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Research Paper

Two-stage thermal pyrolysis of plastic solid waste: Set-up and operative conditions investigation for gaseous fuel production

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ABSTRACT

In response to the escalating global challenge of mounting plastic waste and the imperative to adopt more sustainable practices for resource utilization, our study focuses on the utilization of plastic solid waste (PSW) through a two-stage thermal pyrolysis process. This aims to demonstrate its potential as a high-performance alternative to existing two-stage catalytic pyrolysis methods. The experimentation involved processing real scrap PSW material in a lab-scale batch set-up, emphasizing optimizing residence time in the cracking reactor to maximize gas yield and its lower heating value (LHV). The study underscores the advantages of the employed two-stage thermal pyrolysis apparatus through a comparative analysis with established set-up dedicated to maximizing gas yield. Once the operative conditions were explored, resulting pyrolysis products underwent detailed characterization to assess their suitability as a sustainable fuel source. The study also presents a practical application of the produced gaseous fuel, envisioning its combustion in an internal combustion engine (ICE), known for its flexibility regarding fuel properties. This application is demonstrated through a simulation conducted in Unisim Design©. The successful processing of real PSW material in the two-stage lab-scale experimental set-up showcased optimal gas yield achievements (>65 % w/w) with an LHV (~41 MJ/kg), comparable to that of natural gas. This emphasizes the potential of these sustainable alternatives to replace fossil fuels, especially in the context of ICE applications. The integration of the pyrolysis plant with an ICE demonstrated promising prospects for generating electricity in the transportation sector and facilitating thermal power for heat integration in pyrolysis reactors.

1 Introduction

Various alternatives have been proposed in the literature to reduce the accumulation of plastic waste in landfills to less than 10 % of plastic disposal by 2035 (European Directive, 2018). These alternatives range from direct recycling methods to more advanced energy utilization approaches. One notable strategy is tertiary valorization, focusing on generating fuels and chemicals from plastic waste (Lee and Liew, 2021). This objective can be achieved through two primary approaches: advancing the pyrolysis process and incorporating plastic waste into refinery units (Palos et al., 2021; Rodríguez et al., 2020). The outcome of pyrolysis is significantly influenced by several parameters, such as feedstock variability, temperature, residence time, thermal break-down mechanisms involved (i.e., random scission or chain-end scission), and higher heating rate (Abbas-Abadi et al., 2023; Chaudhary et al., 2023; Mortezaeikia et al., 2021; Zhou et al., 2021). While plastic waste pyrolysis can be considered a viable alternative to produce high yields of liquid fuels, this option requires extensive post-processing to meet commercial fuel standards, particularly in small-scale plants (Faisal et al., 2023; Miandad et al., 2017; Peng et al., 2022). As outlined by Peng et al. (2022), challenges associated with the industrialization of bio-crude involve issues such as the presence of contaminants and the potential interference of certain plastic additives in deactivating downstream catalysts. Essential processes for enhancing liquid fuel quality include filtration, hydrogenation, distillation, liquid–liquid extraction, or blending with conventional fuels. Moreover, Miandad et al. (2017) and Faisal et al. (2023) found out that the pyrolytic oil yield was strongly affected by the kind of feedstock processed. Specifically, when processing polyethylene terephthalate (PET), an increase in char and gas production was registered. On the other hand, blending various plastics

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such as polyethylene (PE), polystyrene (PS), polypropylene (PP), and PET and subjecting them to pyrolysis in a circulating fluidized bed reactor at 400 °C resulted in an increase in gas yield only. Nevertheless, to make the oils produced in both cases suitable for use as automobile engine fuel, further refinement and blending with conventional diesel were deemed necessary. This requirement primarily stems from the elevated presence of aromatic compounds, low flash point, high wax content, sulfur content, and bad odors in the initial pyrolytic oils. It is worth noting that the post-treatments needed to upgrade these oils significantly influences the techno-economic analysis. Notably, Faisal et al. (2023) highlighted that for a small plant capacity (approximately 15,000 tons/year), the breakeven point was achieved after 25 years.

Hence, incorporating waste polyolefins or their derivatives into existing refineries emerges as a promising alternative. The substantial capacity of refinery units ensures that the plastic waste input is minimal, thereby limiting its impact on product distribution (Fulgencio-Medrano et al., 2022; Kasar et al., 2020; Kusenberg et al., 2022). In their analysis, Palos et al. (2019) explored various socio-economic factors and identified refinery units, such as fluidized catalytic cracking reactors or hydro processing units, as viable platforms for valorizing pyrolytic plastic oils. Depending on the composition of these oils, they could be co-fed with vacuum gas oil or light cycle oil. This study revealed that employing a dual approach involving slow pyrolysis of recycled high-density polyethylene (HDPE) plastic, followed by a subsequent catalytic cracking or hydro processing stage in the refinery, yielded promising and economically viable results for large-scale plastic recycling. Consequently, this result suggests the promotion of a large-scale 'waste refinery' concept by integrating primary waste valorization units within refineries. Through this strategy, the industrial implementation of the pyrolysis units would be aided. Nonetheless, the primary challenges lie in the scarcity of experience with full-scale units and the need to guarantee a consistently clean waste polymer to prevent catalyst poisoning. Additionally, plastic wastes are subjected to daily fluctuations in quality, quantity, and physical properties, further complicating the process (Biessey et al., 2023; Lopez et al., 2017; Vollmer et al., 2021).

Non-condensable pyrolytic gases have a high heating value (HHV), comparable to natural gas (~44 MJ/kg) and, therefore, have the potential to be used for heat generation or fulfill the energy needs of an endothermic process (Dwivedi et al., 2019; Kumar Singh et al., 2022). Non-condensable gas can also be directed to the steam reforming process for ethylene/propylene production or as a precursor for carbon nanotubes in a chemical vapor deposition process (Kumar Singh et al., 2022). However, generating excessive gas amount is undesirable due to the associated high transportation costs, unless this product is used on site (Peng et al., 2022). Another drawback is the diverse range of products resulting from the thermal cracking of macromolecules, making their industrial use complex (Berrueco et al., 2005). The combination of pyrolysis plant with catalytic steam reforming is a thermochemical technology that allows to enhance, in a more selective way, the conversion of plastics waste into a H_2-rich gas (Aminu et al., 2023, 2022, 2020; Li et al., 2023).

While catalytic pyrolysis is favored over thermal pyrolysis for promoting gaseous yield and reducing the liquid fraction, it comes with challenges. The mismatch between ideal plastic mixtures in research and real-life plastic wastes hinders commercialization; for example, an economic study regarding H_2 production reveals its complexity (Maroušek et al., 2022). The main hurdles for widespread catalytic pyrolysis implementation include contaminants and non-polymeric species in waste streams (that require pre-sorting unit before process), variability in plastic composition (especially in mixtures), and uncertainties about additives deactivating catalysts or corroding equipment (Abbas-Abadi et al., 2023; Li et al., 2020; Miandad et al., 2019). Catalyst cost becomes crucial in comparing catalytic and thermal pyrolysis economics, emphasizing the need for research on catalyst deactivation, regeneration, and reuse for industrial scalability (Moses et al., 2023; Tan et al., 2023). While catalyst deactivation is often reversible, removing coke on the outer surface is easier than from internal areas, relying on the oxygen's ability to diffuse into the catalyst pores (Daligaux et al., 2021). Thus, single- or double-stage catalytic pyrolysis is a viable technological alternative to maximize gas yield, but it is not economically advantageous since reactor system and cracking catalyst are not always compatible with the changeable requirements of different feedstock logistics, process parameters and target products. Moreover, using this configuration the pyrolysis process would result not cost competitive with fossil fuel production (Vochozka et al., 2020).

Given the entire literature background, our work aims at demonstrating that two-stage thermal pyrolysis could be a high-performance alternative to the use of two-stage catalytic pyrolysis. The main innovation of this proposed configuration is the possibility to obtain experimental data from an easily scalable and economically advantageous configuration set-up. Indeed, the pyrolysis process has been pointed out at lab-scale, reproducing the small-scale configuration of an Auger reactor (first thermal stage), that has notable advantages at industrial scale, such as simple design, homogenous heat profile and easy solid transportation, connected to a second unit (second thermal stage) in which only thermal tars and gaseous products degradation occurs. Moreover, the second stage does not involve the catalysts usage, that is generally employed in the traditional process set-up representing the main challenge in pyrolysis scalability.

Real plastic solid waste (PSW) material was processed using a lab-scale batch set-up, and the effect of residence time in the cracking reactor was studied to maximize the gas yield and its lower heating value (LHV). Moreover, the advantages of the apparatus used in this study, i.e., two-stage thermal pyrolysis, were highlighted through a comparison with the already existing set-up aimed at maximizing gas yield. Once operative conditions were investigated, all pyrolysis products underwent specific characterization to evaluate their features for targeted use as sustainable fuel. A practical application of the gaseous fuel produced was provided: a scenario involving the combustion of the pyrolytic gases into an internal combustion engine (ICE), that is considered as the most suitable power source due to its high flexibility regarding fuel properties.

The experimental campaign is designed to collect a sufficient amount of data in terms of co-products yields and composition. This information serves as a foundational dataset for future work, wherein an integrated process will be developed at an industrial scale to valorize each co-product. The modeled scenarios will facilitate thermal process integration, aiming to reduce carbon footprints associated with electrical production and maximize the reliability on heating capacity of fumes process streams. Then, the outcomes of modeled scenarios will be employed for a technical economic analysis and for the evaluation of environmental impacts according to the methodology supplied by the Annex I of the Delegated Act of European Directive 2018/2001.

2. Materials and methods

2.1. Materials and chemical characterizations

The PSW material processed in these experiments is scrap derived from the densified polyolefin production process, identified by the code EWC150106 (according to European Waste Catalogue). The pristine waste material was heterogeneous (Fig. S1a of the Supplementary Information (SI)), so it underwent pretreatment before characterization and processing. In particular, it was dried using an electric oven set at 105 °C for 2 h and subsequently sieved using a mill to obtain a size distribution characterized by an average value of 8 mm (Fig. S1b of the SI). The characterization of the PSW was performed after being subjected to the quartering technique involving sample homogenization using a clean and dry plastic tray and portioning into four equivalent quarters by tracing two perpendicular axes in the pie with a knife or any other appropriate tool. Thermal characterization of the PSW was conducted through differential scanning calorimetric (DSC) measurements.

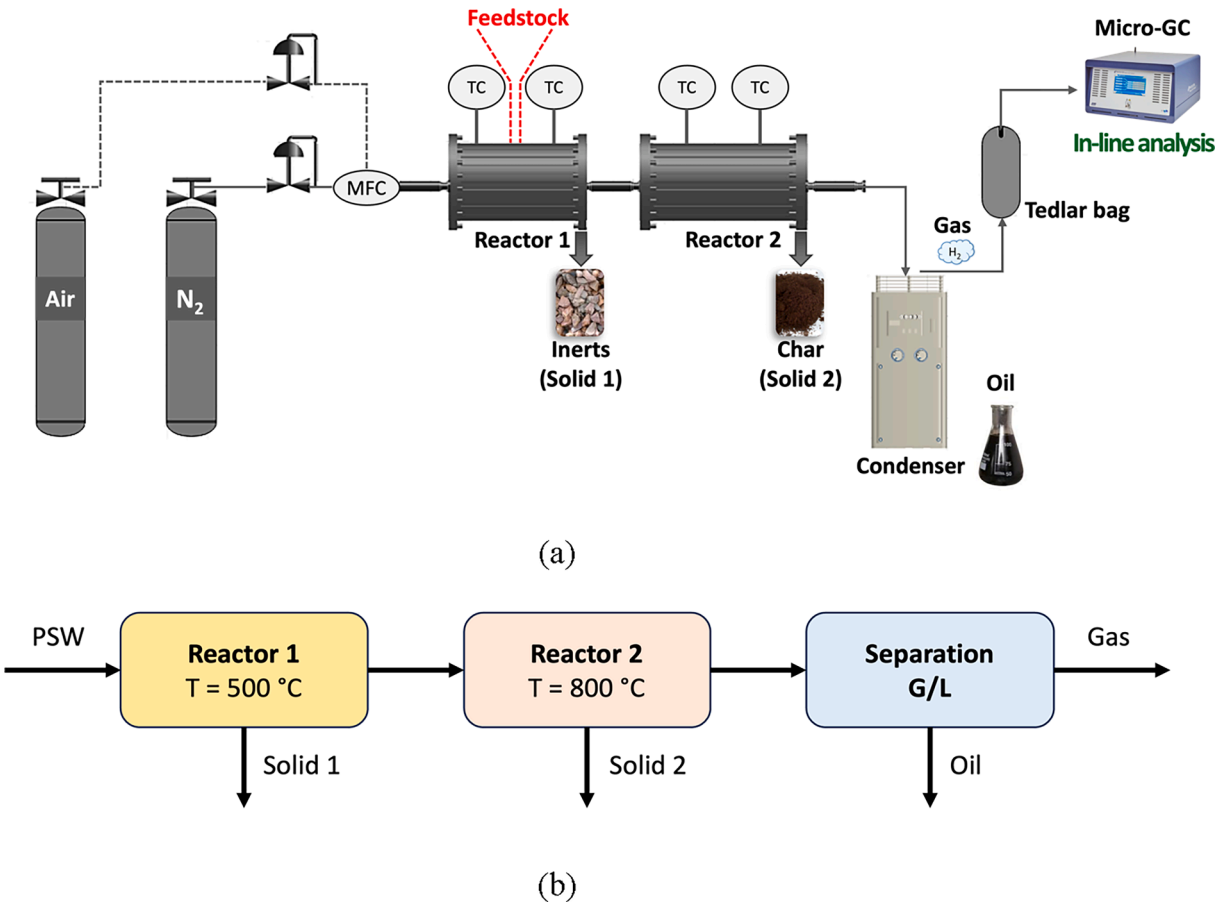

Fig. 1. Process scheme (a) and elemental block scheme (b) of the pyrolysis experimental setup with the measurement scheme performed.

The DSC measurements were carried out using a Mettler Toledo Star DSC 1/700 and nitrogen (N_2) was fed as the inert gas (100 mL/min). The final thermogram was obtained by performing three steps: heating from −20 °C up to 300 °C (heating rate of 10 °C/min), cooling from 300 °C down to −20 °C (cooling rate of −20 °C/min), and heating from −20 °C up to 300 °C (heating rate of 10 °C/min). Elemental analysis was performed using the LECO TruSpec CHN analyzer and the Elementar Vario Macro CHNS analyzer. Eqs. (1) and (2) (Green and Southard, 2019) were employed to estimate the *HHV* and the *LHV*.

$$HHV = 2.326[146.58C + 568.78H + 29.4S - 6.58A(O + N)] \quad (1)$$

$$LHV = (HHV - 206H) \quad (2)$$

H, *C*, *N*, *S*, and *O* represent the mass percentages of hydrogen, carbon, nitrogen, sulfur, and oxygen, respectively. The values of *C*, *H*, and *N* were determined by the elemental analysis; the composition analysis was performed following the standard UNI EN 15002:2015 to calculate *S* content, whereas the value of *O* was obtained from difference. The term *A* was calculated as the ratio of the weighted ash to the total dried mass and was determined by heating the material sample in 3 h in an oven set at 600 °C. The PSW thermal degradation profile was obtained using the thermobalance *TAQ500* combined with the software *Universal Analysis 2000*. The analysis was carried out in an inert atmosphere (N_2) through two-steps analysis: initially heating from 30 °C up to 800 °C (heating rate of 10 °C/min), followed by keeping the temperature constant at 800 °C for 2 h. Each characterization analysis was repeated three times.

2.2. Experimental setup and methods

Once characterized, 5 g of PSW underwent processing using the lab-scale batch set-up, as reported in Fig. 1a, comprising three sections: i.e., reaction, separation, and products analysis.

The reaction section consisted of two reactors: the pyrolysis unit (*Reactor 1*) and the homogeneous cracking unit (*Reactor 2*). The reactor units were equipped with two stainless steel tubes with an internal volume of 0.212 L (*Reactor 1*) and 0.375 L (*Reactor 2*). Each tube was placed in a tubular electric furnace: Carbolite TZF 12/65/550 (with a maximum temperature of 1200 °C) heated up *Reactor 1*, and Carbolite MTF 12/38/250 (with a maximum temperature of 1200 °C) was used for *Reactor 2*. Temperature was measured by J type thermocouples and regulated using Proportional–Integral–Derivative (PID) controllers. Furthermore, *Reactor 2* contained 3.2 mm steel balls (AISI 304), providing a void fraction equal to 0.34; N_2 gas was also fed by a mass flow controller (MFC) to make the reaction environment inert. Temperatures were set at 600 °C and 800 °C for *Reactor 1* and *2*, respectively. Once the two reactors reached the operative temperatures, the PSW sample was placed in a basket, that was, then, fed into the midway of *Reactor 1*. In the first pyrolysis reactor, three co-products were generated: the gaseous product, the vapor product, and the solid product. The solid product, named *Solid 1* in Fig. 1b, was collected in the same basked used for PSW feeding of *Reactor 1*, whereas the other two co-products experienced homogeneous cracking in *Reactor 2*. In the second reactor, the vapor components underwent to chemical bonds breakage leading to two different reaction pathways, namely, the first one led to an increase in gas amount produced (*Gas)*, and the second one led to a further production of solid co-product (*Solid 2* in Fig. 1b). Therefore, by the end of the process, four phases (*Solid 1*, *Solid 2*, *Oil*, and *Gas*) were produced as shown in Fig. 1b. The separation section (*Separation G/L*) divided the *Oil* and *Gas* phases, where the condensable fraction was isolated through cooling. A mixture of ethanol and liquid CO_2 at −80 °C acted as cold utility, and the condensed fraction was weighted at the end

of each test and subjected to CHN analysis. Following this process, the gaseous phase was collected in a 5 L Tedlar Bag, and gas chromatography (Agilent 990) was employed for composition analysis. The solid fraction recovered at the bottom of *Reactor 1* (*Solid 1*) was weighted and subjected to CHN analysis. Simultaneously, the amount of *Solid 2* still present in *Reactor 2* was determined by analyzing its combustion products. At the end of each test, air was fed into *Reactor 2*, and the resulting flue gas was analyzed using the same gas chromatograph (Agilent 990). By measuring the amounts of CO_2 and CO derived from the combustion process, it was possible to evaluate the initial equivalent amount of C. Once the amount of each co-product was determined, the yields of each fraction was evaluated as the ratio between the various-component mass and the PSW total mass fed to the setup. Moreover, the calculated values for the LHVs of pyrolysis gas (LHV_{gas}) and pristine PSW sample (LHV_f), along with the *Gas* yield (Y_{gas}) were used to calculate the process energy efficiency (η) as defined in Eq. (3).

$$\eta = \frac{LHV_{gas} \bullet Y_{gas}}{LHV_f} \tag{3}$$

The objective of the experimental tests was to assess the impact of residence time on product yields by varying the N_2 mass flow rate to identify the value that maximizes the *Gas* yield. Three N_2 flow rates (900 mL/min, 300 mL/min, and 120 mL/min) were examined, corresponding to three different residence times (ca. 2 s, 4 s, and 6 s). Each residence time test was conducted thrice, and the *Gas* yields and compounds identification were determined by averaging the collected data.

At the conclusion of each test, the co-products were characterized. The micro-GC instrument analyzed the composition of collected *Gas*, and the corresponding heating values were evaluated using Eqs. (1) and (2), as previously reported. The micro-GC operates using two independent channels, Channel A and Channel B. Specifically, Channel A separates He, H_2, N_2, O_2, CH_4, and CO using Ar as eluent gas. It consists of a Molsieve 5A molecular sieve column (10 m x 0.32 mm x 30 m) and a heated backflush ejector. Channel B separates CO_2, C_2H_4, C_2H_6, C_2H_2 and C_3 using a Plot U column (8 m x 0.32 mm x 30 m) and He as the eluent gas. The *Solid 1* and *Oil* phases were characterized by elemental analysis, and the results were used to evaluate their heating values using Eqs. (1) and (2).

3. Experimental results and discussion

3.1. Characterization of the plastic solid waste (PSW)

The PSW characterization involved DSC measurements, whose results are reported in Figure S3 of the SI. It reveals that the tested material was mainly composed of PE and PET, with a low content of PP. The polymeric composition of PSW provides a qualitatively prediction about pyrolysis outcomes. The spectrum of pyrolysis products is strongly influenced by the processed polymer structure. For instance, PE, with its linear-branched structure, mainly produces n-alkanes, alkenes, and alkadienes upon thermal degradation. PET, characterized by its aromatic structure, primarily yields gaseous CO and CO_2 products. In contrast, PP, with its linear structure, produces alkenes and lower concentrations of alkanes and alkadienes during devolatilization (Williams and Slaney, 2007).

Moreover, the DSC analysis (Figure S3 of the SI) indicates the absence of PVC and PS, that would be responsible for hydrochloric and sulfuric acid production. This result is also confirmed by composition analysis results collected in Table 1.

Furthermore, the composition analysis was carried out to determine the concentration of elements present in the processed PSW. Indeed, metals and halogens are impurities found in the plastic materials in the range of 1–3000 ppm (Roosen et al., 2022), and they could contribute to corrosion, coke formation, catalysts poisoning, and products contamination (Kusenberg et al., 2022). However, Table 1 indicates that the metals content in the processed PSW was lower than 4.8 ppm. Therefore, the safety risks associated with their presence can be neglected. The results of elemental analysis were compared with the composition of LDPE, HDPE, PET, PP (ie., the main components of the treated PSW), and municipal solid waste (MSW), representing the plastic scrap most extensively tested in the literature scenario. The concentration values of *C*, *H*, *N*, *O*, and *S* characterizing PSW and the other selected materials (Aminu et al., 2023) are collected in Table S1 of the SI. The results of elemental analysis validate the findings obtained from DSC analysis. Indeed, it emerges that the elemental analysis values of the investigated PSW ranged between those characterizing PE and those characterizing PET, confirming the consistency of results obtained from DSC analysis (reported in Figure S3 of the SI). In addition, the *O* content was lower than that of PET but higher than that of MSW. Consequently, the gaseous product of PSW was expected to have higher percentages of carbon monoxide (CO) and carbon dioxide (CO_2) compared to the other scrap. Using these collected results, the LHV of PSW was calculated to be 33.84 MJ/kg. This obtained value falls between the LHVs of PET, LDPE, and HDPE, that are 21.29 MJ/kg, 38.95 MJ/kg, and 34.11 MJ/kg, respectively (Areeprasert et al., 2017). This further confirms the observations from DSC analysis.

Table 1
Composition analysis of the treated PSW.

Metallic Components	Units of Measurement	Value
Chlorine	%w/w	0.173
Sulphur	%w/w	0.01531
Aluminum	mg/kg	3100
Barium	mg/kg	<4.8
Calcium	mg/kg	<4.8
Chromium	mg/kg	<4.8
Magnesium	mg/kg	<4.8
Manganese	mg/kg	<4.8
Nickel	mg/kg	<4.8
Lead	mg/kg	<4.8
Copper	mg/kg	6.6
Tin	mg/kg	<4.8
Zinc	mg/kg	<4.8

The thermal decomposition of PSW obtained through TGA analysis in a N_2 atmosphere is shown in Fig. 2.

The obtained profile demonstrates that most of the sample mass reduction occurred between 370 °C and 495 °C (as indicated in red in Fig. 2), suggesting a potential pyrolysis temperature range. However, the temperature of the first reactor in the experimental setup was increased up to 600 °C to counteract heat loss. Moreover, the weight percentage of solid residue was determined to be 7.7 % w/w. On the contrary, when TGA analysis was performed in air, the ash (*A*) content resulted equal to 2.7 %w/w. This value is expected to be equal to the amount of *Solid 1* recovered in the *Reactor 1*.

3.2. Evaluation of the gas yield

After pre-treatment and characterization, the PSW was fed to the experimental lab-scale set-up to assess the two-stage pyrolysis process and quantify products yields at varying residence times. Three residence times in the second reactor were examined: i.e., ca. 2 s (τ_1), 4 s (τ_2), and 6 s (τ_3). Fig. 3 shows the yields of *Gas*, *Oil*, and *Solid 2,* from left to right, corresponding to the three different tested residence times. *Solid 1* is not reported since it is composed by inert material that does not enhance the total solid energy content.

Fig. 3 shows that upon increasing the residence time from $\boldsymbol{\tau_1}$ up to $\boldsymbol{\tau_2}$, the *Gas* yield increased from 61 % w/w up to 65 % w/w. According to literature investigations, the produced gaseous compounds mainly result from the homolytic dissociation and β-scission of polymer chains (Park et al., 2019). The findings from the same authors also indicated that *Gas* yield increased upon the increase of pyrolysis reactor temperature. The rise in thermal energy led to increased vibration states of polymer molecules, increasing the bond length of C–C and,

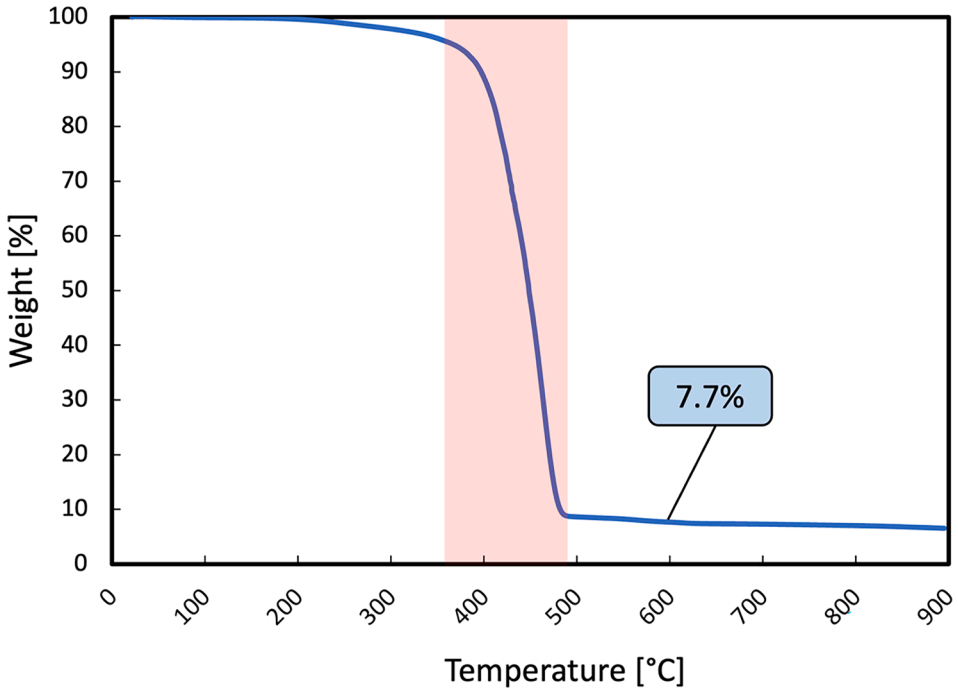

Fig. 2. TGA analysis of PSW carried out in inert atmosphere. In red the potential operability region while on the horizontal phase (on the right) is indicated the residual solid weight percentage.

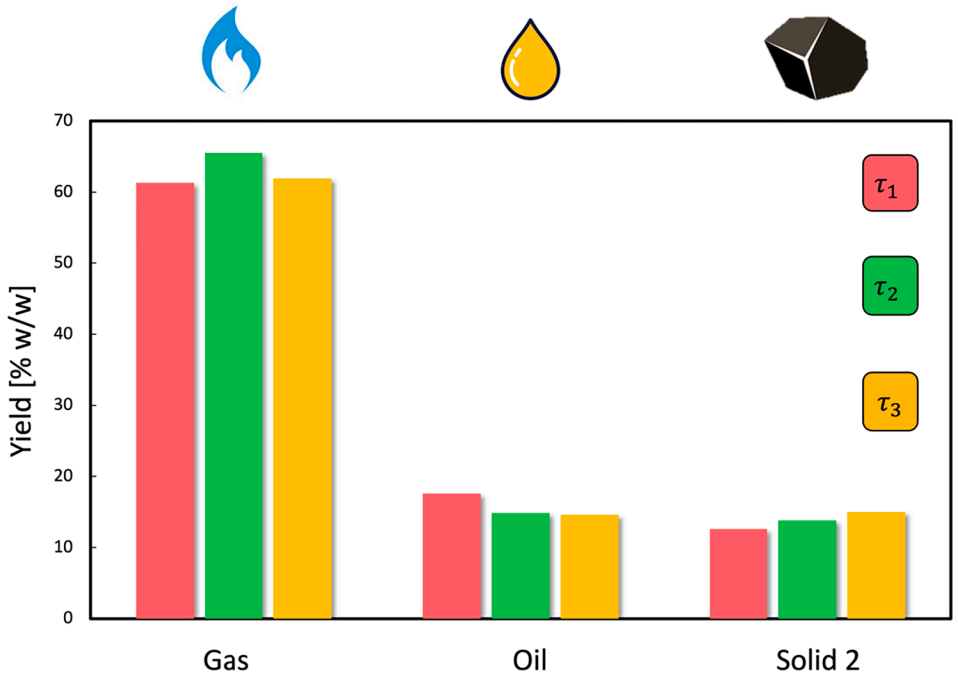

Fig. 3. Comparison between *Gas*, *Oil* and *Solid 2* yields produced at $\tau_1 \cong 2$ s, $\tau_2 \cong 4$ s and $\tau_3 \cong 6$ s. Yields for *Solid 1* are not reported since it represents the inert phase of the process, therefore always equal to ca. 8 %.

consequently, weakening its strength. Moreover, a comparison between one-stage and two-stage reactor by Park et al. (2019) revealed that carrying out pyrolysis in a single reactor resulted in rapid polymer degradation and light olefines production. This could be due to insufficient time for molecules to be excited to higher vibrational states, and the random scission of C–C over short intervals was not favored.

On the contrary, passing from τ_2 up to τ_3, both *Gas* and *Oil* yields slightly reduced, potentially due to *Oil* decomposition and cracking reactions occurring in the vapor phase. Consequently, the recovered amount of *Solid 2* increased from 14 %w/w (for τ_2) up to 15 %w/w (for τ_3).

Several other research studies have focused on maximizing pyrolysis gas production through different approaches and apparatuses. Kordoghli et al. (2017) studied waste tires pyrolysis using a novel catalytic system set at 500 °C, achieving increased gas yield from 25 %w/w up to 31 %w/w due to the presence of Al_2O_3 uniformly distributed on a single layer of oyster shells (OS) particles. However, the formation of H_2S in pyrolysis gases required further optimization of operating conditions

and catalyst bed position, affecting both gas quality and catalyst effectiveness. Honus et al. (2018) produced pyrolysis gases from individual and mixed plastics using a vertical dual-chamber reactor in a laboratory scale, at different temperatures (i.e., 500, 700, and 900 °C). The highest conversion into gaseous fuel and the highest chemical energy yield occurred during PP pyrolysis at 900 °C. Nonetheless, this temperature condition could lead to difficulties in tuning gas composition, and using a single reactor might result in rapid polymer degradation into olefines due to random scission of polymeric chains. Park et al. (2019) carried out PE pyrolysis using a two-stage apparatus consisting of auger and fluidized bed (FB) reactors. The highest gas yield (i.e., 75 wt%) was obtained at 300 °C and 736 °C in the auger and FB, respectively, using N_2 as fluidizing medium. Using this configuration, no catalyst was employed and in the FB a reduction of mass transport limitations occurred. However, issues during mixing and fluidization could potentially arise, and the produced coke should be characterized by specific weight to precipitate and avoid transportation in the gaseous phase. Another example of a two-stage approach was proposed by Zhang et al. (2017), who tested a two-stage pyrolysis catalytic steam reforming process composed of a pyrolysis reactor (500 °C) and a catalytic steam reforming reactor (800 °C). The catalyst was made of Iron (Fe) and Nickel (Ni) using the Mobil Composition of Matter Number 41 (MCM-41) as support. The authors studied the effect of Fe/Ni ratio on gas production, testing five different ratios (i.e., 00:20, 05:15, 10:10, 15:05, and 20:00) and obtaining the highest gas yield (95 % w/w) for the 10:10 ratio. Aminu et al. (2023) studied the pyrolysis/non-thermal plasma catalytic reforming of individual and mixed waste plastics. The experimental setup consisted of a pyrolysis and steam reforming sections, whose temperature were set at 500 °C and 250 °C, respectively. The experiments were carried out in the presence of plasma and catalyst made up using Ni immobilized on MCM-41. Different kinds of individual and mixed waste plastics were investigated; the mineral water bottle plastic provided the best value in terms of gas yield (62.4 % w/w), although the results were significantly affected by the variation in PET fraction. An alternative was proposed by Gao et al. (2020), suggesting the usage of sludge fly ash (SFA) as an additive in an experimental setup equipped with a fixed-bed reactor (700 °C). The MSW was processed, with the highest gas yield obtained equal to 76 % w/w, achieved using a SFA percentage equal to 5 % w/w with respect to the fed material. However, a potential limitation of this apparatus could be related to pyrolysis products contamination with the heavy metal contained in the used ash.

The referenced literature (Aminu et al., 2023; Gao et al., 2020; Honus et al., 2018; Park et al., 2019; Zhang et al., 2017) conducted studies exploring various kind of plastic waste through different experimental methods to optimize the yield of produced gases. These studies revealed notable discrepancies, including the number of process stages (single-stage pyrolysis versus two-stage pyrolysis), the utilization of catalysts or additives, and the specific temperatures and operational conditions employed. The diverse plastic materials tested yielded different outcomes based on the chosen approach. In summary, while single-stage pyrolysis may offer simplicity compared to a two-stage process, the latter allows for two independent reactors and higher process control, particularly at an industrial scale. The use of catalysts or additives might facilitate the production of high-value gaseous products selectively but can present challenges, including high catalyst costs, potential poisoning of catalysts, temperature constraints, and complex regeneration phases. Higher temperatures ensure a faster heating rate and an increase in gas yield. However, at an industrial scale, it is not always possible to work at high temperatures since they may cause technical issues related to the choice of construction materials and equipment seals.

Hence, each experimental set-up exhibited strengths and weaknesses, as summarized in Table 2.

Table 2
Studies on pyrolysis treatment of plastic waste materials, focused on those work whose aim is to enhance gas yields.

Processed material	Technology	Strength	Weakness	References
Mixture of Pure and waste Plastics	Two-stage fixed-bed reactor: pyrolysis and catalytic (Fe-Ni-MCM-41) steam reforming	The high concentration of H_2 and CO and low concentration of CO_2 in tha gas phase	The cost of catalyst usage and regeneration	(Zhang et al., 2017)
Waste tires	One-stage catalytic reactor (Al2O3 dispersed on OS)	Simple design and no segregation problem	Catalyst bed position that affects the presence of acidic gases in the gaseous stream	Kordoghli et al., 2017
European mix Waste	Dual-chamber pyrolysis reactor	Simple design reactor	Possible solid handling problems and possible quick polymer degradation into olefins	Honus et al., 2018
PE pyrolysis	Auger and FB reactors	No catalyst is used and no mass transfer limitations	Possible issues during mixing and fluidization	Park et al., 2019
MSW	Fixed-bed reactor with sludge fly ash (SFA) as additive	The cost-effective of the SFA	The use of SFA can contaminate the pyrolysis products	Gao et al., 2020
Plastic mineral water bottle waste	Two-stage Pyrolysis/ non-thermal plasma catalytic (Ni-MCM-41) reforming	The low temperature of non-thermal plasma catalytic reforming reactor (250 °C)	The cost of use and regeneration of catalyst and the effect of PET fraction on the results	Aminu et al., 2023

3.3. Characterization of pyrolytic gases and their application in ICE

The *Gas* produced was further analyzed in terms of volumetric composition and LHV; its volumetric composition is represented in Fig. 4.

To better analyze these results, the heating time required for the *Gas* to reach the operative temperature of *Reactor 2* (i.e., 800 °C) was evaluated and compared with the residence time. This duration was determined by solving the transient energy balance equation in Eq. (4).

$$mc_p\frac{dT}{dt} = hA(T(t) - 500) \tag{4}$$

Where m, c_p, $T(t)$, and A represent mass, specific heat capacity, temperature, and heat exchange surface respectively.

The coefficient h was derived using the Churchill and Bernstein equation (Green and Southard, 2019), expressed as in Eq. (5).

$$Nu = 2 + 0.6Re^{0.5}Pr^{0.33}\left[1 + \left(\frac{Re}{282}\right)^{0.625}\right]^{0.8} \tag{5}$$

The *Gas* mixture was simulated using Unisim Design© software, assuming that the components in the gaseous stream leaving *Reactor 1* consisted of methane (CH_4), ethylene (C_2H_4), octene, and *trans*-octene. Therefore, the properties of this mixture leaving the first reactor - density (ρ), viscosity (μ), specific heat capacity (c_p), and thermal conductivity (k) - resulted in values of $\rho = 535.5\frac{g}{m^3}$, $\mu = 0.00257cP$, $c_p = 117.93\frac{KJ}{KmolK}$ and $k = 0.0955\frac{W}{mK}$. As reported in Section 2, different

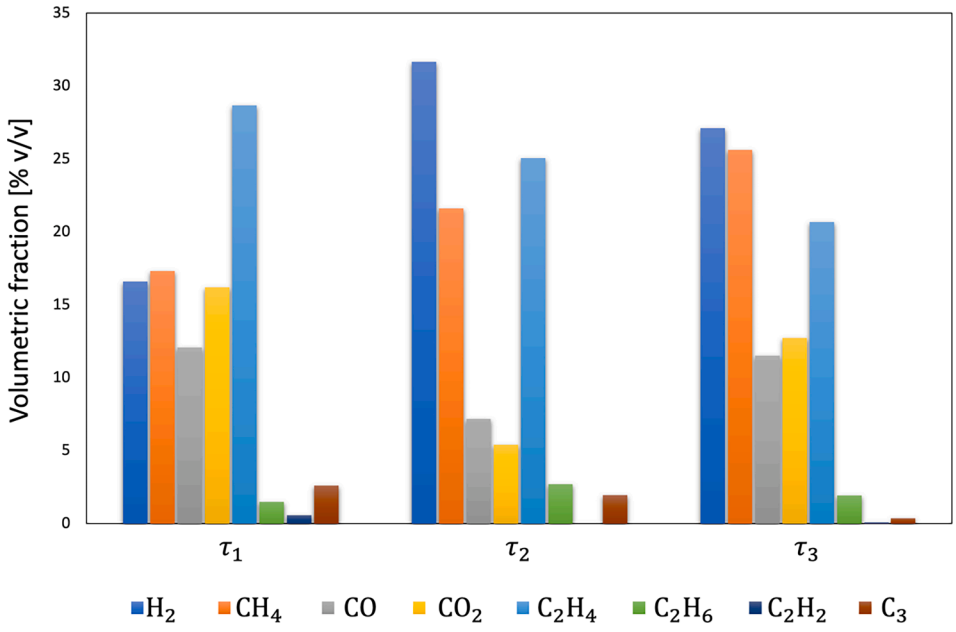

Fig. 4. Comparison between volumetric composition of pyrolysis gases (*Gas*) produced using the three different residence times.

N_2 flow rates (i.e., 900, 300, and 120 mL/min) were used to test various residence times. The gas amounts leaving the first reactor was found out equal to 137.7, 291.7, and 184.7 mL/min, respectively, for the previously reported N_2 flow rates, resulting in gas velocities of $v_1 = 2.35 \frac{cm}{s}$, $v_2 = 0.94 \frac{cm}{s}$, and $v_3 = 0.52 \frac{cm}{s}$. The heat exchange surface required to determine the h coefficient was calculated by multiplying the number of spheres (1806) by their surface area $A = 40.21 mm^2$. The resulting values of h were figured out and resulted in $h_1 = 95.5 \frac{W}{m^2K}$, $h_2 = 81.2 \frac{W}{m^2K}$ and $h_3 = 75.2 \frac{W}{m^2K}$. At this stage, the different times required to heat the *Gas* passing through the *Reactor 2*, from 500 °C up to 800 °C, were obtained by integrating Eq. (4) and resulted in $t_1 = 3.37$ s, $t_2 = 3.63$ s, and $t_3 = 3.90$ s, respectively, for the three different tested flow rates.

Therefore, for the highest value of flow rate, the gas did not have enough time to reach the operative temperature (i.e., 800 °C). Conversely, passing from τ_1 up to τ_2, the cracking reactions that are thermodynamically favored at 800 °C (according to Francis Diagram) were also kinetically enhanced. In particular, the ethylene cracking leading to H_2 production increased (from 17 %v/v up to 32 %v/v), and the random chain scission involving the C_3 decomposition into CH_4 were the predominant reaction pathways (as can be observed in Fig. 4). Continuing to increase the residence time up to τ_3, also the degradation reaction of PET ester bonds was kinetically favored, leading to an increase of CO and CO_2 amount (Fig. 4). Moreover, at the same time range the fraction of longer chains hydrocarbons (C_2 and C_3) reduced as shown in the left part of Fig. 5. This could be due to the mechanism of the homolytic dissociation and β-scission of polymer chains mentioned above (Park et al., 2019), that could lead to an increase of CH_4 and C_2H_4 production as reported in Fig. 4.

At this point, it is important to underline that the pyrolyzed feedstock is a waste derived from a primary process and, consequently, it should undergo to variability that could influence the properties of pyrolysis co-products. In particular, gas composition should vary due to the different PSW chemical composition. However, for the sample batch processed in this work it was possible to figure out a trend in yields value and establish a strong correlation between results provided by DSC and TGA analysis and gas composition.

Given the volumetric composition and the LHV value of *Gas* (calculated using Eqs. (1) and (2)), the process energy yields (using Eq. (3)) were evaluated, and their value are collected in the right part of

Volumetric composition [% v/v]

Type	C_1	C_2	C_3
τ_1	17.32	30.72	2.6
τ_2	21.6	27.74	1.94
τ_3	25.61	22.66	0.37

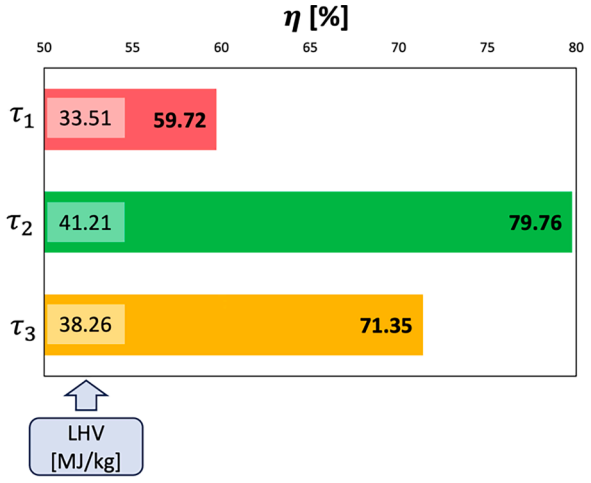

Fig. 5. Comparison between the volumetric composition (on the left) and energy content (on the right) of the pyrolysis gas produced using three different residence times. The energy yields on the right (η) are evaluated using Eq. (3).

Fig. 5.

The highest LHV value was equal to 41.21 MJ/kg, and it was obtained for τ_2. Increasing the residence time from τ_2 up to τ_3 and then reducing it down to τ_1 resulted in an increase in LHV due to the reduction of CO_2 and the increase of H_2 content, that is the gaseous component having the highest LHV value (i.e., 119.93 MJ/kg, (Kahraman et al., 2009)). The concentration of CO_2 also plays an important role in enhancing LHV value of a fuel because it acts as inert gas, reducing the heating value, the combustion speed, and thus the thermal efficiency of the gaseous phase. For this reason, CO_2 removal from fossil fuels is a challenge widely studied in the literature (Rafiee, 2023).

The energy efficiency (reported in the right part of Fig. 5) allowed the collection of both the quantity (yield) and the quality (in terms LHV) of the produced *Gas* in a single term, representing the percentage of energy contained in the initial waste and recovered at the end of the process. The trend of the energy efficiency mirrors those of *Gas* yield and LHV, with both being maximized for τ_2.

The produced *Gas* could be used as fuel to replace the natural gas (NG), mainly composed of CH_4 with an LHV value generally ranging between 44 MJ/kg and 50 MJ/kg (Kahraman et al., 2009). Kakaee et al. (2014) reviewed the impact of NG composition and its effect on energy produced with an internal combustion engine (ICE) and concluded that the CO and CO_2 emissions from NG combustion could be reduced upon H_2 addition to the gas. Therefore, the obtained value of LHV for τ_2 and the high percentage of gas produced in H_2 (see Fig. 4) make this fuel a promising candidate as an electrical and thermal source in ICE. The ICE was simulated using Unisim Design© (as reported in Figure S2 of the SI) and an electrical power (*En-ICE*) of 500 kWe was adopted as the target variable.

First, in a conversion reactor (*R-ICE*), the complete combustion reaction of *Gas* was achieved with a flow rate set at 100 kg/h to simulate an industrial-scale plant, upon addition of air (stream *AIR*). To reach the desired target value of electrical power, a block *Adjust* (*ADJ-1*) manipulated the *AIR* flow rate, whose value resulted equal to 44 kgmole/h based on simulation outcomes. Subsequently, a first cooling step (*E-ICE*) represented the energy production phase, providing a thermal power of 562.5 kW (*En-ICE*). The obtained heat power value was then multiplied by the electrical efficiency of the ICE (0.4) and divided by its thermal efficiency (0.45), resulting in an electrical power of 500 kWe, the chosen target value. The next cooling operation (*E-ICErec*) focused solely on thermal power recovery, extracting 10 kWth from *En-ICErec*, that can be used for heat integration to pre-heat *AIR* from 25 up to 300 °C.

3.4. Characterization of other products and elemental balances

The *Oil* and *Solid 1* fraction produced at τ_2 (i.e., the residence time that provided the best results) underwent elemental analysis, and the results are collected in Table S1 of the SI. The *Solid 1* phase collected in the first reactor exhibited a C/H ratio of 51.81, resulting in a lower heating value. Conversely, the *Oil* fraction showed a high LHV value of 37.6 MJ/kg, due to the absence of ash and due to the lower value of C/H ratio with respect to the *Solid 1* phase. Moreover, the LHV of the liquid fraction closely resembled those of diesel and gasoline, standing at 42.6 MJ/kg and 43.4 MJ/kg, respectively (Hsu, 2012).

To validate the experimental results, elemental material and energy balances were performed for the same residence time (τ_2). Feeding 5 g of PSW, the weight amounts of carbon, hydrogen, oxygen, and ash entering and leaving the set-up were compared. Moreover, the energy content of the feedstock and products was calculated multiplying each product amount by its LHV. These results are collected in Table 3.

As expected, the balances results underline that single elements mass and their energy content were almost completely preserved during the experimentation. As a matter of fact, the maximum value of the absolute normalized error, N Δ, is less than 25 %.

Table 3
Elemental and energy balances results. The last row indicates the absolute normalized error between input and output streams.

	C [g]	H [g]	O [g]	Ash [g]	Energy [MJ]
IN	3.63	0.49	0.73	0.13	169.2
OUT	3.68	0.6	0.73	0.1	164.02
N Δ	1 %	22 %	0 %	23 %	3 %

4. Conclusions

In the face of the escalating global challenge posed by mounting plastic waste, finding viable solutions becomes imperative from both economic and environmental perspectives. This study addresses this critical need, presenting a pioneering two-stage thermal pyrolysis approach for transforming plastic solid waste (PSW) into sustainable fuel alternatives. A real PSW material was successfully processed using a two-stage lab scale experimental set-up with the aim of producing gaseous stream having a high heating value.

The primary objective was to produce a gaseous fuel using a readily scalable pyrolytic setup. This fuel was intended to serve as a potential substitute for fossil fuels in internal combustion engines (ICE), simultaneously offering thermal and electrical outputs, which could be classified as renewable.

However, to evaluate the production viability of the so-called *sustainable fuel* within the European legislative framework, it is mandatory to satisfy the objective criteria reported in the Annex I of the Delegated Act 10/02/23, part C of REDII incorporating assessments of CO_2 equivalent emissions (European Directive, 2018/2001; European Directive, 2023/2413; European Commission Delegated Regulation, 2023).

To this aim, future directions of the work include a comprehensive scale-up of the plant using advanced modeling frameworks to evaluate the emissions factors reported in the Annex I, starting from the preliminary data obtained by the experimental campaign.

It is to be stressed that the simplicity of the proposed scheme, involving only mechanical and pre-heat pretreatments without chemical separation or catalyst-related issues, opens the door to diverse applications of interest for different stakeholders.

The proposed two-stage thermal pyrolysis process offers portability, allowing for a short supply chain of the scrap product. Additionally, the generated electric or thermal energy from the combustion of the produced fuel holds promise for using ICE, directly *in-situ* avoiding gas storage and transportation. This versatility positions the technology as a sustainable solution for plastic waste management, providing an eco-friendly alternative to traditional methods and contributing to the transition toward a circular economy.

CRediT authorship contribution statement

Letizia Marchetti: Writing – original draft, Formal analysis, Data curation. **Mariangela Guastaferro:** Writing – review & editing, Writing – original draft, Conceptualization. **Federica Annunzi:** . **Leonardo Tognotti:** Supervision, Resources, Project administration, Funding acquisition. **Cristiano Nicolella:** Supervision, Resources, Project administration, Methodology, Funding acquisition. **Marco Vaccari:** Writing – review & editing, Validation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2024.03.011.

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