

Article

From Thermal Conversion to Cathode Performance: Acid-Activated Walnut Shell Biochar in Li–S Batteries and Its Impact on Air Quality

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Abstract

The thermal processing of walnut shells was investigated through pyrolysis within the range of 100–650 °C, highlighting the influence of thermal engineering parameters on biomass conversion. The resulting biochar was subjected to chemical activation with phosphoric acid, and its physicochemical properties were evaluated to determine how thermal processing enhances its performance as a cathode material for lithium–sulfur (Li–S) batteries. This approach underscores the role of thermal engineering in bridging biomass valorization with energy storage technologies. In parallel, the gaseous fraction generated during walnut shell fast pyrolysis was collected, and for the first time, volatile organic compounds (VOCs) under atmospheric conditions were identified using solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS). The composition of the VOCs was characterized, quantifying aromatic compounds, hydrocarbons, furans, and oxygenated species. This study further linked the thermal decomposition pathways of these compounds to their atmospheric implications by estimating tropospheric lifetimes and evaluating their potential contributions to air quality degradation at the local, regional, and global scales.

Keywords: thermal conversion of walnut shells; pyrolytic carbon material; acid activation; gas fraction; Li–S battery cathodes based on thermally activated biochar; air pollution



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1. Introduction

To solve or mitigate some of the global environmental problems, it is necessary to seek technological and natural solutions. Within this context, biochar emerges as a nature-based technology that serves as an environmentally friendly tool. In turn, within a circular economy model, in which the conventional sources of certain resources are replaced by recovered waste, biochar can be considered a sustainable replacement for graphite, graphene, and mineral coal, as long as it comes from residual biomass and does not compete with the human food chain or plant nutrition [1,2]. In this way, biomass residues

of very diverse origins can be transformed into raw materials to produce biochar as a new value-added product.

Biochar production originates from the natural absorption of CO₂ by plants, where carbon is fixed within lignocellulosic structures. Through thermal engineering processes such as pyrolysis or gasification, which are carried out under limited oxygen conditions, this fixed carbon can be converted into biochar. In this context, thermal engineering plays a central role in optimizing temperature, heating rates, and residence times to control biochar yield, structural properties, and potential applications [3]. Biochar is a long-lived material, which is considered positive in terms of greenhouse gas emissions [4]. It is characterized by a structure with high porosity and a high specific surface area [5], high carbon content [4,6], a low cost [7], and high adsorption capacity [8]. These physical–chemical characteristics give it the possibility of carrying out a wide variety of functions such as soil amendment and improvers [9], decontamination of soils and aquatic systems [10], elimination of atmospheric contaminants [11], and being part of electrochemical energy storage devices in Li-ion and Li-S batteries [12]. To improve the physical characteristics or catalytic capacity of biochar, it is common to apply physical or chemical activation methods, such as the use of steam, acid and basic treatments, and oxidizing agents [13]. Activating lignocellulosic biomass by chemical methods is mostly used due to its low energy price, lower time of pyrolysis, high surface area, and higher production of activated carbon yield products. Among the chemical activation agents, phosphoric acid is highly used due to its capability of creating mesopores, resulting in higher total pore volumes and diameters [14], and the simplicity in processing steps.

During the production of biochar by pyrolysis, two other products are formed, the bioliquid and the gaseous fraction. According to the raw material and the reaction method, these products will vary in proportion and composition. Both the bioliquid and the gaseous fraction could have different applications; for example, the bioliquid can be used as a raw material to synthesize different chemicals, fertilizers, or fuels [15,16], and the gaseous fraction can contain compounds with different uses, such as furans and derivatives of furans with combustible properties [17]. Generally, the condensable vapors are collected to produce a bioliquid, while the more volatile non-condensable vapors are emitted into the atmosphere. Some investigations observed that the main gaseous products of biomass pyrolysis are CO₂, CO, and H₂ [18], along with some volatile organic compounds such as benzene and acetaldehyde [18,19]. For example, Hadanu et al. [20] identified the VOCs present in the liquid smoke from coconut shell pyrolysis, with phenol derivatives being the most abundant. Hydrocarbons such as heptane and octane, as well as aromatic compounds such as toluene and benzene, were some of the main non-condensable VOCs identified in the pyrolysis of peanut shells [21], where the activation method used in the pyrolysis process can affect the nature and composition of these emissions.

Once released into the atmosphere, these VOCs can be degraded by different fates such as solar photolysis or a reaction with oxidants such as OH, NO₃, and Cl in coastal areas, as well as O₃ in highly polluted areas, as they are capable of contributing to photochemical smog formation and changes in the oxidative capacity of the atmosphere [22]. In this way, despite the benefits mentioned regarding the use of residual biomass for biochar, this technology could have negative impacts in terms of air quality, affecting human health and the biota by releasing CO, CO₂, SO_x, BTX, and other oxygenated VOCs.

Among the aforementioned functions of biochar, one of the most innovative is its incorporation as a carbonaceous matrix within the electrode in energy storage devices, such as Li-S batteries [23,24]. Compared to Li-ion batteries, Li-S batteries represent a promising energy storage system due to their high theoretical energy density of 2600 Wh/Kg and high theoretical specific capacity of 1675 mAh g^{−1}, assuming that sulfur is completely converted

to Li_2S during the battery discharge process [25]. In addition, sulfur is a more abundant, cheaper, and environmentally friendly component. However, this type of battery has certain limitations such as the low conductivity of S, volumetric changes, and the “shuttle” phenomenon where the polysulfides formed dissolve in the electrolyte and migrate to the Li anode, causing corrosion, low coulombic efficiency, and self-discharge of the cells [26,27]. Carbon materials have been widely used to mitigate these problems [28]. Among these, the use of biochar is proposed, since it presents several advantages such as delivering a strong physical and chemical adsorption capacity, low-cost production, high electrical conductivity, tunable pore sizes, high porosity, and a large surface area to hold sulfur [29]. The surface area of biochars ranges from 200 to 2700 m^2/g , and their porosity ranges from 0.26 to 1.5 cm^3/g [24,30,31]. In addition, in the context of sustainability, biochar would be cheaper and has less environmental impact since it replaces materials such as graphite, graphene, and carbon nanotubes that are otherwise used in the electrode [23,32]. Among different biochars, walnut shells present the advantage of being dense and lignocellulosic, providing, in this way, a high yield of carbon upon pyrolysis. It is also an excellent precursor for producing highly porous carbon structures. This is, as stated before, it is an important factor for hosting sulfur and buffering volume expansion during cycling.

Based on the above, we present, for the first time, a comprehensive study on the influence of H_3PO_4 activation on the structural properties of walnut shell biochar, emphasizing the role of thermal engineering to optimize carbon material performance as a Li–S battery cathode. Additionally, we investigate how H_3PO_4 activation affects the non-condensable gaseous emissions of volatile organic compounds during biochar pyrolysis, highlighting the interplay between thermal process conditions and air quality outcomes. Considering the significance of thermally driven conversion processes for sustainable material production, this work aims to evaluate the atmospheric implications of these emissions with respect to air pollution. Consequently, this work provides a global assessment of walnut shell residue valorization under engineered thermal conditions, with a particular focus on how activation strategies influence both material functionality and environmental impact.

2. Materials and Methods

2.1. Biochar Production

The starting raw material was the walnut shell. As other woody biomass, walnut shells are mainly composed of lignin, hemicellulose, and cellulose. First, this shell was washed with distilled water to remove impurities and adhering particles. Further, the shell was crushed with the help of a grinding machine to obtain a homogeneous particle size. The result of grinding and homogenization was subjected to a first pyrolysis for 2 h at 400 °C in an Ar atmosphere.

The next stage was the activation of the resulting first step of pyrolysis with a solution of H_3PO_4 at 85% *w/w* in a ratio of four parts of the acid solution for each part of biochar [33].

This mixture was heated at 85 °C for 90 min during stirring. After filtration, a second activation pyrolysis of the biochar was performed in a glass tubular reactor with dimensions of 23 × 290 mm (internal diameter and height, respectively) at 650 °C for 1 h. Inside it, 2 g of the activated biochar was added. The reactor was placed inside an electric furnace with temperature control. A continuous N_2 stream at a rate of 60 mL/min was controlled by a mass flow meter (El-Flow Base from Bronkhorst) to ensure an inert atmosphere. Condensable vapors were retained in a condenser at −15 °C. The non-condensable fraction was captured in three 5 L Tedlar chambers coupled to the outlet of the reaction system. This fraction was acquired at three temperature ranges: 100–350 °C, 350–500 °C, and 500–650 °C. Pyrolysis reactions were performed in triplicate. Further information on this experimental system is detailed in a previous study [34].

The biochar produced after the second pyrolysis was washed until neutral pH was reached, and then dried, obtaining the acid-activated walnut shell biochar (AWB). A series of physical chemical analyses was carried out to study the structure of biochar with and without acid activation. BET, scanning electron microscopy, X-ray diffraction, and Raman spectroscopy were used for biochar characterization.

2.2. Biochar Characterization

X-ray diffraction (XRD) patterns were collected on a Pan-Analytical diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were identified by a Horiba Jobin-Yvon LabRam HR 800 spectrometer (Horiba, Francia) using $\lambda = 633 \text{ nm}$ with a range of $400\text{--}3400 \text{ cm}^{-1}$. The various biochar morphologies were examined using a field-emission scanning electron microscope (FE-SEM, Sigma Zeiss, (Oberkochen, Germany, LAMARX facilities). The elemental composition was analyzed through energy-dispersive X-ray spectroscopy (EDS) coupled to the FE-SEM. Thermogravimetric analysis (TGA) was conducted with a Q500 analyzer (TA Instrument Corporation, New Castle, DE, USA) under a nitrogen atmosphere, applying a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from ambient temperature up to $600 \text{ }^\circ\text{C}$. Nitrogen gas adsorption (BET, Brunauer–Emmett–Teller) was used to determinate the surface area and total micro- and mesopore volume of the biochars using a Micromeritics ASAP 2020 porosimeter (Norcross, GA, USA) at 77 K . From these measurements the total surface area (Brunauer–Emmett–Teller: BET), pore volume (by Gurvich's rule), micropore volume and area (using the α -plot method with the standard NPC isotherm), and pore size distribution (applying the DFT method with slit/cylindrical pores; QSDFT adsorption branch kernels) were obtained. Samples were vacuum degassed overnight at $160 \text{ }^\circ\text{C}$ prior to analysis. X-ray photoelectron spectra (XPS) were identified with a Thermo Scientific K-Alpha+ X-ray Photoelectron Spectrometer (Thermo Fisher, Waltham, MA, USA). Spectra were recorded at room temperature using non-monochromatized Al-K 1200 W. The fitting of the spectra was performed using the AvantageTM V5 and Igor PRO 6 (Wave Metrics, Lake Oswego, OR, USA) software with a Shirley-type background.

2.3. Electrode Fabrication, Cell Assembly, and Electrochemical Characterization from Biochar

To prepare the carbon/sulfur composite for the electrodes, $30 \text{ wt\%}$ of the AWB and $70 \text{ wt\%}$ of the sulfur powder (Sigma Aldrich, Darmstadt, Germany) were uniformly mixed and heated at $155 \text{ }^\circ\text{C}$ for 6 h in an argon atmosphere to achieve sulfur impregnation. The sulfur content remaining in the impregnated carbon was determined through TGA, and the specific capacity of each material was calculated based on these values. The working electrode was prepared by mixing $80 \text{ wt\%}$ of the attained biochar/sulfur (AWB: S), $10 \text{ wt\%}$ of conductor carbon (carbon super P carbon, Timcal, MTI), and $10 \text{ wt\%}$ of polyvinilidene do fluoride (PVDF) binder, using N-methyl-2-pyrrolidone (NMP) as the solvent. These elements were mixed at 600 rpm for 5 min to obtain uniform slurries. The slurries were spread on an aluminum foil by the Doctor Blade method [34] at a height of $150 \text{ }\mu\text{m}$ and dried in the oven at $80 \text{ }^\circ\text{C}$ for 2 h . The electrodes were punched into circular disks with a diameter of 12 mm and kept inside a glovebox. CR2032 coin-type cells were assembled under an argon atmosphere, using lithium foil as the anode and an electrolyte composed of 1.0 M lithium bis (trifluoromethanesulfonimide) (LiTFSI) and 0.25 M LiNO_3 dissolved in a $1:1 (v/v)$ mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME). Each cell contained $13 \text{ }\mu\text{L}$ of electrolyte per mg of sulfur. The cycling behavior was evaluated with a Biologic battery tester (BioLogic, Seyssinet-Pariset, France) over a voltage window of $1.8\text{--}2.6 \text{ V}$ at room temperature, applying a current density of $50 \text{ }\mu\text{A}/\text{mg}$ for the initial cycle and $100 \text{ }\mu\text{A}/\text{mg}$ for the following cycles. The specific capacity is obtained, taking in consideration the total mass of sulfur in the electrode. In order to evaluate the

rate performance, the batteries were subjected to a progressive increase in current every 10 cycles until 200 $\mu\text{A}/\text{mg}_\text{S}$ was reached.

2.4. Gas Fraction Analysis

The non-condensable gases from the second pyrolysis after activation were captured and pre-concentrated using the solid-phase microextraction (SPME) technique, exposing the fiber to the gases for 10 min. A silica fiber coated with a divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS) adsorbent was used. Finally, the sample was released by exposing the fiber for three minutes in the injector of a Shimadzu QP-2020 gas chromatograph, followed by mass spectrometry (GC-MS) with an apolar MEGA-5 MS column 30 m long, 0.25 μm thick, and 0.25 mm in diameter (Shimadzu, Kyoto, Japan). Compound identification was carried out by matching their spectra with those from the NIST MS and Wiley libraries (match > 90%). Furthermore, a semiquantitative evaluation was conducted based on the average relative chromatographic area (ARCA) corresponding to each compound. The impact of these emissions on air quality was analyzed according to different parameters such as the lifetime of the compounds, toxicity, and the photochemical ozone creation potential (POCP) developed for the main compounds identified.

3. Results and Discussion

3.1. Biochar Characterization

The acid-activated biochars before (black, AWB) and after (red line, AWB-S) sulfur impregnation were characterized by XRD, as can be seen in Figure 1a; the spectrum for AWS only shows two broad peaks, which is typical for highly disordered carbons, located at 25° and 45° , respectively, and related to the (002) and (100) crystallographic planes of graphite [35,36]. After sulfur impregnation, some defined peaks assigned to orthorhombic sulfur (JCPDS 83-2283) are seen [37], which indicates that a fraction of the sulfur is located outside the pores in the form of a crystalline phase, and the broaden peaks match the AWB at the same degree values. Figure 1b shows the Raman spectra of the acid-activated walnut shell, presenting two characteristic peaks observed at around 1343 and 1593 cm^{-1} , which are assigned to the D and G bands, respectively. These are attributed to the structure of defective graphite or disordered carbon, as well as the G band's characteristic peak of the graphite layer, which is generated by the tangential vibration of the sp^2 -bonded carbon atom. It can also be observed in a 2D band at 2700 cm^{-1} , which corresponds to in-plane vibrations of sp^2 hybridized carbon. The ratio of the D and G peaks gives a value of 1.14, correlating with an important amount of structural defects present in the carbon material.

A detailed X-ray photoelectron spectroscopy (XPS) analysis was conducted to investigate the composition and chemical environments of the AWB sample. XPS is a powerful surface analysis technique that offers both qualitative and quantitative insights into surface chemistry. The extended survey spectrum of the AWB sample (Figure 1c) revealed the presence of carbon, oxygen, silicon, nitrogen, and phosphorus, with carbon as the dominant element, followed by oxygen. The relative atomic percentages of Si, N, and P were approximately 2%, representing the surface composition up to a depth of 7–9 nm. To gain insights into chemical bonding, we analyzed the C1s spectrum (Figure 1d). The deconvoluted C1s spectrum of the AWB sample (Figure 1d) revealed seven peaks, corresponding to different carbon species. The main peak at $(284.4 \pm 0.1) \text{ eV}$ was attributed to sp^2 carbon atoms in delocalized C-C bonds, consistent with the anticipated graphitic character of the sample. Due to the significant electrical conductivity of the samples, charge compensation was unnecessary, allowing us to focus on the graphitic features during the fitting process. Peaks between 284.8 eV and $\sim 289 \text{ eV}$ were associated with sp^3 carbon atoms, which were

either bonded to hydrogen or oxygen, along with features indicative of π - π^* excitation energy losses. The peak at 286.3 eV corresponded to C–O bonds, which are linked to ether or phenolic groups, while ester/carboxylic groups (O=C–O) appeared at ~289.2 eV, and carbonyl groups (C=O) were identified at 287.4 eV.

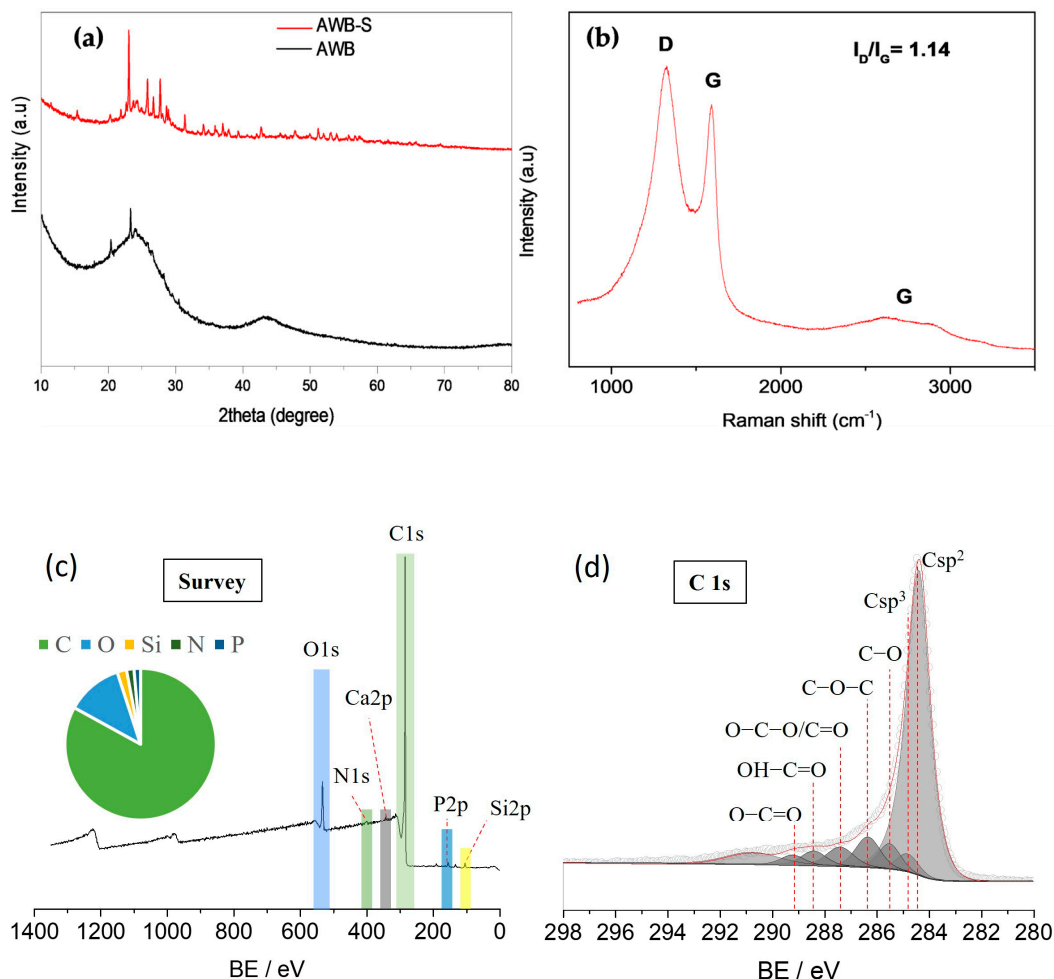


Figure 1. (a) XRD for AWB (black) and AWB-S (red), (b) Raman spectra showing the positions of G, D and 2D-bands; (c,d) XPS survey spectrum, and XPS C1s core-level spectrum of AWB.

The morphological characteristic of the activated walnut shell was studied by SEM and EDS analysis. Figure 2a,b show SEM images of walnut shells before (a) and after (b) being activated with phosphoric acid. As can be seen, the non-activated carbon presents a non-porous structure, while the activated one (b) presents a rougher surface with cavities, showing a microporous structure. The EDS for this last sample (Figure 2c) also confirms the presence of phosphorus in the obtained material. It can also be observed that the sample is composed predominantly of carbon and oxygen. Phosphoric acid functions as an acidic catalyst, facilitating bond cleavage, hydrolysis, dehydration, and condensation processes. These reactions are accompanied by crosslinking between phosphoric acid and the biomass biopolymers, resulting in its integration into the material's structure [38].

Nitrogen adsorption isotherms show an increasing slope below the relative pressure of 0.4, indicating an appreciable amount of mesopores [39]. The isotherm presented in Figure 3a is a type IV one, according to IUPAC, which is characteristic of a mesoporous structure.

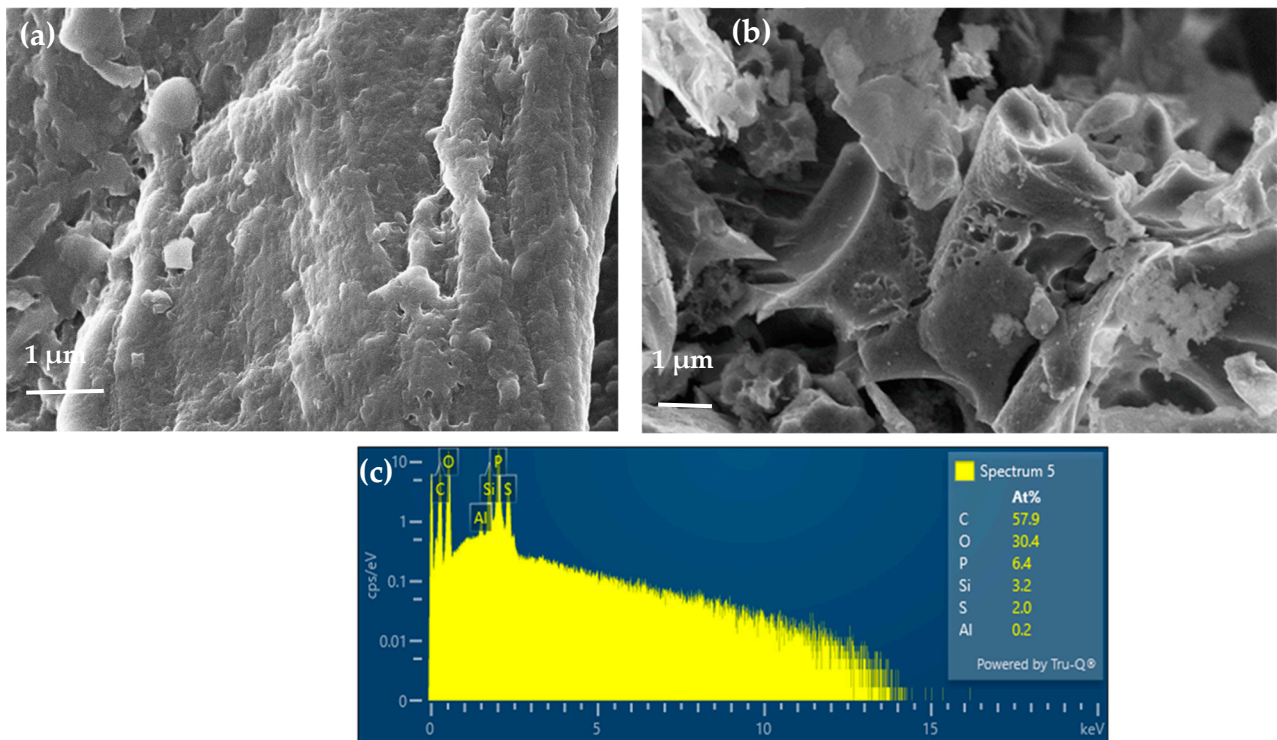


Figure 2. SEM of the (a) non-activated walnut shell and (b) the H_3PO_4 -activated walnut shell. (c) The EDS of the phosphoric acid-activated carbon.

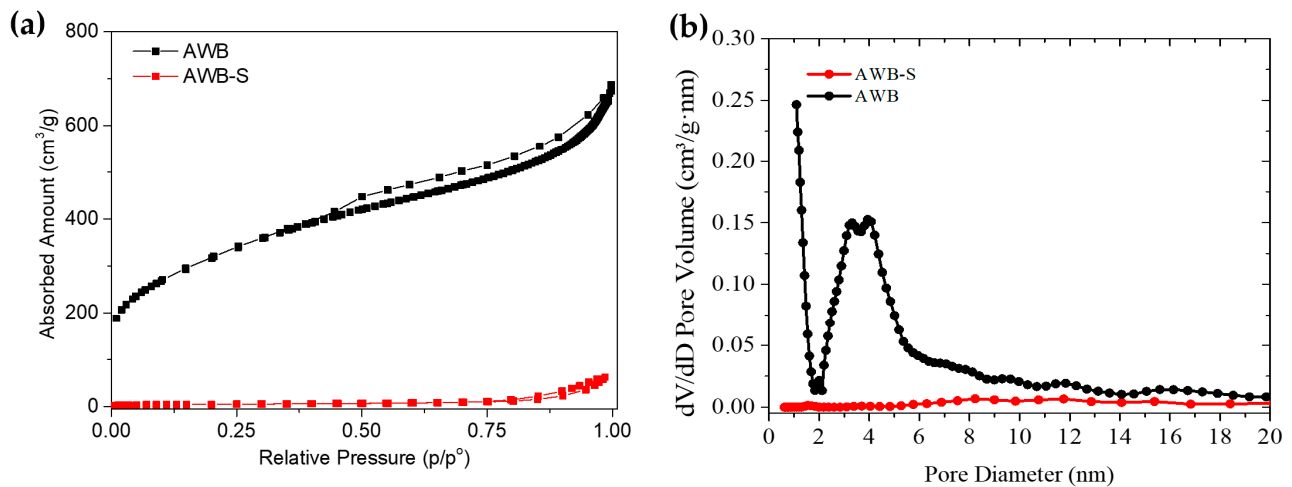


Figure 3. (a) N_2 adsorption–desorption isotherms and (b) pore size distribution for AWB (black) and AWB-S (red).

The H3 hysteresis loop indicates the co-existence of micro- and mesopores (Figure 3a,b). The activation process increases the BET surface area, giving a value of $959 \text{ m}^2/\text{g}$, as depicted in Table 1, and a mean mesoporous diameter of 4.48 nm , as can be seen in Figure 3b; these values are similar to others found in lignocellulosic-activated materials [40,41]. Taking into consideration that the amount of S micro is lower and that the V_{micro} is lower, it can be stated that the carbon matrix is mostly composed of mesoporous structures. The presence of pores in the carbon matrix plays a fundamental role in sulfur loading and Li^+ diffusion when used as a carbon matrix for the Li-S cathode material. For the infiltrated sample (AWB-S), the N_2 adsorption isotherms are flat, indicating that most of the pores were filled with sulfur during the infiltration step. There is important for the diminishing of the total surface, for both micro- and mesopores, where it can also be seen that the

micropores are almost totally filled by sulfur, and almost 99% of the mesopores are also filled. The presence of pores in the carbon matrix plays a fundamental role in sulfur loading and Li⁺ diffusion when used as a carbon matrix for the Li–S cathode material. The pores and the presence of functional groups (P and O groups) [42,43] in the carbon matrix help to accommodate the volume changes [44] suffered during the reduction from S₈ to Li₂S and to avoid the shuttle effect, respectively.

Table 1. BET surface area and pore characteristics of AWB and AWB-S.

Sample	S _{BET}	S _{meso}	S _{micro}	V _{TP}	V _{meso}	V _{micro}
	(m ² /g)			(cm ³ /g)		
AWB	959.00	521.00	438.00	0.907	0.703	0.204
AWB-S	14.00	13.40	0.60	0.082	0.082	0.001

3.2. Electrochemical Performance of Li–S Batteries

The attained activated walnut shell biocarbon was further used as the carbon material for the cathode in Li–S batteries. The real content of sulfur in the carbon–sulfur composite was obtained by thermal gravimetric analysis, which was carried out in the nitrogen atmosphere, as can be seen in Figure 4. The weight loss corresponds to physisorbed water up to around 170 °C, and the rest (70%) corresponds to sulfur sublimation. A pronounced slope is observed starting near 200 °C, which suggests rapid evaporation of sulfur primarily located on the carbon matrix surface. Beyond approximately 300 °C, the weight percentage remained stable in all cases. The value obtained by TGA was further used in the electrochemical characterization of the material.

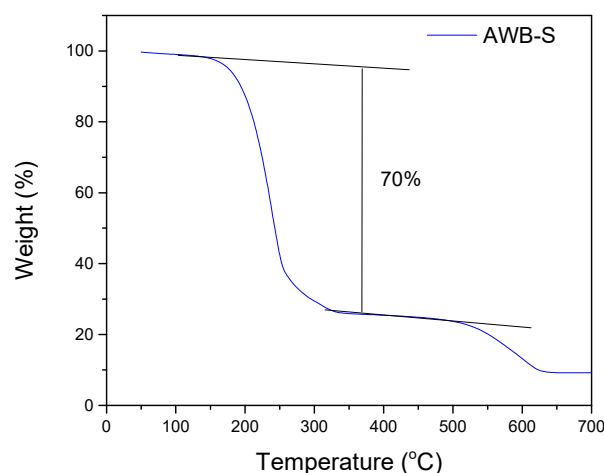


Figure 4. Thermogravimetric analysis (TGA) curve for AWB-S in a nitrogen atmosphere.

Figure 5 shows the electrochemical performance of the attained AWB-S cathode. Figure 5a shows the charge/discharge curves at 50 μ A/mg_S between 2.8 V and 1.8 V. Two plateaus can be seen in the discharge curves, with the first one around 2.28 V corresponding to the reduction of long-chain polysulfides to short-chain polysulfides (Li₂S_x, 4 $\leq$ x $\leq$ 8) and the second one at 2.08 V corresponding to the conversion of short-chain polysulfides to Li₂S₂/Li₂S. The charge curve shows one plateau corresponding to the inverse reaction. As can be seen in cycle performance (Figure 5b), good specific capacity retention is observed, with a capacity of 280 mAh/g even after 100 cycles at 100 μ Ah/mg_S and a good coulombic efficiency of around 98%. These features could be attributed to the presence of the mesopores in the carbon structure and the phosphorous- and oxygen-based functional groups that help in avoiding the shuttle effect.

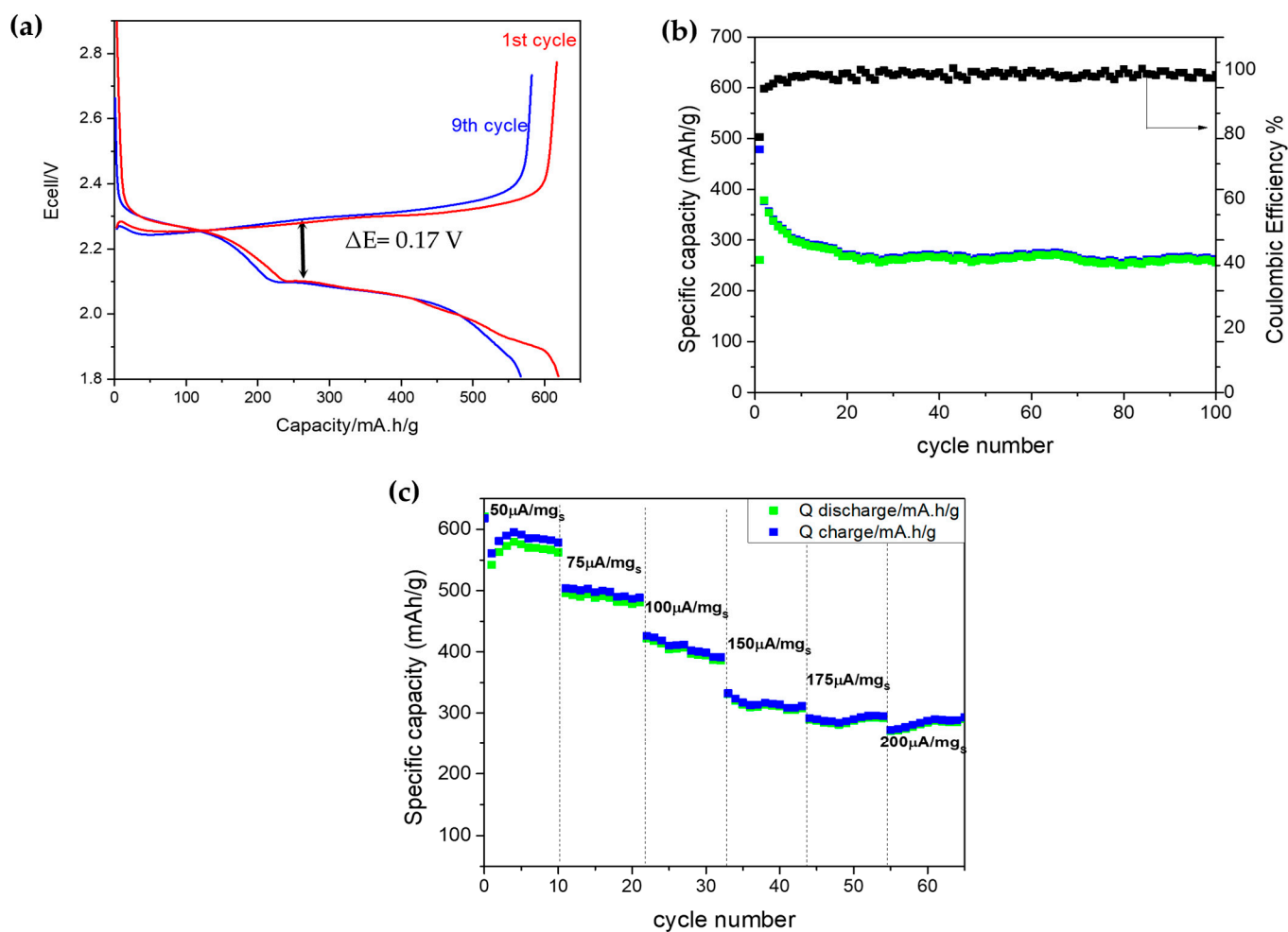


Figure 5. Electrochemical performance of AWB-S. (a) Galvanostatic charge/discharge curves at different cycles recorded at 50 $\mu\text{A}/\text{mg}_\text{s}$. (b) Cycle performance and coulombic efficiency (right axis, black squares) cycled at 100 $\mu\text{A}/\text{mg}_\text{s}$. (c) Specific capacity at different current densities.

Upon evaluating the specific capacity at different current rates, as expected, it can be seen (Figure 5c) that when the current density increases, the specific capacity diminish. Nevertheless, it is important to note that even at high current densities of 200 $\mu\text{A}/\text{mg}_\text{s}$, it still remains with a good specific capacity of around 300 mAh/g .

3.3. Gaseous Emissions

Although the analysis of the gaseous fraction has gained particular importance due to the growing interest in certain compounds present in this phase, there are still few studies focused on their environmental impact. Previous research has reported only a limited set of gases released during the pyrolysis of various biomass residues. Among the identified compounds are H_2 , CO_2 , CO , CH_4 , and some non-methane hydrocarbons, which are detected when pyrolyzing rice husks, wheat straw, wood, and wild reeds, as well as almond, walnut, and peanut shells [45–47]. Gaseous emissions are dependent on the pyrolysis technique and the biomass's nature and composition. The oxygen-free conditions during pyrolysis create an inert atmosphere that leads to higher CO_2 and CO levels through decarbonylation and decarboxylation reactions [48]. The breakdown of aromatic rings and the cleavage of methoxy groups within the lignin structure result in the release of H_2 and CH_4 . Conversely, the decomposition of hemicellulose produces higher amounts of CO_2 due to the oxygen present in its carboxyl groups. Meanwhile, thermal cracking of the carbonyl and carboxyl groups in cellulose leads to an increased CO output [49,50].

Table 2 presents the total compounds identified in the non-condensable gases as a function of reaction temperature and their corresponding average relative chromatographic area (ARCA) before and after activation with phosphoric acid.

Table 2. VOCs detected in the gaseous fraction from walnut shell pyrolysis, both with and without activation, along with their corresponding average relative chromatographic area (ARCA).

Temperature (°C)	VOC Identified Without Activation/ARCA	VOC Identified with Activation/ARCA
100–350	Hexanal/95%	Acetic acid/45.08%
		Benzene 1,2-dimethyl/13.76%
		Benzene, 1-ethyl-3-methyl/4.46%
		Benzene, methyl/3.67%
		Benzene, ethyl/1.68%
		1-heptene 2,4-dimethyl/15.02%
		2-Pentanone, 4-hydroxyl-4-methyl/4.93%
350–500	Hexana/91.04% Furan, 2-methyl/8.96%	Acetic acid/29.25%
		Benzene, methyl/23.6%
		Benzene 1,2-dimethyl/19.09%
500–650	Hexanal/19.2% Benzene, methyl/27.8% Benzene 1,2-dimethyl/15.68% Benzene/4.91% Benzene, ethyl/3.83% Furan, 2-methyl/3.95% Furan, 2,5-dimethyl/2.19% Octane/6.36% 1,3,5,7-Cyclooctatetraene/6.03% Heptane/4.19% Nonane/3.19% 1-Octene/3.17% 1-Heptene/2.66% 2,3-Dimethyl-2-cyclopenten-1-one/3.91%	Benzene, ethyl/12.33%
		Benzene, methyl/29.08%
		Benzene, ethyl/19.55%
		Benzene 1,2-dimethyl/19.18%
		Benzene/11.8%
		Benzene, 1-ethyl-3-methyl/4.38%

Figure 6 shows the selectivity towards the assigned chemical groups at each reaction temperature without the activation process. The gas-phase composition is once more determined by the lignin, cellulose, and hemicellulose contents and the pyrolysis temperature. Aldehydes were observed in the whole range of temperatures evaluated. This group mainly included the presence of hexanal. The maximum value was reached between 350 and 500 °C with 91.04% ARCA. Instead, aromatic derivatives such as benzene and furans represented the second-most abundant group of compounds after aromatics. This pattern is consistent with previous research on the pyrolysis of banana peels [51].

Alternatively, furan derivatives are produced through the thermal breakdown of cellulose and hemicellulose [52–54]. Furans have been previously observed in biomass pyrolysis studies, accounting for up to 50% of the gaseous phase. One possible formation pathway involves the activation of cellulose without mass loss, followed by the generation of low-molecular-weight species such as furans through ring fragmentation [55]. Nevertheless, the depolymerization of polysaccharides could also serve as a source of furan compounds [55,56]. Selectivity towards alkenes and alkanes was observed, showing a slight increase with rising temperatures.

In the presence of phosphoric acid as an activator (Figure 7), acetic acid emissions are observed mainly between 100 and 500 °C, with a percentage between 30 and 45%. Emissions of this acid are considerable, as acetic acid contributes notably to the acidity of

precipitation and cloud water in the troposphere [57–61]. Keene and Galloway [62] and Andreae et al. [63] suggested that carboxylic acids may contribute up to 80–90% of the acidity in precipitation in remote areas of the world. Due to their hygroscopic properties and capacity to function as cloud condensation nuclei [64], they play a role in absorbing and scattering solar radiation, thereby influencing the global thermal balance.

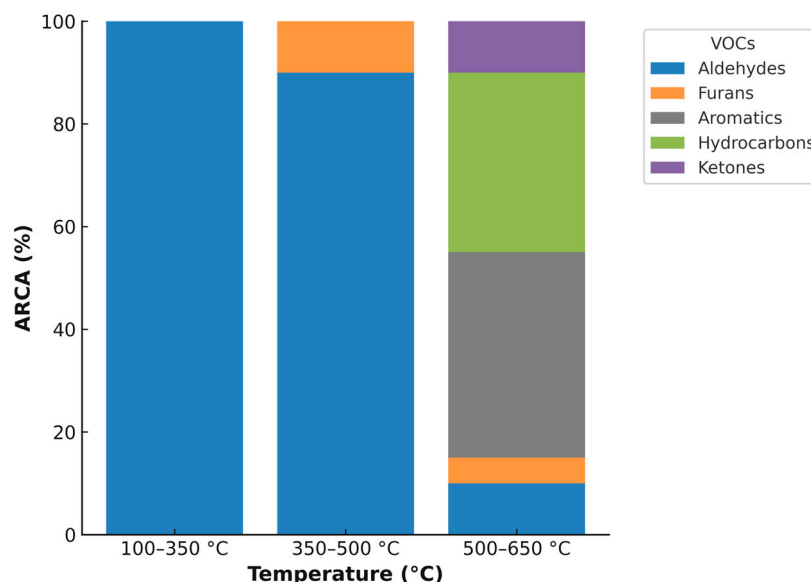


Figure 6. Average relative chromatographic area for the groups of compounds identified in the gas fraction during the pyrolysis of inactivated walnut shells and according to temperature.

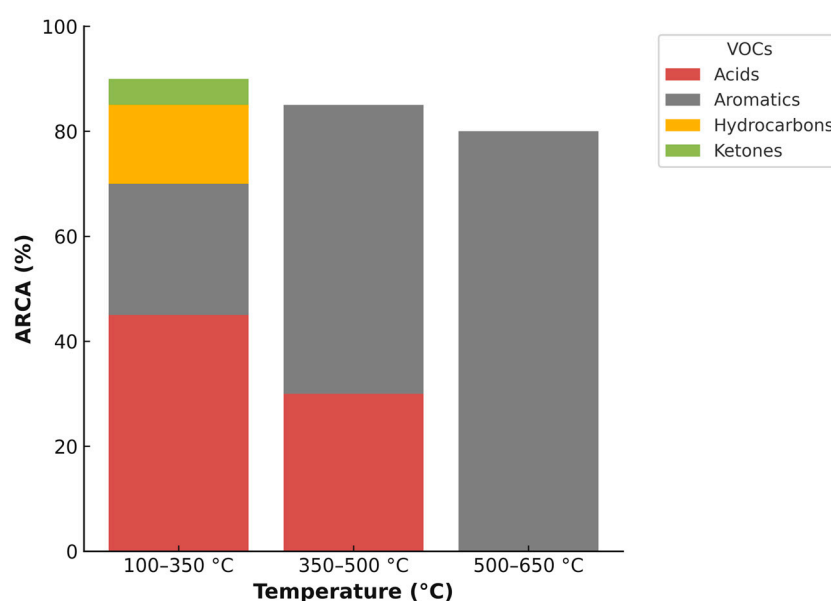


Figure 7. Average relative chromatographic area for the groups of compounds identified in the gas fraction pyrolysis of walnut shells with acid activation of biochar according to temperature.

In addition, methylbenzene and its derivatives were the second prevailing compounds in the whole range of temperatures studied. Benzene 1,2-dimethyl was increasing from 13.76 to 19.18% when the temperature was enhanced. Instead, for methyl benzene the increase was from 3.67 to 29.08% with the increasing temperature. Benzene and ethylbenzene were relevant compounds in the aromatic group between 500 and 650 °C.

In addition to the previously mentioned analytical pyrolysis studies, methylbenzene was identified during the thermal cracking of tars derived from birch, Miscanthus, and

straw [65]. Furthermore, methylbenzene was observed during tar decomposition and coke formation in the fast pyrolysis of woody residues.

A thorough assessment of the atmospheric effects of the detected compounds is needed, considering the composition of the non-condensable gas fraction produced during the thermal pyrolysis of walnut shells. A significant number of identified organic compounds present strong human, animal, and environmental effects.

3.4. Air Pollution Implications

As can be observed from Table 2, in the absence of phosphoric acid, hexanal, methylbenzene, and octane are the main VOCs identified in the gaseous fraction produced in the pyrolysis of walnut shells. On the other hand, in the presence of acid activation, acetic acid, methylbenzene, ethylbenzene, benzene 1,2-dimethyl, 2,4-dimethyl-1-heptene, and benzene were the main VOCs released.

The atmospheric lifetimes (τ) of the VOCs identified in this study were calculated using the equation $\tau_x = 1/(k[X])$, where X represents the OH, NO₃, O₃, and Cl radicals. Table 3 presents the atmospheric lifetimes determined for the degradation of each compound. Kinetic data for the reactions of the identified VOCs with NO₃ radicals, the primary tropospheric oxidant during nighttime, have been reported for all compounds. These calculations assume a typical atmospheric NO₃ radical concentration of 5×10^8 radicals cm⁻³ [66]; this leads to atmospheric lifetimes of 2, 341, 126.5, 40.5, and 61.4 days for hexanal, methylbenzene, octane, acetic acid, ethylbenzene, and benzene 1,2-dimethyl, respectively, and 2.1 years for benzene. Tropospheric lifetimes of the identified VOCs with respect to reactions with OH radicals were calculated assuming a 24 h average OH concentration of 2×10^6 radicals cm⁻³ [67].

Using the rate coefficients at room temperature, the atmospheric lifetimes of these compounds with OH radicals range from 6.21 h to 17.3 days. For reactions initiated by Cl atoms, the estimated atmospheric lifetimes vary from 3 days to 1800 years, assuming a global Cl atom concentration of 1×10^4 atoms cm⁻³ [68]. Nevertheless, in certain marine areas, peak Cl atom concentrations of 1×10^5 atoms cm⁻³ have been recorded [69], making the reaction of Cl with these VOCs a potentially significant atmospheric loss pathway.

The photolytic loss of these volatile organic compounds can be regarded as negligible because they are stable under actinic radiation. Another potential atmospheric removal mechanism is through dry and wet deposition. However, both processes are expected to be minor due to the high volatility and low water solubility of these compounds, with an estimated Henry's law constant of approximately 10 M atm⁻¹ [70].

The relatively short lifetimes, ranging from hours to days, suggest that the gaseous compounds identified during walnut shell pyrolysis will undergo degradation near their emission sources. Consequently, the fate of the products formed through OH-initiated oxidation of these VOCs is significant, as their atmospheric oxidation can also contribute to the formation of ozone and other photooxidants in the troposphere.

Additionally, the photochemical ozone creation potentials (POCPs) for the main VOCs identified in walnut pyrolysis were estimated using a methodology developed by Derwent et al. [71] and Sander et al. [72]. This approach relates the ozone formation potential to the OH reactivity of the VOCs relative to ethene through the following equation:

$$\epsilon^{POCP} = \alpha_1 \cdot \gamma_s \cdot \gamma_R^\beta (1 - \alpha_2 \cdot n_C) \quad (1)$$

In Equation (1), ϵ^{POCP} represents the estimated photochemical ozone creation potential, while α_1 , α_2 , β , γ_s , and γ_R are parameters we calculated by combining the OH rate coefficients presented in Table 3 with the data from [73] and the latest IUPAC recommendation for the rate coefficient of the C₂H₄ + OH reaction. Table 3 presents the calculated values

for the principal VOCs identified, which were provided for comparison. This approach estimates the photochemical ozone creation potential of VOCs relative to ethane, which is assigned a reference value of 100.

Table 3. Assessment of the environmental implications of the main VOCs identified in the gas phase.

Condition	VOC	τ_{OH}	τ_{Cl}	τ_{NO_3}	POCP
Without acid activation	Hexanal	9.92 h	4.5 days	2 days	60.92 ^a
	Benzene, methyl	1.9 days	23.1 days	341 days	63.7 ^b -44 ^c
	Octane	1.4 days	3 days	126.5 days	18.08 ^a -45.3 ^b -34 ^c -13 ^d
	Acetic acid	17.3 days	112.8 years	-	9.7 ^b -9 ^c
With acid activation	Benzene, methyl	1.9 days	23.1 days	341 days	63.7 ^b -44 ^c
	Benzene, ethyl	1.5 days	10 days	40.5 days	73 ^b -46 ^c
	Benzene, 1,2-dimethyl	6.21 h	8.3 days	61.4 days	105.3 ^b -78 ^c -86 ^d
	Benzene	9 days	18,000.17 years	2.1 years	21.8 ^b -10 ^c

^a Values of k_{OH} , k_{Cl} , and k_{NO_3} were extracted from the NIST kinetics database [70]. ^b Derwent et al. [71]. ^c Derwent et al. [74]. ^d Derwent et al. [75].

As shown in Table 3, when compared to ethane as the reference compound, these VOCs may significantly contribute to tropospheric ozone formation, particularly the atmospheric emissions of 1,2-dimethylbenzene and methylbenzene. Moreover, the tropospheric lifetimes provided in Table 3 suggest that these VOCs are likely to be removed rapidly from the gas phase, with OH reactions being their primary sink.

4. Conclusions

The pyrolysis of walnut shells, a widely available lignocellulosic residue, was comparatively analyzed across a thermal processing range of 100–650 °C to generate both solid (biochar) and gaseous products, underscoring the relevance of thermal engineering in biomass valorization. For the first time, the gas fraction produced during fast pyrolysis of walnut shells was characterized under atmospheric conditions, linking product distribution to process temperature and activation steps.

Through phosphoric acid activation followed by controlled carbonization, a porous carbon material with a high surface area, a mesoporous structure, and residual oxygen- and phosphorus-containing groups was obtained. From a thermal engineering perspective, this process demonstrates how activation influence microstructural development. The activated walnut biochar (AWB) effectively enhanced sulfur incorporation and served as a high-performance cathode material in lithium–sulfur batteries by mitigating the polysulfide shuttle effect through combined physical and chemical adsorption.

With regard to the gaseous fraction, this work revealed that in the absence of acid activation, hexanal, methylbenzene, and octane predominated, whereas acid activation promoted the release of benzene, its derivatives, and acetic acid. These findings emphasize how thermo-chemical modifications alter volatile emission profiles. The air quality implications of the major VOCs were further assessed by estimating atmospheric lifetimes (6.21 h to 17.3 days) and identifying oxidation pathways dominated by OH radical reactions near the emission source.

Overall, this work demonstrates that walnut shell pyrolysis, when coupled with acid activation, not only provides a thermally engineered pathway to advanced carbon materials for energy storage but also generates gaseous products with potentially negative environmental impacts. These results highlight the dual role of thermal engineering, enabling the sustainable design of functional materials while simultaneously requiring careful assessments of air quality implications from thermally driven emissions.

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Data Availability Statement: The original data presented in the study are openly available in the UNC repository at <http://hdl.handle.net/11086/12911>, accessed on 10 September 2025.

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References

1. Bora, R.R.; Tao, Y.; Lehmann, J.; Tester, J.W.; Richardson, R.E.; You, F. Techno-Economic Feasibility and Spatial Analysis of Thermochemical Conversion Pathways for Regional Poultry Waste Valorization. *ACS Sustain. Chem. Eng.* **2020**, *8*, 5763–5775. [CrossRef]
2. Ricciardi, P.; Cillari, G.; Miino, M.C.; Collivignarelli, M.C. Valorization of agro-industry residues in the building and environmental sector: A review. *Waste Manag. Res.* **2020**, *38*, 487–513. [CrossRef]
3. Lehmann, J. A handful of carbon. *Nature* **2007**, *447*, 143–144. [CrossRef] [PubMed]
4. Han, M.; Zhao, Q.; Li, W.; Ciais, P.; Wang, Y.-P.; Goll, D.S.; Zhu, L.; Zhao, Z.; Wang, J.; Wei, Y.; et al. Global soil organic carbon changes and economic revenues with biochar application. *GCB Bioenergy* **2022**, *14*, 364–377. [CrossRef]
5. Sun, J.; He, F.; Pan, Y.; Zhang, Z. Effects of pyrolysis temperature and residence time on physicochemical properties of different biochar types. *Acta Agric. Scand. Sect. B Soil Plant Sci.* **2017**, *67*, 12–22. [CrossRef]
6. Wang, J.; Xiong, Z.; Kuzyakov, Y. Biochar stability in soil: Meta-analysis of decomposition and priming effects. *GCB Bioenergy* **2016**, *8*, 512–523. [CrossRef]
7. Fdez-Sanromán, A.; Pazos, M.; Rosales, E.; Sanromán, M.A. Unravelling the Environmental Application of Biochar as Low-Cost Biosorbent: A Review. *Appl. Sci.* **2020**, *10*, 7810. [CrossRef]
8. Rosales, E.; Mejjide, J.; Pazos, M.; Sanromán, M.A. Challenges and recent advances in biochar as low-cost biosorbent: From batch assays to continuous-flow systems. *Bioresour. Technol.* **2017**, *246*, 176–192. [CrossRef] [PubMed]
9. Li, Q.; Cui, K.; Lv, J.; Zhang, J.; Peng, C.; Li, Y.; Gu, Z.; Song, X. Biochar amendments increase soil organic carbon storage and decrease global warming potentials of soil CH₄ and N₂O under N addition in a subtropical Moso bamboo plantation. *For. Ecosyst.* **2022**, *9*, 100054. [CrossRef]
10. Chen, H.; Gao, Y.; Li, J.; Fang, Z.; Bolan, N.; Bhatnagar, A.; Gao, B.; Hou, D.; Wang, S.; Song, H.; et al. Engineered biochar for environmental decontamination in aquatic and soil systems: A review. *Carbon Res.* **2022**, *1*, 4. [CrossRef]
11. Zhao, Z.; Wang, B.; Theng, B.K.G.; Lee, X.; Zhang, X.; Chen, M.; Xu, P. Removal performance; mechanisms, and influencing factors of biochar for air pollutants: A critical review. *Biochar* **2022**, *4*, 30. [CrossRef]
12. Wang, F.; Ouyang, D.; Zhou, Z.; Page, S.J.; Liu, D.; Zhao, X. Lignocellulosic biomass as sustainable feedstock and materials for power generation and energy storage. *J. Energy Chem.* **2021**, *57*, 247–280. [CrossRef]
13. Wang, J.; Wang, S. Preparation, modification and environmental application of biochar: A review. *J. Clean. Prod.* **2019**, *227*, 1002–1022. [CrossRef]
14. Neme, I.; Gonfa, G.; Masi, C. Activated carbon from biomass precursors using phosphoric acid: A review. *Heliyon* **2022**, *8*, e11940. [CrossRef]
15. Jin, X.; Lee, J.H.; Choi, J.W. Catalytic co-pyrolysis of woody biomass with waste plastics: Effects of HZSM-5 and pyrolysis temperature on producing high-value pyrolytic products and reducing wax formation. *Energy* **2022**, *239*, 121739. [CrossRef]
16. Meier, D.; Faix, O. State of the art of applied fast pyrolysis of lignocellulosic materials—A review. *Bioresour. Technol.* **1999**, *68*, 71–77. [CrossRef]
17. Chernyshev, V.M.; Kravchenko, O.A.; Ananikov, V.P. Conversion of plant biomass to furan derivatives and sustainable access to the new generation of polymers. functional materials and fuels, Russ. *Chem. Rev.* **2017**, *86*, 357. [CrossRef]

18. Hwang, S.Y.; Lee, G.B.; Kim, H.; Park, J.E. Influence of mixed methods on the surface area and gas products of activated carbon. *Carbon Lett.* **2020**, *30*, 603–611. [\[CrossRef\]](#)
19. Gu, H.; Bergman, R.; Anderson, N.; Alanya-Rosenbaum, S. Life cycle assessment of activated carbon from woody biomass. *Wood Fiber Sci.* **2018**, *50*, 229–243. [\[CrossRef\]](#)
20. Hadanu, R.; Apituley, D.A.N. Volatile Compounds Detected in Coconut Shell Liquid Smoke through Pyrolysis at a Fractioning Temperature of 350–420 °C. *Makara J. Sci.* **2016**, *20*, 95–100. [\[CrossRef\]](#)
21. Aguirre, F.; Lobos, M.L.N.; Basto, M.A.L.; Teruel, M.A.; Moyano, E.L.; Blanco, M.B. Volatile Organic Compounds Released During the Fast Pyrolysis of Peanut Shells and Environmental Implications. *Bull. Environ. Contam. Toxicol.* **2022**, *108*, 1139–1146. [\[CrossRef\]](#)
22. Finlayson-Pitts, B.J.; Pitts, J.N., Jr. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*; Elsevier: Amsterdam, The Netherlands, 1999.
23. Liu, J.; Liu, B.; Wang, C.; Huang, Z.; Hu, L.; Ke, X.; Liu, L.; Shi, Z.; Guo, Z. Walnut shell—Derived activated carbon: Synthesis and its application in the sulfur cathode for lithium–sulfur batteries. *J. Alloys Compd.* **2017**, *718*, 373–378. [\[CrossRef\]](#)
24. Yuan, H.; Liu, T.; Liu, Y.; Nai, J.; Wang, Y.; Zhang, W.; Tao, X. A review of biomass materials for advanced lithium–sulfur batteries. *Chem. Sci.* **2019**, *10*, 7484–7495. [\[CrossRef\]](#)
25. Lv, Z.-C.; Wang, P.-F.; Wang, J.-C.; Tian, S.-H.; Yi, T.-F. Key challenges, recent advances and future perspectives of rechargeable lithium-sulfur batteries. *J. Ind. Eng. Chem.* **2023**, *124*, 68–88. [\[CrossRef\]](#)
26. Seh, Z.W.; Sun, Y.; Zhang, Q.; Cui, Y. Designing high-energy lithium–sulfur batteries. *Chem. Soc. Rev.* **2016**, *45*, 5605–5634. [\[CrossRef\]](#)
27. Peng, H.-J.; Huang, J.-Q.; Zhang, Q. A review of flexible lithium–sulfur and analogous alkali metal–chalcogen rechargeable batteries. *Chem. Soc. Rev.* **2017**, *46*, 5237–5288. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Li, S.; Jin, B.; Zhai, X.; Li, H.; Jiang, Q. Review of Carbon Materials for Lithium-Sulfur Batteries. *ChemistrySelect* **2018**, *3*, 2245–2260. [\[CrossRef\]](#)
29. Zaini, M.S.M.; Anuar, N.F.; Al-Junid, S.A.M.; Syed-Hassan, S.S.A. Agricultural biomass-based carbon cathode materials for lithium-sulfur batteries: A systematic review. *Mater. Sci. Energy Technol.* **2023**, *6*, 205–225. [\[CrossRef\]](#)
30. Benítez, A.; González-Tejero, M.; Caballero, Á.; Morales, J. Almond Shell as a Microporous Carbon Source for Sustainable Cathodes in Lithium–Sulfur Batteries. *Materials* **2018**, *11*, 1428. [\[CrossRef\]](#)
31. Liu, P.; Wang, Y.; Liu, J. Biomass-derived porous carbon materials for advanced lithium sulfur batteries. *J. Energy Chem.* **2019**, *34*, 171–185. [\[CrossRef\]](#)
32. Li, H.; Pan, L.; Lu, T.; Zhan, Y.; Nie, C.; Sun, Z. A comparative study on electrosorptive behavior of carbon nanotubes and graphene for capacitive deionization. *J. Electroanal. Chem.* **2011**, *653*, 40–44. [\[CrossRef\]](#)
33. Cao, L.; Yu, I.; Tsang, D.C.W.; Zhang, S.; Ok, Y.S.; Kwon, E.E.; Song, H.; Poon, C.S. Phosphoric acid-activated wood biochar for catalytic conversion of starch-rich food waste into glucose and 5-hydroxymethylfurfural. *Bioresour. Technol.* **2018**, *267*, 242–248. [\[CrossRef\]](#)
34. Imwinkelried, G.; Fermanelli, C.S.; Teruel, M.A.; Saux, C.; Blanco, M.B. Comprehensive analysis of soybean residues pyrolysis products. *J. Anal. Appl. Pyrolysis* **2024**, *177*, 106367. [\[CrossRef\]](#)
35. El Hamdouni, Y.; El Hajjaji, S.; Szabó, T.; Trif, L.; Abbi, I.F.K.; Labjar, N.; Harmouche, L.; Shaban, A. Biomass valorization of walnut shell into biochar as a resource for electrochemical simultaneous detection of heavy metal ions in water and soil samples: Preparation, characterization, and applications. *Arab. J. Chem.* **2022**, *15*, 104252. [\[CrossRef\]](#)
36. Raviolo, S.; Bracamonte, M.V.; Ramanzin, M.B.S.; Alburquenque, D.; Oliva, M.I.; Cometto, F.P.; Luque, G.L. Valorization of brewer's spent grain via systematic study of KOH activation parameters and its potential application in energy storage. *Biomass Bioenergy* **2025**, *192*, 107494. [\[CrossRef\]](#)
37. Sevilla, M.; Carro-Rodríguez, J.N.; Díez, N.; Fuertes, A.B. Straightforward synthesis of Sulfur/N, S-codoped carbon cathodes for Lithium-Sulfur batteries. *Sci. Rep.* **2020**, *10*, 4866. [\[CrossRef\]](#)
38. Cherrington, R.; Liang, J. 2—Materials and Deposition Processes for Multifunctionality. In *Design and Manufacture of Plastic Components for Multifunctionality*; Goodship, V., Middleton, B., Cherrington, R., Eds.; William Andrew Publishing: Oxford, UK, 2016; pp. 19–51. [\[CrossRef\]](#)
39. Olivares-Marín, M.; Fernández-González, C.; Macías-García, A.; Gómez-Serrano, V. Thermal behaviour of lignocellulosic material in the presence of phosphoric acid. Influence of the acid content in the initial solution. *Carbon* **2006**, *44*, 2347–2350. [\[CrossRef\]](#)
40. Wang, J.; Kaskel, S. KOH activation of carbon-based materials for energy storage. *J. Mater. Chem.* **2012**, *22*, 23710. [\[CrossRef\]](#)
41. Benítez, A.; Morales, J.; Caballero, Á. Pistachio Shell-Derived Carbon Activated with Phosphoric Acid: A More Efficient Procedure to Improve the Performance of Li–S Batteries. *Nanomaterials* **2020**, *10*, 840. [\[CrossRef\]](#)
42. Chen, H.; Xia, P.; Lei, W.; Pan, Y.; Zou, Y.; Ma, Z. Preparation of activated carbon derived from biomass and its application in lithium–sulfur batteries. *J. Porous Mater.* **2019**, *26*, 1325–1333. [\[CrossRef\]](#)

43. Vélez, P.; Para, M.L.; Luque, G.L.; Barraco, D.; Leiva, E.P.M. Modeling of substitutionally modified graphene structures to prevent the shuttle mechanism in lithium-sulfur batteries. *Electrochim. Acta* **2019**, *309*, 402–414. [\[CrossRef\]](#)
44. Vélez, P.; Rojas, M.D.C.; Velasco, J.; Para, M.L.; Barraco, D.; Leiva, E.P.M.; Luque, G.L. On the role of oxidized graphene interfaces in lithium sulfur batteries: Thermodynamic and kinetic aspects using density functional theory. *Appl. Surf. Sci.* **2021**, *550*, 149358. [\[CrossRef\]](#)
45. Sahore, R.; Levin, B.D.A.; Pan, M.; Muller, D.A.; DiSalvo, F.J.; Giannelis, E.P. Design Principles for Optimum Performance of Porous Carbons in Lithium–Sulfur Batteries. *Adv. Energy Mater.* **2016**, *6*, 1600134. [\[CrossRef\]](#)
46. Hu, X.; Guo, H.; Gholizadeh, M.; Sattari, B.; Liu, Q. Pyrolysis of different wood species: Impacts of C/H ratio in feedstock on distribution of pyrolysis products. *Biomass Bioenergy* **2019**, *120*, 28–39. [\[CrossRef\]](#)
47. Park, Y.-K.; Yoo, M.L.; Heo, H.S.; Lee, H.W.; Park, S.H.; Jung, S.-C.; Park, S.-S.; Seo, S.-G. Wild reed of Suncheon Bay: Potential bio-energy source. *Renew. Energy* **2012**, *42*, 168–172. [\[CrossRef\]](#)
48. Becidan, M.; Skreiberg, Ø.; Hustad, J.E. Products distribution and gas release in pyrolysis of thermally thick biomass residues samples. *J. Anal. Appl. Pyrolysis* **2007**, *78*, 207–213. [\[CrossRef\]](#)
49. Krishna, B.B.; Singh, R.; Bhaskar, T. Effect of catalyst contact on the pyrolysis of wheat straw and wheat husk. *Fuel* **2015**, *160*, 64–70. [\[CrossRef\]](#)
50. Dhyani, V.; Bhaskar, T. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew. Energy* **2018**, *129*, 695–716. [\[CrossRef\]](#)
51. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [\[CrossRef\]](#)
52. Tahir, M.H.; Zhao, Z.; Ren, J.; Rasool, T.; Naqvi, S.R. Thermo-kinetics and gaseous product analysis of banana peel pyrolysis for its bioenergy potential. *Biomass Bioenergy* **2019**, *122*, 193–201. [\[CrossRef\]](#)
53. Cao, J.; Xiao, G.; Xu, X.; Shen, D.; Jin, B. Study on carbonization of lignin by TG-FTIR and high-temperature carbonization reactor. *Fuel Process. Technol.* **2013**, *106*, 41–47. [\[CrossRef\]](#)
54. Ojha, D.K.; Kumar, V.S.P.; Vinu, R. Analytical pyrolysis of bagasse and groundnut shell briquettes: Kinetics and pyrolysate composition studies. *Bioresour. Technol. Rep.* **2021**, *15*, 100784. [\[CrossRef\]](#)
55. Wang, J.; Liu, X.; Hu, B.; Lu, G.; Wang, Y. Efficient catalytic conversion of lignocellulosic biomass into renewable liquid biofuels via furan derivatives. *RSC Adv.* **2014**, *4*, 31101–31107. [\[CrossRef\]](#)
56. Anca-Couce, A.; Mehrabian, R.; Scharler, R.; Obernberger, I. Kinetic scheme of biomass pyrolysis considering secondary charring reactions. *Energy Convers. Manag.* **2014**, *87*, 687–696. [\[CrossRef\]](#)
57. Lu, Q.; Yang, X.; Dong, C.; Zhang, Z.; Zhang, X.; Zhu, X. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: Analytical Py-GC/MS study. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 430–438. [\[CrossRef\]](#)
58. Galloway, J.N.; Likens, G.E.; Keene, W.C.; Miller, J.M. The composition of precipitation in remote areas of the world. *J. Geophys. Res. Ocean* **1982**, *87*, 8771–8786. [\[CrossRef\]](#)
59. Keene, W.C.; Mosher, B.W.; Jacob, D.J.; Munger, J.W.; Talbot, R.W.; Artz, R.S.; Maben, J.R.; Daube, B.C.; Galloway, J.N. Carboxylic acids in clouds at a high-elevation forested site in central Virginia. *J. Geophys. Res. Atmos.* **1995**, *100*, 9345–9357. [\[CrossRef\]](#)
60. Khare, P.; Kumar, N.; Kumari, K.M.; Srivastava, S.S. Atmospheric formic and acetic acids: An overview. *Rev. Geophys.* **1999**, *37*, 227–248. [\[CrossRef\]](#)
61. Vet, R.; Artz, R.S.; Carou, S.; Shaw, M.; Ro, C.-U.; Aas, W.; Baker, A.; Bowersox, V.C.; Dentener, F.; Galy-Lacaux, C.; et al. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmos. Environ.* **2014**, *93*, 3–100. [\[CrossRef\]](#)
62. Zhang, N.; He, Y.; Cao, J.; Ho, K.; Shen, Z. Long-term trends in chemical composition of precipitation at Lijiang, southeast Tibetan Plateau, southwestern China. *Atmos. Res.* **2012**, *106*, 50–60. [\[CrossRef\]](#)
63. Keene, W.C.; Galloway, J.N. Considerations regarding sources for formic and acetic acids in the troposphere. *J. Geophys. Res. Atmos.* **1986**, *91*, 14466–14474. [\[CrossRef\]](#)
64. Andreae, M.O.; Talbot, R.W.; Andreae, T.W.; Harriss, R.C. Formic and acetic acid over the central Amazon region, Brazil: 1. Dry season. *J. Geophys. Res. Atmos.* **1988**, *93*, 1616–1624. [\[CrossRef\]](#)
65. Yu, S. Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (CCN): A review. *Atmos. Res.* **2000**, *53*, 185–217. [\[CrossRef\]](#)
66. Myrén, C.; Hörnell, C.; Björnbom, E.; Sjöström, K. Catalytic tar decomposition of biomass pyrolysis gas with a combination of dolomite and silica. *Biomass Bioenergy* **2002**, *23*, 217–227. [\[CrossRef\]](#)
67. Lauraguais, A.; El Zein, A.; Coeur, C.; Obeid, E.; Cassez, A.; Rayez, M.T.; Rayez, J.C. Kinetic Study of the Gas-Phase Reactions of Nitrate Radicals with Methoxyphenol Compounds: Experimental and Theoretical Approaches. *J. Phys. Chem. A* **2016**, *120*, 2691–2699. [\[CrossRef\]](#)
68. Gour, N.K.; Deka, R.C.; Singh, H.J.; Mishra, B.K. A computational perspective on mechanism and kinetics of the reactions of CF₃C(O)OCH₂CF₃ with OH radicals and Cl atoms at 298 K. *J. Fluor. Chem.* **2014**, *160*, 64–71. [\[CrossRef\]](#)

69. Wang, J.; Zhou, L.; Wang, W.; Ge, M. Gas-phase reaction of two unsaturated ketones with atomic Cl and O₃: Kinetics and products. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12000–12012. [CrossRef]
70. Ye, J.T.; Bai, F.Y.; Pan, X.M. Computational study of H-abstraction reactions from CH₃OCH₂CH₂Cl/CH₃CH₂OCH₂CH₂Cl by Cl atom and OH radical and fate of alkoxy radicals. *Environ. Sci. Pollut. Res.* **2016**, *23*, 23467–23484. [CrossRef]
71. Sander, R.; Acree, W.E.; Visscher, A.D.; Schwartz, S.E.; Wallington, T.J. Henry's law constants (IUPAC Recommendations 2021). *Pure Appl. Chem.* **2022**, *94*, 71–85. [CrossRef]
72. Derwent, R.G.; Jenkin, M.E.; Saunders, S.M.; Pilling, M.J. Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism. *Atmos. Environ.* **1998**, *32*, 2429–2441. [CrossRef]
73. Jenkin, M.E.; Derwent, R.G.; Wallington, T.J. Photochemical ozone creation potentials for volatile organic compounds: Rationalization and estimation. *Atmos. Environ.* **2017**, *163*, 128–137. [CrossRef]
74. NIST Chemical Kinetics Database, (n.d.). Available online: <https://kinetics.nist.gov/kinetics/index.jsp> (accessed on 1 October 2024).
75. Derwent, R.G.; Jenkin, M.E.; Passant, N.R.; Pilling, M.J. Reactivity-based strategies for photochemical ozone control in Europe. *Environ. Sci. Policy* **2007**, *10*, 445–453. [CrossRef]

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