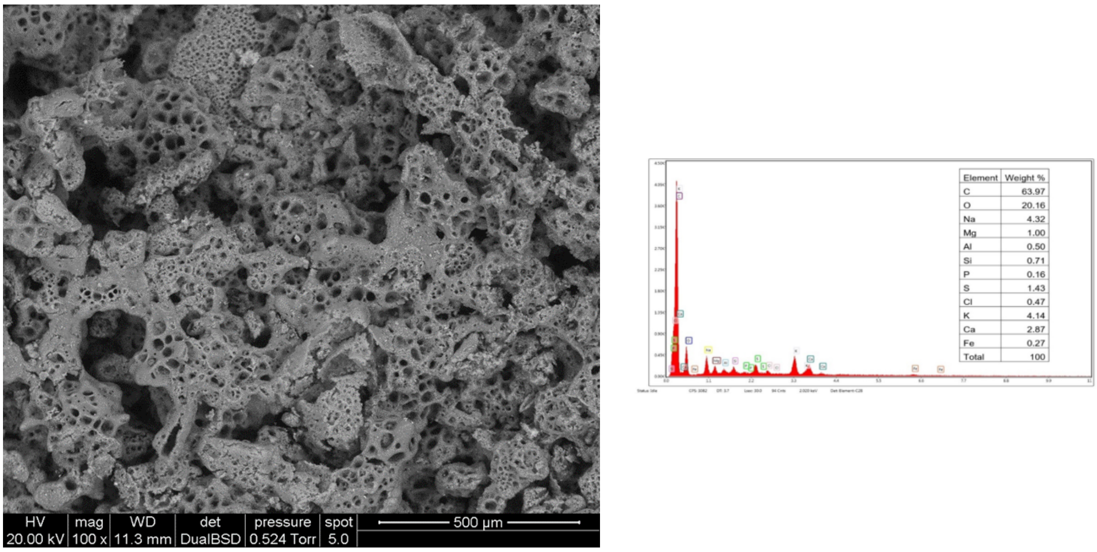
Figure 2. TG, DTG, and DSC analyses for blending (SCG + CLLR, 1:1 wt%) (**A**) and the produced biochar (**B**).

3.2. SEM/EDS Analysis

SEM (100×) of biochar from SCG + CLLR pyrolysis and its EDS spectra are illustrated in Figure 3. Overall, the SEM micrograph of SCG + CLLR (1:1%wt) shows high microporosity. By EDS spectra, biochar is C-rich (ca. 64 wt%) and has essential soil minerals such as Na, K, Ca, and Mg.

By thermal analysis, water content was about 2.5-fold higher in SCG + oven-dried SLC biochar than in SCG biochar. Based on the Proximate analysis, this value was 10-fold higher. Therefore, it was indicated that SLC's alkali metals could catalyze the carbonization of organics in the biomass, producing a more porous material able to retain more water. From elemental composition analysis, biochar from SCG + oven-dried SLC is C-rich and has essential soil minerals such as Na, K, Ca, and Mg.

Chen et al. [18]investigated the effects of eight inorganic additives, including NaOH, NaCl, Na_2CO_3, and Na_2SiO_3, which remarkably increased char yield and made Py-gasses give off earlier. In another work, Wang et al. [11] showed that sodium compounds promote char formation and make pyrolysis more exothermic. To the best of our knowledge, this is the first study to investigate the effects of leachate concentrate on pyrolysis of an agroindustry residue. Thus, recent literature is not available for a reasoning comparative analysis.



Element	Weight %
C	63.97
O	20.16
Na	4.32
Mg	1.00
Al	0.50
Si	0.71
P	0.16
S	1.43
Cl	0.47
K	4.14
Ca	2.87
Fe	0.27
Total	100

(**A**) (**B**)

Figure 3. SEM micrograph (100×) of the obtained biochar from SCG + CLLR (1:1 wt%) pyrolysis (**A**) and its EDS spectra (**B**).

4. Conclusions

This research focused on the slow pyrolysis of SCG using concentrated landfill leachate residue (CLLR) as a pyrolytic additive. Our preliminary findings suggest that inorganic elements in leachate concentrate could catalyse the pyrolysis process of carbon substrates, increasing biochar porosity and its mineral content. High water content is associated with higher porosity. In the case of the more porous biochar, water loss occurred from 20 to 150 °C, followed by the combustion of organics until 550 °C. Data indicated that alkali metals of the CLLR catalyzed the carbonization of organic materials making thermal decomposition faster. From elemental composition analysis, the produced biochar owned essential soil minerals (e.g., Na, K, and Ca); therefore, for practical application, it could be used as a soil amendment for C-sink slow-release inorganic elements or energy storage devices such as batteries and supercapacitors. It must be highlighted that this investigation is at an embryonic stage. Even though it was suggested that co-pyrolysis of leachate concentrate and other substrates could be an exciting way to handle and valorise membrane concentrate streams, our findings cannot be generalized. This research will include the carbon and energy balance of the pyrolysis process and phytotoxicity analysis of biochars. Biochars may also be tested for water purification. Most important, pyrolysis should be performed using actual leachate concentrate samples in future investigations.

Data Availability Statement: Part of this work was previously published as a doctoral thesis: http://objdig.ufrj.br/61/teses/928582.pdf (accessed on).

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