

Article

Refuse-Derived Fuel (RDF) for Energy-Intensive Industries: Characterization and Potential as an Alternative Fuel Source

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Abstract

The transition toward low-carbon cement production requires alternative fuels with improved environmental performance and resource efficiency. Refuse-Derived Fuel (RDF), produced from pre-treated non-recyclable waste streams, represents a promising alternative fuel; however, its heterogeneous and varying composition presents challenges for stable combustion and process optimization. In this study, a comprehensive physicochemical characterization of RDF was performed and compared with pet coke, a conventional, fossil cement kiln fuel. The analysis included manual sorting, particle size distribution, elemental characterization, Scanning Electron Microscopy coupled with Energy dispersive X-ray spectroscopy (SEM/EDS), X-ray Diffraction (XRD), thermogravimetric and differential scanning calorimetry (TGA/DSC), and Higher Heating Value (HHV) determination. The RDF sample exhibited a heterogeneous polymeric-mineral composition dominated by plastics, paper, textiles, and inorganic fractions. TGA revealed a broad multi-stage thermal degradation profile, while calorimetry indicated HHV of 19.2 ± 0.3 MJ/kg and ash content of 11.6 wt.%, compared with 34.57 ± 0.11 MJ/kg and 1.97 wt.% for pet coke, respectively. SEM/EDS and XRD analyses confirmed the coexistence of polymeric and mineral phases in RDF, whereas pet coke exhibited a predominantly carbonaceous and homogeneous composition. The generated dataset supports computational fluid dynamics (CFD)-based cement kiln combustion models and RDF utilization for fossil fuel substitution in the cement industry.

Keywords: Refuse-Derived Fuel (RDF); alternative fuels; fuel characterization; thermogravimetric analysis (TGA); cement industry; waste-to-energy (WtE)



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1. Introduction

Energy-intensive industries, including cement, steel, and chemical production are fundamental to modern economic development but remain major contributors to global greenhouse gas (GHG) emissions. Increased awareness of climate change impacts and strengthened international climate commitments underscore the urgent need for these sectors to adopt sustainable, low-carbon practices. Key mitigation strategies include substituting conventional fossil fuels with alternative ones with a lower or zero carbon footprint, enhancing energy efficiency, and implementing advanced low-emission technologies.

The cement industry, a critical enabler of infrastructure and urban development, is one of the most carbon-intensive industrial sectors. It is estimated that cement production contributes approximately 7–8% of global carbon dioxide (CO₂) emissions, primarily due to fossil fuel combustion and the calcination of limestone during clinker production [1,2]. As the demand for cement continues to grow, particularly in emerging economies, CO₂ emissions from this sector are projected to rise significantly in the absence of large-scale adoption of sustainable practices. This trajectory highlights the pressing need for the sector to transition to low-emission production pathways. One of the most promising strategies for reducing emissions in cement production involves the use of alternative fuels. Traditionally, the cement industry relies on fossil fuels, prominent among which is petroleum coke (pet coke). Pet coke, a byproduct of petroleum refining, is primarily composed of carbon and may contain sulfur, metals, and inorganic residues [3,4]. Its high calorific value and availability make it a prevalent fuel in the cement industry. Waste-derived alternative fuels, such as Refuse-Derived Fuel (RDF), are increasingly used in cement production [5–7]. RDF is produced from the pre-treated, non-recyclable fraction of municipal solid waste (MSW), and commercial, industrial, and agricultural waste streams, in compliance with relevant waste management and fuel quality regulations [8]. The production process involves sorting and mechanical treatments, such as size reduction, sieving, and magnetic separation to recover a high-calorific fraction predominantly composed of paper and plastics [9]. This refined fuel exhibits improved quality compared with untreated waste. The use of RDF provides dual environmental benefits: it facilitates waste valorization and management while concurrently reducing reliance on fossil fuels [10–12]. Due to its partial biogenic content, RDF typically has a measurably lower net CO₂ footprint compared to conventional fossil fuels. Furthermore, its integration into cement manufacturing supports circular economy principles by enhancing resource efficiency and minimizing waste.

The quality of RDF is variable and depends on its composition and treatment. High-grade RDF is characterized by high calorific value and low moisture and ash content. In Europe, Solid Recovered Fuels (SRFs), which represent a standardized and quality-controlled subclass of RDF, are commonly classified according to EN 15359 based on key fuel parameters such as net calorific value, chlorine content, and mercury concentration. These parameters are particularly important for evaluating the suitability of RDF/SRF for industrial co-processing applications, including cement kilns. However, challenges persist regarding the presence of impurities, such as chlorinated compounds, metals, and glass. For instance, RDF may contain chlorinated materials (e.g., polyvinyl chloride, PVC), which can generate harmful compounds during combustion, such as hydrogen chloride, dioxins, and chlorinated Volatile Organic Compounds (VOCs), posing environmental and operational risks [12,13]. These issues underscore the necessity for careful regulation of combustion conditions to mitigate the formation of such pollutants [9].

A detailed understanding of RDF properties, particularly the particle size distribution (PSD) and compositional parameters, is essential for both operational optimization and environmental compliance in cement kilns. The particle size critically influences the combustion kinetics, including the ignition delay, burnout time, and heat release. Smaller

particles tend to combust more completely and efficiently, while larger particles require longer residence times and may result in inefficient combustion that can lead to incomplete burnout and negatively affect kiln thermal stability and clinker quality, thereby impacting both energy efficiency and product quality.

Numerous studies ([6,7] see additional references also in [9]) have investigated RDF as an alternative fuel for cement kilns, and highlighted the significant variability in RDF composition, physicochemical properties, and combustion behavior depending on waste origin, pre-treatment methods, and storage conditions. However, integrated studies combining compositional, morphological, crystallographic, thermal, and calorimetric characterization of RDF together with comparative analysis against conventional kiln fuels such as pet coke remain relatively limited. Such comprehensive characterization not only improves the understanding of RDF fuel quality and combustion behavior but also provides the physicochemical input required for burner design, combustion and emission prediction, process optimization and reliable computational modelling of industrial cement kilns [14,15]. These datasets are therefore essential for developing digital twins capable of supporting the efficient and environmentally sound utilization of alternative fuels in cement production.

To address these challenges, a digital twin of a cement kiln using computational fluid dynamics (CFD) to optimize combustion and facilitate the use of alternative fuels such as RDF, has been developed. A prerequisite for model development is the comprehensive characterization of RDF fuel properties. The current study conducts a detailed analysis of a typical RDF sample to assess its potential as a fuel for clinker kilns. The investigation included particle size fractionation, elemental composition, calorific value, and the content of ash, moisture, and trace elements. A comparative analysis was conducted using pet coke, a commonly used fossil fuel in cement production. Beyond reporting the physicochemical properties of RDF, this work establishes quantitative relationships between fuel composition, morphology, thermal behavior, and energy performance that are directly applicable to combustion modelling and industrial co-firing assessments. In addition to evaluating the fuel properties, the primary objective of this study is to generate high-quality input data to support the development of a combustion simulation model, following similar practices reported elsewhere [16]. This model is designed to optimize kiln operation and enable cleaner and more efficient co-processing of alternative fuels. By evaluating both the technical and environmental implications of RDF use, the present study aims to contribute to the broader discourse on sustainable fuel alternatives in the cement sector. These findings offer insights into RDF's potential to replace conventional fuels, promote waste valorization, and support emissions reduction targets.

2. Materials and Methods

2.1. Materials

Two samples were examined: one RDF sample (Figure 1a,b) and one pet coke sample (Figure 1c), both provided by Titan Cement Company SA, Thessaloniki, Greece. RDF sampling was carried out following the procedures specified in EN 15442 and the sample was prepared following the ISO 21646 standard procedures, i.e., a simple and effective way to obtain a representative subsample without introducing bias. Pet coke sampling was carried out with an automatic POLYSIUS sampler. The RDF sample was used either as received or air-dried and ground down to particle sizes below 0.25 mm using a cutting mill (PULVERISETTE 15, FRITSCH GmbH, Idar-Oberstein, Germany) to achieve homogenization (Figure 1b).

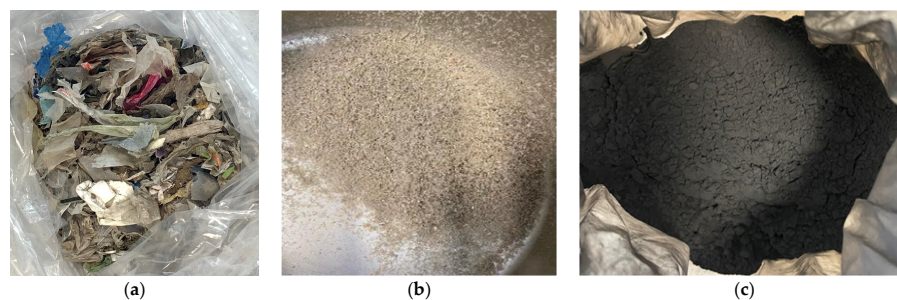


Figure 1. Images of (a) the RDF sample as-received, (b) the RDF sample homogenized after shredding/milling and (c) the pet coke sample in its as-received form.

2.2. Analysis of Fuel Samples

2.2.1. RDF Composition Analysis and Weight-Based Particle Size Distribution

Compositional analysis of RDF was performed on the as-received sample which was processed via manual sorting and classification per size and category of material, including plastics, paper, textiles, glass, metals, and other inorganic fractions. Each size fraction and each material fraction within the corresponding size class were weighed and quantified on a weight percentage basis (wt.%) in order to experimentally determine the weight-based particle size distribution of the RDF sample (based on methodology described elsewhere [12,15]). The manual sorting process was conducted over a period of five days, while final weighing and quantification were performed on the fifth day. Precision weighing was carried out using an analytical balance (Uni Bloc ATX224R, Shimadzu, Kyoto, Japan; max. weight: 220 g, min. weight: 10 mg, accuracy: 0.1 mg).

The Particle Size Distribution (PSD) of the pet coke sample was determined by Laser Scattering and Dynamic Light Scattering (DLS). The Laser Scattering measurements (LA-960 Laser Scattering Particle Size Distribution Analyzer, HORIBA, Kyoto, Japan) were used to determine the size distribution of particle aggregates, whereas the primary PSD was evaluated using DLS measurements performed with a VASCO γ analyzer (CORDOUAN Technologies, Pessac, France).

2.2.2. Alternative and Conventional Fuel Samples Characterization

The RDF and pet coke samples were further characterized in terms of elemental composition, calorific value, ash content, moisture, trace elements, and combustion behavior, morphology and crystallographic structure in order to generate high-quality input data for the combustion simulation model development. Elemental characterization of the two samples was performed using a LECO CHN828 elemental analyzer (LECO Corporation, St. Joseph, MI, USA). The inorganic elemental composition of the pet coke sample was investigated by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using an Optima 4300 DV ICP-OES spectrometer (PerkinElmer, Waltham, MA, USA), equipped with a GemCone (PerkinElmer, Waltham, MA, USA) ultrasonic nebulizer. Morphological and localized elemental analyses were conducted using Scanning Electron Microscopy coupled with Energy dispersive X-ray spectroscopy (SEM/EDS) (InTouchScopeTM JSM-IT 500, JEOL, Tokyo, Japan). Prior to analysis, the samples were coated with a thin conductive gold layer to improve imaging quality and minimize charging effects. The crystallographic structure of the samples was investigated by X-ray Diffraction (XRD) analysis performed with a D8 Advance X-Ray Diffractometer (Bruker, Karlsruhe, Germany).

Moisture content, volatile matter release, fixed carbon combustion, and residual ash content were evaluated using simultaneous Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) (Jupiter STA 449 F3, NETZSCH, Selb, Germany; maximum temperature: 1650 °C). Oxidation behavior was assessed through analysis of

the thermal degradation profiles and heat flow signals obtained during TGA/DSC measurements. The Higher Heating Value (HHV) of the fuel samples was obtained using an isoperibol bomb calorimeter (Parr 6200 Isoperibol bomb Calorimeter, Parr Instrument Company, Moline, IL, USA).

3. Results and Discussion

3.1. Physical Characterization and Particle Size Distribution of RDF and Pet Coke

3.1.1. RDF Manual Sorting, Composition Analysis and Weight-Based Particle Size Distribution

The composition of the RDF sample is presented in Table 1. Plastics constitute the dominant fraction, accounting on average for 41.62 wt.% of the total sample mass, followed by soil-like mineral fraction (29.56 wt.%). Paper (10.41 wt.%) and fabric/textile materials (9.48 wt.%) were present in lower proportions, while wood (3.29 wt.%), glass (1.09 wt.%), rubber and metals (each <1 wt.%) were also identified. The predominance of plastic materials is consistent with the typical composition of RDF reported in the literature, where plastics generally represent the major combustible fraction due to their high calorific value and widespread occurrence in municipal solid waste streams (e.g., [17–20]). In contrast, the relatively high proportion of soil-like mineral material observed in the present study indicates the presence of a significant non-combustible, ash-forming fraction, which can adversely affect the fuel quality and combustion performance of RDF by reducing its effective heating value and increasing ash generation. The origin of this mineral fraction is likely associated with RDF handling and storage practices. RDF stored in bulk form, particularly in open or partially sheltered areas within waste treatment facilities, may accumulate dust, soil particles, and other fine inorganic matter through repeated loading/unloading operations and exposure to environmental conditions. Contact with ground surfaces during mechanical handling may further contribute to the incorporation of mineral fines into the fuel stream. Moreover, insufficient separation at the source has also significant contribution to the amount of the mineral fraction.

Table 1. Weight and percentage of weight of each material in the RDF sample (* indicates all types of plastic).

Material	Weight (g)	wt. %
Metallic	1.6978	0.58
Rubber	2.4252	0.82
Glass	3.2138	1.09
Polymeric foam *	3.3286	1.13
Stones/marble/ceramic	9.2766	3.15
Wood	9.6967	3.29
Thin plastic with aluminum *	11.2981	3.84
Fabric	27.8949	9.48
Paper	30.6357	10.41
Hard plastic *	32.8315	11.15
Thin plastic *	75.0656	25.50
Soil-like mineral	87.0000	29.56
Total	294.3645	100.00

The particle size distribution of the RDF sample was determined by classification into six predefined size fractions (>20 cm, 15–20 cm, 10–15 cm, 5–10 cm, 1–5 cm, <1 cm). Each fraction was weighed using an analytical balance, and the results are summarized in Table 2. The majority of the sample mass was concentrated in the 1–5 cm fraction, accounting for 51.20 wt.% of the total weight. This was followed by the <1 cm (29.56 wt.%)

and 5–10 cm (16.04 wt.%) fractions. The remaining mass was distributed among the 10–15 cm (2.88 wt.%), >20 cm (0.18 wt.%), and 15–20 cm (0.14 wt.%) fractions.

Table 2. Weights and percentages of the weights of each size class of materials.

Size Class (cm)	Weight (g)	wt. %
>20	0.5172	0.18
15–20	0.3976	0.14
10–15	8.4891	2.88
5–10	47.2071	16.04
1–5	150.7535	51.20
<1	87.0000	29.56
Total	294.3645	100.00

Figure 2 presents the weight-based composition (wt.%) of the RDF sample across all particle size fractions. Only thin plastics were identified in the >20 cm fraction. The 15–20 cm fraction comprised exclusively fibers. The 10–15 cm size fraction was predominantly composed of thin plastic (52.10 wt.%), followed by fabric (30.68 wt.%), aluminum-coated thin plastic (13.09 wt.%), hard plastic (3.63 wt.%), and minor amounts of metal (0.49 wt.%). In the 5–10 cm fraction, thin plastic was again the dominant material (43.37 wt.%), with notable contributions from paper (18.69 wt.%), fabric (13.43 wt.%), hard plastic (11.27 wt.%), and aluminum-coated thin plastic (9.21 wt.%). Smaller quantities of wood (1.91 wt.%), metal (1.24 wt.%), and rubber (0.88 wt.%) were also observed. The 1–5 cm fraction exhibited the highest degree of heterogeneity, with thin plastic (32.94 wt.%), hard plastic (18.04 wt.%), paper (14.47 wt.%), and fabric (12.31 wt.%) being the most abundant components. Smaller amounts of stones (6.15 wt.%), wood (5.83 wt.%), aluminum-coated plastic (3.87 wt.%), polymeric foam (2.21 wt.%), glass (2.13 wt.%), rubber (1.33 wt.%), and metal (0.71 wt.%) were also recorded. The <1 cm fraction primarily consisted of fine particulate matter, including soil, small stones, plastic fragments, fine fabric fibers, polymeric foam, and small pieces of paper and metal.

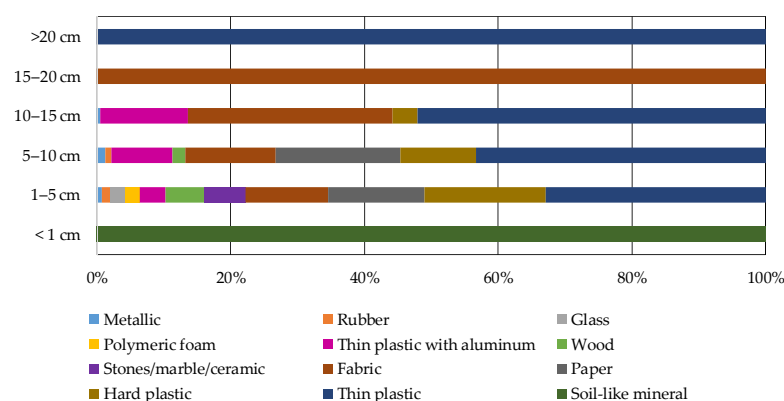


Figure 2. Composition wt.% per material category of all size fractions of the RDF sample.

Figure 3 shows the weight-based particle size distribution of each material identified in the RDF sample. For metals, the majority of the weight was concentrated in the 1–5 cm fraction (63.02 wt.%), followed by the 5–10 cm (34.51 wt.%) and 10–15 cm (2.47 wt.%) fractions. Rubber pieces were similarly concentrated in the 1–5 cm fraction (82.93 wt.%), with the remaining weight in the 5–10 cm fraction (17.07 wt.%). Glass, polymeric foam, and stone particles were exclusively found in the 1–5 cm size range. Wood fragments were predominantly 1–5 cm in size (92.68 wt.%), with only a small proportion (7.32 wt.%) in the 5–10 cm range. Thin aluminum-coated plastics were distributed across three fractions: 51.70 wt.% in the 1–5 cm range, 38.47 wt.% in the 5–10 cm range, and 9.84 wt.% in 10–15 cm

range. Fabric particles were primarily found in the 1–5 cm fraction (67.47 wt.%), with 23.06 wt.% in the 5–10 cm range and 9.47 wt.% in the 10–15 cm range. Paper was mostly present in the 1–5 cm fraction (71.20 wt.%), with the remainder (28.80 wt.%) in the 5–10 cm range. Hard plastic pieces followed a similar trend, with 82.85 wt.% in the 1–5 cm fraction, 16.21 wt.% in the 5–10 cm range, and a minimal amount (0.94 wt.%) in the 10–15 cm fraction. Thin plastic pieces were predominantly in the 1–5 cm size range (66.15 wt.%), followed by 27.27 wt.% in the 5–10 cm range, 5.89 wt.% in the 10–15 cm range, and a small proportion (0.69 wt.%) in the >20 cm range. A visual representation of the distribution of all material types across the various size fractions is shown in Figure 4.

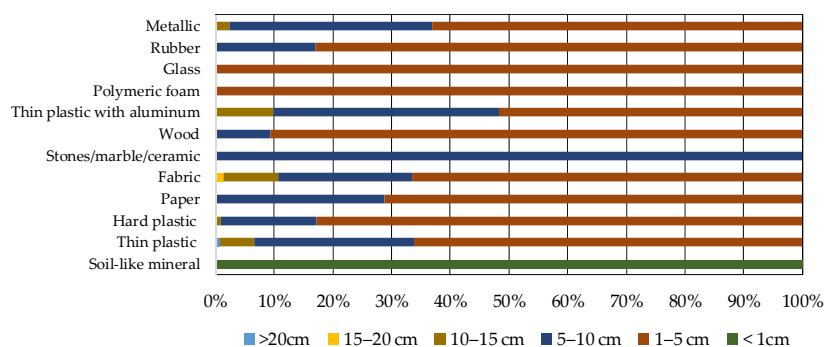


Figure 3. Composition wt.% per material of all size fractions of the RDF sample.

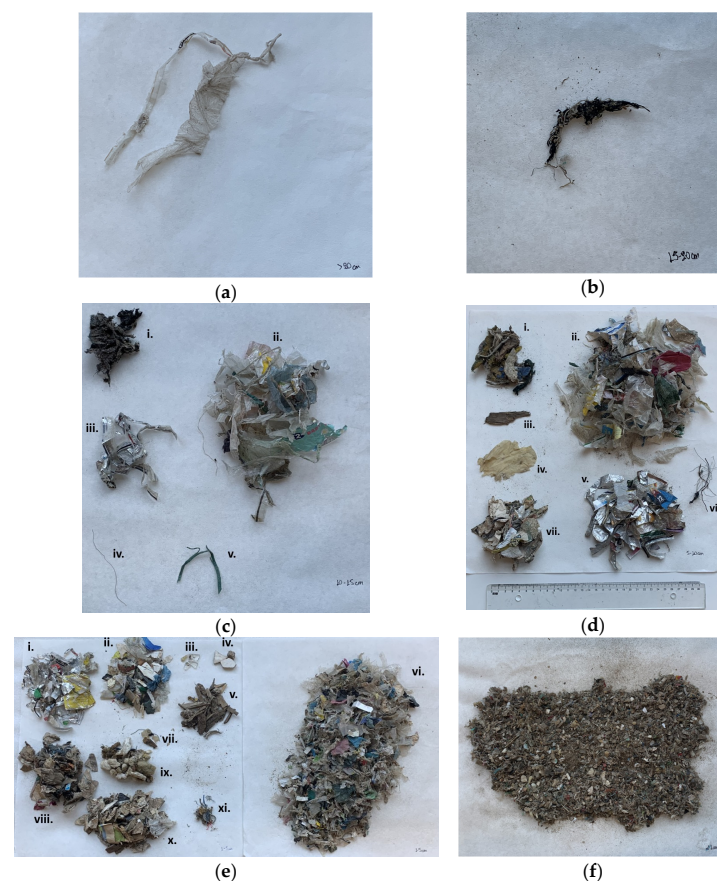


Figure 4. Classification of the RDF sample in size fractions and per material in each fraction: (a) >20 cm: thin plastic, (b) 15–20 cm: fabric, (c) 10–15 cm: i. fabric, ii. thin plastic, iii. thin aluminum-coated plastic, iv. rubber and v. metal, (d) 5–10 cm: i. hard plastic, ii. thin plastic, iii. wood, iv. rubber, v. thin aluminum-coated plastic, vi. metal and vii. paper, (e) 1–5 cm: i. thin plastic with aluminum coating, ii. hard plastic, iii. glass, iv. stone, v. wood, vi. thin plastic, vii. rubber, viii. fabric, ix. polymeric foam, x. paper, and xi. metal, and (f) <1 cm: soil-like mineral fraction.

3.1.2. Volume-Based and Number-Based Particle Size Distribution of Pet Coke

The volume-based particle size distribution (PSD) of the pet coke sample is presented in Figure 5. The particle aggregates ranged from approximately 10 to 100 μm , with a median volume-based diameter (D_v 50%) of 24.76 μm , mean diameter of 38.23 μm and mode diameter of 12.40 μm , as summarized in Table 3. The mode diameter corresponds to the maximum of the distribution curve, whereas the mean diameter is strongly influenced by the selected weighting approach (i.e., intensity-, volume- or number-based distribution) [21]. The number-based PSD describes the distribution of particles according to the number of particles in each size class, while the volume-based particle size distribution weights each particle according to its volume, assuming spherical geometry. Figure 6 illustrates the distribution of the primary particle size in terms of both the particle number and particle volume. Two distinct peaks were observed: the main peak of the number-based distribution appeared at approximately 180 nm, whereas the corresponding peak in the volume-based distribution was located at approximately 650 nm. This behavior indicates that ultrafine particles dominate in terms of particle count, while larger particles account for the majority of the total particle volume and mass. Table 4 summarizes the characteristic size percentiles, including the number-based diameters (D_n 10%, D_n 50%, D_n 90%) and the volume-based diameters (D_v 10%, D_v 50%, D_v 90%). The broad difference between number- and volume-based distributions reflects the heterogeneous particle size characteristics of the ground pet coke sample and highlights the tendency of fine particles to form larger agglomerates.

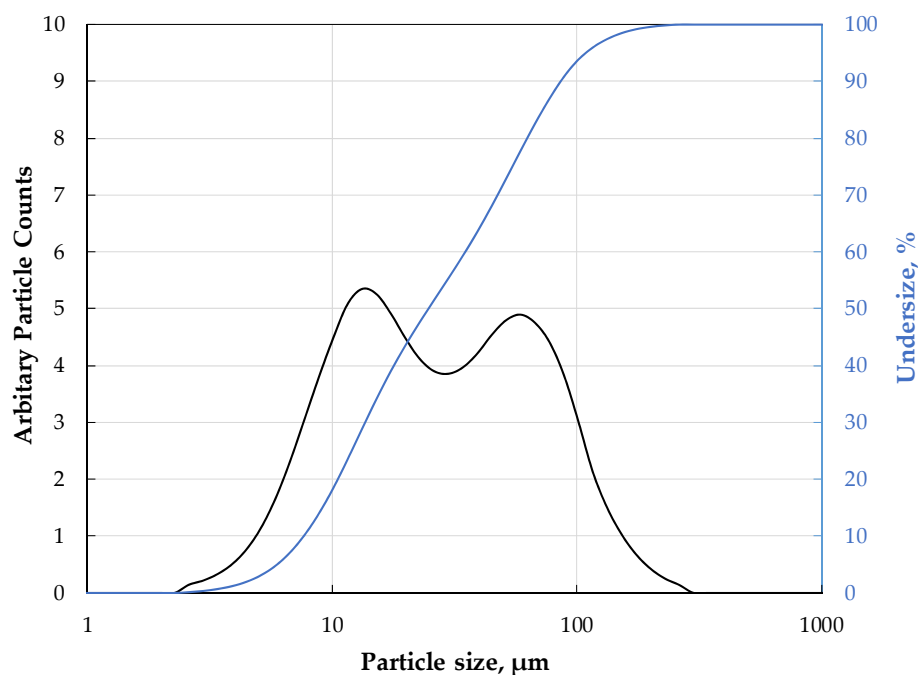


Figure 5. Particle size distribution curve of pet coke particles by Laser Scattering.

Table 3. Volume-based diameter parameters of pet coke measured by Laser Scattering.

Sample	Volume-Based Diameter Parameters (μm)					
	D_v 10%,	D_v 50%	D_v 90%	Median Size	Mean Size	Mode Size
Pet coke	7.64889	24.76153	86.09235	24.76153	38.22618	12.4048

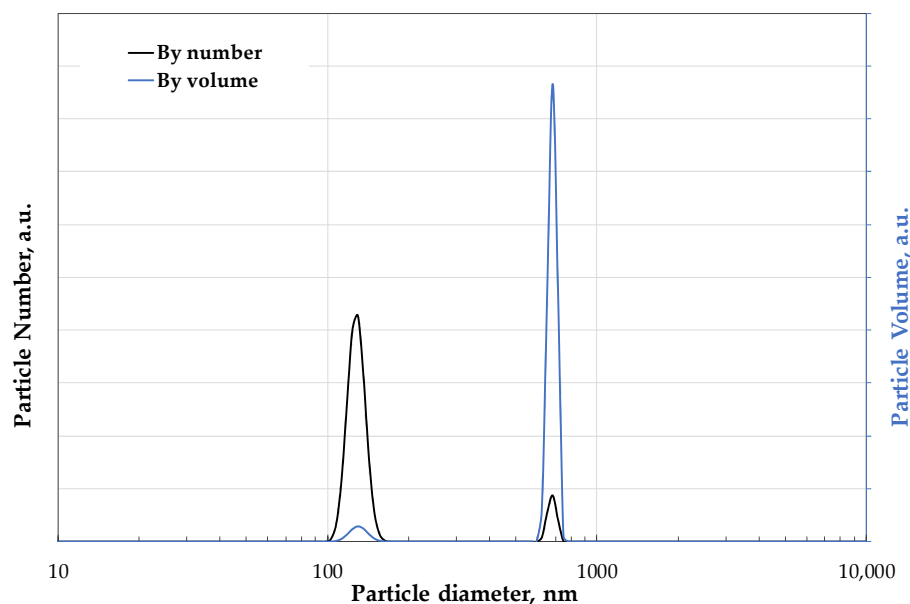


Figure 6. Number-based and Volume-based pet coke particle size distribution curves by DLS (a.u. denotes “arbitrary units”).

Table 4. Number-based and Volume-based diameter parameters of pet coke measured by DLS.

Sample	Number-Based Diameter Parameters (nm)				Volume-Based Diameter Parameters (nm)			
	D _n 10%	D _n 50%	D _n 90%	Mean	D _v 10%	D _v 50%	D _v 90%	Mean
Pet coke	118.11	129.55	155.87	181.16	653.52	684.45	716.84	649.78

The obtained PSD values are generally consistent with particle size distributions reported in the literature for pet coke subjected to mechanical grinding and milling. Similar particle size ranges and bimodal or broad distributions have been associated with grinding conditions, milling duration, and the intrinsic brittleness and carbonaceous structure of pet coke particles [22]. In particular, the measured D_v 50% values fall within the range commonly reported for pulverized pet coke intended for combustion applications in cement kilns and industrial burners, where particle fineness strongly influences ignition behavior, burnout efficiency, and combustion kinetics.

The compositional and particle size characteristics identified in this study are directly relevant to fuel handling, feeding stability, burnout efficiency, and heat release within cement kilns, and therefore constitute essential input parameters for combustion modelling and process optimization.

3.2. Elemental Characterization of RDF and Pet Coke

Elemental characterization provided additional insight into the fuel properties of the RDF and pet coke samples. The results are summarized in Table 5. The RDF sample contained 49.60% carbon, 6.91% hydrogen and 1.64% nitrogen, confirming the presence of a substantial combustible fraction. These values are consistent with the material composition results, particularly the high contribution of plastics, paper, textiles, and biomass-derived components, and support the measured High Heating Value (HHV) (Section 3.6). The elemental composition of RDF reported in the literature spans a relatively broad range, with carbon contents typically varying between approximately 24–60%, hydrogen contents between 1 and 10% and nitrogen contents between 0.04 and 4% [19,23,24]. However, in specific cases where RDF contains elevated fractions of plastics and paper, significantly higher carbon concentrations (>70%) have also been reported [25]. The relatively elevated

hydrogen content of the investigated sample is mainly associated with the significant plastic fraction identified during the compositional analysis, since polymeric materials generally exhibit high hydrogen-to-carbon ratios and contribute positively to the calorific value of RDF [25].

Table 5. Results of qualitative and quantitative determination of elemental analysis of the two fuels investigated.

Elements	Determination of Elements	
	RDF	Pet Coke
C	49.60%	85.10%
H	6.91%	3.67%
N	1.64%	1.58%

In contrast, the pet coke sample exhibited a substantially higher carbon content of 85.10%, together with lower hydrogen content (3.67%) and 1.58% nitrogen. The elevated carbon concentration is characteristic of pet coke and directly explains its significantly higher calorific value and more concentrated exothermic combustion behavior observed in the DSC analysis (Section 3.5). The relatively low hydrogen content reflects the highly carbonized and aromatic nature of pet coke, while the presence of nitrogen may contribute to NO_x formation during combustion, although emission measurements would be required to quantify this effect. The elemental composition of pet coke is in agreement with literature data reported for petroleum-derived solid fuels, which commonly contain carbon concentrations above 80% and relatively low oxygen and volatile contents [24,26].

Preliminary ICP-AES analysis of the pet coke sample confirmed relatively low concentrations of inorganic impurities, with aluminum and copper detected at 452 ± 20 ppm and 9 ± 0.5 ppm, respectively. These findings are consistent with the low residual ash fraction observed during TGA analysis (Section 3.5).

Overall, the elemental analysis confirms the fundamentally different fuel characteristics of RDF and pet coke. RDF behaves as a heterogeneous oxygenated fuel containing mixed biogenic and fossil-derived fractions, whereas pet coke represents a highly carbonaceous and energy-dense fossil fuel with more homogeneous combustion behavior. The elemental composition provides essential information for evaluating fuel quality, calorific potential, and the formation of combustion-related emissions, while also serving as key input for thermodynamic and combustion models.

3.3. Analysis by Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

The morphological and microchemical characterization of both ground RDF and pet coke samples were carried out using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS). SEM micrographs at magnifications ranging from $\times 30$ to $\times 2000$ revealed distinct structural features for each material. The RDF sample exhibited a highly heterogeneous structure, consisting of fibrous materials, irregular fragmented particles, porous regions and fine agglomerates (Figure 7a–c). The coexistence of particles with different morphologies reflects the mixed origin of RDF and is consistent with the manual sorting and compositional analysis results, which identified plastics, paper, textiles, wood-derived materials, and soil-like mineral fractions within the sample, reported also elsewhere [19]. In addition, bright localized regions observed in the SEM images suggest the presence of inorganic or mineral-rich inclusions embedded within the organic matrix.

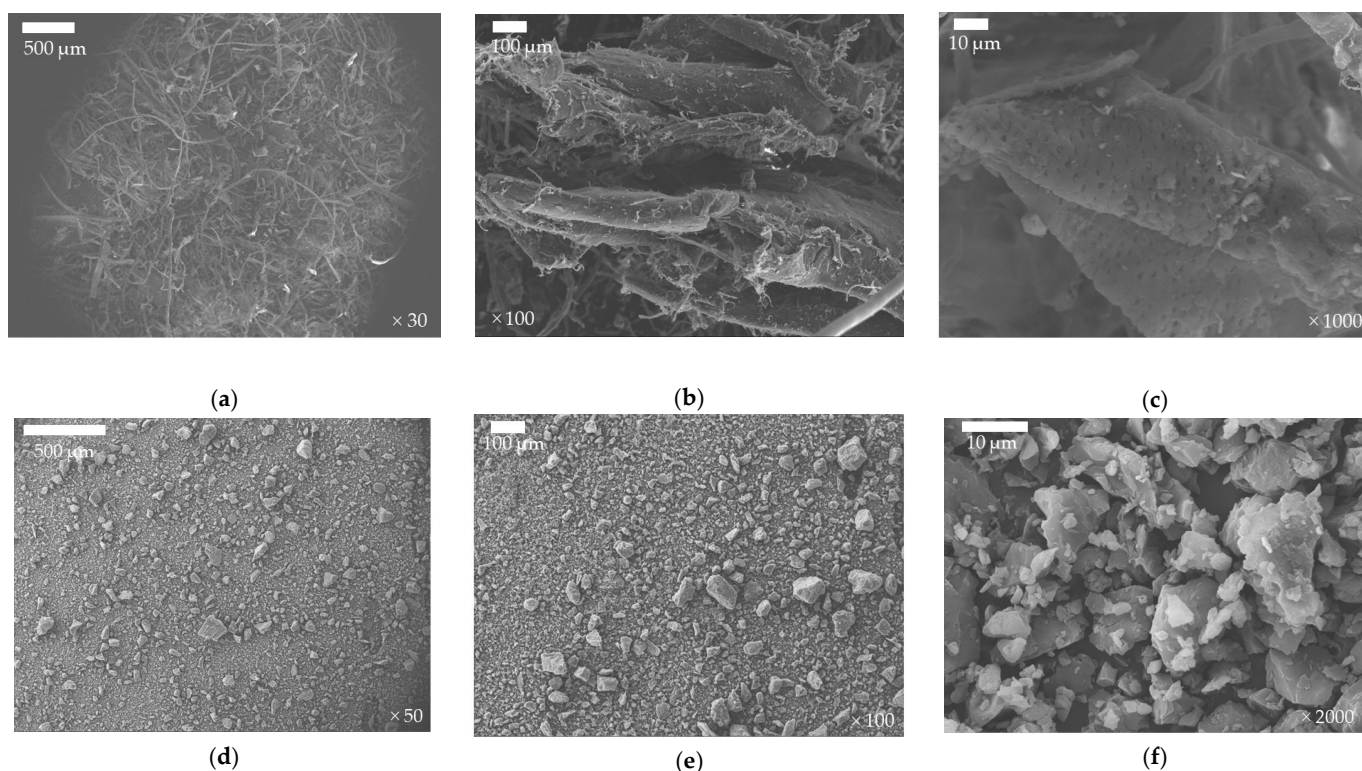


Figure 7. SEM images of ground RDF sample at magnification (a) $\times 30$, (b) $\times 100$, (c) $\times 1000$ and pet coke sample at magnification (d) $\times 50$, (e) $\times 100$, (f) $\times 2000$.

In contrast, the pet coke sample exhibited notably more homogeneous and compact morphology (Figure 7d–f). The particles appeared as relatively dense and well-defined aggregates with characteristic sizes on the order of approximately 10 μm , in agreement with the particle size distribution analysis. The smoother and less porous structure of pet coke is characteristic of highly carbonaceous fossil-derived fuels [27] and is consistent with its concentrated combustion profile and elevated calorific value observed during the TGA/DSC and bomb calorimetric analyses (Sections 3.5 and 3.6).

Multiple EDS point analyses further elucidated the localized elemental composition of the investigated samples. RDF (Figure 8a) exhibited a chemically heterogeneous composition dominated by carbon (C), oxygen (O), and calcium (Ca), along with minor constituents such as silicon (Si), sulfur (S), aluminum (Al), chlorine (Cl), sodium (Na), iron (Fe), magnesium (Mg), potassium (K), and titanium (Ti). The simultaneous presence of carbon-rich and mineral-containing regions further confirms the composite nature of RDF and supports the elevated ash content observed during TGA. Pet coke (Figure 8b) was found to consist primarily of carbon (C), oxygen (O), sulfur (S), and calcium (Ca), with only trace quantities of copper (Cu), silicon (Si), aluminum (Al), and iron (Fe). These findings are consistent with the lower ash content and higher carbon concentration determined through TGA and elemental analysis, respectively. The elements highlighted in red in the EDS spectra correspond to concentrations close to the instrumental detection limits and should therefore be considered indicative rather than quantitatively representative. The elemental composition identified by EDS is generally consistent with literature reports for RDF and pet coke fuels. RDF commonly exhibits substantial heterogeneity due to its mixed waste origin, with major contributions from carbonaceous organic fractions together with varying amounts of calcium-, silicon-, aluminum-, and chlorine-containing inorganic phases [28]. Similarly, petroleum coke is typically characterized by a predominantly carbonaceous composition with relatively low inorganic contamination and limited mineral inclusions [26].

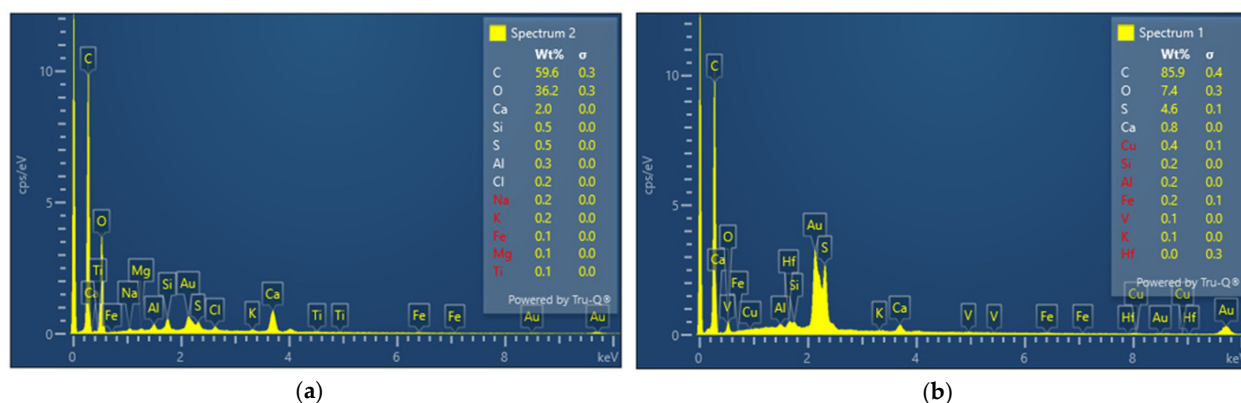


Figure 8. Representative results from EDS results at random points of the (a) RDF sample and (b) pet coke sample. The elements highlighted in red correspond to concentrations close to the instrumental detection limits and should therefore be considered indicative rather than quantitatively representative.

Particular attention was given to the chlorine content detected in the RDF sample, since chlorine is considered one of the most critical elements influencing the environmental performance and industrial applicability of waste-derived fuels [28]. EDS analysis indicated a chlorine concentration of approximately 0.2% in the RDF sample. Conversion to dry basis using the moisture content determined through TGA analysis (Section 3.5) [29] resulted in a similar chlorine concentration, due to low residual moisture content of the preconditioned sample. The presence of chlorine is associated with the potential formation of harmful chlorinated compounds, including polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), particularly under unfavorable combustion conditions. However, the measured chlorine concentration falls within the range considered acceptable for high-quality Solid Recovered Fuels (SRFs), according to the current European classification schemes. In particular, SRFs with chlorine contents ≤ 0.2 wt.% on a dry basis are classified as Class 1 fuels according to ISO 21640:2021 and are generally considered suitable for use in cement kilns [9].

Furthermore, under the high-temperature and strongly alkaline conditions prevailing in cement kilns, the risk of dioxin formation is substantially reduced, contributing to compliance with stringent EU emission regulations [30].

Overall, the SEM/EDS analyses support the compositional, thermogravimetric, and calorimetric characterization results, confirming the heterogeneous and mineral-containing nature of RDF relative to the more homogeneous carbonaceous structure of pet coke. The combined SEM/EDS analyses provide valuable insight into the distribution of combustible and inorganic phases, which influence ash formation, deposition phenomena, clinker quality, and the environmental performance of RDF during industrial co-processing.

3.4. X-Ray Diffraction Crystallography

The X-ray Diffraction (XRD) patterns of the RDF and pet coke samples are presented in Figures 9 and 10. The analyses revealed substantial differences in the phase composition and structural organization of the two fuels, reflecting their distinct origins of physicochemical characteristics. The RDF sample exhibited a highly heterogeneous diffractogram containing multiple crystalline phases superimposed on a broader amorphous background. Distinct diffraction peaks corresponding to polyethylene, calcite (CaCO_3), calcium oxide (CaO) were identified, in agreement with phases commonly reported in RDF and solid recovered fuel (SRF) materials [31]. Additional reflections were tentatively assigned to organic additives and polymer-related compounds, including 3-phenylacetic acid and diphenyl phthalate. The coexistence of polymeric and mineral phases confirms the complex composite nature

of RDF, which originates from mixed municipal and industrial waste streams containing plastics, paper, textiles, mineral fines, and inorganic contaminants.

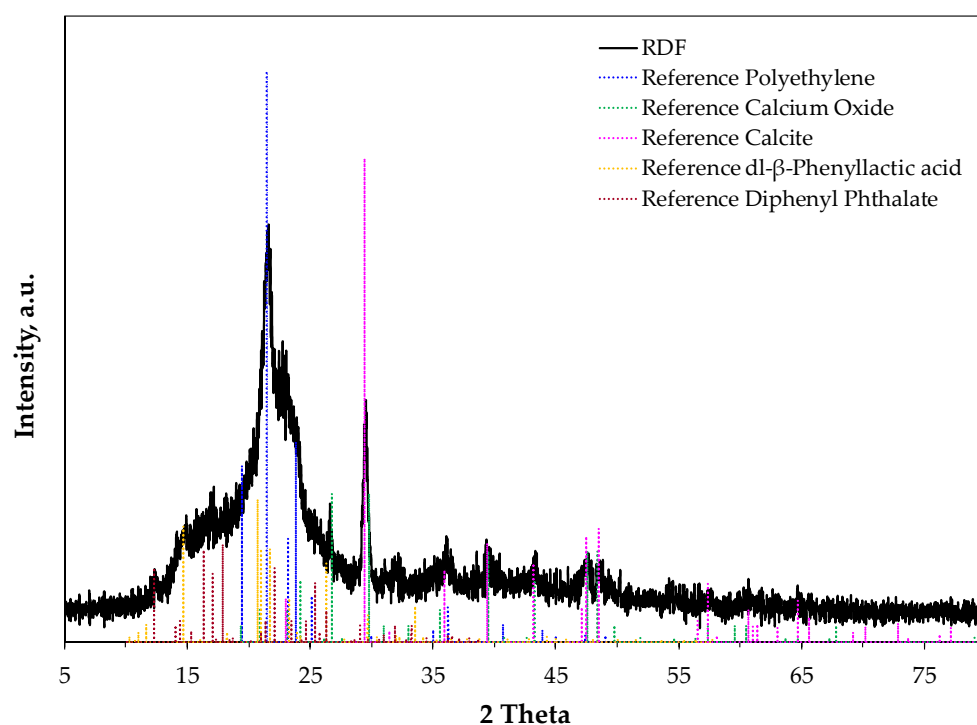


Figure 9. X-ray diffraction results for the RDF sample (a.u. denotes “arbitrary units”).

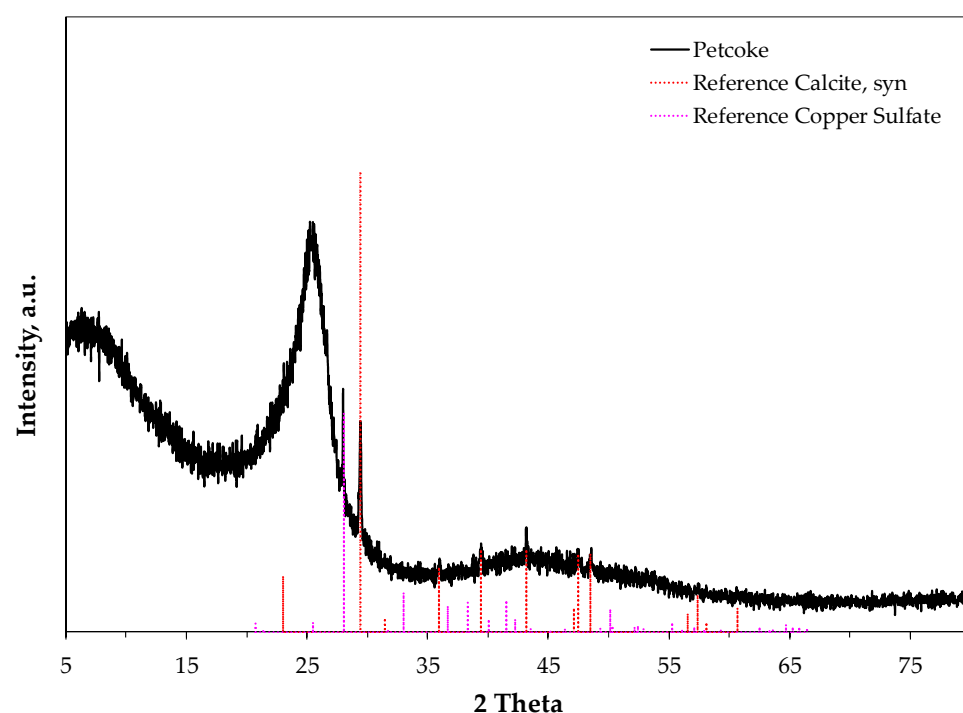


Figure 10. X-ray diffraction results for the pet coke sample (a.u. denotes “arbitrary units”).

The significant contribution of polymeric phases identified by XRD is consistent with the elevated plastic fraction determined during manual sorting and supports the relatively high calorific value measured for the RDF sample. Previous studies have reported that RDF samples containing higher plastic fractions tend to exhibit lower overall crystallinity and enhanced thermal reactivity, which may promote heat transfer and accelerate devolatiliza-

tion during combustion processes [32]. Furthermore, the presence of calcium-containing phases is consistent with the elevated calcium signal observed during EDS analysis and may be associated with mineral impurities, ash-forming constituents, or waste fractions containing construction-derived or carbonate-rich materials.

In contrast, the pet coke sample exhibited a substantially simpler diffraction pattern dominated by a broad amorphous carbonaceous background, as evidenced by the broad hump centered around $26^\circ 2\theta$, characteristic of poorly ordered carbon structures commonly observed in petroleum coke materials [33]. This broad reflection indicates the predominance of disordered aromatic carbon layers and confirms the highly carbonaceous nature of the fuel. In addition to the dominant amorphous carbon background, minor crystalline phases such as calcite and trace quantities of copper sulfate were also identified in the pet coke sample. These phases are likely associated with residual inorganic impurities from the refining and coking processes and are consistent with the low concentrations of inorganic elements detected during SEM/EDS and ICP analyses.

Overall, the XRD results further highlight the markedly heterogeneous composition of RDF relative to pet coke. The RDF sample contains a complex mixture of crystalline polymeric and mineral phases, whereas pet coke exhibits a predominantly amorphous carbon structure with limited inorganic inclusions. These structural differences are consistent with the combustion behavior observed during TGA/DSC analysis, where RDF displayed a broader multi-stage thermal decomposition profile, while pet coke exhibited a more concentrated and homogeneous combustion behavior. Identification of the crystalline phases contributes to understanding the mineral transformations occurring during thermal conversion and provides valuable information regarding ash behavior, clinker compatibility, and the operational performance of cement kilns.

3.5. Combustion Properties

The oxidative thermal behavior of the RDF and pet coke samples was investigated using TGA/DSC, enabling a detailed assessment of moisture release, volatile evolution, and oxidation of the solid residue. Both samples (RDF and pet coke) were heated from ambient temperature to 1300°C at a constant rate of $5^\circ\text{C}/\text{min}$ under continuous air flow. The corresponding mass loss curve for the RDF sample is presented in Figure 11. The RDF sample exhibited a multi-stage mass loss profile, with an initial low-temperature mass loss, followed by two major mass decrease steps in the ranges of $200\text{--}356^\circ\text{C}$ and $356\text{--}638^\circ\text{C}$. An initial mass loss of approximately 1.6% was observed below 100°C and is attributed to moisture. This value is within the lower range of the typical moisture content reported in the literature for RDF samples, which commonly ranges between 1.6 and 24% depending on the waste origin, pre-treatment conditions, and storage practices [9,23,24]. Additionally, interesting results are obtained when the thermal conversion and oxidation characteristics of RDF samples are studied in contrast with its individual compounds (i.e., textile, mixed paper, and mixed plastic) and reveal comparable results [34]. However, the measured value in the present study should not be considered representative of the intrinsic moisture content of the as-received RDF, since the sample had undergone preliminary free drying under ambient atmospheric conditions for approximately five days prior to analysis. This preconditioning step likely resulted in substantial removal of free and weakly bound moisture before the TGA/DSC measurements.

The subsequent mass loss stage between 200 and 356°C is primarily associated with devolatilization and thermal decomposition of the organic fraction, including plastics, paper, textiles and biomass-derived materials. In the higher temperature range ($356\text{--}638^\circ\text{C}$), oxidation of the remaining char and heavier combustible components become the dominant mechanisms. The total weight loss reached 88.4%, corresponding to a residual ash fraction

of 11.6%, consistent with the significant inorganic soil-like mineral content identified during the compositional analysis. It should be noted, however, that the inorganic fraction estimated through manual sorting (>30 wt.%) was higher than the residual ash measured by TGA, likely due to differences in methodology and the partial thermal decomposition of mineral-containing phases during heating. The measured ash content lies within the range of commonly reported values for RDF derived from industrial and mixed waste streams. Literature values indicate that RDF produced from industrial wastes generally exhibits ash content in the range of 10–15%, whereas RDF originating predominantly from municipal or household wastes may present higher ash levels, typically between 15 and 20% [35]. Kara [36] reported an ash content of 7.7% for RDF derived from municipal solid waste (MSW), while Haydary [18] reported 15.6% on a dry basis. Similarly, Sanongraj et al. [37] measured ash contents ranging between 5.97 and 10.02% for RDF samples derived from open-dump solid waste. Standard RDF quality specifications commonly recommend ash content in the range of 8–12% for improved thermal conversion performance and fuel quality [38]. Therefore, the ash content measured in the present study can be considered representative of medium-quality RDF intended for industrial co-firing applications.

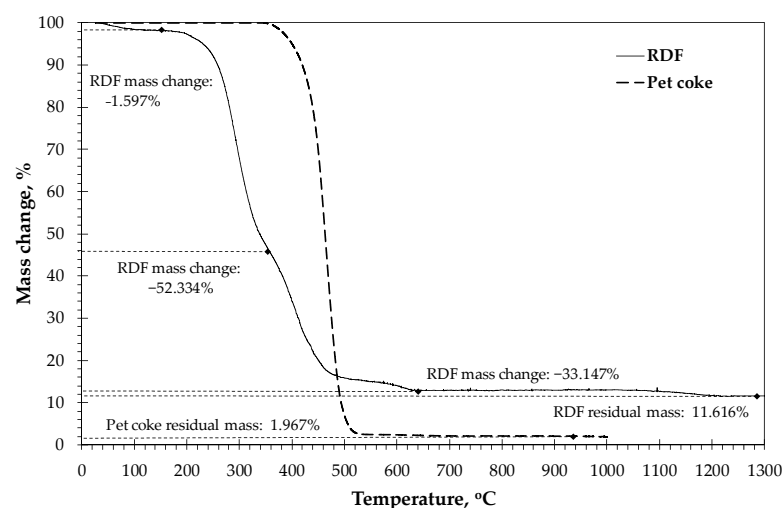


Figure 11. Mass change curves derived from thermogravimetric analysis of RDF and pet coke at a heating rate of 5 °C/min under air atmosphere.

In contrast, pet coke exhibited a substantially different thermal behavior, characterized by a single, sharp oxidation step between 348 °C and 548 °C. During this interval, 98.03% of the sample mass was consumed, reflecting the high fixed carbon content and relatively low volatile fraction of the material, reported also elsewhere [22,26]. Only 1.97% residual ash remained after heating to 1000 °C under identical conditions, confirming the substantially lower inorganic content and higher fuel purity of pet coke compared to RDF. The narrower oxidation temperature window observed for pet coke indicates a more homogeneous carbonaceous structure and a more concentrated oxidation process relative to the broader and more complex mass loss profile of RDF.

Overall, the TGA results demonstrate the markedly heterogeneous oxidative thermal behavior of RDF relative to pet coke. The broader decomposition profile of RDF reflects the co-existence of multiple combustible fractions with different thermal degradation pathways, while pet coke behaves as a more homogeneous carbonaceous fuel with concentrated combustion characteristics. Despite its lower thermal uniformity and higher ash content, RDF remains a promising supplementary fuel due to its contribution to waste valorization and partial substitution of fossil-derived fuels in energy-intensive industrial processes.

The DSC profiles of the RDF and pet coke samples are presented in Figure 12. As expected, pet coke revealed a significantly higher total exothermic enthalpy (16.73 MJ/kg) compared to RDF (6.78 MJ/kg), thereby confirming its superior energy density and more efficient thermal conversion behavior [24]. The lower heat release observed for RDF is consistent with its heterogeneous composition and the presence of non-combustible inorganic material identified during the compositional analysis. The RDF sample exhibited a broader and more complex thermal profile compared to pet coke, particularly within the temperature range of 200–400 °C. Under oxidative conditions, the heat flow variation in this region is attributed to the simultaneous occurrence of two competitive phenomena: (i) devolatilization and thermal decomposition of the organic fraction, and (ii) oxidation of released volatile compounds. During devolatilization, gaseous species are released through predominately endothermic reactions associated with bond cleavage and volatilization phenomena, as similarly reported for waste-derived fuels during pyrolysis under inert atmospheres [20,26]. However, under air atmosphere applied in the present work, these volatile compounds are simultaneously oxidized, generating significant heat through exothermic reactions. As a result, the endothermic and exothermic peaks overlap in the DSC signal and cannot be distinctly separated. The predominance of oxidation reactions over purely thermal decomposition leads to an overall exothermic profile, where the endothermic contribution of devolatilization is masked by the stronger exothermic heat release associated with volatile combustion [39,40]. This overlap phenomenon is particularly pronounced for RDF due to the co-existence of multiple combustible fractions with different thermal degradation pathways and oxidation kinetics. In contrast, pet coke exhibited a narrower and more concentrated exothermic peak, reflecting its homogeneous carbonaceous composition and the predominance of fixed carbon combustion. The simpler DSC profile of pet coke is consistent with the single-stage mass loss behavior observed in the TGA analysis.

Although RDF exhibited lower net exothermic enthalpy and a more complex heat release profile than pet coke, its application as a supplementary fuel remains attractive due to its contribution to waste valorization and its potential to partially substitute fossil-derived fuels in co-firing strategies for energy-intensive industries. The combustion-related properties of RDF and pet coke derived from the TGA/DSC analyses are summarized in Table 6.

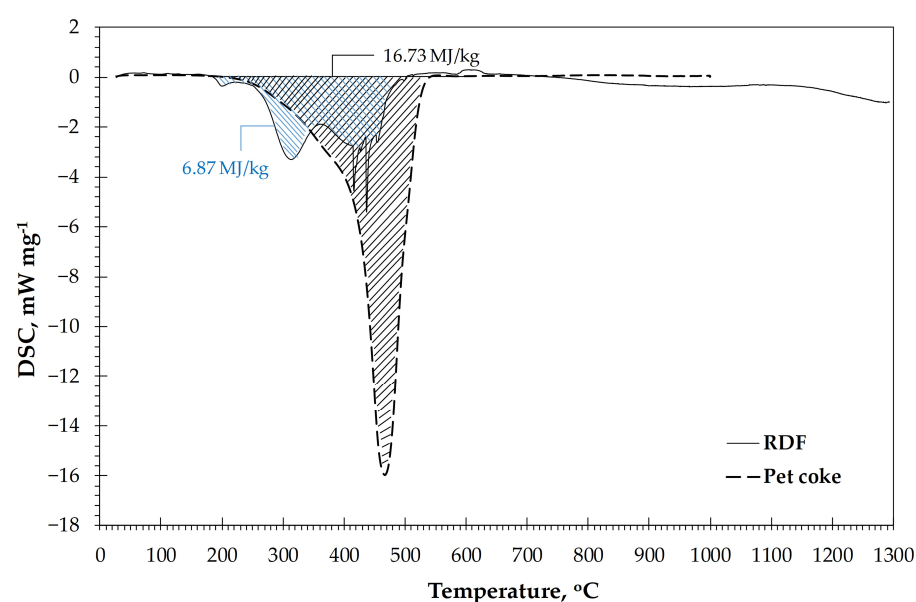


Figure 12. Heat flow derived from the thermogravimetric analysis of both RDF and pet coke samples at a heating rate of 5 °C/min under air atmosphere.

Table 6. Combustion properties of RDF and pet coke samples based on thermogravimetric analysis.

Property	RDF	Pet Coke
Enthalpy (MJ/kg)	6.78	16.73
Main oxidation range (°C)	200–638	348–548
Total mass loss (%)	88.4	98.03
Ash content (%)	11.6	1.97
Combustion profile	Multi-stage	Single sharp stage
Volatile content	High	Low
Fixed carbon reactivity	Moderate	High

The oxidation profiles obtained by TGA/DSC provide valuable information on the thermal reactivity of RDF, supporting the optimization of burner operating conditions and the development of predictive combustion models for industrial applications.

3.6. Heating Value Determination

For the RDF sample, three replicate measurements were conducted, yielding an average HHV of 19.2 ± 0.3 MJ/kg, with individual values ranging from 18.8 to 19.4 MJ/kg (Table 7). This finding aligns with the heterogeneous composition of RDF. In contrast, the pet coke sample exhibited a substantially higher average HHV of 34.57 ± 0.11 MJ/kg, calculated from two independent measurements ranging between 34.47 and 34.68 MJ/kg (Table 7).

Table 7. High Heating Value (HHV) of RDF and pet coke samples based on calorimetry.

High Heating Value (HHV)	RDF	Pet Coke
MJ/kg	19.2 ± 0.3	34.57 ± 0.11

The measured HHV values are generally consistent with literature data reported for both RDF and pet coke fuels. RDF heating values commonly range between approximately 15 and 25 MJ/kg depending on waste composition, moisture content, plastic type and fraction, and pre-treatment conditions [41–43], whereas pet coke typically exhibits HHV values in the range of 30–36 MJ/kg [25,38,43]. The RDF sample investigated in the present study therefore falls within the medium-to-high calorific value range commonly reported for RDF intended for industrial energy recovery applications, particularly in cement kilns and co-combustion systems.

A considerable discrepancy was observed between the energy outputs estimated from DSC analysis and the HHV values determined by bomb calorimetry, with the DSC ones being lower for both cases. This difference is expected and originates from the fundamentally different operating principles and combustion conditions of the two analytical techniques. In TGA/DSC experiments, combustion occurs in an open dynamic system under continuous heating and air flow. Under these conditions, portions of the volatile compounds released during thermal decomposition may escape before complete oxidation occurs, thereby not contributing fully to the measured heat release. Furthermore, devolatilization and oxidation processes occur simultaneously and overlap thermally. Devolatilization is predominantly endothermic, requiring energy for bond cleavage and volatile release, whereas oxidation reactions are exothermic. Consequently, part of the generated heat is internally consumed by thermal decomposition processes, thereby reducing the net exothermic enthalpy measured by DSC. These effects are particularly pronounced for het-

erogeneous fuels such as RDF, where multiple combustible fractions decompose through different reaction pathways and kinetics.

In contrast, bomb calorimetry provides a direct and standardized determination of the total recoverable energy content of a fuel under conditions designed to ensure complete combustion. In the isoperibol bomb calorimeter, combustion occurs in a sealed oxygen-rich environment, while the released heat is quantitatively transferred to a surrounding water bath maintained under controlled thermal conditions [44]. The calorimetric system enables accurate determination of heat release through analysis of the temperature evolution during the initial, combustion, and cooling phases of the experiment. Due to the fact that combustion completeness and heat recovery are maximized, bomb calorimetry is widely regarded as the reference method for calorific value determination.

Similar discrepancies between DSC-derived combustion enthalpies and bomb calorimetric HHV values have been reported elsewhere in the literature for waste-derived fuels and heterogeneous combustible materials. Tsang and Walker [40] noted that DSC-derived combustion energies typically represent only a fraction of the actual calorific value determined through bomb calorimetry. Therefore, while DSC analysis provides valuable information regarding thermal decomposition mechanisms, oxidation stages and reaction kinetics, the HHV values obtained through bomb calorimetry should be considered the most reliable representation of the practical energy content potential of the investigated fuels.

The measured HHV represents one of the most important parameters for evaluating RDF substitution potential, determining thermal input requirements, and assessing fuel replacement ratios in cement kiln operation.

4. Conclusions

The comprehensive characterization of a typical RDF sample presented in this study demonstrates its potential as a viable supplementary fuel for energy-intensive industries, particularly cement production. The composition of the investigated RDF is consistent with literature reports for waste-derived fuels, where plastics, paper, textiles, and inorganic fractions constitute the dominant components. However, the relatively elevated mineral fraction identified in the present work suggests that storage and handling practices may significantly influence RDF quality, ash content, and combustion behavior.

The particle size distribution analysis revealed a predominance of mid-sized fractions (1–5 cm), accounting for more than half of the total sample mass. This size range is generally favorable for industrial co-firing applications and supports stable fuel feeding into combustion systems. Nevertheless, the simultaneous presence of fine (<1 cm) and coarse (>10 cm) fractions indicates the need for improved homogenization and particle size control in order to ensure consistent combustion performance and operational stability.

Morphological, elemental, and crystallographic analyses confirmed the heterogeneous polymeric-mineral nature of RDF. SEM/EDS and XRD analyses identified the co-existence of polymeric phases, fibrous materials, mineral inclusions, and calcium-containing compounds, while elemental characterization confirmed the presence of a substantial combustible fraction associated with plastics and biomass-derived materials. In contrast, pet coke exhibited a predominantly carbonaceous and structurally homogeneous composition with limited inorganic inclusions.

TGA and calorimetric analyses further highlighted the distinct combustion behaviors of RDF and pet coke. RDF exhibited a broad multi-stage thermal degradation profile associated with devolatilization and oxidation of heterogeneous combustible fractions, whereas pet coke displayed a more concentrated and homogeneous combustion profile characteristic of carbon-rich fossil fuels. The RDF sample presented an ash content of approximately 11.6 wt.% and a Higher Heating Value (HHV) of 19.2 ± 0.3 MJ/kg, which

falls within the range commonly reported for medium-quality RDF fuels and confirms its suitability for industrial energy recovery applications. In comparison, pet coke exhibited significantly higher calorific value and combustion completeness due to its elevated fixed carbon content and notably lower ash fraction.

Although RDF demonstrated lower energy density and more complex combustion behavior than pet coke, its application in co-firing systems offers important advantages in terms of waste valorization and partial substitution of fossil-derived fuels. Furthermore, the relatively low chlorine concentration measured in the RDF sample suggests acceptable compatibility with cement kiln applications under current European standards for solid recovered fuels.

The combined analytical approach applied in the present work provides valuable physicochemical input data for thermodynamic and combustion modeling of industrial systems utilizing alternative fuels. Accurate determination of fuel properties, including ash content, elemental composition, particle size distribution, and thermal degradation behavior, provides essential input for reliable simulation of heat transfer, combustion efficiency, oxidation behavior, ash formation, and pollutant emission prediction and specific heat capacity within cement kiln and fluidized bed systems. Although crystallographic and microscopic characteristics are not direct CFD input parameters, they provide valuable complementary information on particle morphology, mineralogical composition, and the distribution of inorganic phases, supporting the interpretation of ash transformation, deposition phenomena, and heterogeneous combustion behavior within the modelling framework. In this context, the present characterization results provide a comprehensive dataset for evaluating RDF performance in industrial co-firing applications and may support future simulation and optimization studies related to RDF utilization in industrial thermal processes, including those reported by Kostarellou et al. [45]. Furthermore, the experimental dataset generated in this work may serve as a valuable basis for future techno-economic assessment (TEA) and life-cycle assessment (LCA) studies aimed at evaluating the economic feasibility and environmental performance of RDF utilization in cement manufacturing under specific industrial operating conditions [46–48]. The integration of comprehensive physicochemical characterization with combustion modelling contributes to the development of digital tools for optimizing alternative fuel utilization, improving process efficiency, and supporting the decarbonization of energy-intensive industries.

Overall, the results support the feasibility of integrating RDF into the fuel mix of energy-intensive sectors such as cement, lime, and power production. However, challenges associated with material heterogeneity, ash-forming constituents, and combustion control remain important considerations and should be addressed through optimized pre-treatment, quality assurance procedures, and advanced process modeling approaches.

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research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AES	Atomic Emission Spectroscopy
DLS	Dynamic Light Scattering
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive X-ray Spectroscopy
GHG	Greenhouse gas
HHV	High Heating Value
ICP	Inductively Coupled Plasma
MSW	Municipal Solid Waste
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzodioxin
PSD	Particle Size Distribution
PVC	Polyvinyl chloride
RDF	Refuse-Derived Fuel
SEM	Scanning Electron Microscopy
SRFs	Solid Recovered Fuels
TGA	Thermogravimetric Analysis
VOCs	Volatile Organic Compounds
XRD	X-Ray Diffraction

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