Pyrolysis of polystyrene using low-cost natural catalysts: Production and characterisation of styrene-rich pyro-oils

David Royuela, Juan Daniel Martínez, María Soledad Callén, José Manuel López, Tomás García, Ramón Murillo, Alberto Veses

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, Zaragoza 50018, Spain

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ABSTRACT

This work aims to study the catalytic pyrolysis of polystyrene (PS) in order to obtain a styrene-rich liquid appealing for re-polymerisation processes. The process was performed in a fixed-bed reactor using low-cost materials such as ilmenite, olivine, calcium oxide (CaO) and dolomite as catalysts at 600 °C. A non-catalytic test with sand was also conducted for comparison purposes. The resulting pyro-oil yield was between 89 and 96 wt%, and consisted mainly of styrene monomer, styrene dimer and styrene trimer, as well as other light aromatic compounds depending on the catalyst used. Olivine and CaO were capable to increase the styrene monomer concentration in the pyro-oil by about 10–12 % compared to non-catalytic pyrolysis, reaching up to 74.5 and 71.4 wt%, respectively. Furthermore, these catalysts reduced the concentration of styrene dimer and styrene trimer in the pyro-oil, which could be useful for further re-polymerisation processes. However, the presence of polycyclic aromatic hydrocarbons (PAHs) in the pyro-oils obtained from ilmenite, olivine and CaO was also identified, and other families such as mono-aromatics, di-aromatics, BTX, and nitrogen heterocyclic compounds were also increased in all pyro-oils obtained with catalysts compared to those obtained by non-catalytic pyrolysis. In addition, several inorganic species in the pyro-oil were reduced by the addition of the catalysts. This effect was observed after the addition of olivine and CaO, especially in the reduction of S, Mg, Ca and Fe. These results clearly demonstrate the potential of pyrolysis to convert PS waste into valuable building blocks for the production of new plastics.

1. Introduction

Plastics have been an important part of innovation and development in various sectors. Their excellent properties have led to massive use worldwide [1,2]. According to Plastics Europe Association [3], the global production of plastics is steadily increasing every year. China leads the list of producing countries with a 32 % share, while Europe has a 15 % share. This large production has significant negative impacts on the environment once the plastics have reached the end of their useful life. It is estimated that approximately 60 % of all plastics produced between 1950 and 2015 were landfilled or released into the environment [4]. In 2020, 29.5 Mt of plastic waste were collected in the EU (EU27 plus Norway, Switzerland and the United Kingdom), of which only 34.6 % were recycled (10.2 Mt), 42 % used for energy recovery (12.4 Mt) and 23.4 % landfilled (6.9 Mt). In addition, between 1.5 % and 4 % of the world’s plastic production ends up in the oceans each year, i.e. about 5–13 Mt of plastic per year [5]. There is also a great concern about microplastics, tiny plastic fragments less than 5 mm in size, which accumulate in the environment and enter into the food chain, posing potential threats to both the environment and human health.

Plastics can be recycled in a number of ways, including mechanical and chemical recycling [6–8]. Mechanical recycling comprehends the reduction in size and extrusion of recycled plastics into pellets. This practice results in the polymer degradation over time, which reduces the performance of recycled plastic when compared to the virgin one; and therefore, limits the number of reuse cycles [8–10]. This recycling method requires sorting and cleaning steps, which increases the cost of recycling. Thus, the ability to meet the expected market demand for recycled plastics is limited [11,12]. On the other hand, chemical recycling involves depolymerisation (methanolysis, hydrolysis, glycolysis) and thermochemical (pyrolysis, gasification) processes. These technologies are expected to lead to different circular economy pathways such as recycling and remanufacturing. The efficiency of these processes is strongly dependent on the presence of chemical stabilisers, which are added to the plastics to prevent polymer degradation during transportation or storage.

* Corresponding author.
E-mail address: a.veses@icb.csic.es (A. Veses).
as plastic-to-fuel, plastic-to-intermediates, or plastic-to-plastics. Among other reasons, chemical recycling is critical to meeting the ambitious recycled plastic targets set by the EU. For example, by 2030, 60 % of municipal waste should be prepared for reuse and recycling (Revision of the Waste Framework Directive) and at least 70 % of all packing waste and 55 % of all plastic waste should be recycled (Directive EU/2018/852). It is worth noting that the use of plastic waste as fuel in energy-intensive facilities is not considered recycling, and is therefore not a sustainable solution from a circular economy perspective in the long term [11].

Pyrolysis is a thermochemical conversion technology capable of producing several families of hydrocarbons that can be used as precursors for chemical commodities or fuels. This technology is becoming increasingly relevant, especially for the recovery of contaminated plastics and complex and mixed streams of plastics that are hard to recover by conventional methods [7,13,14]. Furthermore, pyrolysis offers an integrated solution for waste management and greenhouse gas reduction without polluting water, soil and air, while contributing significantly to the circular economy [15–18]. Particularly, pyrolysis of plastic waste induces the thermal degradation of polymer chains into molecules of smaller size and less complexity [6,18,19]. For example, poly styrene (PS) or polymethyl methacrylate (PMMA) can produce high yields of the original monomer, while polyolefins such as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP) produce mainly hydrocarbon products in the form of waxes, oils and gases. Operating conditions, composition of derived products and key process information have been recently reviewed as found elsewhere [6,11,13,19].

PS is used in packaging, electronic devices, household items, insulation, medical equipment and automobiles because of its low cost and good properties such as heat resistance, lightness, durability and strength [7,11,13,20]. Global production of this polymer reached 29 Mt in 2019, of which 3.6 Mt were produced in Europe (6.2 % of total plastics demand). In contrast, global waste generation in 2019 was 18 Mt and it is forecasted to increase in the future [20–22]. As a result, the chemical recycling of PS by pyrolysis is highly attractive because the embedded styrene can be recovered, maximizing the circularity degree of this commodity rather than permanently landfilled or combusted in energy facilities.

PS is made of styrene monomer with a chemical structure consisting of long hydrocarbon chains with phenyl groups [19,23,24]. Styrene is a widely used building block in the manufacture of many products, and about 60 % of all styrene produced worldwide is used to make PS [25]. However, the success of pyrolysis of PS still faces a number of challenges. On the one hand, pyrolysis has heat and mass transfer limitations, so reactor type and optimal process conditions are still key variables that need to be optimised. Many studies show important differences in the yields and properties of the resulting liquid fraction, herein referred to as pyro-oil [26]. Several types of reactors have been studied to carry out the pyrolysis of PS. The most common are fixed bed reactors [23,27–33], fluidised bed reactors [13,34–40], and semi-batch reactors [41–47], conical spouted reactors [48,49] and those assisted by microwaves [50,51]. On the other hand, the styrene concentration and the presence of impurities are probably the main obstacles to overcome in order to introduce the pyro-oil into a polymerisation process [27,49,50,52].

The use of catalysts can promote a high concentration of valuable compounds in the pyro-oil. In particular, the use of solid acid catalysts such as those used in the petrochemical industry (zeolites and FCC), has been studied in numerous works [27,29,39,53–56]. However, the use of these types of catalysts has shown a reduction not only in the pyro-oil yield but also in the selectivity towards styrene, favouring the production of monoaromatics such as benzene, toluene or ethylbenzene [27,56–59]. According to a study by Ukei et al. [57], the yield of styrene obtained using HZSM5 was 50 wt%, compared to 56 wt% for thermal pyrolysis, and 71 wt% for BaO catalyst. At this point, basic catalysts are reported with potential to promote styrene recovery, as with several low-cost natural catalysts such as CaO, bentonite clays or dolomite. While catalytic pyrolysis studies of PS using these catalysts widely available is scarce, some authors report higher styrene selectivities compared to thermal pyrolysis [57,60,61]. Thus, it has been reported that styrene production from PS pyrolysis using CaO was 62.5 wt% [57]. In addition, there is a lack of information in the literature on the role of contaminants in the pyro-oil, and the presence and composition of trace metals is still a largely unexplored area [26]. Metals are considered hazardous and undesirable inorganic elements due to their persistence and toxic and bioaccumulative effects [62–64]. Although there are some works in the literature dealing with the presence of these compounds for different applications [26,30,65,66], strategies to reduce their concentration while increasing the styrene monomer are hardly reported. The presence of certain aromatic compounds or metallic components in the pyro-oil can act as chain transfer agents, reducing the average molecular weight of the resulting polymer [27]. Therefore, a detailed characterisation to assess the presence of possible inhibitors and to investigate their potential for further repolymerisation is necessary to improve the knowledge of the composition of pyro-oil. In this way, catalytic pyrolysis has the potential not only to promote styrene selectivity but also to enhance and facilitate its repolymerisation. It is therefore vital to address this challenge and provide a complete database for further pyrolysis work in which most of the components in the pyro-oil are determined and quantified.

This work deals with the pyrolysis of PS using low-cost and natural catalysts such as ilmenite, olivine, calcium oxide (CaO) and dolomite to obtain a complete pyro-oil characterisation including both aromatic components and metals. The experiments were conducted in a laboratory scale fixed bed reactor process and the resulting pyro-oil was fully characterised by GC, GC/MS for chemical species, and XRF for inorganic elements.

2. Materials and methods

2.1. Feedstock

PS waste from fish packaging was used in this study. The material was supplied by ACTECO in granular form (particle size between 2 and 4 mm) and was characterised by ultimate analysis according to UNE-EN 15407:2011 (Thermo Flash 1112 and LECO 628). Proximate analysis was also performed in order to determine the content of moisture, ash and volatile matter in accordance with UNE-EN 15414–3:2011, UNE-EN 15403:2011 and UNE-EN 15402:2011, respectively. Fixed carbon was determined by balance. Additionally, the calorific value was measured in accordance with UNE-EN 15400:2011 (Parr 6400). The ash composition of PS was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Xrebluex-EOP-TI FMT26 (Spectro). The results obtained for the main properties of the PS sample are shown in Table 1.

As it can be seen in Table 1, PS is a carbon-rich feedstock (92.1 wt%) mainly composed of volatiles (98.4 wt%). Thus, the proximate analysis suggests a very suitable and promising feedstock to be subjected to a thermochemical recycling process such as pyrolysis, which implies high pyro-oil yields and very high styrene concentrations. It is also worth noting that the ultimate analysis fails to detect sulphur, as well as the very low concentration of nitrogen and a virtually negligible presence of oxygen. The absence of sulphur cannot be assumed as it is detected in the ash composition analysis, which may be due to additives or even organic residues. According to the literature, the nitrogen is likely to come from organic residues that have been in contact with the PS [26,67]. In general, all these elements (sulphur, nitrogen, and oxygen) along with metals, are the major contaminants in plastics that must be considered for the successful implementation of a thermochemical recycling process [26].

On the other hand, the calorific value of the PS used in this work is
high (HCV = 41.2 MJ/kg), greater than solid fuels such as coal, and comparable to petroleum-based hydrocarbons such as gasoline and diesel [68,69]. Additionally, an analysis of the chemical composition of the ash was carried out. For this purpose, the sample was calcined, homogenised and ground in an agate mortar. The sample was then dissolved in HCl 1/20. The sample was then filtered through a 0.45 μm membrane. The concentrations of Ca, Mg, and Ti were determined by ICP analysis. The concentrations of Al, Si, P, S, Fe, K, Mn, Na, and Zn were determined by ICP-MS analysis. The concentrations of other elements were determined by XRF analysis. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.32</td>
</tr>
<tr>
<td>Ca</td>
<td>11.8</td>
</tr>
<tr>
<td>Fe</td>
<td>5.2</td>
</tr>
<tr>
<td>K</td>
<td>0.55</td>
</tr>
<tr>
<td>Mg</td>
<td>2.3</td>
</tr>
<tr>
<td>Mn</td>
<td>0.06</td>
</tr>
<tr>
<td>Na</td>
<td>0.5</td>
</tr>
<tr>
<td>P</td>
<td>0.04</td>
</tr>
<tr>
<td>S</td>
<td>0.10</td>
</tr>
<tr>
<td>Si</td>
<td>0.45</td>
</tr>
<tr>
<td>Ti</td>
<td>16.3</td>
</tr>
<tr>
<td>Zn</td>
<td>3.08</td>
</tr>
</tbody>
</table>

Table 1: Characterisation of PS.

2.2. Thermogravimetric analysis

The aim of the thermogravimetric study was to evaluate the thermal behaviour of the PS sample under pyrolysis conditions by determining the weight loss and rate of weight loss, namely TGA and DTG respectively. This study began at room temperature and progresses to 700 °C at a heating rate of 100 °C/min in an N2 atmosphere. These conditions were chosen to match those of the fixed bed reactor during the pyrolysis experiments, rather than to facilitate to perform a proper kinetic or detailed decomposition analysis. This analysis was performed in a Netzsch Libra F1 thermobalance. The sample weight used in all experiments was approximately 9 mg, and the carrier gas was N2 at a flow rate of 50 Nml/min.

2.3. Catalysts

Four different natural minerals (ilmenite, olivine, calcium oxide and dolomite) that are inexpensive, readily available and have no environmental impact associated with their synthesis were selected as catalysts for this study. Ilmenite (general formula: FeTiO3), consists mainly of Fe and Ti oxides although it also contains Mn, Mg, V, Ni and Cr as trace elements [73-75]. On the other hand, the composition of olivine is defined by the chemical formula (Mg,Fe)2SiO4, and is characterised by high amounts of MgO and SiO2 (51.6 wt% and 36.5 wt%, respectively), as well as a significant Fe2O3 content (10.2 wt%) [76]. Calcium oxide consists mainly of CaO (95 wt%), which is also found in dolomite (CaMg (CO3)2) together with MgO (47.6 wt%, and 33.2 wt%, respectively) [77]. The particle size of the sand, dolomite and CaO used is 300–600 μm, while that of olivine is between 400 and 600 μm, while ilmenite is between 100 and 300 μm. It should also be noted that all the catalysts were dried, and the dolomite and CaO were calcined previously.

2.4. Fixed bed reactor

Pyrolysis experiments were carried out in a stainless steel fixed-bed reactor (52.5 cm long and 5 cm internal diameter). A brief diagram of the process is shown in Fig. 1. This process was designed with the peculiarity of having a vertical moving piston, known as a liner, into which the sample is introduced. The reactor is heated by an external electrical resistance. Once the required temperature is reached in the reactor zone, the liner is moved down into the reaction zone, ensuring fast heating rates for the devolatilisation process (around 100 °C/min). Samples of 10 g of PS previously mixed with different catalysts at a PS-to-catalyst ratio of 3–1 by weight were pyrolysed at 600 °C using N2 as a carrier gas (400 mL/min).

Although the introduction of catalysts into the pyrolysis process is expected to reduce the temperature, the highest styrene selectivity was found at 600 °C based on previous studies carried out in this specific reactor. Similar results have been reported using fixed bed or fluidised bed reactors, where optimum temperatures for styrene production have been identified at 550 °C or 600 °C without the addition of catalysts [37, 52]. The temperature used in this work may appear higher than those reported in the literature, but it should be noted that many factors also affect the selection of this value, such as the influence of the reactor configuration and the role of mass and energy transfer. Therefore, there is not necessarily a single value for temperature, although this is the key parameter in pyrolysis. In addition, it is worth mentioning that the aim of this work is to elucidate the behaviour of readily available materials in promoting styrene selectivity under reasonable conditions, and 600 °C is quite promising and assertive for further exploration at high technological readiness levels.

On the other hand, the duration of the experiments was set to 25 min. However, a short residence time of the volatiles is ensured in order to reduce the occurrence of cracking reactions. A tailor-made water reflux condenser at 7 °C was used to collect the condensable fraction, referred to as pyro-oil, while the non-condensable gases were sampled for gas chromatographic analysis. The yields of pyro-oil and of any residual carbonaceous solids were determined by weight. In contrast, the yield of non-condensable gases was calculated from the composition of the sampled gas. It should be noted that no non-condensable fractions were detected in the subsequent cold sections of the plant prior to gas sampling. Furthermore, the quantification of non-condensable compounds was nearly 100 vol%, which confirms the complete condensation of the pyro-oil. Each run was performed three times, maintaining a relative standard deviation (RSD) of less than 5 % in the product yields. Only those experiments with a mass balance of 100 ± 5 % were considered as valid.

2.5. Product characterisation

The non-condensable gases were analysed in a Bruker 450 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Separation was performed by using two stainless steel packed columns in series (Molsieve 13X and HayeSep Q). An oven temperature of 60 °C was maintained for 10 min. The carrier gas was Argon at a constant column flow rate of 30 Nml/min. The TCD temperature was...
200 °C. The permanent gases analysed included H₂, CO₂, O₂, N₂ and CO. Certified gas mixtures (Air Products) were used for identification and quantification purposes. Subsequently, light hydrocarbons (C₁–C₄) were analysed in a PerkinElmer Clarus 590 gas GC equipped with a flame ionisation detector (FID). Separation was performed by a 30-m-long and 0.32-mm-wide alumina chloride capillary column. The light hydrocarbons analysed included methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), propane (C₃H₈), propylene (C₃H₆), isobutene and n-butane (C₄H₁₀), and trans-2-butene, 1-butene, isobutene, cis-2-butene and 1,3-butadiene (C₄H₆). Peaks corresponding to hydrocarbons with more than 4 carbon atoms (C₅+) are also observed at the end of the chromatogram. These were quantified using a response factor based on the carbon number, which was previously calculated for the FID. An initial oven temperature of 40 °C was maintained for 2.5 min, after which a heating rate of 5 °C/min was implemented to reach an oven temperature of 90 °C. The heating rate was then increased to 15 °C/min to reach the final oven temperature of 180 °C. This temperature was maintained for 4.5 min. The carrier gas was helium with an initial pressure of 9 psi for 16 min, then raised to 18 psi. The injector and FID temperatures were both 250 °C. Certified gas mixtures (Air Products) were used for identification and quantification purposes.

The pyro-oils were characterised by gas chromatography (GC) using a Perkin Elmer Clarus 590 equipped with a wide-range FID detector and a 60-m DB-5 ms capillary column (0.25 mm ID and 0.25 μm df). The initial oven temperature (40 °C) was maintained for 1 min. Then, a heating rate of 5 °C/min was set in order to reach a final oven temperature of 290 °C. Helium was used as carrier gas at a constant column flow rate of 1 Nml/min. 300 °C and 325 °C were the split/splitless injector and wide-range FID temperatures, respectively. The sample volume injected was 0.5 μl with an auto sampler and a split ratio of 1:30. Thus, the concentration of benzene, toluene, ethylbenzene, styrene monomer, ethylvinyl benzene + divinyl benzene, and styrene dimer and trimer was determined.

On the other hand, a Clarus 690 gas chromatograph coupled to a Clarus SQ8 quadrupole mass spectrometer (Perkin-Elmer) (GC/MS) was used for the qualitative analysis of the chemical composition of the pyro-oils. The system was equipped with a capillary column, Elite-5 ms (5 % diphenyl-/95 % dimethylpolysiloxane; 60 m x 0.25 mm, 0.25 mm; Perkin-Elmer). The oil was diluted 10 times with dichloromethane/ethanol (1:1) Volume. 1 microliter of sample was automatically injected with an auto-sampler at 280°C with a split flow of 25 ml/min. The oven temperature program was: 40°C constant for 4 min, 40–300°C at a rate of 4°C/min and then constant for 21 min. Helium was used as the carrier gas at a constant pressure of 39 psi). The temperatures of the source and the inlet line were kept at 250°C and 260°C, respectively. The mass spectrometer operated in the electron ionisation mode (70 eV) and full scan mode (35–305 m/z range). ass spectra interpretation was performed using an automatic search in the NIST2020 library. Additionally, metal content in the pyro-oil was determined on a Malvern-Panalytical Epsilon 3 × ED-XRF instrument using the OMNIAN (internal standards) methodology. The results were normalized to 100 % using the appropriate balance composition. The results represent the average of three determinations. The error, which is below 2 %, has not been included for clarity.

3. Results and discussion

3.1. Thermogravimetric analysis

The results obtained for weight loss and rate of weight loss for the PS sample are shown in Fig. 2. PS degradation is observed to occur in a single step within a narrow temperature range (400 – 500 °C), with very rapid devolatilisation. The presence of a single peak in the DTG curve indicates not only that the sample consists of a single polymer but also that the degradation of the monomer present, in this case styrene, is occurring. Similar observations are reported elsewhere [78,79]. In addition, the maximum rate of mass loss is observed at 440 °C. As pointed out by several authors, the thermal degradation by pyrolysis of this polymer is roughly explained by random scission to form macroradicals and macromolecules, followed by chain-end scission reactions that finally lead to the monomer [23,80–83].

3.2. Products yields

A summary of the yields of pyro-oil and gas fraction after the pyrolysis experiments is shown in Fig. 3. It is worth noting the high
production of pyro-oil, and the apparent absence of a carbonaceous and inorganic solids, despite the ash content reported in Table 1. The lack of solids after pyrolysis of PS has been observed elsewhere [18,19,27,49]. Under proper pyrolysis conditions, PS decomposition does not lead to the formation of carbonaceous complexes in the resulting solid fraction as the amount of fixed carbon is practically negligible, but inorganic matter in the ash could be transferred either to the pyro-oil or gas, to the catalyst bed, or be trapped within the reactor walls. However, although it was not possible to quantify this accurately, the ash content will need to be considered in future scale-ups of pilot plant processes. The highest pyro-oil yield was obtained in the non-catalytic experiment (using an inert solid such as silica sand), reaching 96.9 wt%. However, after catalytic experiments, the pyro-oil yield slightly decreased. For ilmenite, olivine and CaO, these yields were between 94 and 96 wt%. The lowest pyro-oil yield (89.3 wt%) was found using dolomite. Compared to the other catalysts, dolomite appears to have a higher catalytic effect regarding the increase in the yield of low molecular weight compounds.

Table 2 shows the gas composition expressed in g of each component/100 g of PS. In general, the gas from the non-catalytic PS pyrolysis consist mainly of H2 and hydrocarbons, especially C4H4, C4 and >C4 compounds. This composition is in line with the literature, which states that the pyrolysis of PS results in a gaseous product rich in CH4, C2H2, C2H4, C3H6, and C6H6 [19,27,37,49]. The presence of CO2 can also be observed, which may be associated with the presence of organic residues, various oxygenated additives or even a minor content from catalysts [26,27]. On the other hand, the role of basic metal oxide catalysts as a deoxygenation and cracking pathway is well documented and is related to the higher presence of CO and CO2, as reported elsewhere [84]. It can also be seen that the H2 content increased with the use of all catalysts, which may be associated with cracking reactions that could favour styrene production [35,49]. Table 2 also shows the ratio between each gas for each experiment using catalysts and that produced without any catalyst, indicating whether there was an increase (+) or a decrease (-). It is observed that the gas yield increases when the ilmenite, olivine, CaO and dolomite are added to the pyrolysis, in full agreement with the yields shown in Fig. 3.

The highest gas yield is found with dolomite (10.6 g/100 gPS), followed by ilmenite (5.8 g/100 gPS) olivine (4.9 g/100 gPS) and CaO (3.8 g/100 gPS). This pattern suggests a clear effect of these catalysts on the pyrolysis of PS, at least towards the production of gases, and an indicator of selectivity can be elucidated from the ratios shown in Table 2. H2 production is strongly pronounced in the case of the CaO, which could result in higher styrene recovery, as shown elsewhere [85]. It is also worth highlighting the high presence of hydrocarbon compounds (C3, C4 and > C4) for all catalysts, particularly those produced when dolomite is used.

### 3.3. Pyro-oil characterisation

#### 3.3.1. GC analysis

Fig. 4 shows the main composition of the pyro-oils obtained after pyrolysis in terms of styrene, styrene dimer, styrene trimer, ethylvinylbenzene + divinylbenzene, benzene, toluene and ethylbenzene, which account for 75–80 wt%. It can be observed that the most abundant compound in all the pyro-oils is styrene monomer (between 65 and 75 wt%), followed by styrene dimer (between 2.1 and 5.1 wt%) and styrene trimer (between 0.3 and 5.7 wt%). The highest concentrations of styrene dimer and styrene trimer in the pyro-oils are found in the non-catalytic pyrolysis (5.1 and 5.7 wt% respectively), and are significantly lowered when ilmenite, olivine, CaO and dolomite are used, while the styrene concentration is increased. The basic catalysts are expected to produce carbonabions (intermediates in the depolymerisation of PS) formed by the removal of hydrogen atoms adsorbed on the base sites of

<table>
<thead>
<tr>
<th>Gas</th>
<th>PS-Sand</th>
<th>PS-Ilmenite</th>
<th>PS-Olivine</th>
<th>PS-CaO</th>
<th>PS-Dolomite</th>
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</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.048</td>
<td>0.083</td>
<td>1.73 (+)</td>
<td>0.113</td>
<td>2.35 (+)</td>
</tr>
<tr>
<td>CO</td>
<td>0.000</td>
<td>0.325</td>
<td>(+)</td>
<td>0.335</td>
<td>0.183</td>
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<td>CO2</td>
<td>0.853</td>
<td>1.420</td>
<td>1.66 (+)</td>
<td>1.628</td>
<td>1.91 (+)</td>
</tr>
<tr>
<td>CH4</td>
<td>0.095</td>
<td>0.155</td>
<td>1.63 (+)</td>
<td>0.139</td>
<td>1.46 (+)</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.045</td>
<td>0.039</td>
<td>0.87 (-)</td>
<td>0.033</td>
<td>0.73</td>
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<td>C2H4</td>
<td>0.125</td>
<td>0.362</td>
<td>2.90 (+)</td>
<td>0.320</td>
<td>2.56 (+)</td>
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<tr>
<td>C3</td>
<td>0.063</td>
<td>0.163</td>
<td>2.59 (+)</td>
<td>0.137</td>
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<tr>
<td>C4</td>
<td>0.087</td>
<td>0.000</td>
<td>(+)</td>
<td>0.000</td>
<td>0.090</td>
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<tr>
<td>&gt;C4</td>
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<td>Total</td>
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<td>5.8</td>
<td>1.87 (+)</td>
<td>4.9</td>
<td>1.58 (+)</td>
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</table>

The Gas composition (g/100 g PS feeding).
The concentration of the styrene dimer in the pyro-oil was reduced by half, regardless of the catalysts used. In addition, the reduction in styrene trimer concentration with respect to non-catalytic pyrolysis was more pronounced, being reduced up to 15 times in the case of olivine. This catalyst also leads to the highest styrene monomer concentration in the production of styrene monomer. Therefore, these carboxanions are thought to lead to more styrene monomer rather than carbo-cations (generated by acidic catalysts) or carbo-radicals intermediates [57, 87–89].

The presence of these styrene oligomers is not considered beneficial for polymerisation reactions [91,92]; therefore they need to be reduced in order to promote the use of pyro-oil as a feedstock for the manufacture of new PS products. CaO also leads to a high concentration of styrene monomer in the pyro-oil (74.5 wt%), which implies a 12 % increase over the non-catalytic test. This is a very interesting outcome because all styrene-containing compounds are considered to be the primary pyrolysis products of PS pyrolysis, so styrene dimer and styrene trimer are not formed by the recombination of styrene monomer [90]. Furthermore, the presence of these styrene oligomers is not considered beneficial for polymerisation reactions [91,92]; therefore they need to be reduced in order to promote the use of pyro-oil as a feedstock for the manufacture of new PS products. CaO also leads to a high concentration of styrene monomer in the pyro-oil (74.5 wt%), which indicates a 12 % increase over the non-catalytic test. This catalyst also leads to the highest styrene monomer concentration in the production of styrene monomer. Therefore, these carboxanions are thought to lead to more styrene monomer rather than carbo-cations (generated by acidic catalysts) or carbo-radicals intermediates [57, 87–89].

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On each compound can be found in the supporting information (Table S1–S5). Interestingly, similar compounds were identified for the non-catalytic test and the dolomite test. However, the number of these compounds increased for the remaining catalysts. Thus, 27 compounds were identified for the non-catalytic test, 28 for dolomite, 43 for ilmenite, 46 for CaO, and 53 for olivine.

Fig. 5 reveals the notorious presence of styrene-containing compounds such as styrene dimer, styrene trimer, as well as α-methyl-styrene, which was not identified by GC. It is observed that styrene dimer and styrene trimer follow the same tendency found in the GC results, as their presence decreases for all catalysts, being more pronounced for ilmenite, olivine and CaO. It is also seen that the presence of α-methylstyrene in the pyro-oil, even for that obtained in the non-catalytic pyrolysis, seems to increase regardless of the catalyst used. Fig. 5 also shows the presence of mono-aromatics and BTX in all the pyro-oils, which are present in higher proportions in all the pyro-oils obtained by using these catalysts, in agreement with the GC results. The presence of di-aromatics is also observed in the pyro-oils. With respect to the non-catalytic pyrolysis, these compounds are increased in those obtained with ilmenite, olivine and CaO, and to a lesser extent in that obtained with dolomite. These outcomes support the catalytic activity when low-cost natural materials are used during the pyrolysis of PS, as discussed above.

On the other hand, the nitrogen heterocyclic compounds consist mainly of compounds of 2,3-diazabicyclo and 1 H-2,3-benzodiazepine. It should be noted that the presence of these nitrogen compounds is linked to the presence of possible organic residues, as mentioned above. The relevance of this family group is that it can have a deteriorating effect during the repolymerisation processes. According to Mandal [93], nitroxide radicals could be responsible for preventing the onset of styrene polymerisation. Oxygenated compounds within the group of nitrogen heterocyclic compounds such as 2,3-diazabicyclo[2.2.1]hept-2-ene,1,4-diphenyl-, n-oxide are also observed in all the samples. In addition, the presence of 1,3,5,7-cyclooctatetraene-1-propanol was found in the pyro-oil of olivine, ilmenite and CaO, as well as aceto phenone in the pyro-oil with CaO. In addition, 5-H-dibenzo[a,d]cyclo hepten-5-one was detected in the pyro-oil with ilmenite. The relevance of these oxygen compounds in the pyro-oils makes sense because they could react with carbon radicals leading to the formation of peroxy radicals during the repolymerisation process [93].

A large number of PAHs are also observed in the pyro-oils derived from ilmenite, olivine and CaO, as shown in Fig. 5. Interestingly, no PAHs are found in the pyro-oil obtained with dolomite or in the pyro-oil from the non-catalytic pyrolysis. The importance of these compounds in the pyro-oils lies in the fact that they are moderately persistent in the
environment and are potentially bio-accumulative, carcinogenic, mutagenic and potent immunosuppressants. In this sense, it is interesting to note that PAHs appeared in the pyro-oils with the highest styrene monomer concentration. Single-ring compounds such as styrene and benzene can be considered PAHs precursors, which can be formed via the HACA mechanism [94,95]. Naphthalene, the simplest PAH, is only present in the pyro-oils from catalytic pyrolysis. Of all the PAHs, via the HACA mechanism [94,95]. Naphthalene, the simplest PAH, is and benzene can be considered PAHs precursors, which can be formed about 92 % for the ilmenite with naphthalene being the most abundant 2-ring PAH. For the olivine, on the other hand, only 5 % of 4-ring PAHs are reported, all of which are pyrene.

It should be noted that the increased complexity of pyro-oil samples from catalytic pyrolysis could be used as an opportunity to facilitate the purification of styrene. In this way, compounds with different boiling points such as PAHs, could easily be separated into a heavy fraction along with α-methylstyrene and the styrene dimer and trimers, which could negatively affect the repolymerisation process. The resulting fraction from this separation process can be upgraded by hydrocracking or even recycled back into the pyrolysis reactor as a source of styrene [49,96]. On the other hand, compounds such as benzene (boiling point 80.1 °C), ethylbenzene (boiling point 136 °C) and toluene (boiling point 110.6 °C) could be separated into a light fraction. This would isolate styrene (boiling point 145 °C) from these aromatics that act as chain transfer agents in polymerisation processes.

3.4. Inorganic elements in the pyro-oil

The presence of inorganics in the pyro-oils is closely related to the nature of the feedstock, and also to the permanent deactivation of a large number of active sites in the catalysts [14,67]. As mentioned above, these elements could have a negative effect on the repolymerisation processes, as they are likely to be carried out of the reactor and to some extent into the pyro-oil, as it is found elsewhere [26,36,97]. In this sense, Table 3 shows the main inorganics identified and quantified in the pyro-oils using the low-cost natural catalysts targeted in this work. It is observed that some of the metallic elements present in the feedstock (see Table 1) such as Na, Si, Al and K, were not detected in the pyro-oils. However, it is interesting to note the presence of other metals such as Cd, Mo, Ag, Cu, Ni, Sn, and V, which are below 1 ppm. These inorganic elements may be linked to the composition of the PS or the catalyst or, a lesser extent, to contamination from the fixed-bed reactor itself. The presence of these elements, especially V and Ni are considered as undesirable because they are difficult to remove, often in the form of porphyrins or asphaltene [98]. Ba, Cr, Mn, Pb and Sb were also detected in the range of 1–5 ppm. To the best of the authors’ knowledge, there are no studies in the literature that demonstrate the negative effect of these elements on the re-polymerisation process of PS.

The main species identified in the pyro-oil obtained from the non-catalytic experiment were S (395 ppm), Mg (26.5 ppm), Ca (17.9 ppm), Fe (7 ppm) and Zn (2.6 ppm). Therefore, the resulting pyro-oil from the pyrolysis of PS using these natural catalysts is expected to minimise interference with the molecular weight of the final polymer [99,100]. The above elements were reduced by the use of the catalyst. Thus, the pyro-oil from the non-catalytic experiment presents 395 ppm of S, and was reduced to 26 and 58 ppm using CaO and olivine, respectively. In this case, hydrodesulphurisation or selective oxidation, two of the most important common desulphurisation processes, could be avoided or minimised [101]. However, this significant reduction of S may lead to a sharp reduction of the catalytic effect of these catalysts [102]. A high S content may hinder the use of these materials in future applications, so this issue should be the subject of future studies.

Mg was also reduced from 26.5 ppm to 16.3 ppm in the case of CaO and to less than 5 ppm in the case of olivine. Ca was also reduced from 17.9 ppm to 8.6 ppm by the use of olivine, while the pyro-oil with CaO resulted in less than 1 ppm. The use of dolomite (CaMg(CO3)2) resulted in Ca and Mg in the resulting pyro-oil of 1334 ppm and 3252 ppm, respectively. These values represent the maximum concentrations of all samples. Although this behaviour may be related to experimental error due to the minimum sample amount used in these analytical techniques, future studies are needed to clarify this issue. Both elements have been reported to cause some reactions, reducing the yield of pyro-oil from the pyrolysis of PS [28]. Their presence in the pyro-oil with dolomite is in full agreement with the results shown in Fig. 3, since the pyro-oil yield is the lowest. According to the literature, Ca and Mg can also increase the content of mono-aromatics in the pyro-oils [28,67].

Zn is commonly used as an additive in plastics, and its presence was confirmed in Table 1. Zn was present in the resulting pyro-oil obtained without catalysts (2.6 ppm) and was also reduced to negligible levels (<1 ppm) in the pyro-oils with ilmenite, olivine, and CaO. Other authors have also demonstrated the presence of Zn in the pyro-oil from plastic waste and packaging [103–105], stating that distillation is the main step for upgrading pyro-oil. Fe in the pyro-oil acts as an inhibitor of styrene polymerisation [93], and was reduced from 7 ppm (for the non-catalytic experiment), to less than 1 ppm for olivine and to a lesser extent by CaO (5.1 ppm). The presence of Fe is critical in some thermochemical post-treatments, as the allowed limits are quite low, requiring various removal technologies such as hydrodemetallisation, solvent extraction or membrane filtration [98,106]. In this line, distillation and acid demetallisation have also been reported as upgrading steps for the oil obtained from the pyrolysis of plastic waste, capable of reducing the load of metal contaminants and even saturate olefinic and aromatic compounds through catalytic hydrotreatment [70,107,108]. Although Cu in Table 3 shows negligible values, cupric halides have also been reported to act as polymerisation inhibitors. In particular, CuCl2 is considered to be a stronger chain terminator than FeCl3. In their ionic form, these metals also retard polymerisation by oxidative termination.

It is also interesting to highlight the presence of P in the pyro-oil with the natural catalysts. P was present in the feedstock (see Table 1), and levels of less than 1 ppm were found in the pyro-oil obtained after the
non-catalytic test. However, the concentration of P increased in the pyro-oils from the catalytic experiments. Unfortunately, the presence of halogenated metals was not investigated, but the presence of Cl and Br, both present as adsorbed salts from food packaging, cannot be excluded [26,70]. The presence of these metals is considered detrimental to many other applications of pyro-oil. In summary, not only has the styrene fraction been increased and some aromatics reduced, but also the metal content of some species has also been reduced through the use of different low-cost natural catalysts. In particular, both olivine and CaO have been shown to have a positive effect on the quality of the pyro-oil obtained from the pyrolysis of PS.

4. Prospects for future studies

The results of this study provide a useful database for product characterisation, particularly for the pyro-oil. This work validates the potential use of inexpensive natural catalysts to promote styrene concentration and reduce oligomers and metals in the resulting pyro-oil. However, there appear to be several challenges in making this strategy more comprehensive:

- Further work is required to adjust the optimal operating conditions, such as temperature and the catalyst-to-feedstock ratio, as the process is scaled up to higher technological readiness levels. Although this study provides initial values, further work should include other critical variables such as reaction time, pressure, and feedstock composition. By systematically varying these parameters, the conditions that maximise styrene yield and selectivity can be identified. Additionally, the influence of catalyst type and its properties, such as surface area and active sites, should be investigated to improve catalytic performance.
- As the catalytic effect of these materials is expected to decrease significantly over time, a comprehensive study is required to evaluate the stability and reusability of the catalyst over multiple operating cycles due to the deactivation or poisoned problems associated with metal/sulphur retention. The effect of potential impurities in the feedstock on the performance of the catalyst and the overall reaction should also be assessed. Through such comprehensive optimisation, the process can be fine-tuned to achieve the highest efficiency and productivity.
- Rather than focusing solely on regeneration, further studies exploring new alternatives for these materials, for example in the materials sector, also offer an interesting opportunity to improve circularity [109]. The regeneration processes commonly used for synthetic catalysts do not appear very attractive given the high energy and economic input involved. Fillers/additives in cement production, light aggregates, etc. are likely to be other applications for these spent catalysts [109,110].
- The ultimate goal of using these natural catalysts is to facilitate the pyro-oil upgrading steps before it can be used in repolymerisation processes. At this point, repolymerisation studies of enhanced pyro-oil obtained from the use of ilmenite, olivine, CaO and dolomite are required. In this way, the effect of the compounds present in the pyro-oil should be considered in future studies focused on the repolymerization of pyro-oil obtained from the PS pyrolysis.

5. Conclusions

A thermal and catalytic pyrolysis process of PS waste was successfully carried out in a laboratory-scale fixed bed reactor facility. The interest in PS pyrolysis lies in the production of styrene monomers as building blocks for new PS production. Experiments were performed with four different low-cost and widely available natural catalysts (ilmenite, dolomite, olivine and CaO) to maximise the yield of styrene monomer. The results demonstrate the clear potential of these materials to produce a valuable styrene-rich pyro-oil. The main product of PS pyrolysis was mainly styrene monomer, followed by styrene dimer and trimer. For ilmenite, olivine and CaO, the styrene concentration exceeds 70 wt%, reaching the maximum styrene using olivine (74.5 wt%), while the concentration of styrene oligomers is reduced. The reduction in metal content has also been demonstrated, particularly when olivine and CaO are used. These inexpensive natural catalysts are therefore seen as the most promising way of improving styrene production. The characterisation of the pyro-oils obtained in this work is expected to provide a useful database for the further development and use of pyrolysis of PS waste to achieve plastics circularity.

CRediT authorship contribution statement

David Royuela: Writing – original draft, Methodology, Investigation, Formal analysis. Juan Daniel Martínez: Writing – review & editing, Validation, Supervision, Data curation, Conceptualization. María Soledad Callén: Writing – review & editing, Software, Formal analysis. Jose Manuel López: Software, Formal analysis. Tomás García: Writing – review & editing, Validation, Supervision, Resources, Conceptualization. Ramón Murillo: Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. Alberto Veses: Writing – review & editing, Validation, Supervision, Investigation, Data curation, 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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2024.106690.

References

