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Article

Valorization of Spent Coffee Grounds Using KOH and Concentrated Leachate as Activating Agents in Slow Pyrolysis at 600 °C—A Comparative Analysis of Char Properties

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Abstract: The coffee industry and landfill leachate treatment generate residual waste streams, known as spent coffee grounds (SCG) and landfill leachate membrane concentrate (LLMC). Current practices for managing these residues, including open burning, incineration, and landfilling as a final disposal method, represent a waste of resources and pose a challenge to sustainability. Due to the high pollution potential of solid waste SCG and LLMC, cost-effective management solutions are urgently needed. The present research investigates the slow pyrolysis of SCG using potassium hydroxide (KOH) (weight ratio of 1:1) and LLMC residue (weight ratio of 1:1) as activating agents. The high content of alkali and alkaline earth metals in LLMC could promote the activation of the resulting char and improve the quality of the carbon-based material produced in pyrolysis. The use of LLMC as an activating agent could be a sustainable alternative for valorizing SCG and landfill wastes, potentially replacing ingredients such as steam, CO₂, and chemical additives used on an industrial scale. 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 exhibited a higher surface area than the LLMC-activated char, measuring 1,960 m² g⁻¹ compared to 1,138 m² g⁻¹ – a difference of about 72%. On the other hand, the combustion enthalpy of the LLMC-activated material was estimated at 22.04 MJ kg⁻¹. The combustion enthalpy of LLMC-activated char was about 21.7% and 19.8% higher than that of SCG and KOH-activated chars, which had values of 18.11 and 18.40 MJ kg⁻¹, respectively. 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 value of combustion enthalpy. This work showed that both activated chars had superior energetic and morphological properties compared to the non-activated char made from SCG biomass. Among the activating agents, KOH led to better performance in terms of char yield and morphological properties. Meanwhile, utilizing LLMC residue as an activating agent highlights its potential for converting landfill waste into high-value material.

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

1. Introduction

Landfill leachate treatment plants have employed nanofiltration and reverse osmosis to remove contaminants, complementing or replacing conventional methods. However, managing the landfill leachate membrane concentrate (LLMC) challenges operators [1,2]. LLMC is a high-salinity residual stream containing recalcitrant organic contaminants like lignin-like substances, unsaturated hydrocarbons, and humic substances (conductivity of 16,130–98,000 $\mu\text{S cm}^{-1}$; 890 – 15,400 mg L^{-1} sodium; 210 – 9,600 mg L^{-1} potassium; 719 – 4,500 mg L^{-1} total organic carbon; 1,393 – 1,501 mg L^{-1} humic substances), making it highly polluted and complex [3]. When used to handle LLMC, thermal processes like evaporation generate a mother liquor that requires further management [4]. Likewise, evaporation ponds, used in warm regions to reduce the LLMC volume, produce secondary pollutants such as air pollution and sludge [5]. These residues, which consist of inorganic salts like K, Na, Mg, and Ca, pose environmental risks and contribute to equipment deterioration. At the same time, the disposal of secondary pollutants, such as sludge, into landfills exacerbates contamination, highlighting the need for better treatment and disposal methods [6].

Likewise, one of the emerging waste challenges is handling spent coffee ground (SCG) residues. SCG is a solid waste by-product from the coffee processing industry – the second-largest traded commodity after petroleum. Individuals, coffee shops, and food services also generate it. It is estimated that only about 30% of the mass of coffee beans is extracted into the brewed coffee, meaning that a large portion of the beans remains as solid waste in the form of SCG. Approximately six million tons of SCG annually are generated globally [7,8]. If disposed of in the environment, SCG causes contamination since it contains caffeine, tannins, and polyphenols, making it a toxic residue [9]. The SCG waste is typically landfilled, incinerated, burned with other coffee residues, or mixed into animal feed [10]. Open burning is an unsustainable destination, while landfilling and incineration release greenhouse gases [11]. Current SCG management practices contribute to a significant carbon footprint and raise sustainability concerns. Therefore, cost-effective and green management solutions are urgently needed.

Pyrolysis 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 [12–14]. 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. This process yields a solid carbon-rich substance known as biochar, volatile organic compounds that can be condensed into a liquid form (bio-oil), and various non-condensable gases (such as CO, CO₂, CH₄, and H₂) collectively referred to as syngas [15]. Pyrolysis technology is classified into fast, intermediate, and slow types based on heating rate, peak temperature, and residence time. Slow pyrolysis, also known as carbonization, is the most widely used method for producing char due to its ability to achieve the highest recovery of carbon-based material [16,17].

The char properties are affected by the biomass characteristics and the activating method. The latter changes the char porosity, surface area, and thermal stability [18]. Conventionally, activated chars are produced using chemical and physical activation methods. An external activation agent such as ZnCl₂, H₃PO₄, KOH, HNO₃, and NaOH is employed in chemical methods. In contrast, continuous CO₂ or H₂O gas incorporation into the pyrolysis reactor is performed in physical processes. As a disadvantage of these techniques, washing and neutralizing steps generate wastewater with toxic chemicals from the activation step, increasing costs for pollution control and equipment maintenance [19]. Thus, finding novel approaches to activate the carbon-based material produced in pyrolysis is imperative.

It is acknowledged that inorganic compounds, such as alkali and alkaline earth metals (mainly Na, Mg, and Ca), can activate carbon oxidation, enhancing the morphological properties of the resulting solid material produced in the pyrolysis [20–24]. However, the potential use of residual

streams for this purpose has not been fully explored. Due to the high Na and K content of LLMC residue, this landfill wastewater is a potential candidate for activating biomass conversion in pyrolysis. This approach is an innovative strategy to promote the valorization of LLMC and different kinds of biomass, including solid waste SCG.

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 [25–29]. Besides, the landfill leachate co-pyrolysis has been assessed in lab-scale experiments. Ben Hassen-Trabelsi et al. [30] 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 CnHm). 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 [30]. In a recent study, landfill leachate sludge was pyrolyzed to produce an adsorbent for chromium removal [31].

Using 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 the LLMC residue in the pyrolysis of SCG. The concentrated leachate residue could be used as an activating agent to improve the char quality produced in the pyrolytic conversion due to the parallel biomass carbonization and oxidation of the resulting carbon structure. In that direction, this research comparatively analyzes the slow pyrolysis of SCG using KOH and LLMC residue as activating agents. KOH is one of the most effective activating agents for preparing activated carbon with a high specific surface area [32]. Therefore, KOH was used as the reference activating agent for comparative analysis. 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 activating agent in pyrolysis. This research extends and complements our previous findings [33], shedding light on possible alternatives and ranging the spectrum for solid waste valorization.

2. Materials and Methods

2.1. Biomass and Activating Agents

The LLMC was prepared following the procedure proposed by [34]. The sample was subsequently oven-dried at 105°C for 24 h. The dried residue had a water content of 2 wt% and a volatile solids/total solids (VS/TS) ratio of 51%. The LLMC solid was then powdered and used in pyrolysis tests. The proximate and ultimate analyses of the LLMC residue are detailed in Table 1.

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

Proximate analysis (wt%)					*Ultimate analysis (dry basis, wt%)						
MC	VM	Ashe s	FC	C	O	Na	K	Mg	Cl	S	
LLM C resid ue	2.46	23.55	51.23	22.76	13.32±2. 23	33.99±4. 33	39.28±1. 99	8.085±0. 78	0.256±0. 08	3.83±0.6 6	0.745±0.4 35

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

A local Italian company supplied the SCG (100% Arabica blend). The sample was sieved to remove impurities, stirred to obtain a homogenous sample, oven-dried overnight at 110°C, and stored in glass bottles for pyrolysis tests. The KOH powder (≥85%) was sourced from Sigma-Aldrich (Stainheim, Germany). KOH is commonly used as an activating agent to develop porosity during thermal processes [21]. This work employed KOH as the reference activating agent for comparative analysis. After pyrolysis, the obtained chars were filtered through a Gooch 4 filter and washed with deionized water until the pH reached neutral. It was then oven-dried at 110°C for 24 hours.

2.2. Pyrolysis Experimental Set-Up

Slow pyrolysis experiments were conducted using a lab-scale pyrolyzer at a heating rate of 4.5°C min⁻¹. The pyrolyzer is an automated tubular alumina reactor (Carbolite) connected to a nitrogen cylinder. The bench-scale reactor was positioned within an exhaust system operating at atmospheric pressure and ambient temperature (±20°C) [21]. 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 experimental conditions were established based on preliminary pyrolysis tests and a thorough review of the relevant literature [16,17,35]. 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 our preliminary findings [35]. Below 500°C, biomass pyrolysis may produce biochar with low structural stability [17].

The SCG and activating agents (i.e., KOH and LLMC residue) were pyrolyzed in a 1:1 ratio by weight. The mass ratio of the activating agent to the carbon precursor is critical in the activation process. An equal mass ratio was adopted because our previous study confirmed that the chemical activation of SCG with KOH produced a carbon material with a high surface area (up to 1199 m² g⁻¹) [21]. The present study uses KOH as the reference activating agent for comparative analysis; therefore, the SCG and LLMC mass ratio follows the same proportion.

The chars were washed with deionized water on a paper filter at a neutral pH 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.

$$Yield (\%) = \left(\frac{m_i}{m_0} \right) \times 100 \quad (1)$$

Where m_0 (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 analyzed. MC was measured by heating a 1,000 mg sample at 105±5°C for one hour in an oven. VM was determined by heating the remaining residue at 950°C for 6 minutes. Ash content was obtained by placing the samples in a furnace at 750°C for 6 hours. FC was calculated by difference according to ASTM method D1762 – 84/2021[36].

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 of SCG and prepared chars was calculated based on the N₂ adsorption-desorption isotherms measured using a gas sorption analyzer (AutoChem II Modelo 2920, Micromeritics Instrument Ltd.). The pore size distribution was derived from BET isotherms using the Density Functional Theory (DFT) method [37].

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.

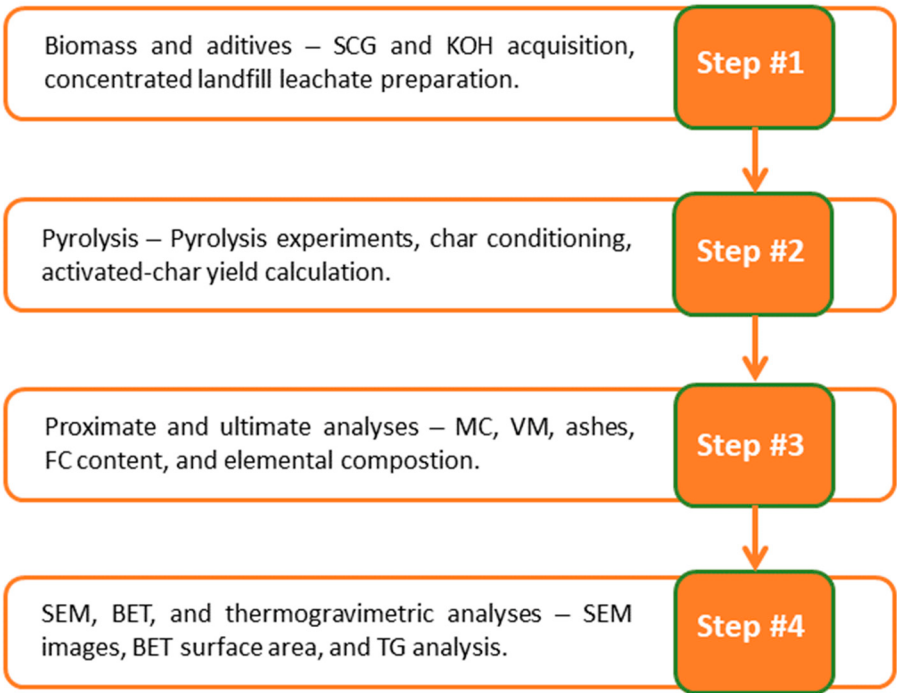


Figure 1. Schematic diagram of the research steps conducted in this study. BET = Brunauer-Emmett-Teller surface area. FC = fixed carbon. SCG = spent coffee grounds. SEM/EDS = Scanning electron microscopy with energy-dispersive X-ray spectroscopy. TG = Thermogravimetric. VM = volatile matter.

3. Results and Discussion

3.1. Char Yield, Proximate Analysis, and Elemental Composition

Table 2 shows char yield and proximate content (wt%) for SCG, biochar, and the produced activated chars.

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/or 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 [24]. For example, Wang et al. [20] 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 yield of volatiles, and reduces the temperature of the maximum weight loss rate [24]. The lower yield when concentrated leachate residue was employed could be due to the synergistic interactions between different LLMC metals (mainly Na and K) and the SCG [38]. Optimizing the mass ratio of SCG and LLMC could be a promising strategy to enhance char yields, as the interaction between these materials influences the activation process. Adjusting this ratio may make it possible to maximize char yield while minimizing the loss of volatiles during the activation reaction.

Briefly, KOH catalyzes the decomposition of the volatile components of SCG, driving the reaction toward char formation. Meanwhile, the mixture of metals from LLMC enhances the carbonization of SCG by interacting with the biomass, increasing the thermal decomposition rate. These metals are supposed to facilitate oxidation reactions, which could lead to a faster loss of volatiles than KOH activation. They promote faster carbonization but also result in a lower char yield because the reaction shifts more toward volatile product formation. Studies have explored the kinetics of pyrolysis reactions in the presence of various activating agents [39–41]. Modeling the pyrolysis kinetics and activation process using computational methods could further explain the underlying interaction mechanisms between SCG and KOH or LLMC.

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 [28]. 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 [42].

SEM/EDS was employed to observe the morphology of SCG, concentrated leachate residue, and prepared materials. EDS spectra were used to determine biomass and char composition (Table 3).

Table 3. Ultimate analysis of biomass and chars from EDS spectra.

Material	Elemental composition (dry basis, wt%)								
	C	O	Na	K	Mg	Ca	Al	Cl	S
SCG	47.73	47.49	n.d	3.19	n.d	0.91	n.d	n.d	0.68
LLMC residue	14.55	37.04	40.86	2.26	n.d	n.d	0.78	2.63	1.55
SCG char	46.06	45.26	n.d	3.87	0.40	n.d	n.d	n.d	0.52
KOH-activated char	85.30	13.70	n.d	0.87	0.02	n.d	n.d	n.d	0.10
LLMC-activated char	63.97	20.16	4.32	4.14	1.00	2.87	n.d	0.47	1.43

n.d = not detected. KOH = potassium hydroxide. LLMC = landfill leachate membrane concentrate. SCG = spent coffee ground.

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%). 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%). Despite the samples being washed with deionized water under neutral

conditions, the residual salts from the LLMC activator may have persisted in the activated carbon's structure. Due to the high salt content of the LLMC residue, primarily Na and K, the washing process may not have been thorough enough to remove all the residual salts. The remaining chemical constituents in the carbon network can affect the material's surface area, chemical reactivity, electrochemical properties, and adsorption capabilities, thus limiting its effectiveness in various applications. Therefore, purification steps (e.g., acid or alkaline washing) may be necessary to remove these residues and enhance the material's functionality, especially when purity and specific surface properties are critical [32,43]. In addition, sulfur content in the LLMC-activated char (1.43 wt%) raises concerns about potential sulfur dioxide (SO_2) emissions during combustion. Likewise, addressing sulfur removal through additional purification steps may be crucial for ensuring the material's environmental sustainability when used as a fuel or in combustion processes.

3.2. SEM Images and Porosity

Scanning electron microscopy (SEM) was used to analyze the biomass and LLMC residue structure and surface topography (Figure 2). 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.

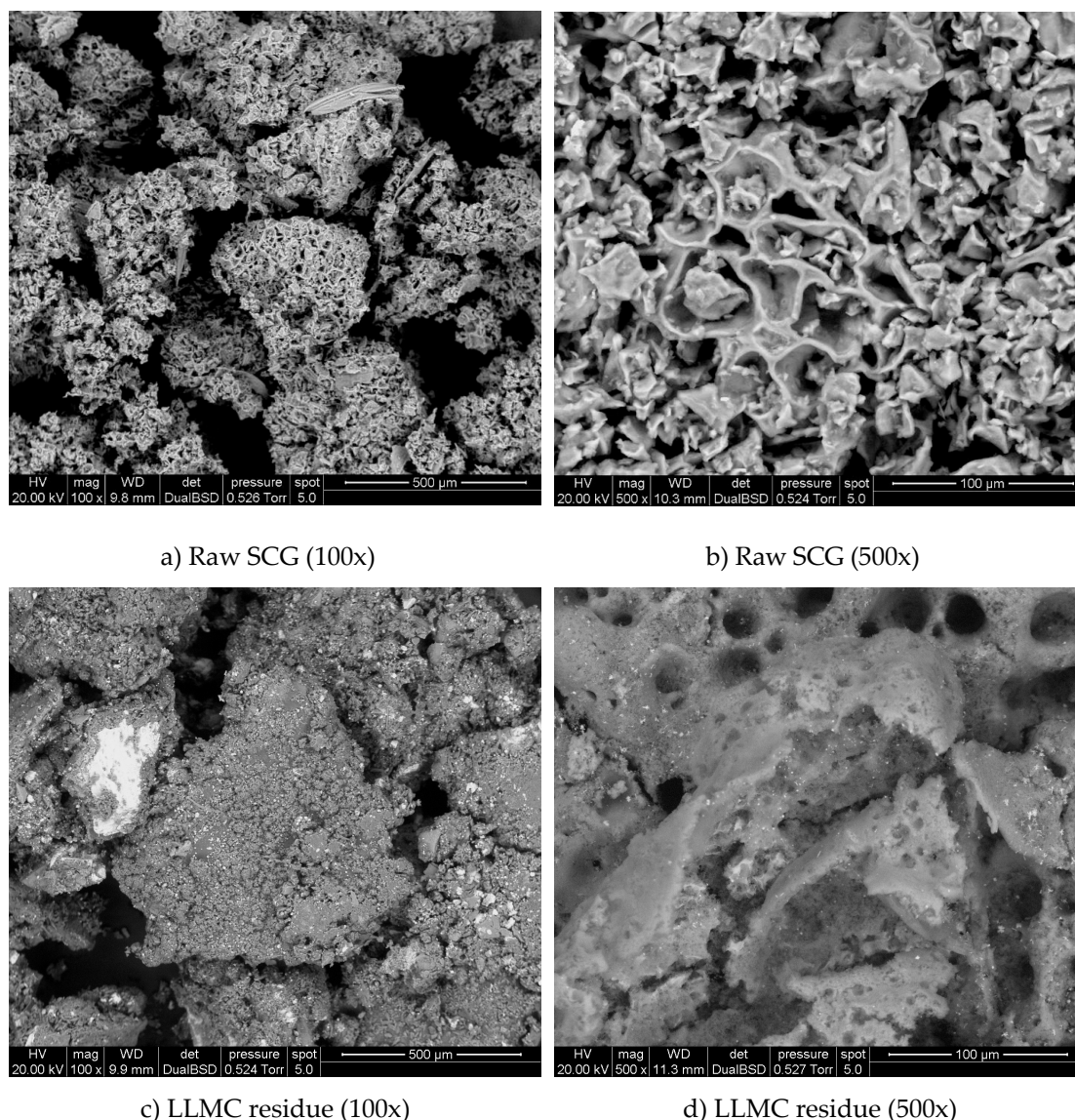
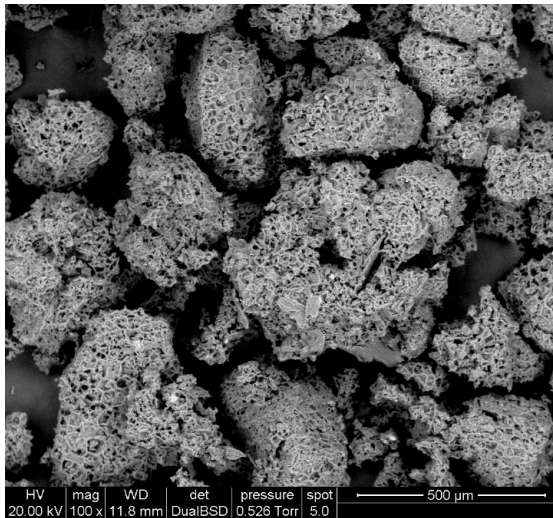
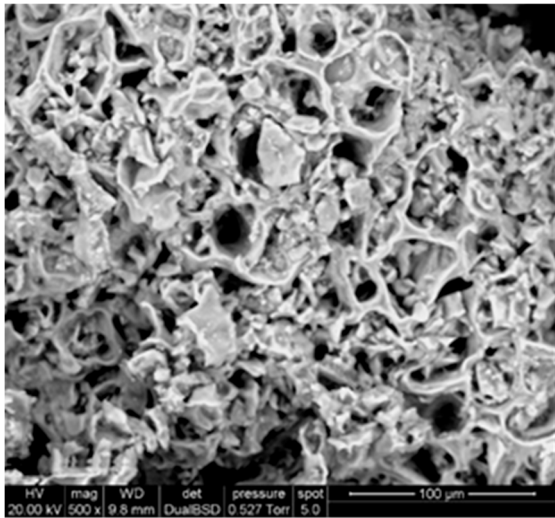


Figure 2. SEM images of starting materials. LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds.

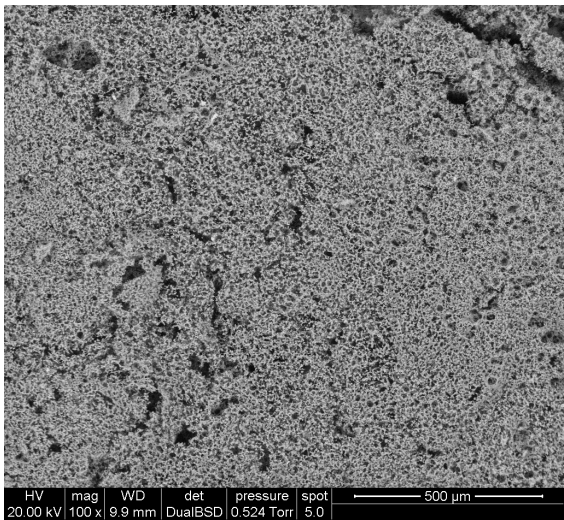
Following slow pyrolysis, biomass undergoes a notable transformation, manifesting a darker hue. SEM images of SCG, KOH-activated, and concentrated leachate-activated chars are illustrated in Figure 3. The SCG char was denser than the precursor. Larger porous structures are observed in the SEM images. In the LLMC-activated char, larger dispersed pores were also observed, and discontinuous structures impregnated with inorganic elements were portrayed. This portrayal suggests a unique structural arrangement compared to the other char samples.



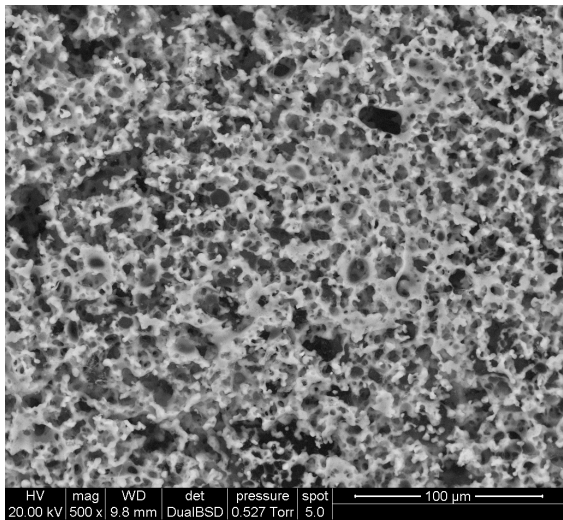
A) SCG biochar (100x)



B) SCG biochar (500x)



C) KOH-activated char (100x)



D) KOH-activated char (500x)

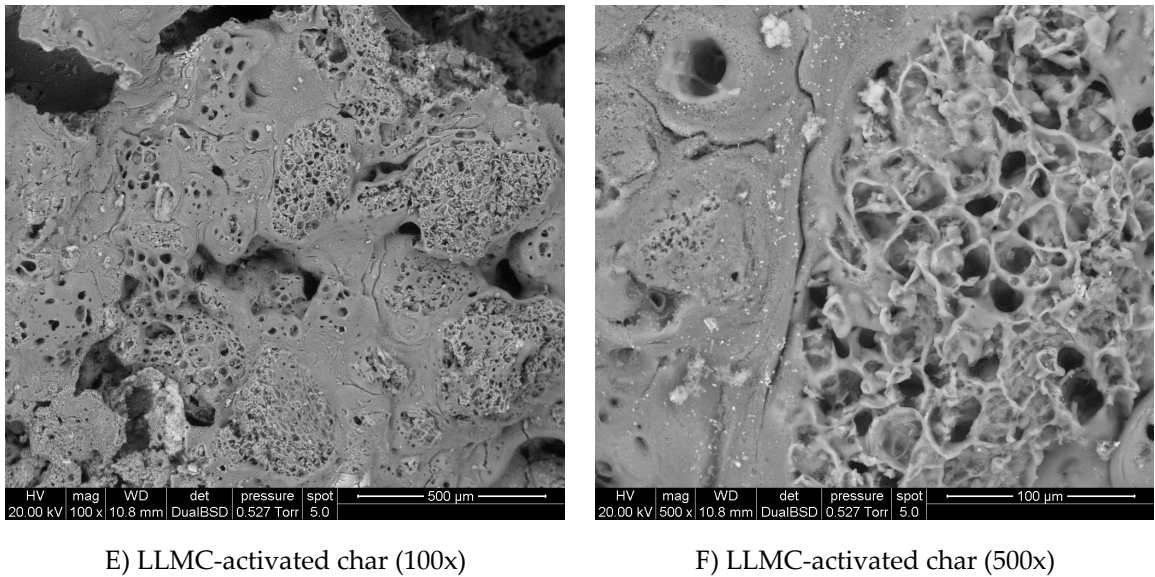


Figure 3. SEM images of SCG char and activated chars. LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds.

Table 4 shows the BET surface area and average pore diameter of SCG and prepared chars at isothermal pyrolysis (600°C) of 1 h.

Table 4. BET surface area and average pore diameter of SCG and prepared chars.

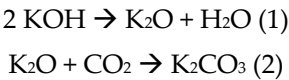
Sample	BET surface area (m ² g ⁻¹)	Average pore size (nm)
SCG	4.5	10.7
SCG char	463	4.8
KOH-activated char	1960	1.8
LLMC-activated char	1138	5.9

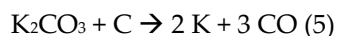
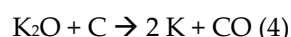
LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds.

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. 1138 m² g⁻¹). KOH is one of the most effective activating agents for preparing activated carbon with a high specific surface area. 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 m² g⁻¹) [44,45].

The mechanism of KOH activation involves the conversion of KOH into potassium oxide (K₂O) at 400°C and then complete conversion into potassium carbonate (K₂CO₃) at 600°C (Equations 1 – 2) [32]. The K₂CO₃ is also produced during the activation process (Equation 3). Afterward, metallic potassium may be generated by K₂CO₃ or K₂O reduction (Equations 4 – 5).

The interaction between SCG and KOH occurs due to the strong ionic and electrostatic forces, which influence the carbon surface structure [43]. As a result of intermolecular force compensation, the energy of molecules inside is lower than that of surface molecules [46,47]. Potassium ions from KOH can break the π-bonds in the aromatic layers of SCG, further activating the carbon surface and increasing the available reaction sites. It penetrates the internal structure of the carbon lattice to create new pores and expand the char surface area [48]. Additionally, the enhanced wettability and reduced surface tension facilitate better penetration of KOH into the carbon matrix, thereby promoting the overall reactivity of the system [32].





On the other hand, the higher ash content of LLMC-char might justify why the surface area was smaller than KOH-activated char (7.0 vs. 1.3 %wt). The inorganic formed by the ash component occupies the material's pore structure, reducing the surface area [49]. Therefore, the subsequent washing step is essential to remove remaining chemical constituents from the carbon network, improving the porous structure and material surface area [32].

Regarding pore structure, KOH- and LLMC-activated materials have 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 [50].

3.3. Thermal Analysis

Figure 4 presents the TG, derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) profiles for SCG and the resulting biochar. The thermal analysis of SCG indicates an initial loss of free water between 20 and 150 °C, followed by the combustion of organic matter around 580 °C. The first DTG peak and its corresponding endothermic DSC response at 150 °C are associated with the evaporation of free water. Subsequent DTG peaks and exothermic DSC signals observed from 150 to 580 °C correspond to the combustion of organic compounds in SCG.

The most significant peaks in the DTG thermal decomposition of SCG include cellulose, lignin, and hemicellulose degradation [23]. Wachter et al.[8] 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°C, 451°C, and 505°C [8]. 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. [51], 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 [51].

Similar behavior was observed for the produced char from that biomass. However, DTG and DSC peaks from 150 to 390 °C are absent for SCG char, which the hemicellulose loss during the SCG pyrolysis can explain. Hemicellulose has a temperature decomposition of around 220°C [7]. 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. The last stage was probably the thermal decomposition of carbonaceous residues, that is, stable components with high molecular weight and refractory carbon [52]. 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 the work of [53].

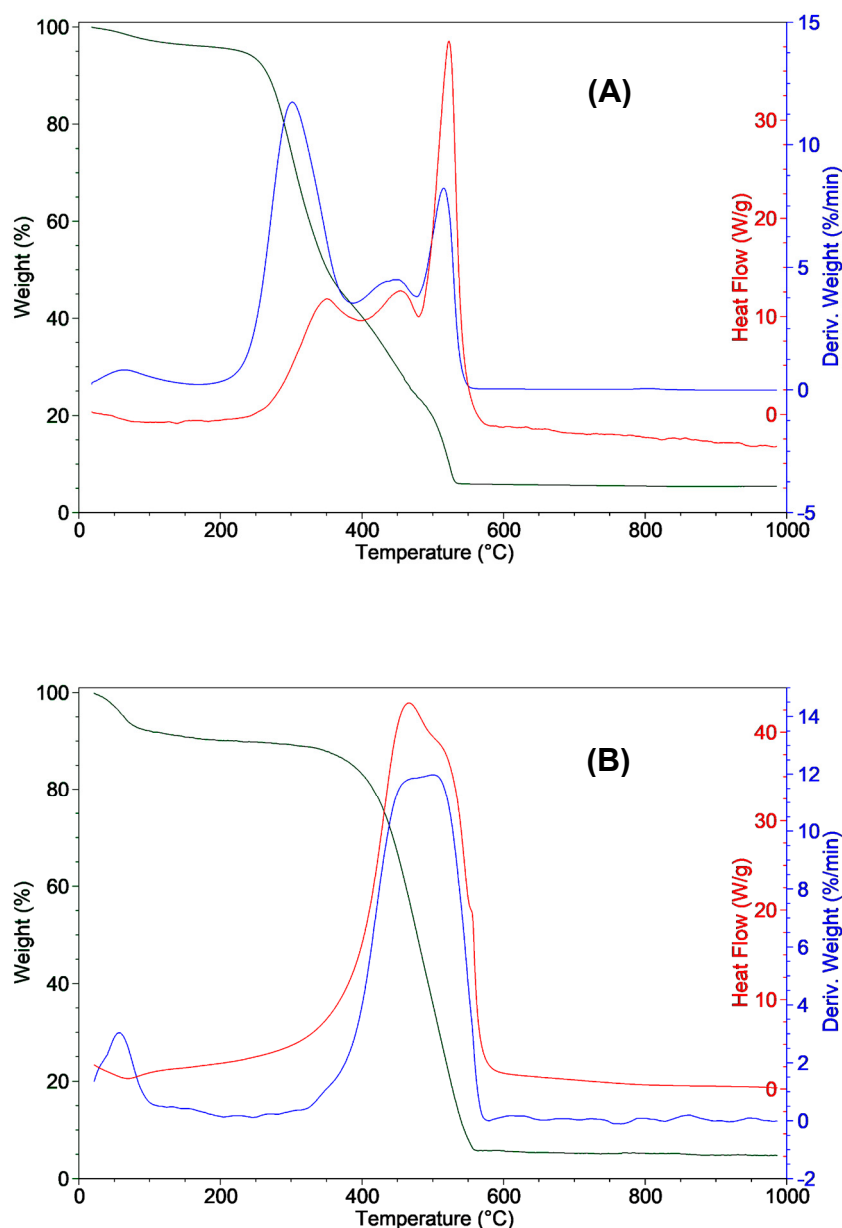


Figure 4. TG, DTG, and DSC curves for SCG (A) and the produced char (B). DSC = differential scanning calorimetry. DTG = derivative thermogravimetry. SCG = spent coffee grounds. TG = thermogravimetry.

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 [54]. The high stability results in more complete combustion and higher energy release during combustion. Besides, the augmented surface area of char (463 vs. 4.5 m² g⁻¹) enhances combustion kinetics, enabling more effective utilization of its carbon content and releasing more energy [55].

TG, DTG, and DSC curves of SCG + LLMC residue (1:1) and LLMC-activated char are illustrated in Figure 5. 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 [56].

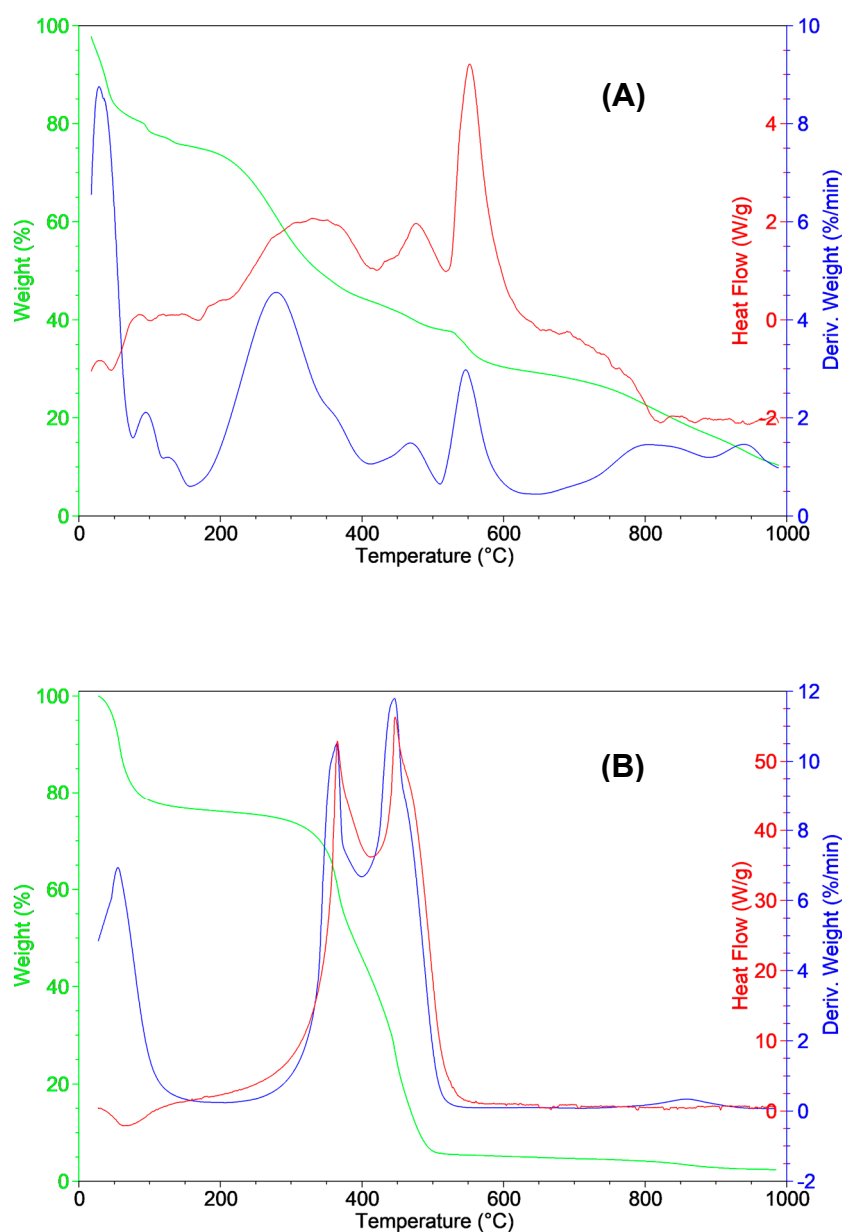


Figure 5. TG, DTG, and DSC curves for SCG+LLMC residue (1:1) (A) and the LLMC-activated char (B). DSC = differential scanning calorimetry. DTG = derivative thermogravimetry. LLMC = landfill leachate membrane concentrate. SCG = spent coffee grounds. TG = thermogravimetry.

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 metals, such as Na and K, alter the char reactivity and shift the thermal oxidation of carbon materials to lower temperatures [20]. 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 [23]. 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 6). Besides, it was registered that the energy of the char activated using KOH was similar to the SCG char (18.40 MJ kg⁻¹). These results are consistent with the literature [51,57]. In sum, combustion enthalpies of SCG (raw biomass), SCG char, KOH-, and LLMC-activated chars were 11.55, 18.11, 18.40, and 22.04 MJ kg⁻¹, respectively.

Activated carbons with a well-developed microstructure (i.e., balanced porosity and graphitic domains) exhibit high thermal stability and a favorable energy enthalpy. However, a well-developed microstructure may also reduce the energy enthalpy by increasing the proportion of oxygenated functional groups and decreasing carbonization efficiency [58,59]. El-Hendawy et al. [59] confirmed the presence of an open-pore structure and various functionalities on the carbon surfaces of cotton stalk chars prepared with KOH, H₃PO₄ and steam as activating agents. KOH produced a carbon with higher microporosity and the highest specific surface area among the prepared chars (1307 m² g⁻¹). In contrast, despite the lower surface area of the H₃PO₄-activated char (841 m² g⁻¹), it exhibited higher thermal stability. FTIR analysis confirmed a high amount of oxygen-functional groups on the surface of the KOH-activated carbon, which could contribute to its lower energy enthalpy.

Moreover, the material may become less dense as microporosity increases, and the carbon content per unit mass can decrease. Microporous carbons may also release more volatile organic compounds during combustion. These volatiles can reduce the combustion enthalpy of the carbon, as they might not contribute as much energy as the solid carbon structure itself [58–60]. Even though, all prepared chars had combustion enthalpy 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 [61].

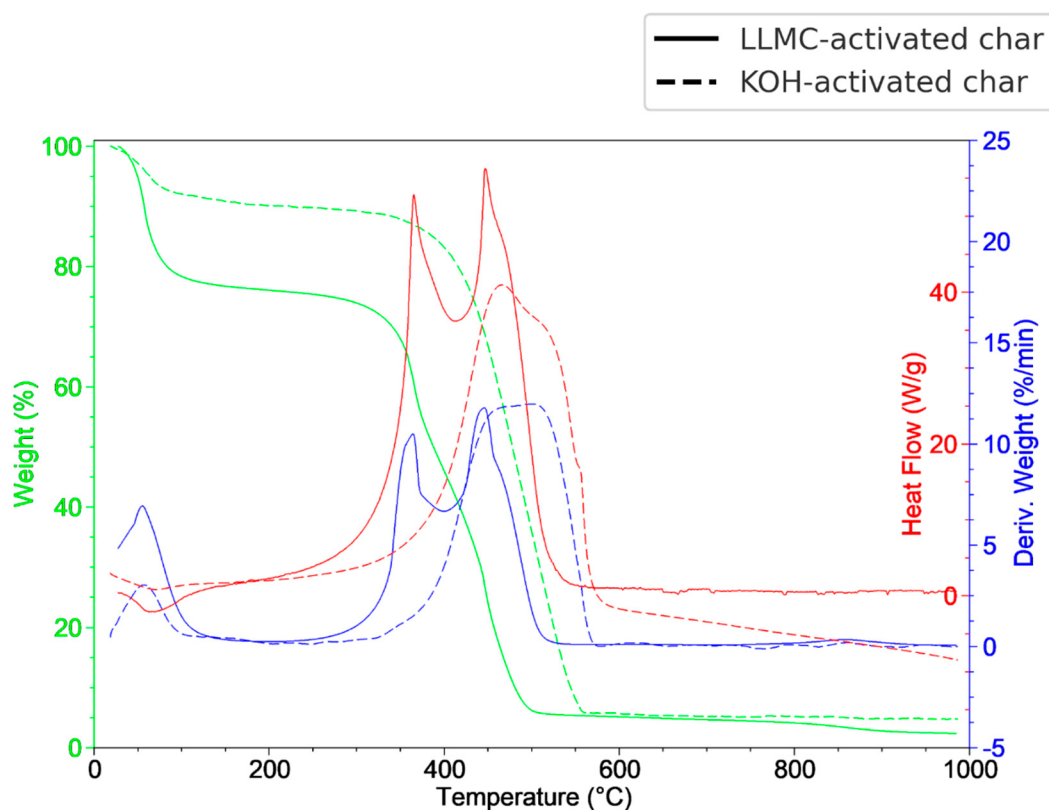


Figure 6. TG, DTG, and DSC curves for KOH-activated char and LLMC-activated char. DSC = differential scanning calorimetry. DTG = derivative thermogravimetry. LLMC = landfill leachate membrane concentrate. TG = thermogravimetry.

4. Conclusions

This research focused on the slow pyrolysis of SCG using KOH and LLMC residue as activating agents. The conclusions from this work are: #1) The char yields in slow pyrolysis ranged from 18 to 24%. The mass yield of LLMC-activated char was 18.6%, while KOH-activated char produced a higher yield of 21.2%. Alkali metals, such as K, Na, and Li, have been shown to induce a so-called synergistic effect that promotes the yields of volatiles at the expense of char and oil recovery. The lower yield observed when LLMC residue was employed in pyrolysis could be due to the synergistic interactions between different LLMC metals (mainly Na and K) and the SCG, which intensifies carbon oxidation during the activation process compared to using KOH alone; #2) The KOH-activated char exhibited a higher surface area than the LLMC-activated char, with a surface area of 1138 m² g⁻¹, approximately 72% greater than the 1960 m² g⁻¹ surface area of the LLMC-activated char.

In addition, the elemental composition of the KOH-activated sample identified the material as C-rich (85.30 wt%). These features 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 22.04 MJ kg⁻¹, making it possible for usage as a biofuel. The results showed that both activated chars had better energetic and morphological properties than the non-activated char prepared from SCG biomass. Comparing the KOH and LLMC as activating agents, the slow pyrolysis performed better in the presence of KOH. It provided a higher char yield and a material with higher carbon content and surface area.

Meanwhile, using LLMC residue as an activating agent depicts the possibility of valorization of landfill waste by producing a potential biofuel. Future studies for this research are crucial, including optimizing the pyrolysis and, most importantly, exploring analytical techniques to understand the

char surface chemistry and functional groups. Studies on practical applications for the prepared activated chars are also on the horizon.

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

Data Availability Statement: The data supporting this study's findings are available from the corresponding author upon reasonable request.

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