



Research Paper

Application of an integrated pyrolysis and chemical leaching process for pulper waste conversion into coal, hydrogen and chemical flocculating agent

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ABSTRACT

This work aims to investigate the potentials of integrating slow pyrolysis and chemical leaching to recycle pulper waste (PW), the waste generated by paper mills, and consists of plastics, metallic films, and biobased polymers. The concentration of chlorine and metals is a barrier against PW valorisation by combustion or high temperature thermochemical processes. In this study, PW was tested by slow pyrolysis at 400 °C and 500 °C. Chemical leaching tests were performed by processing both chars in a 1.4 M HCl solution, at 80 °C for 2 h, to remove inorganic compounds and upgrade the char to a coal-like material. Then, precipitation by NaOH was conducted on the leachate. Slow pyrolysis led to a char mass yield around 30 %. Due to the high inorganic matter concentration (almost 36 %, mainly including chlorine, calcium, and aluminium), the char retained only 25 % of the feedstock's chemical energy, while the remaining 75 % was recovered in the pyrogas. Leaching of the 500 °C pyrolysis char led to extract 93 % of aluminium, and almost 100 % of calcium and chlorine, resulting in an upgraded char containing 15.5 % ash, comparable to a fossil coal. By char leaching, the oxidation reaction of aluminium could produce 8 kg hydrogen per dry ton PW. The effectiveness of the precipitated compounds as flocculating agents was demonstrated, enabling a closed-loop recycling in the same paper mill. In conclusion, the proposed process demonstrated to be an effective solution to convert PW into high quality products.

1. Introduction

The European Union (EU) pulp and paper industry generates an annual turnover of 95 billion euros, adding 21 billion euros to the EU gross domestic product (GDP) and providing 179,000 direct jobs. Around 55 million t of paper waste are treated to produce recycled paper and board (Cepi, 2022). The recycling process of paper waste consists in introducing bales of recycled paper into a mixing tank called “pulper” which, through the mechanical action of rotating blades and the presence of water, brings the cellulose fibres into liquid suspension. Unfortunately, bales of paper from separated collection contain a large fraction of waste materials made up of plastics, composites (polymers, paperboard and aluminium), wood, glass, cotton and numerous other foreign compounds. After “pulping”, the waste material is separated by means of hydro-cyclones, hydro-classifiers and drums washing

processes. The waste, named pulper waste (PW) and identified by EWC 030307, amounts to around 6–7 % of the processed paper (Italia, 2018) and it is composed of plastics, not converted bio-based polymers, inorganic compounds, and aluminium. According to (Agenzia Regionale Recupero Risorse, 2015; Cepi, 2022), only in Tuscany, about 111000 t/y of PW were produced in 2015. Of this, half is incinerated, while the rest is disposed in landfill. At the same time, paper mills require large quantities of energy in the form of both steam and electricity to run the manufacturing process (Ouadi, 2012); for that, many research activities focused on energy recovery of the PW by co-combustion, gasification, and pyrolysis (Ouadi, 2012; Ouadi et al., 2018, 2013; Win et al., 2019). According to previous experiences, the heterogeneity of such solid waste, the agglomeration of the plastics, and the low-melting temperatures of the inorganic compounds represented a limit during gasification (Fazil et al., 2023; Ouadi et al., 2013). More interesting results have been collected by testing PW through slow pyrolysis, where, as opposed to

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Nomenclature

Pulper Waste (PW)	Residue of the pulper paper recycling plants.
EWC	European Waste Code.
Char	Solid obtained as product of slow pyrolysis process.
Ash 550	Ash content determined at 550 °C.
Ash 710	Ash content determined at 710 °C.
Char 400	Char produced at 400 °C pyrolysis temperature.
Char 500	Char produced at 500 °C pyrolysis temperature.
Aqueous Phase (AP)	Pyrolysis aqueous phase.
Oil Phase (OP)	Pyrolysis oil phase.
Leaching solution	Solution of demineralized water and reagent used for leaching.
Leaching liquid	Liquid phase produced by leaching process.
Recycled Coal 1 (RC1)	Solid obtained after char chemical leaching in test 1.
Recycled Coal 2 (RC2)	Solid obtained after char chemical leaching in test 1.
PC 1	Precipitate obtained at pH 4 from first chemical precipitation test.
PC 2	Precipitate obtained at pH 12 from first chemical precipitation test.
PC 1b	Precipitate obtained at pH 4 from second chemical precipitation test.
PC 2b	Precipitate obtained at pH 12 from second chemical precipitation test.

gasification, whose target is to produce syngas as single product, the feedstock is decomposed in the absence of oxygen, at temperatures between 300 and 900 °C (Czajczyńska et al., 2017; Zhang and Brown, 2019), aiming to maximize the production of the solid product; at these conditions, the material is converted into a solid residue (char), a mixture of condensable compounds (water and organic compounds) and a mixture of permanent gases (CO, CO₂, CH₄, H₂, etc.). Compared to combustion process, pyrolysis generates smaller amount of flue gases, with reduced pollutants and dioxins concentration (Czajczyńska et al., 2017; Paz-Ferreiro et al., 2018; Zhang and Brown, 2019). Since most inorganics are inert to pyrolysis, an effect of PW pyrolysis is the accumulation of inorganic compounds in the char (Paz-Ferreiro et al., 2018).

According to (Ouadi et al., 2018), a solid yield of about 30 % on a dry basis is achievable by PW slow pyrolysis. In the study, a char with an ash content of about 26 % db is produced. The composition of the ashes is not assessed by the author, which however underlines that the valorisation of the char by combustion should be improved by reducing inorganics. Similar results were obtained by (Nel, 2021), which processed PW at temperatures between 450 and 550 °C, obtaining a char mass yield of 35–25 % wt, decreasing with the process temperature. In both the cited studies, the pyrolysis of PW brought to obtain a char with a relevant ash content (between 26 % wt and 41 % wt). In the study of (Nel, 2021), the char is considered as marketable like a petroleum coke, but it does not include a characterization of the inorganics, nor of the chlorine. On the contrary, the present study analysed the concentration of inorganics, thus proving that the obtained char is an impure material containing, in addition to carbon, metals, and other inorganic compounds, thus not usable in the steelmaking sector as produced. For this reason, PW char processing by chemical leaching represents a potential strategy to separate metals and reduce inorganic elements in the solid. In fact, a common application of chemical leaching is low-grade coal cleaning, for ashes and sulphur content reduction (Behera et al., 2018; Dhawan and Sharma, 2019). Chemical leaching can be performed by acids or alkalis in one step or in step-wise processes, or by a combination of both (Dhawan and Sharma, 2019), to remove carbonates, metals, and oxides (Behera et al., 2018). The integration of slow pyrolysis and

chemical leaching was already successfully tested on sewage and industrial sludge, containing a relevant concentration of carbon, and inorganic elements (Salimbeni et al., 2023b, 2020).

The proposed study aims to demonstrate the opportunities offered by the integration of slow pyrolysis and chemical leaching for the complete valorisation of PW by an experimental campaign, and the analysis on the obtained products. The specific objectives are then: (i) assess the PW slow pyrolysis at different temperatures; (ii) determine char mass yield and energy content; (iii) demonstrate the effectiveness of acid leaching process as char upgrading system; (iv) assess the potential application of inorganic materials recovered as flocculating agents.

The novelty of this work is that, unlike any previous experience on PW management, the proposed integrated process can recover not only energy, but also carbon, aluminium, and hydrogen as by-product. In fact, to the best of the authors' knowledge, this is the first study that proposes to combine pyrolysis and leaching, with a complete valorisation of PW, for the concurrent recovery of materials (recycled coal, inorganic chemicals), hydrogen, and energy, without any solid residual waste stream.

2. Materials and methods

2.1. Pulper waste sampling and pre-treatment

The plant that supplied the PW processed in this study (Fig. S-1, left) is an Italian paper mill, producing approximately 4500 t PW per year. Given the heterogeneity of the waste material, a specific sampling activity (described in the supplementary material) was carried out (Gerlach and Nocerino, 2003). The sampled material was shredded (Fig. S-1, right) using a knife mill equipped with a 10 mm sieve.

2.2. Characterization of materials

The shredded material, the char, and the chars from leaching (recycled coals, RC) were characterized in their proximate and ultimate composition and concentration of metals. Proximate analysis was conducted in a thermo-balance (LECO TGA 701) according to UNI EN ISO 18134-2; 2017 for moisture, UNI EN ISO 18122; 2016 and UNI EN ISO 1860-2; 2005 for ash at 550 °C (ash 550) and 710 °C (ash 710), UNI EN ISO 18123; 2016 for volatiles. Fixed carbon was calculated as difference between 100 and the sum of moisture, volatiles and ash at 550 °C according to UNI EN ISO 1860-2; 2005.

Ultimate analysis allowed to determine carbon, hydrogen, nitrogen, sulphur and chlorine contents, and it was conducted by a CHN-S analyser (LECO TruSpec CHN-S) according to UNI EN ISO 16948; 2015 and, to determine chlorine, by a bomb calorimeter (LECO AC500), for pre-treatment, and an ion chromatography system (Metrohm 883 Basic IC plus) according to UNI EN ISO 16994; 2017. The higher heating value (HHV) was determined analytically by a bomb calorimeter (LECO AC500) according to UNI EN ISO 18125; 2018 and used, by mean of moisture and hydrogen content, to derive the lower heating value (LHV) as per UNI EN ISO 18125; 2018 and UNI EN ISO 16948; 2015. The characterization of the material was completed using microwave plasma atomic emission spectroscopy (Agilent 4200 MP-AES), in order to quantify the concentration of metals according to UNI EN ISO 16967; 2015 and UNI EN ISO 16968; 2015. Leachates were analysed by MP-AES to determine their composition in metals and calculate element extraction efficiency (EE). In addition, aiming to evaluate RCs quality, their atomic H/C and O/C ratios were defined (calculating their oxygen content as difference between 100 and the sum of C, H, N and ash 550). Where possible, 3 replicates of proximate and ultimate analysis were performed. Given the heterogeneity, the measurements of ash content of PW, and of raw char samples, was obtained as a mean value of 7 replicates.

Fourier-transform infrared spectroscopy (FTIR) was used to determine the type of materials in the PW and to evaluate the precipitated

compound. A Shimadzu IR Tracer-100 was used to acquire the spectra (Transmittance-mode, wavelength from 600 to 4000 cm^{-1}), that were compared with the instrument library and literature reference for identification of compounds.

The condensed products from slow pyrolysis trials, recovered from the condensation system of the pilot plant, were collected and mixed, then the aqueous phase (AP) was separated from the oil phase (OP) gravimetrically. To characterize the OP, its carbon, hydrogen and nitrogen content (by a LECO TruSpec CHN-S analyser), its HHV (by a LECO AC500 bomb calorimeter) and LHV, its water content (by an automatic titrator Metrohm 848 Titrino Plus, by Karl Fischer titration method), Cl and S content (by bomb calorimeter LECO AC500 for pre-treatment, and an ion chromatography system Metrohm 883 Basic IC plus) were determined. Cl, S, and SO_4^{2-} content in the AP were determined by an ion chromatography system (Metrohm 883 Basic IC plus). The COD (chemical oxygen demand) was determined after oxidation in presence of $\text{K}_2\text{Cr}_2\text{O}_7$ through the photometric COD Cell Test 25–1500 mg/l (COD)(Spectroquant) and by measuring the absorbance at 605 nm (Shimadzu UV-1800) according to EPA 410.4.

2.3. Thermo-gravimetric analysis

To evaluate the potential behaviour of the material during pyrolysis, a thermo-gravimetric analysis of shredded PW was performed in a LECO TGA 701 by heating it in N_2 controlled atmosphere under a constant heating rate (7 $^\circ\text{C}/\text{min}$) up to 900 $^\circ\text{C}$, measuring weight loss over temperature.

2.4. Slow pyrolysis

2.4.1. Pyrolysis pilot unit

A pilot scale slow pyrolysis unit, coupled with a condensation unit, was operated for the pyrolysis tests. The unit (Fig. S-2), a shaftless auger-type pyrolyzer, is described elsewhere (Salimbeni et al., 2023a, 2023c) While char is collected in a sealed vessel and condensable gases are recovered by a condensation system, non-condensable gases are burnt and vented outside.

2.4.2. Slow pyrolysis tests

In this work, two pyrolysis tests have been performed in the pilot plant at different temperatures: 400 $^\circ\text{C}$ and 500 $^\circ\text{C}$. The rotating speed of the reactor screw was set at 0.3 rpm to achieve a solid residence time of 1 h. At the end of both trials, the char produced was weighted and analysed. The condensed products from each test were collected, weighted, gravimetrically separated in an AP and OP and analysed. After both trials, the mass and energy balance of the process were calculated from the mass and properties of PW and collected products (solid and liquids) and attributing the difference to the gas. The energy balance consisted in the calculation of the input chemical energy to the plant in the form of dry shredded PW, multiplying its mass by its HHV. The chemical energy recovered as char, in the oil phase (OP) and in the aqueous phase (AP) was similarly calculated. The chemical energy recovered as permanent gases was calculated subtracting char's and OP's energy content from the input chemical energy.

2.5. Chemical leaching experiments

2.5.1. Methodology

Chemical leaching experiments were conducted at laboratory scale to extract the desired inorganic compounds from the pyrolyzed PW. The selection of the chemical leaching process parameters was based on results from literature (Yang et al., 2019), and previous tests performed (Salimbeni et al., 2023a), adapted to this specific case study. HCl was used as acid reagent, having demonstrated high leaching performances on several heavy metals (Fe, Al, Ca) in previous experiments (Ajiboye et al., 2019; Jadhav and Hocheng, 2015).

The char was initially oven dried at 105 $^\circ\text{C}$ to constant weight. The leaching solution was prepared by mixing in a beaker demineralized water and HCl, dosed as a solution (Carlo Erba, 37 % HCl). The beaker, with a magnetic stirred inside, was immersed in a silicone oil bath kept at the selected temperature on a heating plate. Subsequently, the char was added into the beaker. The temperature was monitored by a thermocouple immersed in the silicon batch and stirring was kept for the entire duration of the process. After the test, the content of the beaker was vacuum filtered to separate the solid from the liquid phase (leachate). The solid was subsequently washed with demineralized water to remove the residual reagent, again separating the washing water through a vacuum filter. The solid material was finally oven dried at 105 $^\circ\text{C}$ to constant weight.

Two leaching tests were performed, processing the chars obtained at 400 $^\circ\text{C}$ (test 1) and 500 $^\circ\text{C}$ (test 2). For both tests, 10 g char and 100 ml of solution containing 5 % w/w of HCl and 95 % w/w of demineralized water were dosed. A contact time of 2 h and a temperature of 80 $^\circ\text{C}$ was maintained. Hereinafter, the chars produced by leaching will be referred to as recycled coals (RC).

2.5.2. Performance indicators

The performances of the leaching tests were evaluated by two indicators. The first is the degree of demineralization (DD), which expresses the char ash content decrease after leaching:

$$DD(\%) = \frac{\text{ash}_{char,i}(\%d.b.) - \text{ash}_{RC,f}(\%d.b.)}{\text{ash}_{char,i}(\%d.b.)} \quad (1)$$

Where $\text{ash}_{char,i}$ is the ash content (710 $^\circ\text{C}$) in the processed char, and $\text{ash}_{RC,f}$ is the ash content (at 710 $^\circ\text{C}$) in the recycled coal.

The second indicator is the element extraction efficiency (EE), which expresses the percentage of extracted element against the initial element content in the processed char:

$$EE(\%) = \frac{\text{Element}_{LL,f}(\text{mg})}{\text{Element}_{char,i}(\text{mg})} \cdot 100 \quad (2)$$

Where $\text{Element}_{LL,f}$ is the element mass extracted by leaching in the leaching liquid, and $\text{Element}_{char,i}$ is the element mass in the processed char.

The $\text{Element}_{LL,f}$ was calculated multiplying the concentration of element in the leachate (from MP-AES analysis) by the recovered leaching liquid mass. The $\text{Element}_{char,i}$ was calculated starting from the concentration of the element in the char (from MP-AES analysis) and the dry char mass processed.

2.6. Chemical precipitation experiments

Two double-step precipitation tests were conducted on the leachate from leaching test 2, selected as the most effective. Precipitation was performed by adding, through progressive dosage, a 4 M NaOH solution, produced by dissolving NaOH pellets (Merck, purity $\geq 98\%$) into demineralized water. Known volumes of the basic solution were added to the acid leachate, previously introduced into a conical bottom test tube, maintaining the system stirred. The pH of the system was monitored, using a pH meter, for the entire duration of the addition process. The basic solution was dosed until precipitation of the dissolved compounds was observed. Since a precipitation occurred at a still acidic pH, two precipitation stages were carried out, thus obtaining two fractions of precipitate. In the first stage, the pH was increased from 0.2 to 3.9–4.0. After that, the precipitated salt (PC 1) was separated by centrifugation, and a second precipitation step was performed on the liquid until a pH of 12.0 was achieved, producing a second precipitated salt (PC 2). The test was replicated to produce enough precipitated salts (PC 1b, from step 1, and PC 2b, from step 2) for flocculating tests.

2.7. Flocculation tests

To prove the usability of the precipitated compound as flocculating agents, a flocculation test was performed. The tests were conducted on an agricultural waste digestate, previously filtrated at 1 mm, with a COD of 997 mg/l. A first test was performed adopting a commercial flocculant (Chimpex, 18–20 % Al_2O_3) (PAC20), while a second and a third tests were conducted with PC 1b and PC 2b respectively. For each test, a beaker was filled with 300 ml of digestate and kept at 350 rpm by a magnetic stirrer. A pH-meter was used to continuously measure the pH. After PAC20 dosage, the stirrer was stopped and a pH of 5 was measured. The solution was left to settle for 30 min. In flocculation tests by PC 1b and PC 2b, each precipitated salt was dosed at intervals of 1 g, continuously adjusting the pH by adding a 1 M HCl solution until the same pH of the PAC20 test was reached (pH 5). Then the solution was left to settle.

3. Results

3.1. Results of pulper waste characterization

3.1.1. Shredded pulper waste chemical-physical composition

The results of the shredded PW chemical and physical analysis performed in the laboratory are reported in Table 3.

The material has a high carbon content (almost 64 %) and a high hydrogen content (around 9 %), both typical of plastic polymers, which make it potentially promising for a use in energy sectors. However, a large amount of inorganic compounds is present in the material, with a concentration of Al and Ca of about 1.2 and 1.9 % respectively, and chlorine higher than 1 %. The presence of chlorine is probably due to the chemical agents (CaCl_2 , NaCl) used for de-inking and bleaching the paper waste in the pulping process (Costa and Rubio, 2005; Yilmaz et al., 2021). In the three analyses carried out, chlorine content varied between 0.6 % and 2.0 %. This variability can be due to the distribution of chlorine-polymers (e.g. polyvinylchloride) in the sample and to sample's inhomogeneity. The high concentration of aluminium in metallic form is attributed to the presence of packaging materials, including aluminium films in food packaging. On the contrary, sulphur is rather neglectable, with a concentration of about 0.09 %.

3.1.2. Thermo-gravimetric analysis

Fig. S-3 shows the test temperature (temperature, x axis), the 0–100 % scale for the residual mass (mass yield, left y axis) and weight loss over temperature (degree of volatilisation, right y axis). The graph consists of two characteristic curves: mass yield curve (%) and degree of volatilisation curve over temperature (%/°C). The thermo-gravimetric analysis of shredded PW led to identify a first de-volatilization peak at 300 °C, and a second peak at 500 °C. After this analysis, the two pyrolysis temperatures (400 and 500 °C were selected).

3.2. Results of slow pyrolysis trials

3.2.1. Mass balance

In the tests carried out at 400 and 500 °C, 2.7 kg and 2.5 kg of material were processed in the pyrolysis pilot unit respectively. The mass balance of the two trials is reported in Table 1.

d.b. – dry basis.

The two tests produced a similar char mass yield, equal to 31 % at 400 °C and 33 % at 500 °C. This result denotes a substantial invariance in the yield of solid against temperature. However, the main reason for this result lies in the inhomogeneity of the processed material, as PW contains compounds of different nature, from low-density polyethylene to cotton, including composite materials, and a large amount of inorganics.

Table 1

Mass balance of the slow pyrolysis trials.

Material	Trial at 400 °C	Trial at 500 °C	Unit
Shredded PW processed	2718	2456	g
Dry shredded PW	2463	2225	g
Moisture	255	231	g
Dry char produced	765	733	g
Condensates produced	812	953	g
Aqueous phase (AP)	380	886	g
Oil phase (OP)	432	67	g
Dry char mass yield ^a	31 %	33 %	% d.b.

^a Referred to input dry shredded PW.

3.2.2. Energy balance

For the trial at 400 °C, the total chemical energy theoretically introduced into the plant, in the form of PW dry matter, resulted equal to approximately 70.3 MJ. The energy recovered as char was equal to 19.7 MJ. As a result, the char extracted after pyrolysis at 400 °C contained about 28 % of the initial energy content, while about 72 % was converted during the process into pyrogas (Fig. 1, left). In the 500 °C test, around 63.5 MJ chemical energy were introduced as shredded PW dry matter, recovering 15.9 MJ as char. This char retained about 25 % of the initial energy content and, therefore, about 75 % of the initial energy content was converted during the process into pyrogas (Fig. 1, right).

The main difference observed between the two tests lies in the appearance of the oil phase, which is highly dense and black from the test at 400 °C, but shows a lower viscosity and a semi-transparent colour, with a reduced yield, when produced at 500 °C. These results are in line with other experiments performed on different polymers, which demonstrated that, at temperatures of around 500 °C, the oil is cracked to a larger extent to gas (around 47.0 %) with a corresponding decline in oil yield (Abdullah et al., 2018; Onwudili et al., 2009). Furthermore, despite the higher char mass yield (33 % compared to 31 %), the test at 500 °C produced a char with a lower calorific value and an energy balance more in favour of the gaseous component. Both tests demonstrate how the volatility of plastics contributes to the production of a large fraction of pyrogas.

3.2.3. Condensates composition

Both tests produced two-phases condensates. The high production of water steams from the reactions taking place during pyrolysis of oxygenated materials is the result of both feedstock moisture content, and of dehydration reactions occurring during the pyrolysis process, when O and H are released from the organic compounds (Jerzak et al., 2023). The composition of the two phases of the condensates from the trials is reported in Table 2.

Chlorine concentration in the APs of both trials resulted greater than 1 %. The high presence of chlorine in the AP represents a possible criticality in the combustion phase, due to the potential production of dioxins (Gullett et al., 2000). On the contrary, the presence of sulphur is limited and less problematic. Nonetheless, any potential energy valorisation solution of the condensates would require including an exhaust treatment line.

3.2.4. Char composition

The results of the characterization of the char from the slow pyrolysis trials performed at 400 and 500 °C, and of the shredded PW, are reported in Table 3.

The chars show a calorific value from 21 to 25 MJ/kg d.b., similar to the input material, and a high carbon content. The char produced at 500 °C, as expected, shows a reduced volatile content which makes it a fuel of potential interest for sectors that require carbon to be stable at high temperatures, such as steelmaking. However, the high chlorine content prevents a safe use of the char as fuel, due to the potential dangerous emissions produced. Moreover, the high amount of ash, made of both oxides and metals, is another important barrier. Chars ashes are

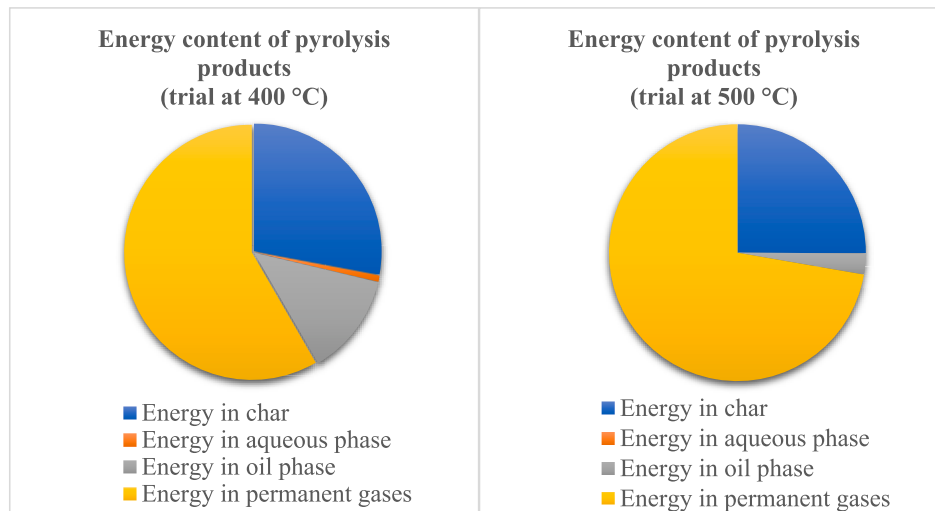


Fig. 1. Energy balance of the two pyrolysis trials (at 400 °C, left, at 500 °C, right).

Table 2
Composition of the OP and AP from two pyrolysis trials.

Parameter	OP 400 °C	AP 400 °C	OP 500 °C	AP 500 °C	Unit
Water content	41.50 ± 2	89.33 ± 0.8	43.55 ± 0.4	96.74 ± 2	% w.b.
HHV	21.59 ± 0.9	1.43 ± 0.1	25.13 ± 0.3	b.d.l.	MJ/kg w.b.
C	41.86 ± 4	3.59 ± 0.1	56.60 ± 1	0.49 ± 0.03	% w.b.
H	10.80 ± 0.07	10.11 ± 0.3	8.96 ± 0.1	9.90 ± 1	% w.b.
N	0.17 ± 0.04	b.d.l.	0.30 ± 0.07	b.d.l.	% w.b.
Cl	1.09 ± 0.2	1.48	0.80 ± 0.04	1.38	% w.b.
S	0.12 ± 0.04	0.1	0.05 ± 0.00	0.02	% w.b.

b.d.l. – below detection limit.
w.b. – wet basis.

Table 3
Chemical-physical composition of the chars and of the shredded pulper waste.

Parameter	Shredded PW	Char 400 °C	Char 500 °C	Unit
Ash 550	8.76 ± 2	26.57 ± 8	37.89 ± 2	% d.b.
Ash 710	7.80 ± 2	25.61 ± 8	35.52 ± 2	% d.b.
Volatiles	82.84 ± 3	28.44 ± 2	17.52 ± 0.1	% d.b.
Fixed C	8.40	44.99	44.59	% d.b.
HHV	28.56 ± 0.4	25.66 ± 0.2	21.73 ± 0.03	MJ/kg d.b.
LHV	26.72 ± 0.4	24.93 ± 0.2	21.36 ± 0.03	MJ/kg d.b.
C	63.94 ± 8	64.16 ± 0.8	55.64 ± 0.5	% d.b.
H	8.92 ± 1	3.50 ± 0.05	1.79 ± 0.04	% d.b.
N	0.18 ± 0.1	0.55 ± 0.02	0.71 ± 0.1	% d.b.
Cl	1.27 ± 0.7	1.43 ± 0.05	2.44 ± 0.1	% d.b.
Al	12,462	37,828	88,574	mg/kg d.b.
Ca	19,452	40,696	75,721	mg/kg d.b.
Cu	36	92	143	mg/kg d.b.
Fe	713	2317	3597	mg/kg d.b.
K	1129	5683	6188	mg/kg d.b.
Mg	630	4190	6022	mg/kg d.b.
Mn	23	90	130	mg/kg d.b.
Na	355	1040	1861	mg/kg d.b.
Pb	13	77	116	mg/kg d.b.
Si	1402	3262	2914	mg/kg d.b.
Zn	65	253	2212	mg/kg d.b.

d.b. – dry basis.

mainly composed of calcium and aluminium. Chlorine concentration increases in both chars compared to shredded PW and also in the char produced at 500 °C compared to that produced at 400 °C; this could be attributed to chlorine inorganic state in the PW, since it did not devolatilize despite the high process temperatures. It is for this reason that, to enable the use of char as alternative to fossil coal, inorganics extraction by chemical leaching is necessary.

3.3. Results of chemical leaching

3.3.1. Chemical leaching performance

The aim of the leaching tests was to maximise the extraction of the most concentrated elements (Al, Ca, Cl), and therefore of ash, from the feedstock to the resulting leachates. A degree of demineralization of 41.9 % and 56.4 % was obtained from the leaching trials on char produced at 400 and 500 °C respectively. The result is also reported in Table S-1. Fig. 2 shows the extraction efficiency obtained for the elements having a concentration higher than 1000 mg/kg d.b. in the raw chars. From Table 4, a reduction of the concentration of almost all the inorganic elements in the RCs is observed compared to the starting chars. The main leaching target elements, that are aluminium and calcium, have been efficiently removed, likewise iron, potassium, magnesium and sodium.

Tests 2, showing the best result in terms of leaching performances, was chosen for further process assessment studies and for the following chemical precipitation tests. Fig. S-4 shows the char produced at 500 °C, and the RC produced by leaching test 2.

3.3.2. Mass balance of the leaching trial

From the leaching test 2, a dry RC mass yield of 89.7 % was obtained, due to ash extraction. Gas phase production was about 0.3 % of the total input solution.

3.3.3. Recycled coals characterization

The results of RC from test 1 (RC1) and 2 (RC2) characterization are shown in Table 4. In addition to the parameters shown in Table 4, the chlorine content was analysed for RC 2. The chlorine content in the char resulted of 0.74 % db. The residual chlorine content could have been reduced with a more intensive washing system.

3.3.4. Leachate characterization

The elemental composition of the leachate produced by leaching test 2 (Table S-2) shows that the inorganic elements extracted from the treated char are found in the liquid fraction. The elements present in

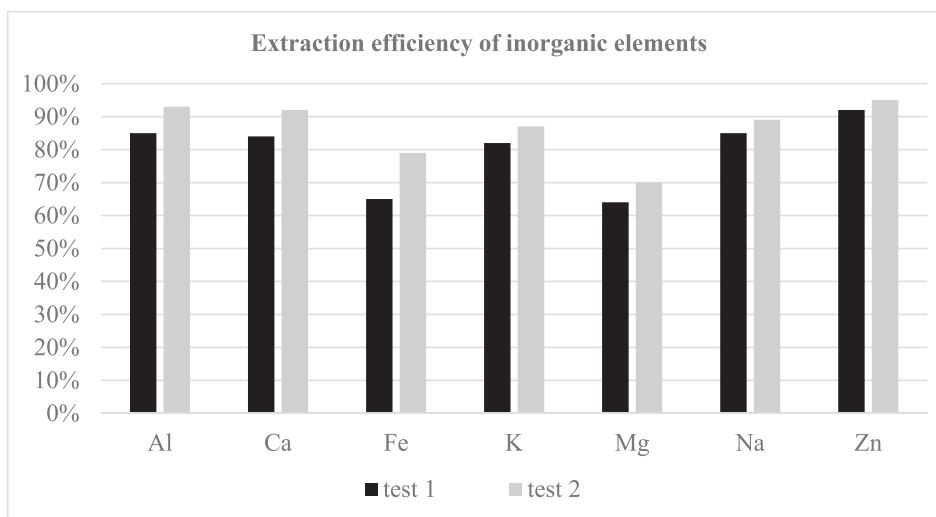


Fig. 2. Elements extraction efficiency obtained by the two leaching tests.

Table 4
Chemical-physical composition of RC1 and RC2.

Parameter	RC1	RC2	Unit
Ash 710	14.89 ± 0.2	15.48 ± 0.2	% d.b.
Volatiles	39.10	18.4	% d.b.
Fixed C	45.96	66.23	% d.b.
C	68.65 ± 0.2	72.52 ± 0.3	% d.b.
H	4.97 ± 0.03	2.26 ± 0.03	% d.b.
N	0.60 ± 0.03	0.93 ± 0.04	% d.b.
O ^a	10.83	8.77	% d.b.
Atomic H/C	0.86	0.37	–
Atomic O/C	0.12	0.09	–
HHV	29.45 ± 0.1	27.69 ± 0.3	MJ/kg d.b.
LHV	28.43 ± 0.1	27.22 ± 0.3	MJ/kg d.b.
Al	15,747	8187	mg/kg d.b.
Ca	13,728	8092	mg/kg d.b.
Cu	91	276	mg/kg d.b.
Fe	1432	1069	mg/kg d.b.
K	1270	1096	mg/kg d.b.
Mg	2535	2546	mg/kg d.b.
Mn	38	31	mg/kg d.b.
Na	315	273	mg/kg d.b.
Pb	50	b.d.l.	mg/kg d.b.
Si	3390	2919	mg/kg d.b.
Zn	206	143	mg/kg d.b.

b.d.l. – below detection limit.

d.b. – dry basis.

^a Calculated as 100-(ash 550 + C + H + N).

higher concentrations are chlorine (around 4.8 %, due to the use of HCl), aluminium (0.7 %) and calcium (0.6 %), in line with what has been observed in the starting material.

3.4. Results of chemical precipitation

3.4.1. Products characterization

PC 1, obtained from the first precipitation stage, had a jelly texture and contained mainly Al (7.06 % d.b.), Ca (2.31 % d.b.) and Na (8.09 % d.b.); additionally, Fe, K, Mg were identified, with concentrations of 1.89, 1.84, 2.65 g/kg respectively. PC 2 showed a reduced Al concentration (2.40 % d.b.), higher Ca (5.54 % d.b.) and higher Na (13.8 %). The concentration of Fe, K and Mg was 0.59 g/kg d.b., 2.27 g/kg and 1.36 g/kg respectively. The characterization of the solid precipitation products, compared against the elemental composition of the treated leachate (Table S-2), shows that precipitation with NaOH had an effect on the recovery of aluminium, calcium, iron, magnesium, zinc. PC 1b showed a concentration of 12.8 % d.b. of Al, and 3.8 % d.b. of Ca; PC 2b

showed a similar concentration of Al (12.1 % d.b.) and Ca (4.4 % d.b.) (Table S-3). As shown in Table S-6, the obtained liquid contained mostly chlorine (35.4 g/l) and sodium (18 g/l).

3.4.2. Mass balance of precipitation trial

As reported in Table S-4, the precipitation trial showed that about 2.62 g NaOH were needed for the precipitation of 80.7 g of liquid, equal to 3.48 % of inlet leachate. As a result, about 0.9 g of PC 1b and 2.9 g of PC 2b were recovered, equal to 0.75 % and 3.5 % of the processed leachate respectively.

3.4.3. Precipitates analysis by FTIR

FTIR analysis was performed on the PC 1 and PC2 to gather information regarding the chemical structure of the samples starting from the spectrum obtained (Fig. 3). The strong broad bands at 3356 in Fig. 7(a), and 3396 cm⁻¹ in Fig. 7 (b) could be attributed to stretching of hydroxyl group, mixed with vibrations of H₂O. The peak appearing at 1633 cm⁻¹ in Fig. 3 (a) can indicate O–H bending of water; the same can be stated for the peak at 1627 cm⁻¹ visible in Fig. 3 (b). The peaks at a wavelength of 1404, 873 and 780 cm⁻¹, identified in the second precipitate, are characteristics of carbonate and of carboxylic groups (Pranata Putra et al., 2014; Vagenas et al., 2003).

3.5. Results of flocculation tests

The results of the flocculation tests are showed in Fig. 4. The flocculation tests showed that, to achieve the same effects of the commercial flocculating agent (PAC20), of which 3 g/l were dosed for the trial, 13 g/l of PC1b and 40 g/l of PC 2b were necessary. COD concentrations are reported in Table S-5. PAC20 and PC2b dosages resulted in the same COD removal efficiency, equal to 89.8 %. PC1b demonstrated a better performance, showing a higher COD removal efficiency (95.7 %).

4. Discussion

4.1. Recycled coal quality

The characteristics of the RC samples shown in Table 4 were examined in order to determine their applicability as coal substitutes in the steelmaking sector. A first quality assessment was performed by the Van Krevelen diagram (van Krevelen, 1993), reported in Fig. S-5 which shows the classification of coals on the basis of their atomic H/C and O/C ratio. This essential classification provides information about coal stability and, thus, volatility. High H/C and O/C ratios correspond to a

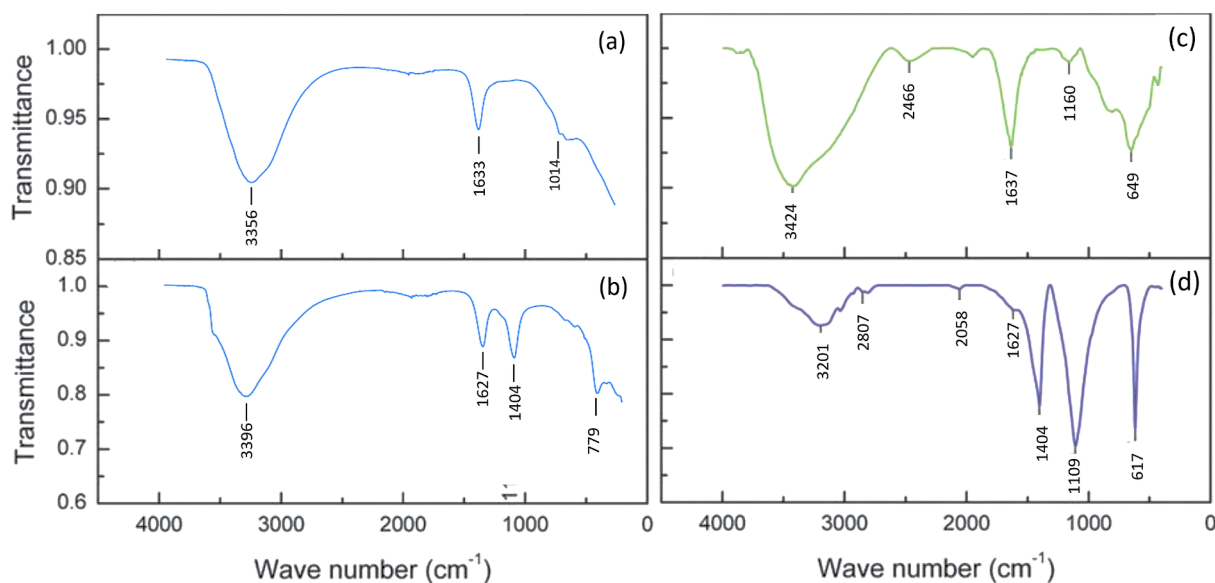


Fig. 3. (a) IR spectrum of PC 1. (b) IR spectrum of PC 2. (c) IR spectrum of commercial poly-aluminium chloride (PAC) and (d) IR spectrum of commercial flocculant: Suffloc-1010 (Lal and Garg, 2017).

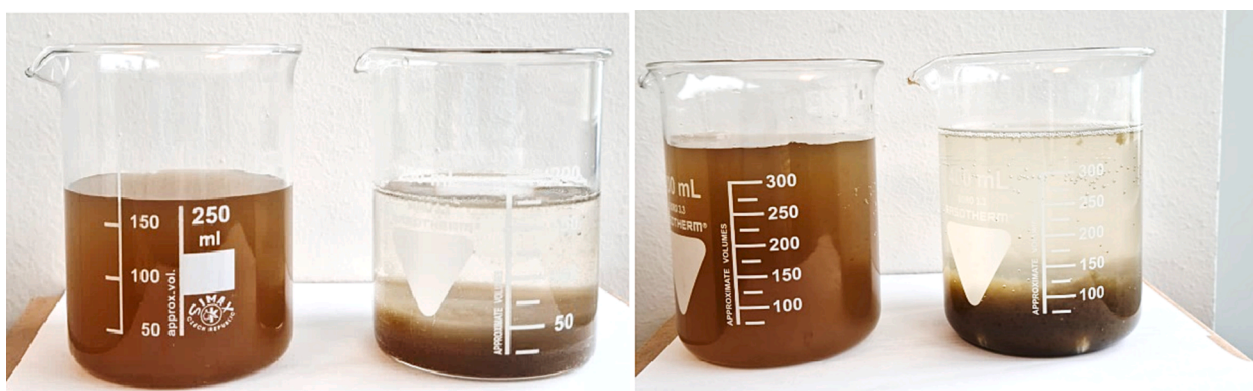


Fig. 4. Agricultural digestate before and after flocculation with PC1b and PC2b.

high volatiles content, which makes coal easier to ignite. As visible in Fig. S-5, RC2 is similar to anthracite, so having a reduced volatility and, by consequence, a higher stability. On the contrary, RC1, could be classified as common, thermal coal. However, coal requirements for the steel sector change depending on the specific use. Typically, low moisture content, ranging (2–3 %) and a low ash content, (8–10 %) must be respected, with a volatiles content from 15 to 30 % (Sahu et al., 2014). In the study presented by (Campos et al., 2019), different coal samples to be used as pulverized coal in blast furnaces are characterized. According to (Campos et al., 2019), all recycled coal samples produced in this work could be suitable. On the contrary, as explained by Zhang et al. (2021), to fully or partially replace anthracite, or coke in sintering process, the admitted ash content is higher, but volatility must be reduced. For this reason, a quality assessment of the produced coal samples was performed in collaboration with a steel manufacturing industry, which stated that RC2 could replace about 15 % of hard coal in sintering process. A low concentration of Al and Cl is considered crucial to enable the use of RC1 and RC2 as reducing agents in steelmaking. Moreover, Cl is a precursor of dioxins (Stanmore, 2004) formation in combustion gases. By virtue of these considerations, RC2 was identified as the best in terms of quality and of potential market value.

4.1.1. Chlorine distribution and management

Of the chlorine initially contained in the PW was mostly found in the

AP of the pyrolysis process (1.38 %wt) and in the raw char (2.4 % db). After the leaching, where HCl was used, the chlorine content determined in RC2 was 0.7 % db, lower than the Cl contained in the corresponding char. However, despite this concentration is in line with other residue derived fuels (Vounatsos et al., 2015), it is considered critical for the application of RC 2 as biofuel or reducing agent in iron making processes. At the same time, it is supposed that the residual chlorine content in the RC 2 could be furtherly reduced by a more intensive washing process. During the leaching process, a high amount of chlorine is consumed as HCl. After the precipitation process, as reported in Table S-6, a high concentration of Cl and Na was found in the liquid phase. To facilitate the water reuse, reverse osmosis could represent a valid solution to treat the water and to remove the ions concentrated in the spent liquid.

4.2. Precipitated compound quality

The similarity of the infrared spectrum of the precipitates to that of aluminium polychloride suggested the possibility of having obtained a coagulant to be used for wastewater treatment. This consideration is based on the similarity of different coagulants used for treating pulping effluents (Lal and Garg, 2017). The flocculation tests performed showed that both precipitated compounds could be used as flocculating agents, replacing costly, commercial polyaluminium chloride. The need of a

higher amount of product (13 g/l for PC1b and 40 g/l of PC2b against 3 g/l of PAC20), is supposed to be related to precipitated salts humidity, and thus to the reduced Al_2O_3 concentration in PC 1b (2.24 %) and PC 2b (2.41 %) in comparison with PAC 20 (20 %). In fact, the mass of Al_2O_3 dosed in the three tests is 0.6 g/l for PAC20, 0.3 g/l for PC 1b and 0.96 g/l for PC 2b.

4.3. Hydrogen production

Hydrogen production through metals corrosion is a well-known process, currently widely investigated (Liang et al., 2016; Wang et al., 2009). In particular, aluminium was identified as the most suitable metal due its low atomic mass, negative value of standard electron potential, abundance and low cost. One g of aluminium can theoretically produce 1360 ml of H_2 at standard atmospheric pressure, equal to about 122 g H_2 per kg of Al, according to reaction (3) (Ho, 2017):



According to Pourbaix diagram, the aluminium oxide can be destroyed in strong acidic and alkaline solutions ($4 > \text{pH} > 9$) (Ahmad, 2006). An oxidation–reduction reaction occurs when metallic aluminium reacts with hydrochloric acid. Balanced equation (4) is reported below:



However, several factors influence the production of H_2 from Al corrosion, so that the actual production rate is lower. Razali H. et al., estimated that around 108 g of hydrogen can be produced by processing 1 kg of aluminium (Razali et al., 2014). Similar hydrogen yield was obtained by (Coronel-García et al., 2020), where Al was leached in a 1.4 M HCl solution and heated at 60 °C for 20 min. These conditions, similar than those adopted in this study, enabled to produce around 1300 ml of H_2 per gram of Al. It is therefore estimated that, by processing 1 dry ton of char produced by PW pyrolysis, about 8 kg of hydrogen could be reasonable produced.

4.4. Mass balance of the process

Considering the experimental results, from 1 t of dry PW, around 297 kg of dry RC and 263 kg of dry precipitate could be produced, including about 2.9 kg of hydrogen. The reagents used include about 446 kg of HCl (37 % solution) and 198 of pure NaOH. In the case of an industrial-size plant, part of the liquid from precipitation, at high pH, could be reused as an additive to the bubbling unit for leaching vapours condensation. The rest of the liquid is supposed to be processed into a reverse osmosis unit to minimize water consumption. The mass balance of an industrial facility is the [supplementary material \(Fig. S-6\)](#).

4.5. Critical aspects of the proposed process

The process tested in this study has three major limitations. First, the heterogeneity of the feedstock could be a major barrier against the industrial implementation of the proposed process. Despite no critical aspects have been identified in the processed samples, heavy metals and contaminants, such as Zn, Cr, Cu, Pb, could affect the chemical composition, and thus the marketability of the two main products (the coal and the flocculating agents). Secondly, the chlorine content of the feedstock and the use of HCl as leaching reagent represent a key point to consider to avoid chlorine concentration in the RC, and in the wastewater. Finally, the hydrogen obtained as by-product of the leaching reaction, even after the condensation of vapours from the gas phase, could be not easy valorised as H_2 but only as an energy source, because of the expensive gas storage and utilization systems to be implemented.

5. Conclusion

The study provided evidence about the heterogeneous composition of PW, which was characterized by a valuable calorific value, but had limited possibility to be used as a fuel due to the high concentration of chlorine, and of low-temperature melting metals (aluminium).

Moreover, the behaviour of PW during slow pyrolysis process at 400 °C and 500 °C was assessed in real environment, demonstrating that about 75 % of the input feedstock energy content could be recovered in the form of pyrogas (permanent and condensable gases), obtaining at the same time a solid mass yield of more than 30 %. The pyrolysis trials showed that the aluminium contained in PW was not oxidized during pyrolysis process and could be recovered as part of the solid product.

The chemical leaching test demonstrated to effectively remove aluminium, and other inorganic compounds, such as calcium, and chlorine, obtaining a demineralization efficiency of more than 56 %. At these leaching conditions, the ash and contaminants in the char were reduced.

Thanks to the low H/C ratio, the low volatility, and the reduced ash content, the RC could be defined a coal-like material, usable as alternative to fossil coal in hard-to-abate sectors such as sintering, or blast furnaces steelmaking processes.

Moreover, the utilization of NaOH to precipitate the inorganic compound in the leaching liquid brought to the production of a solid salt with a spectrum similar to those of aluminium polychloride and other commercial flocculating agents used by pulp and paper industry. The potential application of the precipitated salts as flocculating agents was confirmed by flocculation tests, which showed a COD removal efficiency >89 %, although a higher quantity was required compared to PAC20.

In summary: about 297 kg of recycled coal could be produced from 1 ton of dry PW; the RC presents a chemical composition in line with fossil coals used in metallurgy; considering an average concentration of about 8 % d.b. of aluminium, 2.9 kg of hydrogen could be obtained from 1 ton of dry PW; 5.9 MWt could be produced by the energy recovery of the pyrogas produced from 1 ton of dry PW; 263 kg of dry flocculating agent could be produced from 1 ton of dry pulper waste, considering the consumption of 165 kg of pure HCl and 198 kg/h of pure NaOH; the precipitated salt obtained has the properties of a flocculating agent.

To validate the process from an economic and technical point of view, additional studies and trials in real environment are planned. However, the quality of the obtained materials demonstrated that it is possible to transform PW into high quality products.

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

The most significant data generated and/or analysed during this study are included in this published article. Additional datasets are available from the corresponding author on reasonable request.

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Author contributions

All authors contributed to the study conception and design. Material preparation, tests conduction, data collection and analysis were performed by Andrea Salimbeni, and Marta Di Bianca. The first draft of the manuscript was written by Andrea Salimbeni, and edited and commented by Andrea Maria Rizzo, Marta Di Bianca and all other authors. All authors read and approved the final manuscript.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2023.12.038>.

References

- Abdullah, N.A., Novianti, A., Hakim, I.I., Putra, N., Koestoe, R.A., 2018. Influence of temperature on conversion of plastics waste (polystyrene) to liquid oil using pyrolysis process. *IOP Conf. Ser. Earth Environ. Sci.* 105, 012033 <https://doi.org/10.1088/1755-1315/105/1/012033>.
- Ahmad, Z., 2006. Basic concepts in corrosion. In: *Principles of Corrosion Engineering and Corrosion Control*. Elsevier, pp. 9–56. doi: 10.1016/B978-075065924-6/50003-9.
- Ajiboye, E.A., Panda, P.K., Adebayo, A.O., Ajayi, O.O., Tripathy, B.C., Ghosh, M.K., Basu, S., 2019. Leaching kinetics of Cu, Ni and Zn from waste silica rich integrated circuits using mild nitric acid. *Hydrometall.* 188, 161–168. <https://doi.org/10.1016/j.hydromet.2019.06.016>.
- Behera, S., Kumari, U., Meikap, B., 2018. A review of chemical leaching of coal by acid and alkali solution. *J. Min. Metall. A: Min.* 54, 1–24. <https://doi.org/10.5937/JMMA1801001B>.
- Campos, A.M.A., Novack, K., Assis, P.S., 2019. Selection of materials for blast furnace injection using quality indicators. *REM - Int. Eng. J.* 72, 119–123. <https://doi.org/10.1590/0370-44672018720025>.
- Cepi, 2022. Key Statistics 2021. European pulp & paper industry.
- Coronel-García, M.A., Salazar-Barrera, J.G., Malpica-Maldonado, J.J., Martínez-Salazar, A.L., Melo-Banda, J.A., 2020. Hydrogen production by aluminum corrosion in aqueous hydrochloric acid solution promoted by sodium molybdate dihydrate. *Int. J. Hydrogen Energy* 45, 13693–13701. <https://doi.org/10.1016/j.ijhydene.2020.01.122>.
- Costa, C.A., Rubio, J., 2005. Deinking flotation: influence of calcium soap and surface-active substances. *Miner. Eng.* 18, 59–64. <https://doi.org/10.1016/j.mineng.2004.05.014>.
- Czajczyńska, D., Anguilano, L., Ghazal, H., Krzyżyńska, R., Reynolds, A.J., Spencer, N., Joughara, H., 2017. Potential of pyrolysis processes in the waste management sector. *Therm. Sci. Eng. Prog.* 3, 171–197. <https://doi.org/10.1016/j.tsep.2017.06.003>.
- Dhawan, H., Sharma, D.K., 2019. Advances in the chemical leaching (inorganic leaching), bio-leaching and desulphurisation of coals. *Int. J. Coal Sci. Technol.* 6, 169–183. <https://doi.org/10.1007/s40789-019-0253-6>.
- Fazil, A., Kumar, S., Mahajani, S.M., 2023. Gasification and Co-gasification of paper-rich, high-ash refuse-derived fuel in downdraft gasifier. *Energy* 263, 125659. <https://doi.org/10.1016/j.energy.2022.125659>.
- Gerlach, R., Nocerino, J., 2003. Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples. Environmental Protection Agency. EPA/600/R-03/027. United States.
- Gullett, B.K., Sarofim, A.F., Smith, K.A., Procaccini, C., 2000. The role of chlorine in dioxin formation. *Process Saf. Environ. Prot.* 78, 47–52. <https://doi.org/10.1205/095758200530448>.
- Ho, C.-Y., 2017. Hydrolytic reaction of waste aluminum foils for high efficiency of hydrogen generation. *Int. J. Hydrogen Energy* 42, 19622–19628. <https://doi.org/10.1016/j.ijhydene.2017.06.104>.
- Italia, C., 2018. Italy: Technologies and Prospects for the Recycling of Plastics from Pulper Waste. Paper Industry World.
- Jadhav, U., Hocheng, H., 2015. Hydrometallurgical recovery of metals from large printed circuit board pieces. *Sci. Rep.* 5, 14574 <https://doi.org/10.1038/srep14574>.
- Jerzak, W., Bieniek, A., Magdziarz, A., 2023. Multifaceted analysis of products from the intermediate co-pyrolysis of biomass with Tetra Pak waste. *Int. J. Hydrogen Energy* 48, 11680–11694. <https://doi.org/10.1016/j.ijhydene.2021.06.202>.
- Lal, K., Garg, A., 2017. Physico-chemical treatment of pulping effluent: characterization of flocs and sludge generated after treatment. *Sep. Sci. Technol. (Philadelphia)* 52, 1583–1593. <https://doi.org/10.1080/01496395.2017.1292294>.
- Liang, J., Gao, L.J., Miao, N.N., Chai, Y.J., Wang, N., Song, X.Q., 2016. Hydrogen generation by reaction of Al-M (M = Fe Co, Ni) with water. *Energy* 113, 282–287. <https://doi.org/10.1016/j.energy.2016.07.013>.
- Nel, J.L., 2021. Technical and economic comparison of pyrolysis and pelleting for valorisation of pulper rejects from a secondary tissue mill, as alternative to disposal.
- Onwudili, J.A., Insura, N., Williams, P.T., 2009. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time. *J. Anal. Appl. Pyrol.* 86, 293–303. <https://doi.org/10.1016/j.jaap.2009.07.008>.
- Ouadi, M., Brammer, J.G., Kay, M., Hornung, A., 2013. Fixed bed downdraft gasification of paper industry wastes. *Appl. Energy* 103, 692–699. <https://doi.org/10.1016/j.apenergy.2012.10.038>.
- Ouadi, M., Greenhalf, C., Jaeger, N., Speranza, L.G., Hornung, A., 2018. Thermo-catalytic reforming of pulper rejects from a secondary fibre mill. *Renew. Energy Focus* 26, 39–45. <https://doi.org/10.1016/j.ref.2018.07.004>.
- Ouadi, M., 2012. Sustainable energy from paper industry waste.
- Paz-Ferreiro, J., Nieto, A., Méndez, A., Askeland, M., Gascó, G., 2018. Biochar from biosolids pyrolysis: a review. *Int. J. Environ. Res. Public Health* 15, 956. <https://doi.org/10.3390/ijerph15050956>.
- Pranata Putra, W., Kamari, A., Yusoff, N.M., Fauziah Ishak, C., Mohamed, A., Hashim, N., Md Isa, I., 2014. Biosorption of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions using selected waste materials: adsorption and characterisation studies. *J. Encapsul. Adsorp. Sci.* 04, 25–35. <https://doi.org/10.4236/jeas.2014.41004>.
- Razali, H., Sopian, K., Mat, S., 2014. The application of aluminum and hydrochloric acid to produce hydrogen for internal combustion engine via hydrogen mixture with gasoline based on specific fuel consumption. *Adv. Mat. Res.* 875–877, 1804–1811. <https://doi.org/10.4028/www.scientific.net/AMR.875-877.1804>.
- Sahu, S.G., Mukherjee, A., Kumar, M., Adak, A.K., Sarkar, P., Biswas, S., Tiwari, H.P., Das, A., Banerjee, P.K., 2014. Evaluation of combustion behaviour of coal blends for use in pulverized coal injection (PCI). *Appl. Therm. Eng.* 73, 1014–1021. <https://doi.org/10.1016/j.applthermaleng.2014.08.071>.
- Salimbeni, A., Di Bianca, M., Lombardi, G., Rizzo, A.M., Chiaramonti, D., 2023a. Opportunities of integrating slow pyrolysis and chemical leaching for extraction of critical raw materials from sewage sludge. *Water (Basel)* 15, 1060. <https://doi.org/10.3390/w15061060>.
- Salimbeni, A., Di Bianca, M., Rizzo, A.M., Chiaramonti, D., 2023b. Activated carbon and P-rich fertilizer production from industrial sludge by application of an integrated thermo-chemical treatment. *Sustainability* 15, 14620. <https://doi.org/10.3390/su151914620>.
- Salimbeni, A., Rizzo, A.M., Chiaramonti, D., 2020. Integration of two-stage thermochemical treatment and chemical leaching for extraction of advanced biochar and high value critical raw materials from sewage sludge.
- Salimbeni, A., Lombardi, G., Rizzo, A.M., Chiaramonti, D., 2023c. Techno-economic feasibility of integrating biomass slow pyrolysis in an EAF steelmaking site: a case study. *Appl. Energy* 339, 120991. <https://doi.org/10.1016/j.apenergy.2023.120991>.
- Stanmore, B.R., 2004. The formation of dioxins in combustion systems. *Combust. Flame* 136, 398–427. <https://doi.org/10.1016/j.combustflame.2003.11.004>.
- Vagenas, N., Gatsouli, A., Kontoyannis, C.G., 2003. Quantitative analysis of synthetic calcium carbonate polymorphs using FT-IR spectroscopy. *Talanta* 59, 831–836. [https://doi.org/10.1016/S0039-9140\(02\)00638-0](https://doi.org/10.1016/S0039-9140(02)00638-0).
- van Krevelen, D.W., 1993. *Coal - Typology, Physics, Chemistry, Constitution*, third ed. Elsevier, Amsterdam, New York.
- Vounatsos, P., Agraniotis, M., Grammelis, P., Kakaras, E., Skiadi, O., Zampoutis, T., 2015. Refuse-derived fuel classification in a mechanical-biological treatment plant and its valorization with techno-economic criteria. *Int. J. Environ. Sci. Technol.* 12, 1137–1146. <https://doi.org/10.1007/s13762-014-0509-z>.
- Wang, H.Z., Leung, D.Y.C., Leung, M.K.H., Ni, M., 2009. A review on hydrogen production using aluminum and aluminum alloys. *Renew. Sustain. Energy Rev.* 13, 845–853. <https://doi.org/10.1016/j.rser.2008.02.009>.
- Win, M.M., Asari, M., Hayakawa, R., Hosoda, H., Yano, J., Sakai, S., 2019. Characteristics of gas from the fluidized bed gasification of refuse paper and plastic fuel (RPF) and wood biomass. *Waste Manag.* 87, 173–182. <https://doi.org/10.1016/j.wasman.2019.02.002>.
- Yang, Q., Li, Q., Zhang, G., Shi, Q., Feng, H., 2019. Investigation of leaching kinetics of aluminum extraction from secondary aluminum dross with use of hydrochloric acid. *Hydrometall.* 187, 158–167. <https://doi.org/10.1016/j.hydromet.2019.05.017>.
- Yılmaz, U., Tutus, A., Sönmez, S., 2021. An overview of the waste paper recycling system. In: Berkan, B. (Ed.), *Current Studies in Agriculture, Forestry and Aquaculture Sciences*. Duvar Publishing.
- Zhang, X., Brown, R.C., 2019. Introduction to thermochemical processing of biomass into fuels, chemicals, and power. In: *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*. Wiley, pp. 1–16. doi: 10.1002/9781119417637.ch1.
- Zhang, X., Zhong, Q., Liu, C., Rao, M., Peng, Z., Li, G., Jiang, T., 2021. Partial substitution of anthracite for coke breeze in iron ore sintering. *Sci. Rep.* 11, 1–12. <https://doi.org/10.1038/s41598-021-80992-4>.