

Article

Comparative Analysis of Pyrolysis and Anaerobic Digestion as End-of-Life Options for Used Cork Stoppers

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Abstract

The cork industry generates valuable by-products and residues with significant potential within a circular bioeconomy framework. This study evaluated the energy-driven valorization of two post-consumer cork residues—natural cork stoppers (NCS) and technical cork stoppers (TCS)—through anaerobic digestion and pyrolysis. Both NCS and TCS exhibited low moisture and ash content, a high heating value of 25.14 and 29.88 MJ/kg, respectively, a carbon content exceeding 58 wt% and low nitrogen, sulfur and chlorine concentrations. These characteristics highlight the suitability of NCS and TCS for energy recovery applications. Anaerobic digestion produced biogas containing 68.5 vol% of methane after alkaline pretreatment of TCS. However, the maximum biochemical methane potential was low, reaching only 19.5 L CH₄/kg VS. The resulting digestates contained nitrogen, phosphorus and potassium at levels compatible with agricultural use. Slow pyrolysis of the cork residues resulted in high biochar yields, with NCS achieving an average yield of 64.8 wt%. Combined with carbon contents of up to 66.3 wt%, the biochars produced from NCS and TCS show strong potential for valorization as solid energy carriers, as well as for applications such as activated carbon production and soil amendment. Overall, thermochemical conversion via pyrolysis proved to be the most effective pathway for energy valorization of the tested cork residues, whereas the performance of anaerobic digestion remained limited unless more intensive pretreatment strategies were applied.

Keywords: post-consumer cork residues; thermochemical conversion; biochemical conversion; biochar; methane



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1. Introduction

Cork is the bark of the cork oak tree (*Quercus suber* L.), a raw material harvested without causing long-term damage to the tree, thereby allowing bark regeneration and repeated extractions over time. As such, cork represents a renewable resource associated with long-lived trees (up to 200 years) that contribute to carbon sequestration while supporting ecosystems that mitigate desertification and provide multiple ecosystem services [1]. Nevertheless, cork production is constrained by a long biological cycle—requiring at least 25 years for the first harvest, followed by a second harvest after an additional 9 years, both

of which are unsuitable for some applications, and subsequent 9-year cycles thereafter—and by the limited geographical distribution of the cork oak. Consequently, supply is inherently restricted and depends on sustainable forest management. Reflecting these constraints, cork has been classified as a near-critical biotic raw material by the European Union [2].

Given these limitations, the cork industry has historically prioritized minimizing material losses to maximize the value of this high-cost raw material. Pre-consumer by-products are almost entirely reintegrated within industrial processes through cascading use and continuous development of new applications across sectors such as aerospace, automotive, construction, footwear, and cosmetics [3]. In contrast, the management of post-consumer cork waste, particularly cork stoppers, remains more challenging. Although local collection schemes have been implemented—often initiated by cork product companies—these efforts are primarily focused on recovering used cork stoppers, which remain the most significant cork product globally in terms of both economic value and volume [4–6]. When recycling is not feasible on a high scale, common waste management practices include landfill disposal and incineration, with or without energy recovery, both of which are associated with well-documented environmental impacts [7,8]. Furthermore, future supply limitations in primary cork production may increase the relevance of recycling as a source of secondary raw materials, particularly from post-consumer streams such as cork stoppers [4]. While the use of recycled cork in new stoppers is limited by stringent quality requirements related to food contact, these materials can be repurposed for alternative applications, including construction products. Cork stopper recycling also faces significant sustainability challenges, particularly at the collection stage. The relatively low volume of cork waste compared to other waste streams reduces its attractiveness under current recyclability criteria, such as those defined in the Packaging and Packaging Waste Regulation (PPWR) [9]. This issue is exacerbated by the geographical mismatch between production and consumption: cork stopper production and recycling facilities are largely concentrated in the Iberian Peninsula, whereas consumption is globally dispersed. As a result, collection systems lack scalability, limiting economic viability. Moreover, centralized transport to processing facilities contributes to greenhouse gas (GHG) emissions, rendering collection environmentally and economically unfeasible in certain regions, even when infrastructure is available [10]. To address these constraints, efforts are underway to integrate cork stopper collection into broader waste management systems. In Portugal, for example, the National Environmental Agency recommends collecting corks together with glass waste to prevent them from getting lost during the sorting process due to their size.

Considering the limitations associated with conventional recycling and disposal, biological and thermochemical conversion offer complementary alternatives for the valorization of post-consumer cork. The interest in these approaches stems from the distinctive composition of cork, which combines biodegradable structural carbohydrates with high proportions of recalcitrant components, particularly suberin and lignin. These characteristics make cork a challenging substrate for biological conversion but also provide a carbon-rich feedstock with potential for thermochemical valorization. Anaerobic digestion (AD) can recover the biodegradable organic fraction as biogas, while pyrolysis can convert the more recalcitrant fraction into biochar and gaseous and condensable products. Thus, the two technologies offer different valorization opportunities, with their suitability depending on cork composition, the required pretreatment, process conditions, and the desired end products.

Understanding the potential of these valorization pathways requires consideration of the physicochemical characteristics of cork, as its unique cellular structure and chemical composition strongly influence both its biodegradability and thermal conversion. The physical properties of cork are primarily ruled by its cellular structure, characterized by

a closed-cell, honeycomb-like arrangement of gas-filled cells. Cork is hydrophobic and absorbs water slowly, maintaining dimensional stability under varying environmental conditions. Additionally, its low thermal conductivity (approximately 0.03–0.05 W/m·K) makes it an effective insulating material [11]. Mechanically, cork exhibits high compressibility and resilience, allowing large deformations under compression with substantial recovery after load removal, which is essential for sealing applications [12]. Suberin is the main structural component of cork, accounting for approximately 40–50% of its total mass, and consists of a highly cross-linked aliphatic polyester formed by long-chain fatty acids and glycerol-derived units [13]. Lignin, representing about 20–25% of the material, is an aromatic, three-dimensional polymer that provides mechanical strength and rigidity [13]. The predominance of suberin and lignin in cork has important implications for its behavior during both thermochemical conversion and biological processes. The relatively high lignin content, characterized by its aromatic and condensed structure, enhances the suitability of cork for biochar production through pyrolysis. During thermal treatment, lignin undergoes progressive aromatization and carbonization, leading to the formation of stable, carbon-rich structures with high structural integrity [14]. In contrast, the high content of suberin and lignin render cork inherently resistant to microbial degradation, which directly affects both biogas yields and the characteristics of the resulting digestate. As a result, untreated cork residues generally produce lower methane yields compared to more readily degradable biomass, such as agricultural residues or food waste [15]. To overcome this limitation, pretreatment strategies have been proposed to enhance substrate accessibility and improve digestion efficiency. Existing studies largely focused on cork boiling wastewater report relatively low conversion efficiencies, including chemical oxygen demand (COD) removal rates of approximately 36–40% and limited methane yields. These limitations are primarily attributed to the presence of inhibitory phenolic compounds and the low bioavailability of the substrate [16,17]. Similar challenges are observed for lignocellulosic biomasses, such as cork residues, where methane production is constrained by the recalcitrant nature of the lignocellulosic structures, requiring efficient hydrolysis of cellulose and hemicellulose [18]. To enhance process performance, pretreatment methods involving mechanical, thermal (steam explosion, liquid hot water) or chemical (acid, alkaline) pretreatments, applied alone or combined, are essential, as they improve the digestibility (by enzymes and bacteria) of lignocellulosic biomass, resulting in methane yield increases of 20–100% [19]. Alternatively, slow pyrolysis of used cork stoppers represents a promising circular bioeconomy strategy. This thermochemical process converts biomass under limited oxygen conditions into biochar, condensable liquids, and gaseous products [20,21]. Cork-derived biochar typically exhibits a highly porous structure and a high degree of carbonization and aromaticity, enabling its application as a soil amendment, an adsorbent for contaminants (including heavy metals), and a carbon sequestration material [20–23]. However, the yield and properties of the resulting pyrolysis products depend on operating parameters such as temperature, residence time, heating rate, and feedstock characteristics. Therefore, optimization of process conditions is necessary to maximize the value of the resulting products and ensure favorable energy and environmental performance.

Given the challenges associated with current cork waste management practices and the complementary nature of biological and thermochemical conversion routes, this study evaluated the potential of AD and pyrolysis as decentralized valorization pathways to address collection scalability constraints and reduce the environmental and economic burdens of centralized recycling systems. Their integration with other lignocellulosic waste streams could further improve collection efficiency, supporting circular resource management strategies that minimize transport-related impacts while recovering valuable energy and material products from cork residues.

2. Materials and Methods

2.1. Cork Residues Under Study

This study investigated two types of cork residue: shredded natural cork stoppers (NCS) and shredded micro-agglomerated cork stoppers, referred to herein as technical cork stoppers (TCS). Both NCS and TCS were obtained from a normal production workflow from a cork factory, except for marking/branding with either ink, heat or laser. The full extent of chemical composition and process details are confidential and cannot be disclosed, as per request by the manufacturer. As these materials originate from different manufacturing processes, it is expected that there will be differences in their physical and chemical properties. NCS are produced from cork planks which are initially sorted and graded according to quality parameters. The suitable planks are then cut into strips and punched into cylindrical stoppers [24]. Subsequent finishing operations include polishing, dimensional calibration, washing, drying, and surface treatments (e.g., paraffin or silicone coatings) to enhance sealing performance [25]. This process preserves the cellular structure of cork. In contrast, TCS are manufactured by grinding cork into granules with a controlled particle size distribution. These granules are then cleaned, dried, and mixed with polymeric binders, typically polyurethane-based adhesives [26]. The resulting mixture is homogenized and molded under controlled pressure and temperature to promote interparticle bonding and ensure structural cohesion [27]. After curing, the material is removed from the molds, and finishing steps may include surface treatment, polishing, and dimensional standardization.

2.2. Physical and Chemical Characterization of the Cork Residues

Bulk density and moisture content (reference method) were determined for the shredded NCS and TCS as received, in accordance with ISO 17828 [28] and ISO 18134-1 [29], respectively. For the bulk density test, a 32 L cylindrical container was used; its volume was determined from the mass and density of water under laboratory temperature conditions. After compaction in the container, the sample mass was obtained as the difference between the mass of the container filled with sample and the mass of the empty container. Bulk density was calculated as the ratio of sample mass to container volume. The moisture content was determined directly after oven-drying at 105 ± 2 °C, in a Venticell 55 oven with forced-air circulation (MMM Medcenter Einrichtungen GmbH, Munich, Germany), in 60 min cycles until constant mass. Particle size distribution was determined by an oscillating sieving procedure based on ISO 17827-2 [30]. Retsch sieves with apertures of 3.15 mm, 2.0 mm, 1.0 mm, 0.6 mm, and 0.212 mm were used in combination with an automatic Retsch vibratory sieve shaker (RETSCH GmbH, Haan, Germany). For physical and chemical characterization, except for moisture content (reference method), the samples were milled to a particle size below 1 mm using a Retsch SM 300 cutting mill. Analytical results obtained for these milled samples were converted to a dry basis using the moisture content after particle-size reduction, determined according to ISO 18134-3 [31]. The results were further converted from dry basis to as-received basis by considering the moisture content of the as-received sample, following the calculations established in ISO 16993 [32].

Ash content at 815 ± 10 °C was determined from the mass of the remaining residue relative to the initial sample mass (1 g) after calcination under strictly controlled furnace time and temperature conditions. The test was performed in a Heraeus M110 muffle furnace (Heraeus Instruments GmbH, Hanau, Germany), enabling controlled heating according to ISO 18122 [33], using platinum crucibles (60 mm diameter and 20 mm height). Carbon (C), nitrogen (N), hydrogen (H), and sulfur (S) were determined using an Elementar vario MACRO cube elemental analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany), following ISO 16948 [34] and the manufacturer's instructions to ensure traceability and reliability of the results. For each analysis, approximately 20–30 mg of sample,

previously enclosed in a tin capsule, was introduced into the analyzer. The furnace was heated to 1150 °C under a constant flow of helium (He) as the carrier gas and oxygen gas (O₂) as the ignition gas, and the generated gases were passed through reduction columns at 850 °C prior to measurement by a thermal conductivity detector. Chlorine (Cl) content was determined following a procedure based on ISO 16994 [35]. Pelletized samples (≈1 g) were combusted in an IKA C7000 calorimeter (IKA-Werke GmbH & Co. KG, Staufen, Germany), and chloride ions in the absorption solution were quantified by potentiometric titration with standardized AgNO₃ using a silver sulfide membrane ion-selective electrode. The oxygen (O) content was calculated by difference (%O = 100 – (%C + %H + %N + %S + %Cl + %ash)). As an indirect determination, the calculated oxygen value incorporates the cumulative analytical uncertainties associated with the measurement of elemental composition and ash content.

The macromolecular composition of the NCS and TCS samples was assayed after determination of extractives by successive Soxhlet extractions with water and ethanol. The carbohydrates (cellulose and hemicelluloses) and lignin were determined in extractive-free samples by quantitative hydrolysis (in duplicate) with sulfuric acid in two stages (the first with 72 wt% acid, at 30 °C for 1 h; and the second with 4 wt% acid, for 1 h at 121 °C) according to the method described by Browning [36]. The acid-insoluble residue was considered as Klason lignin, after correction based on acid-insoluble ash. This methodology did not allow the separation of suberin from the acid-insoluble residue, therefore the result as determined was presented as Klason lignin + suberin content.

The higher heating value (HHV), at constant volume, was determined according to ISO 18125 [37]. A sample portion (0.3–0.6 g) was combusted in a high-pressure Parr oxygen bomb installed in a 6400 Isoperibol Automatic Calorimeter (Parr Instrument Company, Moline, IL, USA). After combustion, the bomb was rinsed with water. The resulting solution was diluted to 100 mL and used for chlorine analysis by potentiometry. The HHV was calculated based on the corrected temperature rise and the effective heat capacity of the calorimeter, considering contributions from ignition-wire energy and applying corrections for the formation of nitric and hydrochloric acids, as well as sulfur.

2.3. Chemical Characterization of the Fractions Obtained After Alkaline Pretreatment and of the Digestate from Anaerobic Digestion

Volatile solids (VS) were determined according to SMEWW 24th Edition, Method 2540 E [38]. Samples were dried at 104 ± 1 °C using a MMM Venticell 55 drying oven (MMM Medcenter Einrichtungen GmbH, Planegg/Munich, Germany) and subsequently ignited at 550 ± 50 °C in a Nabertherm LVT 15/11/B510 ashing furnace (Nabertherm GmbH, Lilienthal, Germany). The VS content was calculated from mass loss after ignition. Kjeldahl nitrogen was determined according to the Portuguese Standard NP EN 25663 [39]. Samples were digested with sulfuric acid (10 mL) in the presence of a catalyst mixture containing selenium (0.5 g) and potassium sulfate (9.5 g), using a DK 20 Kjeldahl Digestion Unit (VELP Scientifica, Usmate Velate, Italy). The mixtures were heated at 190 °C for 3.5 h and subsequently at 290 °C for 1 h. After dilution to 100 mL and alkalization to pH 9.5 with sodium hydroxide, the solutions were distilled using a VELP UDK140 unit. The released ammonia was trapped in a boric acid solution and titrated with standardized HCl to calculate the Kjeldahl nitrogen content. Chemical oxygen demand (COD) was determined according to the Portuguese Standard NP 4329 [40] based on open-reflux digestion of the sample with a known amount of potassium dichromate under strongly acidic conditions. Mercury (II) sulfate was used as a complexing agent and silver sulfate as a catalyst. The mixture was refluxed at 148 ± 3 °C for 110 min, using a BEHROTEST CSB 12, TRS200 system, (behr Labor-Technik GmbH, Düsseldorf, Germany) and the residual dichromate was titrated with a standardized ammonium iron (II) sulfate solution to quantify the oxygen equivalent consumed. Phosphorus (P) and potassium (K) were determined in the digestate,

after microwave-assisted digestion of the samples, in an ETHOS PLUS Microwave Digestion System (Milestone Srl, Sorisole, Italy), performed according to EN 13346:2000, Method C [41], with adaptations. The digested solutions were analyzed as described in SMEWW 24th Edition, Method 4500-P D, sections 4a, b, c [42], for P determination by molecular absorption spectrometry, and SMEWW 24th Edition, Method 3111 B [43], for K determination by flame atomic absorption spectrometry, using an UNICAM UV300 Spectrophotometer (Thermo Spectronic, Cambridge, UK) and a Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometer (Thermo Fisher Scientific, Cambridge, UK), respectively.

2.4. Alkaline Pretreatment of the Cork Residues

An alkaline pretreatment with sodium hydroxide was applied to NCS and TCS prior to AD. For this purpose, each sample was suspended in aqueous solution of 8% (*w/v*) NaOH, at a solid/liquid ratio of 1:6 [250 g (dry basis) of residue with 1.5 L of 80 g/L NaOH solution, in 2 or 5 L-Schott flasks], and was incubated for 4 h at 85 °C in a thermostatic bath. At the end of the incubation, the suspension was centrifuged at $13,700\times g$, 15 min, 4 °C (SIGMA 6-16KS, Osterode am Harz, Germany). The supernatant obtained (PTL fraction) (Figure 1) was directly used for AD assays, after adjusting pH to 7. In turn, the recovered solid (PTS fraction) was used for AD after extensive washing with water, until pH 7 was obtained in the washing water. AD using the whole slurry obtained at the end of the pretreatment (PTWS fraction), i.e., with no solid–liquid separation, was also performed, providing the evaluation of the combined digestibility of the pretreated solid fraction together with the components solubilized in NaOH.

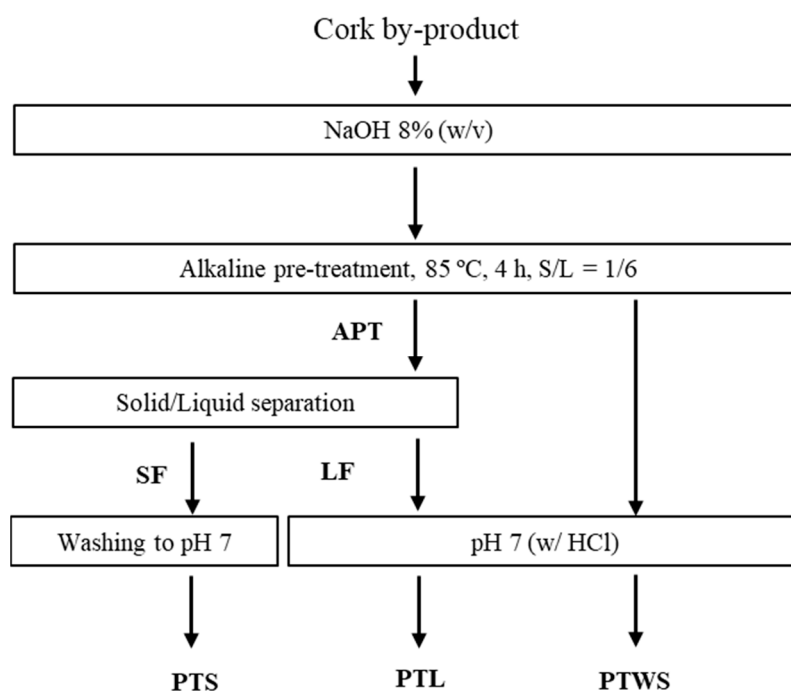


Figure 1. Scheme of the alkaline pretreatment applied to the shredded cork stoppers, including the pretreated fractions recovered. APT—alkaline pretreated; SF—solid fraction; LF—liquid fraction; PTS—pretreated solid fraction; PTL—pretreated liquid fraction; PTWS—pretreated whole slurry (non-separated).

2.5. Experimental Set-Up for Anaerobic Digestion of the Cork Residues

Anaerobic digestion assays were conducted at laboratory scale in batch mode using sealed vials with a total volume of 72 mL and a working volume of 40 mL. A sludge collected in a municipal anaerobic digester plant (SIMARSUL, Quinta do Conde, Portugal)

was used as the inoculum. The substrates tested were the PTL, PTS, and PTWS fractions after pH neutralization. The substrates were stored at 4 °C until use.

Each assay was inoculated at 30 vol%, with a substrate-to-inoculum ratio of 2.3, expressed as chemical oxygen demand to volatile solids (COD/VS) for the PTL fractions and as VS/VS for the PTS fractions and PTWS samples [44]. Blank control units contained only inoculum, with no added substrate. All experiments were performed in triplicate. Prior to incubation, the vials were purged with N₂ to ensure anaerobic conditions, then sealed using butyl rubber stoppers. Incubation was carried out under mesophilic conditions (37 °C), and the process was maintained until no further increase in biogas production was observed. Biogas production was monitored daily through manometric measurements using a handheld pressure transducer, previously calibrated to the headspace volume of the vials. The recorded values were converted to standard temperature and pressure conditions (STP: 0 °C, 1 bar), as defined by the International Union of Pure and Applied Chemistry (IUPAC). Cumulative biogas production was calculated by adding up the individual gas volumes measured at each time interval, during the AD process:

$$V_{cum}(t) = \sum_{i=1}^n V_i \quad (1)$$

where:

V_i —Individual biogas volumes measured during each i -time interval.

n —Total number of days measured up to time t .

At each incubation time, the average biogas production from the inoculum triplicates was used as a background correction and subtracted from the average biogas volume measured for the tested samples. Methane accumulated in the headspace was quantified on a weekly basis by injecting a 0.5 mL gas sample into a gas chromatograph (Agilent/HP 6890, Santa Clara, CA, USA) equipped with a gas sampling valve, two packed columns (Molecular Sieve 5A and Porapak Q), and two detectors (a thermal conductivity detector and a flame ionization detector) fitted in series. The quantitative analysis of the gaseous compounds was determined by comparing the peak area of each compound in the sample with the area of that compound in standard calibration mixtures.

Biogas and methane yields were calculated based on the cumulative gas production of each sample relative to the initial mass of VS of the substrate added at the beginning of the assay (specific methane potential, SPM; L CH₄/kg VS_{in}) and tracked throughout the AD process. The biochemical methane potential (BMP) of each sample was defined as the maximum methane yield achieved. The energy content was calculated by converting the yield of the recovered energy product (methane), expressed per unit mass of input substrate, into its corresponding energy content (MJ/kg of pretreated cork residue or by-product). The HHV of methane was used for this conversion [45].

2.6. Experimental Set-Up for Slow Pyrolysis of the Cork Residues

Three independent slow pyrolysis tests of NCS and TCS were performed in a laboratory-scale PARR batch reactor. Cork powder (CP) was also tested for comparison purposes. The experimental parameters used were optimized in previous work [46]: reaction temperature of 450 °C, initial N₂ pressure of 0.7 bar, and reaction time of 30 min. To determine the gas production, the reactor was weighed both before and after the reaction. The total gas yield was calculated as the difference between the weight of the reactor at the beginning and at the end of each assay. The gas fraction was analyzed by gas chromatography (GC) (as described in Section 2.5). Quantitative analysis of gaseous compounds was determined by comparing the peak area of each compound in the sample with the area of that compound in calibration mixtures. Elemental analysis was performed on the biochar

using the same method applied in the characterization of the cork samples. The oxygen content was calculated by difference, as described in Section 2.2. The quantification of sulfur and chlorine in the biochar was not performed, as both elements were present at concentrations below or close to the analytical detection limits in the original cork residues. The energy content was calculated by converting the yield of the recovered energy products (biochar and pyrolysis gas), expressed per unit mass of input substrate, into its corresponding energy content (MJ/kg of cork residue or by-product). The HHV of the respective individual components in the pyrolysis gas were used [45]. The energy content of the biochar was calculated according to [47] using the modified Dulong–Berthelot correlation.

3. Results and Discussion

3.1. Characterization of the Cork Residues

The shredded NCS and TCS samples were almost visually indistinguishable, except for the subtle reddish tone exhibited by the former (Figure 2). The particle size distribution of both samples was predominantly concentrated in the 2.0–3.15 mm size range, accounting for 48.9 wt% and 53.5 wt% for NCS and TCS, respectively, followed by the 1.0–2.0 mm fraction (42.7 wt% and 37.1 wt%) (Table 1). Fine particles (<1.0 mm) represented only a small fraction of the total mass (<8 wt%), while particles larger than 3.15 mm accounted for less than 2 wt%. Overall, TCS exhibited a slightly coarser particle size distribution than NCS, with a higher proportion of particles in the 2.0–3.15 mm range.

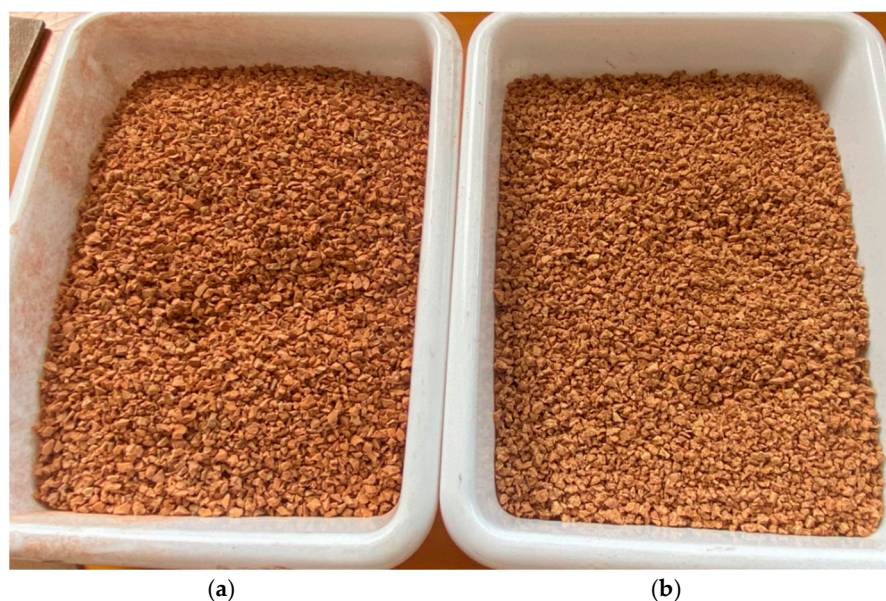


Figure 2. Shredded cork stoppers used in this study: (a) natural cork stopper; (b) technical cork stoppers.

Table 1. Particle size distribution of the cork residues.

Cork Residue	Particle Size Distribution (wt%)					
	<0.212 mm	0.212–0.6 mm	0.6–1.0 mm	1.0–2.0 mm	2.0–3.15 mm	>3.15 mm
Natural stoppers	0.8	1.0	4.8	42.7	48.9	1.9
Technical stoppers	0.5	1.9	5.2	37.1	53.5	1.8

Cork residues showed low moisture contents, ranging from 3.62 to 5.11 wt% (Table 2). NCS exhibited the highest moisture content (5.11 wt%) and ash content (1.29 wt%), as well as the lowest bulk density (93 kg/m³) and heating value (25.14 MJ/kg). In contrast, TCS

showed the highest bulk density (112 kg/m^3) and higher heating value (29.88 MJ/kg), together with relatively low ash content ($0.76 \text{ wt}\%$). All the samples exhibited physical and chemical properties typical of structurally stable lignocellulosic materials, with low inorganic content. Carbon and hydrogen were predominant elements in both cork residues (Table 2). Particularly, TCS exhibited the highest carbon ($65.77 \text{ wt}\%$) and hydrogen ($7.36 \text{ wt}\%$) contents. Nitrogen and chlorine content was low in both NCS and TCS, while sulfur was below the detection limit for both samples. Overall, the high carbon content and low concentrations of nitrogen, sulfur, and chlorine indicate favorable fuel characteristics and a reduced potential for pollutant emissions during thermochemical conversion.

Table 2. Physical and chemical analysis of the cork residues.

Cork Residue	Moisture	Bulk Density	Ash, d.b. ²	HHV ¹ , d.b. ²	C ³	H ⁴	N ⁵	O ⁶	S ⁷	Cl ⁸
	(wt%)	(kg/m^3)	(wt%)	(MJ/kg)	(wt%, d.b. ²)					
Natural stoppers	5.11 ± 0.06	93	1.29 ± 0.03	25.14 ± 0.62	58.75 ± 0.96	6.08 ± 0.21	0.92 ± 0.10	32.16 ± 1.30	<0.6	0.20 ± 0.01
Technical stoppers	3.62 ± 0.08	112	0.76 ± 0.04	29.88 ± 0.04	65.77 ± 0.08	7.36 ± 0.13	1.46 ± 0.08	23.83 ± 0.08	<0.6	0.22 ± 0.00

¹ HHV—high heating value; ² d.b.—dry basis; ³ C—carbon; ⁴ H—hydrogen; ⁵ N—nitrogen; ⁶ O—oxygen; ⁷ S—sulfur; ⁸ Cl—chlorine.

According to Table 3, the analysis of the lignocellulosic fraction of both cork residues was characterized by a high Klason lignin + suberin content, accounting for $79.88 \text{ wt}\%$ in NCS and $75.22 \text{ wt}\%$ in TCS. The predominance of suberin- and lignin-rich structural polymers is consistent with previous studies, which also reported higher ash contents and lignocellulosic-suberin fractions in NCS than in TCS [48]. In contrast, cellulose and hemicellulose contents were relatively low, ranging from 1.98 – $2.21 \text{ wt}\%$ and 4.95 – $5.80 \text{ wt}\%$ in NCS and TCS, respectively. Freitas et al. [48] reported a substantially higher percentage of total monosaccharides (17.29% dry weight) in TCS. The differences to the values presented in Table 3 may be attributed to variations in the analytical methodologies employed for extraction and chemical fractionation, together with variations in raw material origin, stopper manufacturing processes, and prior use history. NCS also exhibited a higher soluble lignin content ($3.64 \text{ wt}\%$) than TCS ($2.52 \text{ wt}\%$). Extractives constituted a significant fraction of the biomass, particularly ethanol-soluble compounds, which reached $8.46 \text{ wt}\%$ and $9.69 \text{ wt}\%$ for NCS and TCS, respectively, while water-soluble extractives ranged between 2.65 and $3.12 \text{ wt}\%$. Overall, the results confirmed the high content of insoluble lignin + suberin of the cork residues and the presence of considerable amounts of extractives, both of which contribute to their distinctive chemical and fuel properties.

Table 3. Lignocellulosic composition and extractives of the cork residues before alkaline pretreatment.

Cork Residue	Cellulose	Hemicelluloses	KL ¹ + Sub. ²	Soluble Lignin	Extractives (Water)	Extractives (Ethanol)
	(wt%, d.b. ³)					
Natural stoppers	2.21 ± 0.07	5.80 ± 0.18	79.88 ± 0.14	3.64 ± 0.31	2.65 ± 0.29	8.46 ± 0.91
Technical stoppers	1.98 ± 0.03	4.95 ± 0.13	75.22 ± 0.53	2.52 ± 0.14	3.12 ± 0.17	9.69 ± 0.07

¹ KL—Klason lignin; ² Sub.—suberin; ³ d.b.—dry basis.

Given the results of the quantitative acid hydrolysis assay performed with the residual cork samples, exhibiting polysaccharides (cellulose + hemicelluloses) contents less than or equal to $8 \text{ wt}\%$, no enzymatic hydrolysis step was accomplished before the AD process. Indeed, the cost of enzymes is widely recognized as one of the main critical factors hampering the economic viability of lignocellulosic biorefineries based on the sugar (biochemical) platform, and thus the potential sugars titers obtainable from these constituent polysaccharides do not justify the introduction of an enzymatic hydrolysis stage [49].

3.2. Anaerobic Digestion of the Pretreated Cork Residues

Alkaline pretreatment, as applied to NCS and TCS before AD, has been extensively used for lignocellulosic biomass with the purpose of increasing its digestibility towards enzymatic hydrolysis and microbial degradation. Alkaline pretreatment promotes saponification and solvation reactions, generating a swollen state of the biomass that is more accessible for enzymes and bacteria. Also, some hemicellulose solubilization occurs, together with partial solubilization, redistribution and condensation of lignin and modifications in the crystalline state of the cellulose [19]. Following pretreatment of NCS and TCS, the resulting slurries were subjected to centrifugation to separate the supernatant and solid fractions. The collected solid fractions were extensively washed with distilled water until pH 7 was reached. The pH of the supernatant, so as a third, non-separated fraction in the form of the pretreated slurry, was adjusted to pH 7 with 0.1N HCl before AD. Table 4 presents the chemical analysis of the fractions obtained after alkaline pretreatment, showing the main parameters for admission to the AD process. CP obtained from the initial process of cork grinding to produce granules in an industrial setting was used as reference material for comparison purposes in the stage of AD. Although all samples exhibited very low nitrogen content, they were still considered suitable for AD, as the calculated C/N ratios fell within the typical optimal range of 10–60 [50]. However, they also showed low COD and carbon levels, indicating a limited availability of organic matter for digestion.

Table 4. Chemical analysis of key parameters for the anaerobic digestion of the pretreated cork residues.

Parameter	Inoculum	Natural Stoppers			Technical Stoppers			Cork Powder		
		PTL ¹	PTS ²	PTWS ³	PTL ¹	PTS ²	PTWS ³	PTL ¹	PTS ²	PTWS ³
COD ⁴ (g/L)	3.60 ± 0.04	40.76 ± 0.54	-	-	55.00 ± 0.20	-	-	51.78 ± 2.61	-	-
VS ⁵ (g/L)	4.00 ± 0.05	54.96 ± 1.80	-	-	63.92 ± 0.94	-	-	83.92 ± 5.84	-	-
N-Kjeldahl (g/L)	0.36 ± 0.00	≤1.5	-	-	<1.5	-	-	1.54 ± 0.04	-	-
C ⁶ (wt%)	-	-	9.59 ± 0.35	9.04 ± 0.38	-	10.42 ± 0.71	10.31 ± 0.44	-	8.27 ± 0.13	8.10 ± 0.13
N ⁷ (wt%)	-	-	<0.2	<0.2	-	<0.2	<0.2	-	<0.2	<0.2
C/N ⁸	10.0	29.8	48.0	45.2	43.7	52.0	51.5	33.6	41.4	40.5

¹ PTL—pretreated liquid fraction; ² PTS—pretreated solid fraction; ³ PTWS—pretreated whole slurry (non-separated); ⁴ COD—chemical oxygen demand; ⁵ VS—volatile solids; ⁶ C—carbon; ⁷ N—nitrogen; ⁸ C/N—carbon/nitrogen ratio.

The biogas accumulation profile was determined for all the pretreated cork fractions along the digestion time. Cumulative biogas production was observed from the start of AD, showing a similar profile across all tested substrates (Figure 3a,b). No initial lag phase was detected, with biogas volumes ranging from 2.5 to 7.0 mL by the end of the third day. This behavior suggested the absence of inhibitory factors. From the third or the fourth day onward, no further biogas accumulation was observed in NCS-PTS or in any of the PTL and PTWS samples (Figure 3a); therefore, these tests ended on the eighth day of the AD process. In these cases, monitoring the methane content in the small volume of biogas produced, as well as evaluating biogas or methane yields, was deemed unnecessary.

Occasional decreases in cumulative biogas production were observed during the experimental period. These apparent reductions are likely attributable to variability among replicates, particularly when one of the triplicates exhibited lower biogas production while the remaining replicates continued to generate biogas. This inter-replicate variability also contributed to the relatively large standard deviations observed (Figure 3a,b). Nevertheless, the mean cumulative biogas production did not exhibit a consistent upward trend beyond day 3 in Figure 3a and beyond day 16 in Figure 3b, respectively. It was considered that biogas generation had plateaued after these points. The biogas production curves shown in Figure 3b did not display plateaus as distinct as those observed in Figure 3a. Nonetheless, both TCS-PTS and CP-PTS samples exhibited slope values greater than 1.1 during the first 16 days of digestion, after which the slope decreased to approximately 0.5, indicating a

nearly 50% reduction in the biogas production rate. For this reason, the digestion assay was maintained until day 25. Biogas generation in TCS-PTS and CP-PTS assays (Figure 3b) reached maximum cumulative productions of 25 mL and 26 mL after 18 and 22 days of digestion, respectively.

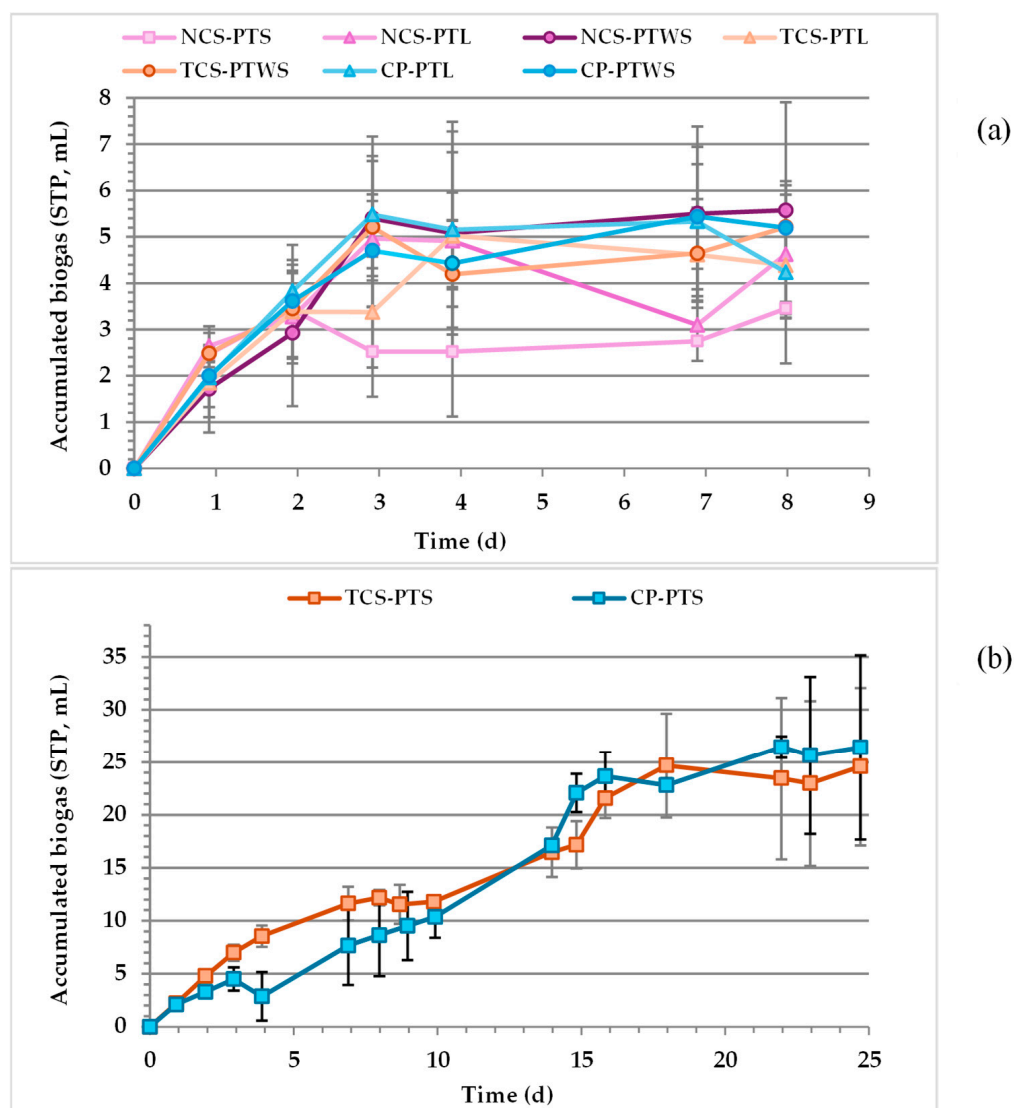


Figure 3. Profiles of biogas accumulation during the anaerobic digestion of the pretreated samples of natural and technical cork stoppers and cork powder over 8 days (a) and 25 days (b). NCS—natural cork stoppers; TCS—technical cork stoppers; CP—cork powder; PTL—pretreated liquid fraction; PTS—pretreated solid fraction; PTWS—pretreated whole slurry (non-separated); STP—Standard Temperature and Pressure, according to IUPAC, air at 0 °C and 1 bar. For improved clarity, different colors were used to distinguish the standard deviation associated with each sample in (b).

Figure 4 illustrates the evolution of methane content and cumulative methane yield throughout AD. Approximately 61% of the total methane production was achieved within the first 15 days of digestion for both substrates. The highest cumulative methane yields, corresponding to the BMP, were estimated at 19.5 and 26.1 L/kg initial VS for the PTS fractions of TCS and CP, respectively, with methane contents in the produced biogas reaching 68.5% and 63.9%, respectively. The maximum yield values obtained for each sample are summarized in Table 5.

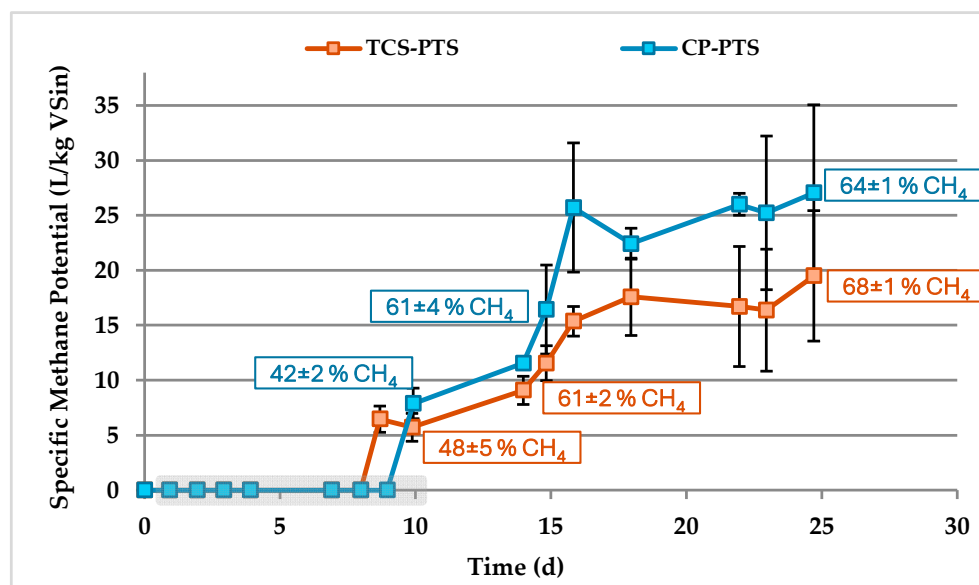


Figure 4. Specific methane potential as a function of time during the anaerobic digestion of pretreated technical cork stoppers and cork powder, with indication of the methane content in the biogas samples. Shaded data indicate that the methane content was not analyzed in this period. TCS—technical cork stoppers; CP—cork powder; PTS—pretreated solid fraction; VS_{in}—initial volatile solids.

Table 5. Maximum biogas and methane yields obtained after anaerobic digestion of the cork technical stoppers and cork powder solids that were separated after alkaline pretreatment.

Cork Residue or By-Product	Pretreated Fraction	VS _{in} ²	Biogas Yield	Methane	Methane Yield
		(g/L)	(L/kg VS _{in} ²)	(%)	(L CH ₄ /kg VS _{in} ²)
Technical stoppers	PTS ¹	21.60	28.5 ± 8.7	68.5 ± 0.8	19.5 ± 5.9
Cork powder	PTS ¹	15.61	42.3 ± 14.0	63.9 ± 0.6	26.1 ± 8.9

¹ PTS—pretreated solid fraction; ² VS_{in}—initial volatile solids.

Anaerobic digestion of cork residues has been scarcely investigated in the literature. Table 6 compares the methane yields, accumulated biogas volumes, and biogas quality obtained in this study with those reported for other substrates used in AD. The digestion of lignocellulosic biomasses, such as cork residues, rice husk, and wood waste, is a promising approach for biogas production; however, its efficiency remains severely limited by the structural recalcitrance of these materials, which makes them resistant to microbial degradation [51–53]. For wood waste, NaOH pretreatment coupled with anaerobic co-digestion with pig manure resulted in a 75.8% increase in cumulative methane yield compared to the untreated biomass [51]. Similarly, hydrothermal pretreatment of rice husk at 230 °C successfully disrupted its rigid outer silica layer and lignin matrix, achieving a maximum methane yield of 153 mL/g VS (representing a 5.7-fold increase relative to untreated rice husk) [53]. These findings highlight that the efficiency of biochemical conversion is highly dependent on selecting a substrate-specific pretreatment capable of overcoming the unique physical and chemical barriers of each biomass type [53]. Cork residues and by-products (including TCS and CP) exhibit extreme biological recalcitrance due to a chemical composition dominated by suberin (ca. 40–50 wt%) and Klason lignin (ca. 20–25 wt%) [54,55]. Mild alkaline pretreatment with NaOH at 85 °C proved ineffective, as it resulted in limited biogas production from NCS and methane yields of only 19.5 and 26.1 L CH₄/kg VS for TCS and CP, respectively. On the other hand, the pretreatment using acidic deep eutectic solvents (DES), consisting of choline chloride and formic acid (ChCl:formic acid) at 130 °C, demonstrated high efficacy in deconstructing the hydrophobic suberin–lignin matrix. This

pretreatment enabled a 125% increase in the biogas yield of cork dust, achieving a methane potential of 81 mL/g VS [54]. In contrast, liquid agricultural and industrial waste streams, such as piggery effluent with an inherent methane yield of 434 L CH₄/kg VS, or yogurt-milk processing sludge with 209 L CH₄/kg VS, bypass lignocellulosic recalcitrance entirely, providing excellent nutrient availability and pH buffering capacity [56,57]. This suggests that combining efficiently pretreated solid wastes with highly buffered liquid effluents represents an optimal strategy to balance carbon-to-nitrogen ratios and advance circular bioeconomy goals.

Table 6. Comparative table showing the methane yield, volume and quality of the accumulated biogas resulting from the anaerobic digestion of various types of biomasses, including the pretreated technical stoppers and cork powder used in the present study.

Biomass	Pretreatment Process	Methane Yield	Accumulated Biogas	Methane	Refs.
		(L CH ₄ /kg VS _{in} ¹)	(L)	(%)	
Technical stoppers	NaOH, 85 °C	19	0.025	68	This study
Cork powder	NaOH, 85 °C	26	0.025	64	This study
Cork powder without pretreatment	-	35	-	-	[54,55]
Cork powder with pretreatment	DES ²	81	-	-	[54,55]
Rice husk without pretreatment	-	27	-	-	[53]
Rice husks with pretreatment	Hydrothermal, 230 °C	153	-	-	[53]
Wood waste without pretreatment	-	175	-	-	[51]
Wood waste with pretreatment	NaOH, 90 °C	243	-	-	[51]
Piggery effluent	-	434	0.780	71	[56]
Liquid sludge from chestnut processing plant	-	152	0.106	63	[57]
Liquid sludge from dairy processing industry plant	-	209	0.114	70	[57]
Liquid sludge from fruit and cereals processing industry plant	-	190	0.144	53	[57]

¹ VS_{in}—initial volatile solids; ² DES—deep eutectic solvents.

In terms of co-product valorization, AD produced a nutrient-rich digestate (Table 7). Although a full evaluation was not performed in this study, it is unlikely that the original feedstock is contaminated with heavy metals. Therefore, due to its high N, K and P content, the produced digestate has the potential for agricultural applications.

Table 7. Chemical analysis of the digestate obtained from the cork technical stoppers and cork powder solids that were separated after alkaline pretreatment.

Cork Residue or By-Product	Pretreated Fraction	Total Solids (g/L)	Volatile Solids (g/L)	N ² (g/L)	K ³ (mg/L)	P ⁴ (mg/L)
Technical stoppers	PTS ¹	21.4	19.0	0.43	51.0	75.8
Cork powder	PTS ¹	21.4	18.9	0.30	44.7	91.4

¹ PTS—pretreated solid fraction; ² N—nitrogen; ³ K—potassium; ⁴ P—phosphorus.

Due to the lignocellulosic nature of the feedstock, the digestate from AD of cork stoppers is more similar to crop digestate than to manure or slurry digestate [58]. The digestates obtained in this study contained measurable concentrations of the three primary macronutrients—with TCS-PTS sample being richer in N (0.43 g/L) and K (51.0 mg/L), and CP-PTS richer in P (91.4 mg/L)—along with high VS content, indicative of high organic matter content with potential soil conditioning value. However, these nutrient levels are substantially lower than those reported for digestates derived from more readily biodegradable substrates, such as agricultural residues or food waste [59]. Nonetheless, several treatments can be applied to enhance the potential use of digestate, including solid/liquid phase separation (with various levels of complexity), as described by Rizzioli et al. [60], composting and use as a slurry substitute [59]. More advanced applications even involve ammonia stripping and scrubbing to produce ammonium sulfate [61].

3.3. Slow Pyrolysis of the Cork Residues

Due to their high carbon content, elevated heating value, and substantial proportions of lignin and suberin, cork residues are particularly suitable feedstocks for pyrolysis. Furthermore, the unique chemical composition of cork favors the production of biochar with a high carbon content and a porous structure, making it an attractive material for soil application as well as adsorption, carbon sequestration and energy storage applications. Slow pyrolysis was conducted on NCS, TCS and CP, the latter for comparison purposes. The product yields ranged from 61.6–75.0 wt% of biochar and 25.0–38.4 wt% of pyrolysis gas, with no detectable liquid fraction under the conditions applied (Figure 5). The sample CP with the finer particle size produced the largest amount of biochar (75.0 wt%). However, all samples exhibited a high biochar yield, suggesting that cork contains significant amounts of lignin and suberin that are resistant to thermal decomposition. The operating parameters can be adjusted to further optimize either the biochar or gas yield. The biochar yields obtained in this study are in agreement with previous reports on the pyrolysis of cork residues [14,20,62], although some variations can be attributed to differences in feedstock origin, particle size and reactor operating conditions. Cork biochar exhibits a high fixed carbon content (typically ~80 wt%) [20] comparable to biochar types derived from other lignocellulosic feedstocks, reflecting the inherent thermal resistance of its unique biochemical structure, particularly the presence of lignin and suberin.

Table 8 highlights the carbon-rich nature of the biochar obtained from the slow pyrolysis of cork residues. The biochar produced from NCS and TCS exhibited slightly higher carbon contents than that derived from CP, suggesting a greater extent of carbonization with oxygen and hydrogen being released to the gas phase, whose yield was higher. On the contrary, the higher oxygen content observed for CP biochar may indicate the persistence of oxygenated functional groups and a comparatively lower degree of thermal conversion. Low hydrogen and nitrogen contents, as observed in all samples, are consistent with devolatilization, dehydration and aromatization reactions during pyrolysis [63]. Chemically, cork biochar is composed predominantly of aromatic carbon structures, resulting from the progressive condensation of lignin-derived phenolic units. As pyrolysis temperature

increases, the biochar typically becomes more carbonized, with a higher carbon content and a reduction in oxygen-containing functional groups [20]. These changes influence key properties such as surface reactivity and affinity for polar versus non-polar compounds. Structurally, cork biochar retains much of the native cellular architecture of cork, characterized by a honeycomb-like arrangement of closed cells. During pyrolysis, this structure evolves into a highly porous network, with both micro- and mesopores contributing to an enlarged specific surface area (increasing from 2.37 m²/g to 489.1 m²/g) [14]. The extent of porosity development depends strongly on pyrolysis temperature: lower temperatures tend to preserve structural features with limited pore development, while higher temperatures (450–550 °C) enhance pore formation through secondary degradation and volatilization [14]. The release of oxygen- and hydrogen-containing species during thermal conversion is reflected in the composition of the pyrolysis gas. As shown in Figure 6, the gaseous product obtained from the pyrolysis of cork residues is mainly composed by CO₂, CH₄, CO, H₂, and light hydrocarbons, consistent with trends reported in the literature for lignocellulosic biomass [14,20]. In most published studies on cork and similar biomass materials, CO₂ is typically the dominant component, as the removal of oxygen from the biomass structure occurs primarily through the formation of CO₂.

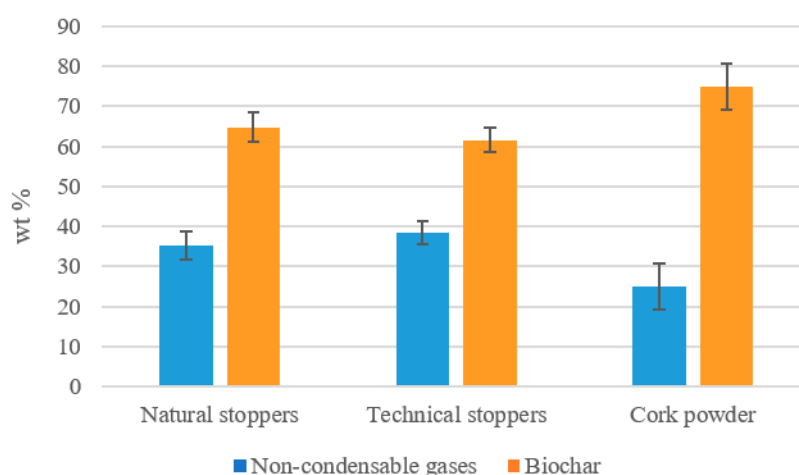


Figure 5. Biochar and gas yields obtained in the slow pyrolysis of natural and technical cork stoppers and cork powder.

Table 8. Elemental analysis of the biochar obtained after slow pyrolysis of natural and technical cork stoppers and cork powder.

Biochar	C ¹	H ²	N ³	O ⁴
	(wt%, d.b. ⁵)			
Natural stoppers	65.4 ± 6.0	4.8 ± 0.8	0.9 ± 0.1	25.9 ± 6.5
Technical stoppers	66.3 ± 2.9	4.9 ± 0.6	1.2 ± 0.1	24.7 ± 2.1
Cork powder	62.0 ± 3.6	5.0 ± 0.1	1.4 ± 0.2	27.4 ± 3.4

¹ C—carbon; ² H—hydrogen; ³ N—nitrogen; ⁴ O—oxygen; ⁵ d.b.—dry basis.

The comparison between the elemental compositions of the raw cork residues (Table 2) and the corresponding biochars (Table 8) demonstrates the carbonization effect of pyrolysis, reflected by increased carbon contents and reduced hydrogen and oxygen contents, particularly for NCS. This effect was evident in the NCS biochar, which exhibited an increase in carbon content from 58.75 to 65.4 wt%, accompanied by decreases in hydrogen and oxygen contents. This trend is consistent with the release of H₂ (6.80 vol.%), CO₂ (60.40 vol.%), and CO (6.83 vol.%) during pyrolysis (Figure 6). Nitrogen content remained

essentially unchanged within the reported experimental variability. TCS already exhibited a comparatively high initial carbon content (65.77 wt%); consequently, pyrolysis resulted in only a marginal increase to 66.3 wt%. The most pronounced change was the reduction in hydrogen content, from 7.36 to 4.9 wt%, indicating the occurrence of dehydrogenation reactions and corroborated by the higher production of gaseous hydrocarbons (Figure 6). Overall, these results confirm that cork-derived biochars are predominantly stable carbonaceous materials with considerable potential for use in soil applications, as adsorbents or carbon-sequestration products. The use of biochar as activated carbon for the adsorption of pollutants in different media has been investigated in the literature [64,65]. Its high adsorption and retention capacity, combined with environmental benefits (e.g., carbon sequestration and the use of residues), makes this use a promising possibility for agriculture, water treatment, and industrial processes.

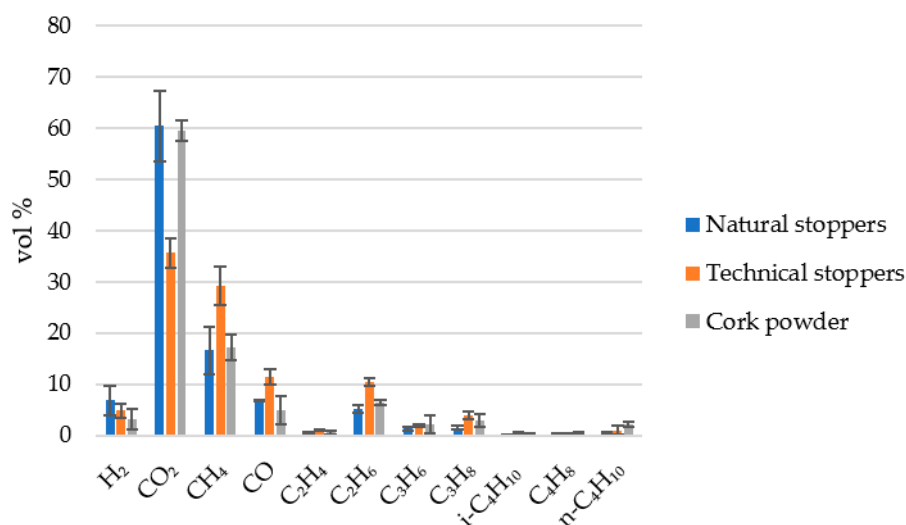


Figure 6. Non condensable gas composition obtained after slow pyrolysis of natural and technical cork stoppers and cork powder. H₂—hydrogen; CO₂—carbon dioxide; CH₄—methane; CO—carbon monoxide; C₂H₄—ethylene; C₂H₆—ethane; C₃H₆—propene; C₃H₈—propane; i-C₄H₁₀—isobutane; C₄H₈—butene; n-C₄H₁₀—n-butane.

3.4. Final Considerations on the Sustainable Valorization of Used Cork Stoppers

Table 9 presents a comparison of the potential energy recovery achieved through AD (methane production) and pyrolysis (biochar and pyrolysis gas production) on a per-unit-mass basis of the input substrate. From an energy recovery perspective, pyrolysis consistently outperformed AD yielding approximately 22–27 MJ/kg input substrate through the combined production of biochar and pyrolysis gas, compared with only 1.19–1.38 MJ/kg as methane. Regarding pyrolysis, the results showed a good energetic potential. Most of the energy was concentrated in the biochar fraction, whose values of recovered energy (16.36–18.71 MJ/kg) are comparable to those of some low-rank coals. The values for the pyrolysis gas were between 5.22–10.76 MJ/kg and were highly correlated with the CO₂ concentration. TCS pyrolysis gas presented a much lower CO₂ concentration, of about 35.6 vol% compared with 60.4 and 59.6 vol% obtained with NCS and CP, respectively (Figure 6). These observations are in line with previous studies showing that cork pyrolysis generates an energy-dense biochar and a combustible gas stream rich in H₂, CH₄, CO and light hydrocarbons [20,66].

Table 9. Potential energy recovered in the final products of anaerobic digestion and pyrolysis per input substrate.

Cork Residue or By-Product	Anaerobic Digestion	Slow Pyrolysis	
	Methane (MJ/kg Pretreated Cork)	Biochar (MJ/kg Cork)	Pyrolysis Gas
Natural stoppers	-	16.83 ± 2.29	5.39 ± 0.79
Technical stoppers	1.19 ± 0.36	16.36 ± 0.99	10.76 ± 0.55
Cork powder	1.38 ± 0.46	18.71 ± 1.28	5.22 ± 0.01

In addition to its higher energy recovery potential, biochar is a versatile material that offers a wider range of valorization opportunities than digestate generated through AD. From a vast list of potential applications currently being investigated, two can be highlighted as the currently more applied in industrial settings: as low-cost adsorbent for water or wastewater treatment or as soil amendment (with or without carbon sequestration credit potential) [67]. Several studies have explored the potential of cork-derived biochar as a low-cost adsorbent for heavy metals and gaseous pollutants, assessing the influence of different activation procedures on its adsorption properties [68]. However, to the best of the authors' knowledge, no other studies have tested the influence of the type of cork stopper on the yield of biochar. Further tests on its performance as adsorbent would be required. Regarding its use in soil applications, cork-derived biochar benefits from the high lignin content of the original feedstock, resulting in elevated carbon content, high aromaticity, and enhanced structural stability, all of which are favorable attributes for long-term carbon sequestration [69]. Despite its numerous environmental benefits, the main driver for the application of biochar to soils is the addition of nutrients and organic carbon, enabling the valorization of waste streams through the generation of a value-added product suitable for organic markets and capable of partially replacing fossil-based fertilizers [70].

It is important to compare the two tested pathways for used cork stoppers with the most common waste treatment options of incineration and landfill. From a life cycle perspective, issues regarding biogenic carbon, dynamic and/or consequential modelling can strongly affect the comparison. From a purely attributional perspective, the environmental impacts of incineration and landfilling depend strongly on whether energy recovery is implemented, either through direct combustion in incineration facilities or through biogas capture and utilization in landfills. Still, even with energy recovery, incineration leads to high emissions of biogenic carbon as well as fossil carbon from the fossil-origin fraction of cork stoppers such as polyurethane, inks and coatings, as well as particulates, nitrogen oxides (NO_x) and sulfur oxides (SO_x). Furthermore, although the energy produced could displace grid electricity, this benefit can be very limited in low-carbon grid and does not compensate for the CO₂eq emissions, particularly if biogenic carbon is considered. Landfill of cork stoppers is more complex, as the lignin content of its cork main material strongly limits degradation, as well as the coating used. However, it is known that biogas recovery is not 100% efficient particularly for landfills operating for several decades [71], with fugitive emissions of methane as well as emissions connected to leachate treatment [72]. As methane is such a powerful GHG, only a small amount of its emissions rapidly overtakes the amount of carbon capture that remains in the part of the cork stopper that does not degrade. Furthermore, biogas capture is not necessarily implemented in all sanitary landfills where cork stoppers are used. Estimates indicate that only 10% of methane produced in landfills is captured and used to produce electricity worldwide [73].

Anaerobic digestion more closely resembles landfill, as both create anaerobic conditions and produce biogas. However, despite the increased emissions associated with the required pretreatment, AD as evaluated in this study would be conducted under much

more controlled reactor conditions than landfilling, greatly reducing fugitive emissions and enhancing biogas production yields. Further reductions in GHG emissions would depend on the use given to the digestate, as it contains recalcitrant carbon and can be used to substitute, even if partially, fertilizers of fossil origin. The use of biogas is particularly relevant because it is typically cleaner than landfill gas [74] and can substitute natural gas, thereby reducing reliance on fossil fuels and the associated GHG emissions. Finally, the thermochemical conversion of used cork stoppers produces high-quality pyrolysis gas with low contamination. This pyrolysis gas can be used to substitute natural gas, in a process similar to AD, but with a higher yield. This higher yield compensates for the energy (and associated carbon emissions) required to heat the material to the necessary temperature. The climate change mitigation potential of this end-of-life treatment is strongly dependent on the quality of the biochar produced and its final application. When applied under suitable conditions, biochar can contribute to long-term carbon sequestration and may offer additional benefits through the generation of carbon credits [75,76].

Despite its potential, the present results suggest that AD of cork materials may not be suitable for increased industrial scale, as indicated by other authors [77], given its relatively slow kinetics, the difficulty of controlling the microbial process, the need for pretreatment and the lower methane production when compared to other feedstocks. The scalability of pyrolysis, on the other hand, is influenced by multiple factors, notably the energy source employed and the availability of suitable feedstocks. Novel solar-thermal-assisted pyrolysis systems, for example, have demonstrated potential advantages associated with the use of a low-carbon and potentially low-cost energy source [78]. Feedstock supply is also a critical consideration, and construction, renovation, and demolition waste, consisting primarily of wood but also including cork-based insulation materials, has been shown to represent a suitable feedstock source for pilot-scale pyrolysis applications [79]. Techno-economic assessments of the scale-up of slow pyrolysis systems processing lignin-rich biomass have indicated favorable economic performance, with returns on investment exceeding commonly accepted thresholds for bioprocess ventures and comparatively low payback periods [80]. Although material recycling and the recovery of potential value-added compounds from cork extractives should be prioritized, the tested conversions, particularly the thermochemical solution, can provide sustainable alternatives that can be integrated into existing systems while the recycling process is still being developed or improved.

Beyond the individual advantages of each technology, further opportunities may arise from integrating pyrolysis and AD within a biorefinery framework. Pyrolysis is especially suited to lignin- and suberin-rich solid fractions, while AD can recover energy and nutrients from liquid residues, wastewater and pretreated biomass. Additional synergies, such as using cork-derived biochar to enhance AD performance or thermochemically upgrading digestate, can further improve resource efficiency. Furthermore, the incorporation of digestate into cork-derived biochar may increase its suitability for agricultural applications.

4. Conclusions

This study demonstrates that cork residues can be valorized through both AD and slow pyrolysis. Pyrolysis proved particularly effective, yielding high amounts of carbon-rich biochar (61.6–75.0 wt%), with properties that varied according to the cork residue or by-product. The results highlight the suitability of NCS, TCS and CP as feedstocks for biochar production, generating materials with potential applications in soils, adsorption processes, carbon sequestration and other environmental uses. From a comparative perspective, pyrolysis exhibited greater valorization potential than AD under the conditions investigated, owing to its efficient conversion of the recalcitrant cork matrix into a high-yield, carbon-rich product with potential energy applications. In contrast, the low biogas yields obtained by AD suggest

that significant improvements in biodegradability would be required for this route to become competitive for cork as a standalone substrate. Nevertheless, AD may become more attractive when cork is co-digested with readily biodegradable substrates or subjected to optimized pretreatment strategies. Overall, the findings support the integration of cork residues into circular bioeconomy strategies, promoting their conversion into energy or value-added products. Future research should focus on optimizing pyrolysis conditions, including temperature, residence time, and particle size, to tailor biochar properties to specific applications and maximize the valorization potential of cork-derived materials.

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