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Article

Characterization of Concentrated Leachate-Activated Char Prepared from Spent Coffee Ground in Slow Pyrolysis

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Abstract: The pyrolysis process has emerged as an attractive option for waste treatment. In this technology, inorganic compounds play catalytic effects in the pyrolytic reaction of organic materials, increasing the char's yield, porosity, and physicochemical properties. The present research investigates and compares the slow pyrolysis of spent coffee grounds (SCG) using potassium hydroxide (KOH) (weight ratio of 1:1) and landfill leachate membrane concentrate (LLMC) residue (weight ratio of 1:1) as pyrolytic additives. We hypothesized that the high content of alkali and alkaline earth metals in LLMC could enhance the yield or improve the quality of the carbon-based material produced in pyrolysis. This strategy could be a sustainable alternative for valorizing SCG and landfill wastes, replacing catalyzing agents such as steam, CO₂, and chemical additives used on an industrial scale. The char yields in slow pyrolysis ranged from 18 to 24%. The SCG had a low specific surface area (4.5 m² g⁻¹), contrasting with the notable surface areas observed in both activated chars. In particular, the KOH-activated char displayed a higher surface area than the LLMC-activated char (1960 vs. 1130 m² g⁻¹). On the other hand, the combustion enthalpy of the LLMC-activated material was estimated at 22 MJ kg⁻¹. This value was 22% higher than the energy enthalpy of SCG and KOH-activated char used for comparison. Our findings confirm that pyrolysis of SCG with KOH produces a microporous material with a high specific surface area. In contrast, the resulting LLMC-activated char demonstrates a higher calorific value. Our findings could contribute to establishing potential industrial applications for SCG and LLMC residues to produce energy and high-value materials.

Keywords: landfill leachate; membrane concentrate; spent coffee grounds; thermogravimetric analysis; waste-derived char

1. Introduction

Due to the disposal standards and the need to protect the environmental quality of ecosystems, landfill leachate treatment plants adopt membrane separation processes (MSP), such as nanofiltration and reverse osmosis, to remove macro and micro-contaminants, complementing or replacing

conventional treatment methods [1]. However, the destination of landfill leachate membrane concentrate (LLMC) – the residual stream of MSP – is a critical aspect of the landfill leachate treatment loop and is challenging for landfill operators [2]. The common practice in handling the LLMC is infiltration into landfilled waste. However, the recent literature indicates that membrane concentrate infiltration tends to impact the environmental and economic performance of the leachate treatment chain [3–5].

Generally, membrane concentrates generated in landfills are high-saline streams (conductivity of 16,130–98,000 $\mu\text{S cm}^{-1}$; 890 – 15,400 mg/L sodium; 210 – 9,600 mg L^{-1} potassium) and, depending on the leachate composition and its treatment layout, refractory organic pollutants such as lignin-like, lipids/proteins-like and unsaturated hydrocarbons are presented on it in high-level (719 – 4,500 mg L^{-1} total organic carbon; 1,393 – 1,501 mg L^{-1} humic substances) [6]. Therefore, due to its complex nature and high pollution potential, cost-effective options for managing LLMC are urgent.

Thermal technologies such as submerged combustion evaporation and mechanical vapor recompression handle leachate concentrate streams [7]. In these systems, an evaporation mother liquor is generated and should be managed appropriately [2]. Likewise, evaporation ponds, used in warm regions to reduce the membrane concentration volume, produce secondary pollutants such as sludge directed to the landfill body [8]. Inorganic salts of leachate evaporation residues are mainly K, Na, Mg, and Ca. Due to the complexity of these wastes, there is currently no feasible path for their treatment and disposal. The accumulation of evaporation residues leads to significant environmental contamination, equipment deterioration, and lack of economic benefit [9].

The pyrolysis process has emerged as a management solution for valorizing different waste streams, such as sewage sludge, crop and agro-industrial residues, and industrial and municipal solid wastes [10–12]. In this context, one of the emerging waste challenges is handling spent coffee ground (SCG) residues, which is a significant concern. SCG is a solid waste by-product from the coffee processing industry – the second-largest traded commodity after petroleum. The SCG waste is usually landfilled, open-burned with other coffee residues, or mixed with animal fodder. The carbon footprint and environmental burdens associated with the existing management practices challenge sustainability [13,14].

Pyrolysis is the thermochemical decomposition of carbon-based biomass under deficient concentration or absence of oxygen at a temperature higher than 400°C and atmospheric pressure. Solid carbonaceous material named biochar, volatile organic substances that 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 [15]. The pyrolysis technology is categorized as fast, intermediate, and slow depending on heating rate, peak temperature, and residence time. Slow pyrolysis, also named carbonization, is the most employed method for char production because it offers the highest recovery of carbon-based material [16,17].

In recent scientific investigations, research has concentrated on utilizing char derived from commercial or specially prepared biochar sourced from organic feedstocks to purify landfill wastewater [18–22]. Besides, the landfill leachate co-pyrolysis has been assessed in lab-scale experiments. Ben Hassen-Trabelsi et al. [23] tested the co-pyrolysis of LLMC and sewage sludge for bio-oil and syngas recovery. The authors explored the possibility of recycling organics in biofuels, which could be exported or used as an energy source for the pyrolysis treatment. The results showed that adding LLMC into sewage sludge increased the bio-oil yield (from 25 wt% of sludge pyrolysis to 31 wt% for LLMC: sludge at 30:70 ratio by weight). In addition, the syngas had a sound hydrogen concentration and high light hydrocarbon content (methane and C_nH_m). The heating value increased from 8.48 MJ kg^{-1} for sludge pyrolysis to 12.29 MJ kg^{-1} for LLMC: sludge-30:70 co-pyrolysis [23]. In a recent study, landfill leachate sludge was pyrolyzed to produce an adsorbent for chromium removal [24]. Utilizing leachate waste streams in pyrolytic processes is promising, but literature on this topic is scarce. Therefore, our study contributes to this area of research by exploring the utilization of landfill leachate residues in the pyrolysis of SCG. It is acknowledged that inorganic compounds, such as alkali and alkaline earth metals (mainly Na, Mg, and Ca), can catalyze the pyrolytic reaction of biomasses, enhancing the char yield and morphological properties of the carbonaceous material

produced [25–29]. In that direction, we hypothesized that the concentrated leachate residue could be used as an additive to boost the yield and/or improve the char quality produced in the pyrolytic conversion. This research comparatively analyzes the slow pyrolysis of SCG using potassium hydroxide (KOH) and LLMC residue as additives. Morphological and thermal characterization were performed to discuss environmental benefits and potential applications. The experimental study showcased here represents the pioneering investigations into using LLMC as an additive in pyrolysis. This research extends and complements our previous findings [30], shedding light on possible alternatives and ranging the spectrum for solid waste valorization.

2. Materials and Methods

2.1. Biomass and additives

The LLMC was prepared following the procedure proposed by Grossule et al. [31]. Hereafter, the sample was oven-dried at 105°C for 24 h. The oven-dried residue presented water content and volatile solids/ total solids (VS/TS) ratio of 2 wt% and 51%, respectively. The LLMC solid was powdered and used in the pyrolysis tests. The proximate and ultimate analyses of LLMC residue are presented in Table 1.

Table 1. Proximate and ultimate analyses of the LLMC residue.

	Proximate analysis (wt%)				*Ultimate analysis (dry basis, wt%)						
	MC	VM	Ashes	FC	C	O	Na	K	Mg	Cl	S
LLMC residue	2.46	23.55	51.23	22.76	13.32±2.2	33.99±4.3	39.28±1.9	8.085±0.7	0.256±0.0	3.83±0.6	0.745±0.43
					3	3	9	8	8	6	5

FC = fixed carbon. LLMC = landfill leachate membrane concentrate. MC = moisture content. VM = volatile matter. *Mean ± standard deviation of three determinations.

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. The potassium hydroxide (KOH) powder was obtained from Sigma-Aldrich. KOH is commonly used as an activating agent to develop porosity during thermal processes [26]. This work employed KOH as the reference catalyzing agent for comparative analysis.

2.2. Pyrolysis experimental set-up

Slow pyrolysis experiments were conducted using a lab-scale pyrolyzer at a heating rate of 45°C min⁻¹. The bench-scale pyrolyzer was positioned within an exhaust system operating at atmospheric pressure and ambient temperature (±20°C). Pyrolysis conditions included an isothermal temperature of 600°C, an inert gas flow of 100 cm³ N₂ min⁻¹, and a residence time of 1 h. The peak temperature is a critical factor in the slow pyrolysis, significantly influencing the characteristics of the char product. Elevating the peak temperature appears to result in carbon materials with increased aromaticity, fixed carbon content, and porosity [16]. At the same time, at temperatures higher than 800°C, the quantity of carbon left on char is minimal, as observed in previous findings [32]. Below 500°C, biomass pyrolysis may produce biochar with low structural stability [17]. The SCG and additives (i.e., KOH and LLMC residue) were pyrolyzed in a 1:1 ratio by weight. Experimental conditions were defined according to our preliminary results [32]. Obtained chars were washed with deionized water on a paper filter and left to dry at ambient temperature (±20°C). The activated-carbon yield was determined as a mass fraction of the initial biomass (Equation (1)). The activated-carbon materials were stored for morphological and thermal characterization.

$$Yield\ (\%) = \left(\frac{m_i}{m_0}\right) \times 100$$

(1)

Where m₀ (in mass unit) is the initial mass of SCG and m_i (in mass unit) is the mass of activated carbon produced in slow pyrolysis.

2.3. Characterization of biomass and the activated materials

Moisture content (MC), volatile matter (VM), ash content, and fixed carbon (FC) were determined. The MC was measured by heating 1,000 mg of a sample at 105±5°C for one hour in an oven; the VM was determined by heating the left residue at 950°C for 6 min. Last, ash content was obtained by heating the samples in a furnace at 750°C for 6 h. FC was calculated by difference following the ASTM method D1762 – 84/ 2021 [33].

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) of biomass and prepared activated-carbon materials was performed with a FEI-QUANTA200 instrument (Milan, Italy). The Brunauer-Emmett-Teller (BET) surface area and average pore size of SCG and prepared chars were calculated based on the N₂ adsorption-desorption isotherms measured using a gas sorption analyzer (AutoChem II Modelo 2920, Micromeritics Instrument Ltd.).

Thermogravimetric (TG) analysis and decomposition profile were performed using TA Instruments equipment, model SDTQ600. The samples were weighed to around 5 mg. After that, they were heated from 20 to 1000°C (in an alumina pan) at 20 °C min⁻¹ under an air gas flow rate of 100 mL min⁻¹. Figure 1 illustrates a schematic diagram of the research steps.

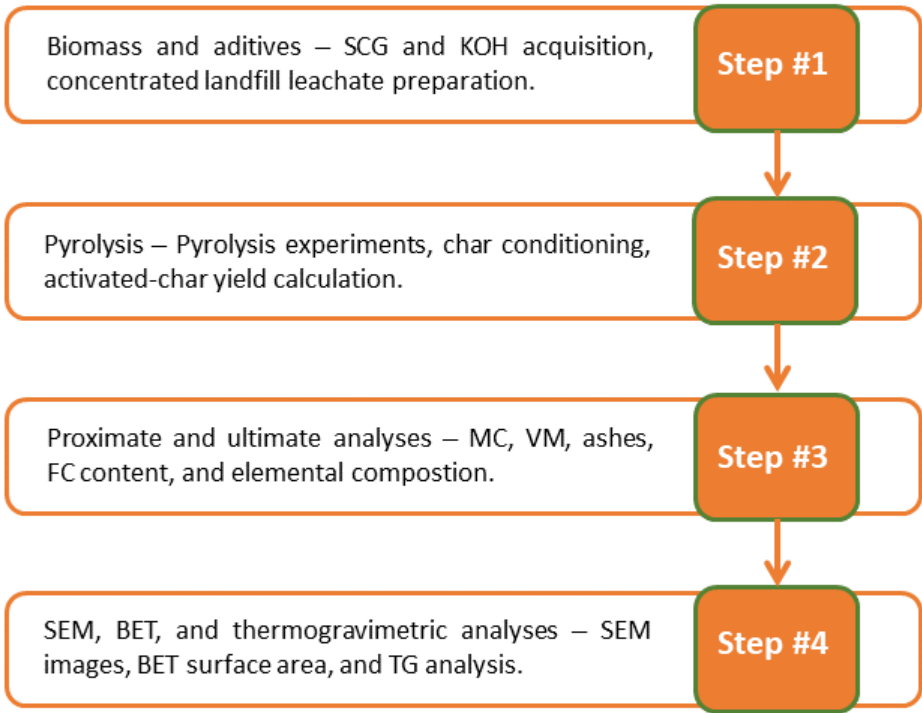


Figure 1. Schematic diagram of research steps performed in this work. BET = Brunauer-Emmett-Teller surface area. FC = fixed carbon. SCG = spent coffee grounds. SEM/EDS = Scanning electron microscopy with energy-dispersive X-ray spectroscopy. TG = Thermogravimetric. VM = volatile matter.

3. Results and Discussion

3.1. Char yield, proximate analysis, and elemental composition

Table 1 shows char yield and proximate content (wt%) of SCG, biochar, and activated chars using KOH and LLMC residue.

Table 2. Yield and proximate analysis..

	SCG	Biochar	KOH- activated char	LLMC- activated char
Mass yield (wt%)	–	23.9	21.2	18.6
MC (wt%)	3.78	9.2	5.8	23.3
VM (wt%)	94.91	58.4	47.9	44.4
Ashes (wt%)	1.26	5.8	1.3	7.0
FC (wt%)	1.25	33.0	25.6	20.4

FC = fixed carbon. LLMC = landfill leachate membrane concentrate. MC = moisture content. SCG = spent coffee ground. VM = volatile matter.

The biochar yields produced from SCG and activated chars were 23.9, 21.2, and 18.6%, respectively. A low mass yield of activated chars is obtained because of the high release of volatile matter catalyzed by oxidizing agents in slow pyrolysis (i.e., KOH and concentrated leachate residue). Alkali and alkaline earth metals shift the decomposition of biomass to lower temperatures while increasing the char and gas yields at the expense of bio-oil. As far as potassium additives in particular, they have been shown to promote the yields of low molecular compounds and gaseous species, which could justify the lower yield of KOH-activated char than SCG char in this study [29]. For example, Wang et al. [25] showed that potassium and sodium compounds promoted the reduction of char formation and made pyrolysis more exothermic.

Besides, the LLMC-activated char had a relatively lower mass yield than that obtained from KOH activation (18.6 vs. 21.2%). Alkali metals have been shown to induce a so-called synergistic effect that decreases the apparent activation energy of the pyrolysis reaction, promotes the yields of volatiles, and reduces the temperature of the maximum weight loss rate [29]. Lower yield when concentrated leachate residue was employed could be due to the synergetic interactions between different LLMC metals (mainly Na and K) and the SCG [34].

The proximate content of the SCG biomass is primarily dominated by volatile matter (94.91 wt%), moisture (3.78 wt%), ashes (1.26 wt%), and fixed carbon (1.25 wt%). The volatile matter was significantly reduced to 44 – 47 wt% for both activated chars, producing materials with a high fixed carbon content (20 – 33 wt%). High fixed carbon, closely related to stable carbon content, represents a beneficial feature that shows higher stability against environmental oxidation and thermal degradation [21]. On the other hand, the high ash content of LLMC-activated char indicates that it may not be appropriated for cofiring or use as boiler fuel, as that may lead to fouling and corrosion in combustors [35].

SEM/EDS was employed to observe the morphology and pore size of SCG, concentrated leachate residue, and prepared materials. EDS spectra were used to determine biomass and char composition (Table S1). The biochar obtained from SCG presented 46% wt% of carbon, and both activated chars were highly C-rich. The results showed similar carbon content in activated chars (>60 wt%) (Figure 2). The final elemental composition of the LLMC-activated sample was the following (wt%): carbon (C) content of 63.97%, oxygen (O) content of 20.16%, sulfur (S) content of 1.43%, chloride (Cl) content of 0.47%, sodium content of 4.32%, potassium (K) content of 4.14%, calcium (Ca) content of 2.87%, and magnesium (Mg) content of 1%. Foreign elements were observed in the three prepared materials (i.e., Na, K, or S, <5% wt%).

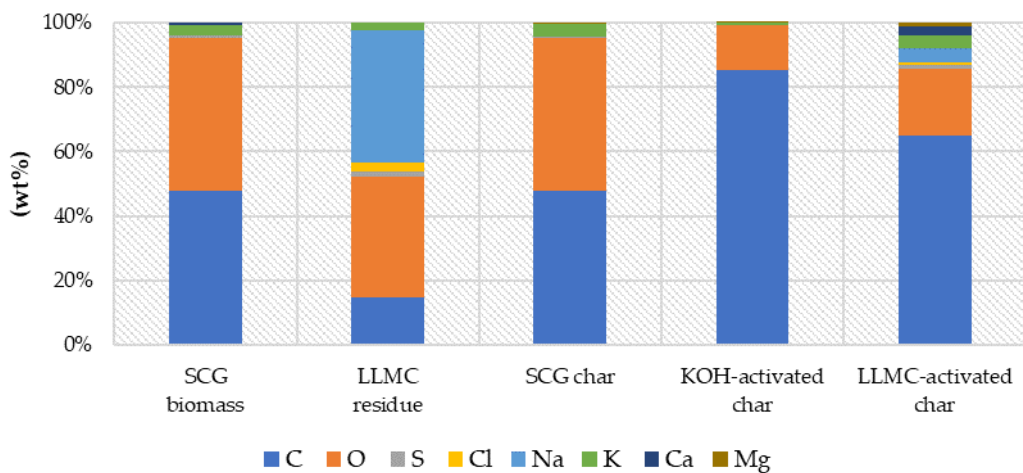
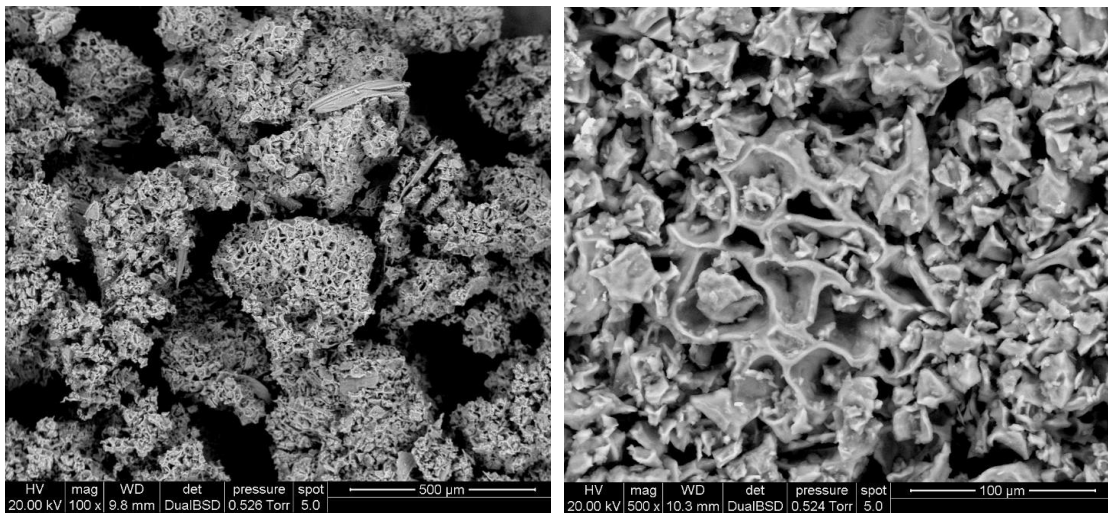


Figure 2. Elemental composition of biomass and chars from EDS spectra.

3.2. SEM images and porosity

Scanning electron microscopy (SEM) was used to analyze the biomass and LLMC residue structure and surface topography (Figure 3). The surface of the SCG is slightly porous and has a high surface roughness. The LLMC residue was brown and had an amorphous structure and irregular shape. From SEM images, many fractured particles with flaky substances are attached to them.



A) Raw SCG (100x)

B) Raw SCG (500x)

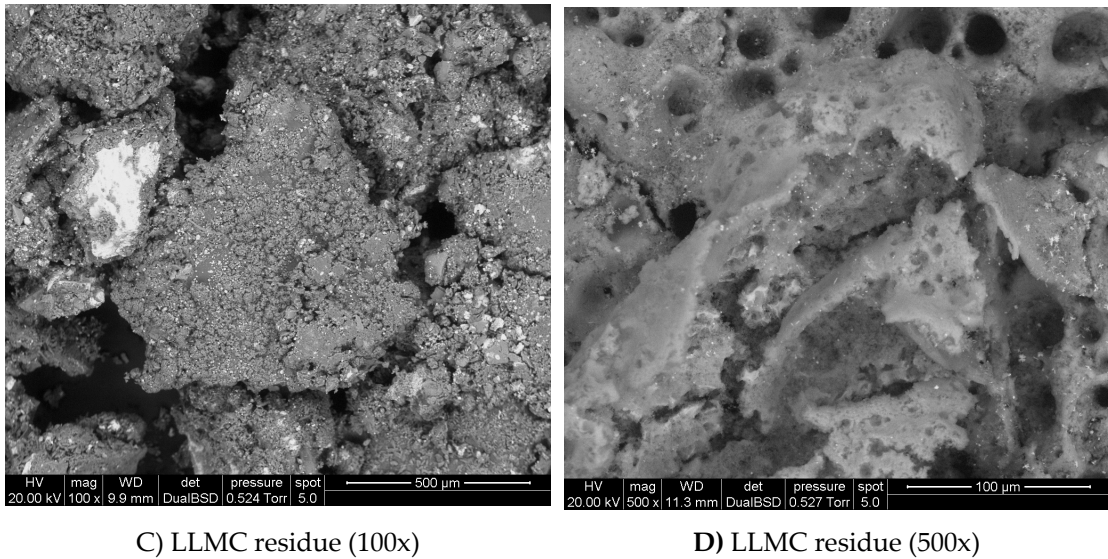
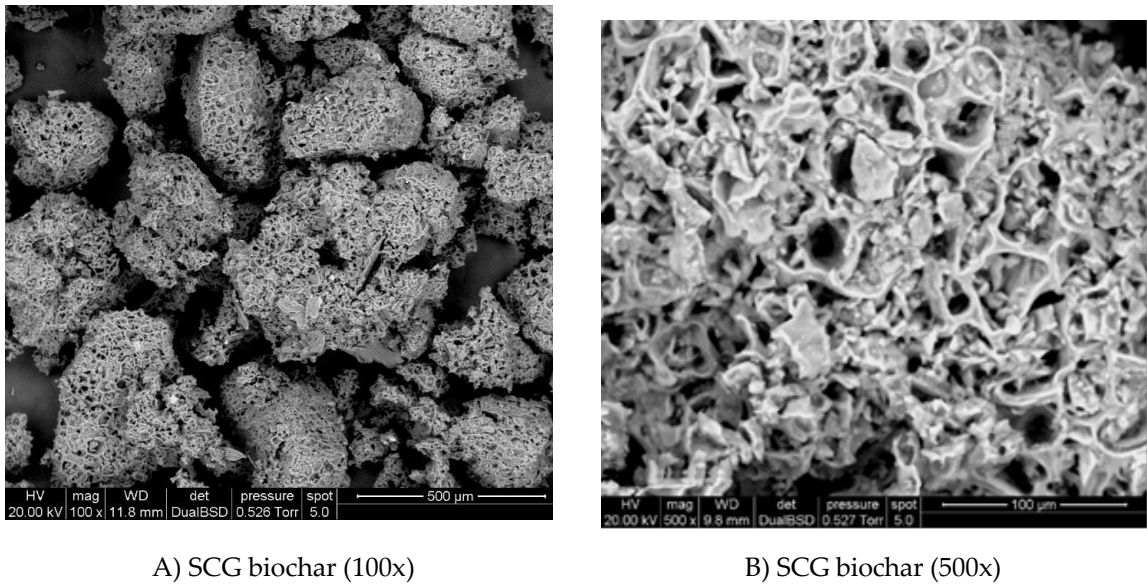


Figure 3. SEM images of starting materials. LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds.

Following slow pyrolysis, biomass undergoes a notable transformation, manifesting a darker hue. SEM images of SCG, KOH-activated, and concentrated leachate-activated chars are illustrated in Figure 4. The SCG char was denser than the precursor. From the SEM images, it owns a macro-porous structure. In contrast, the KOH-activated char has many micropores under its surface. In the LLMC-activated char, larger dispersed pores were observed, and discontinuous microstructures impregnated with inorganic elements were portrayed. This portrayal suggests a unique structural arrangement compared to the other char samples.



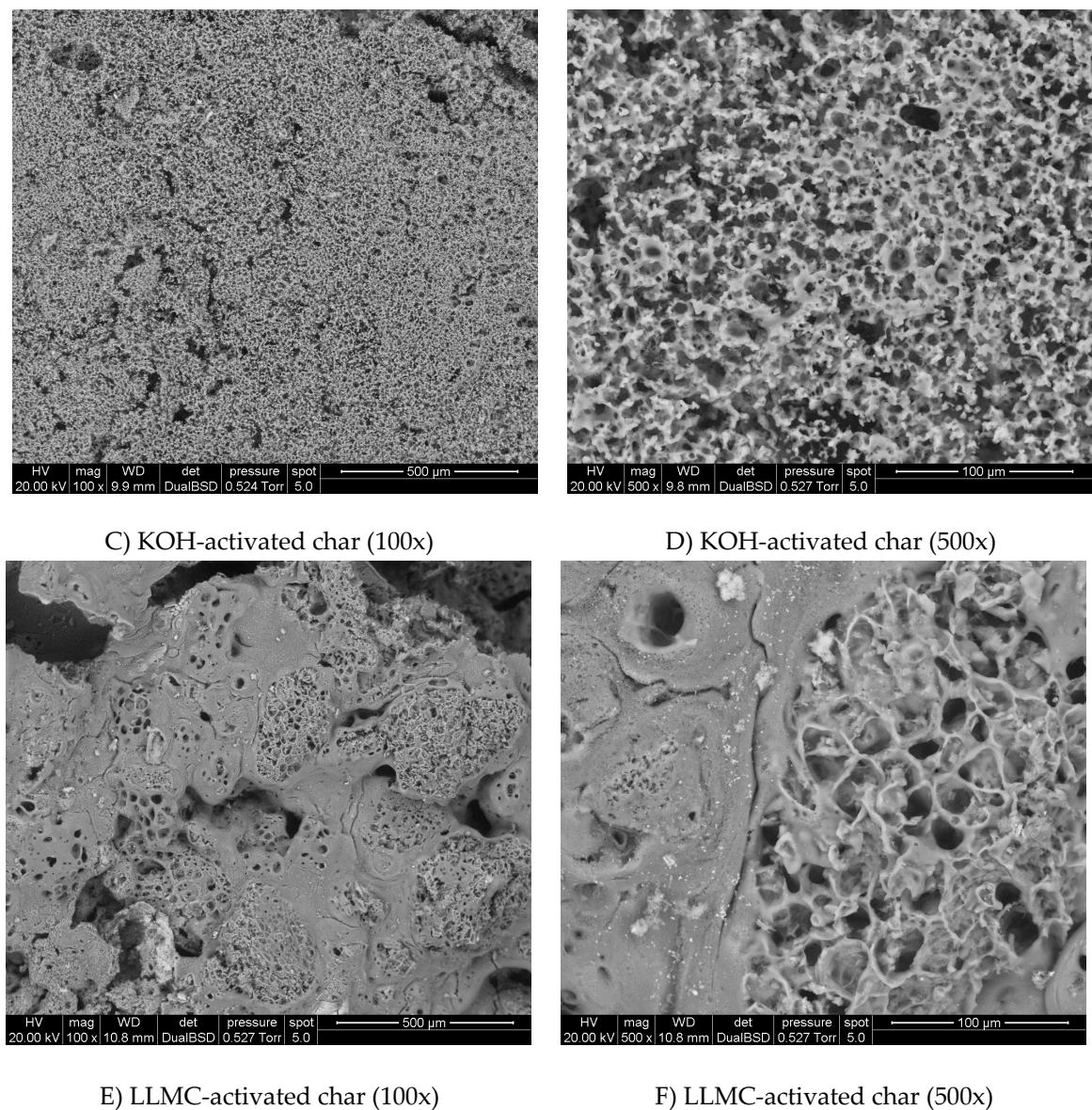


Figure 4. SEM images of SCG char and activated chars. LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds.

Table 3 shows the BET surface area and average pore diameter of SCG and prepared chars at isothermal pyrolysis (600°C) of 1 h.

Table 3. BET surface area and average pore diameter of SCG and prepared chars.

Sample	BET surface area (m ² g ⁻¹)	Average pore size (nm)
SCG	4.5	10.7
SCG char	463	4.8
KOH-activated char	1960	1.8
LLMC-activated char	1138	5.9

LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds.

The N₂ physisorption isotherms revealed that the SCG had a low BET surface area (4.5 m² g⁻¹). On the other hand, both activated chars exhibited high surface areas. In particular, the KOH-activated char displayed a higher specific surface area than the LLMC-activated char (1960 vs. 1130 m² g⁻¹). The

BET surface areas for SCG and KOH-activated chars in this study were consistent with values reported in the literature (4.3 to $2230 \text{ m}^2 \text{ g}^{-1}$) [36,37].

In terms of pore structure, KOH and LLMC-activated materials presented average pore diameters of 1.8 and 5.9 nm , respectively. According to the International Union of Pure and Applied Chemistry (IUPAC), KOH-activated char is classified as microporous. In contrast, LLMC-activated char is a mesoporous material [38].

3.3. Thermal analysis

Figure 5 shows the TG, derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) curves 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 free water vaporization. DTG and exothermic DSC peaks from 150 to 580°C are connected to the combustion of SCG organic compounds.

The most significant peaks in the DTG thermal decomposition of SCG include cellulose, lignin, and hemicellulose degradation [28]. Wachter et al. [39] also described three thermogravimetric peaks of the SCG in airflow. The first DTG peak was assigned to the degradation of hemicellulose, the second (lower) peak to cellulose, and the third peak to lignin decomposition. DTG peaks were observed at 337 , 451°C , and 505°C [39]. These values are very similar to those shown in Fig.5(A) (300°C and 425°C , 520°C).

This study utilized the SCG biomass derived from Arabica coffee, and three distinct phases were observed during combustion. The first two peaks have almost the same heat flow, about 12.5 W g^{-1} , and the last peak has a higher heat flow of about 40 W g^{-1} . This finding corroborates the findings of Bejenari et al. [40], who investigated the combustion of SCG from Arabica and Robusta coffee varieties. The combustion of Arabica coffee occurs in three stages. In addition, similar heat flows were recorded in their study [40].

Similar behavior was observed for the produced char from that biomass. However, DTG and DSC peaks from 150 to 390°C are not presented for SCG char, which the hemicellulose loss during the SCG pyrolysis can explain. Hemicellulose has a temperature decomposition of around 220°C [13]. Thus, the pyrolysis to which the SCG was submitted (600°C) provided the total decomposition of hemicellulose and modified it thermally. In the char, it can be assumed that the first peak is linked to the thermo-oxidation of cellulose and lignin, and the last stage was probably the thermal decomposition of carbonaceous residues. Both the width of the curves and the width of the peaks are higher in the SCG char. It should be highlighted that the fixed-carbon content of char was more than 25-fold higher than that in the SCG (Table 2). High-fixed carbon content materials often exhibit a heterogeneous structure with different types of bonds and functional groups. Thus, the decomposition process may break various chemical constituents over various temperatures, contributing to broader peaks in the DTG curve, as observed in this work [41].

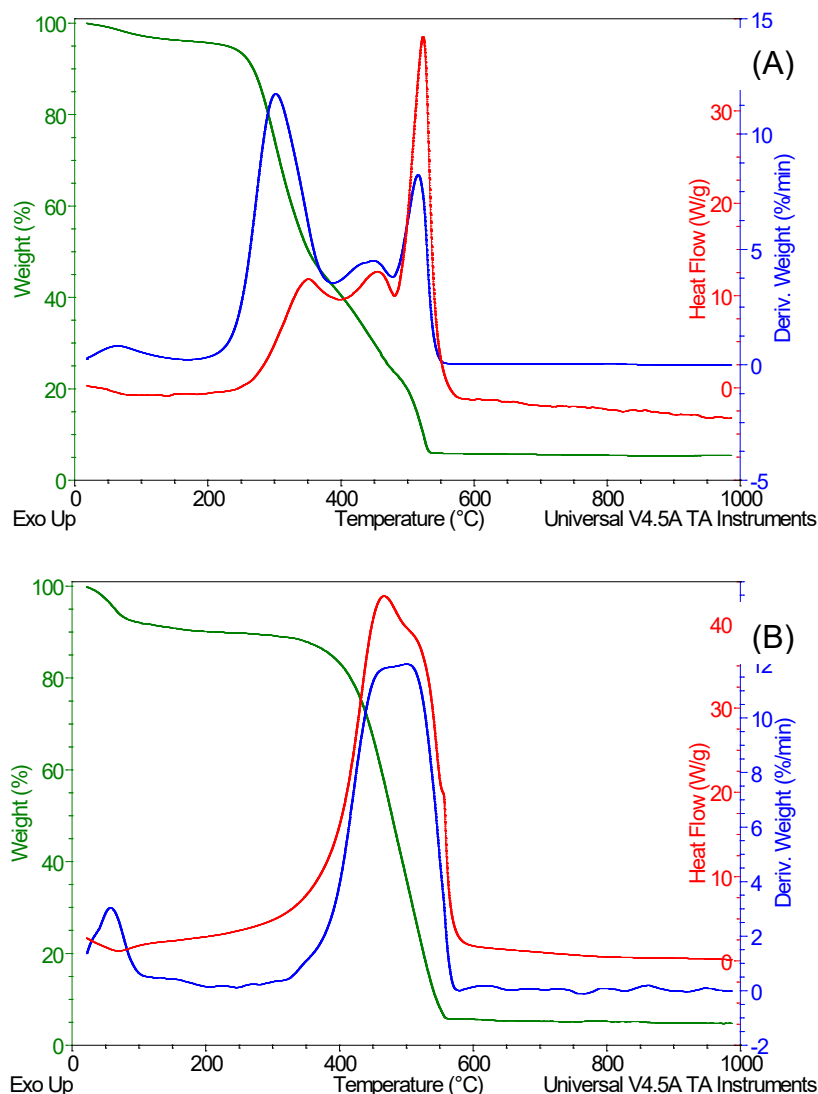


Figure 5. TG, DTG, and DSC curves for SCG (A) and the produced char (B).

The amount of free water in SCG char was 9.18%. In the raw SCG, it is 3.87%, indicating that the SCG char can absorb more water on its external and internal surfaces due to its higher porosity. By DSC peak areas, the combustion enthalpy of SCG char is 18.11 MJ kg^{-1} . For SCG, it is 11.55 MJ kg^{-1} , showing that biochar will release more energy upon combustion. The enhanced SCG char stability and higher surface area than the raw biomass can explain this. Char formation is frequently promoted by intramolecular and intermolecular rearrangement processes, culminating in a material characterized by enhanced thermal stability [42]. The high stability results in more complete combustion and higher energy release during combustion. Besides, the augmented surface area of char ($463 \text{ vs. } 4.5 \text{ m}^2 \text{ g}^{-1}$) enhances combustion kinetics, enabling more effective utilization of its carbon content and releasing more energy [43].

TG, DTG, and DSC curves of SCG + LLMC residue (1:1) and LLMC-activated char are illustrated in Figure 6. For the LLMC-activated char, water loss occurred from 20 to 160 °C. Organics were combusted from 160 to 650°C. The curves showed that the hemicellulose degradation shifts toward lower temperatures (c.a. 280°C), which indicates that the presence of the LLMC residue influences the thermal oxidation of the SCG. Inorganic salts, mainly in the LLMC residue, melt and vaporize above 650 °C. For example, magnesium chloride, potassium chloride, and sodium chloride have melting points of around 700, 770, and 800°C, respectively [44].

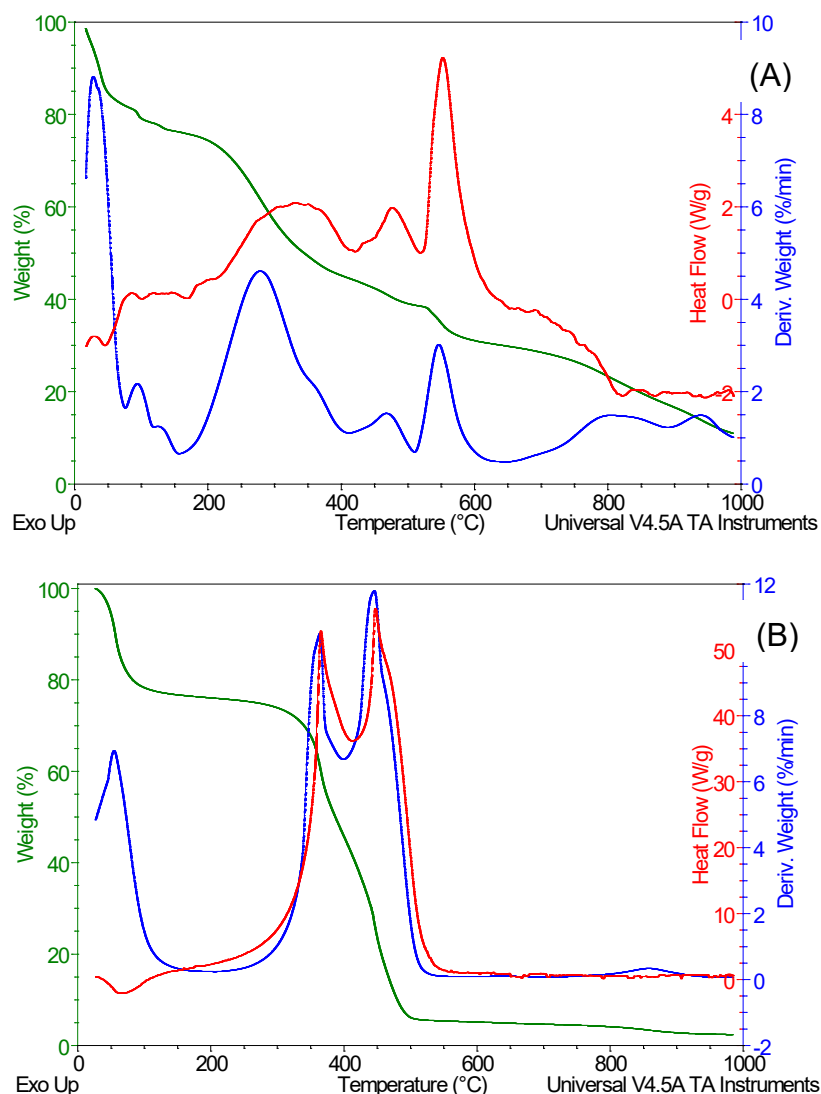


Figure 6. TG, DTG, and DSC curves for SCG+LLMC residue (1:1) (A) and the LLMC-activated char (B).

The LLMC-activated char exhibited loss of free water from room temperature up to 150 °C, identified by the DTG peak and endothermic DSC peak, followed by the combustion of pyrolyzed organic products between 150 °C and 580 °C, determined by the two DTG peaks and two exothermic DSC peaks. It was observed that the SCG char underwent combustion in a single DTG peak with two overlapping stages, peaking at around 500 °C (Fig. 5B). In contrast, the LLMC-activated char exhibited combustion in two stages, identified by two DTG peaks, peaking at temperatures of 360 °C and 445 °C (Fig. 6B). It has been underlined that alkali and alkaline metals, such as Na and K, alter the char reactivity and shift the thermal oxidation of carbon materials to lower temperatures [25]. These elements on the carbon surface could act as the active sites for oxygen chemisorption, weakening C=C surface bonds and promoting the desorption of monoxide and carbon dioxide [28]. We assumed that the content of alkali and alkaline metals in the LLMC residue contributed to the results obtained in this work. From thermal analysis, the water content and the combustion enthalpy in the LLMC-activated char were estimated at 23.25 wt% and 22.04 MJ kg⁻¹.

Comparing both activated chars, the DSC peaks of the LLMC-activated char were more substantial, meaning that the thermal oxidation of the LLMC-activated char is more exothermic than the KOH-activated char (Figure 7). Besides, it was registered that the energy of the char activated using KOH was similar to the SCG char (18.4 MJ kg⁻¹). These results are consistent with the literature

[40,45]. All materials had net calorific values higher than the lowest limit of 16.50 MJ kg⁻¹ stated in ISO 17225-1:2021, making it possible to direct them for usage as solid biofuels [46].

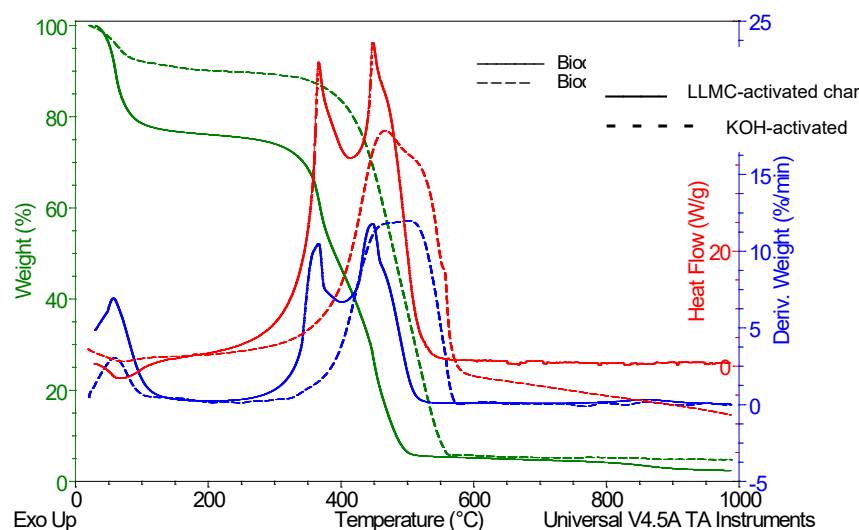


Figure 7. TG, DTG, and DSC curves for KOH-activated char and LLMC-activated char.

4. Conclusions

This research focused on the slow pyrolysis of spent coffee ground biomass (SCG) using concentrated landfill leachate membrane concentrate (LLMC) as a pyrolytic additive. The conclusions from this work are: #1) The char yields in slow pyrolysis ranged from 18 to 24%. The char activated by LLMC demonstrates a mass yield lower than that achieved through KOH activation. Alkali metals have been shown to induce a so-called synergistic effect that promotes the yields of volatiles at the expense of char and oil recovery. Lower yield when LLMC residue was employed in pyrolysis could be due to the synergetic interactions between different LLMC metals (mainly Na and K) and the SCG; #2) Both activated chars showcased remarkable surface areas, with the KOH-activated char notably surpassing the specific surface area of the LLMC-activated char. This feature could render it invaluable for applications such as the adsorption of pollutants, catalyst support, and energy storage devices; and #3) the LLMC inorganic components catalyzed the carbonization of SCG, making thermal decomposition faster. By DSC peak areas, the combustion enthalpy of the activated char was estimated at 22 MJ kg⁻¹. In addition, the elemental composition of the LLMC-activated sample identified the material as C-rich (64 wt%). Our results may aid in identifying potential industrial applications for SCG and LLMC residues, enabling the production of energy and high-value materials.

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Conflicts of Interest: The authors declare no conflict of interest.

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