



Cite this: *Sustainable Energy Fuels*,  
2023, 7, 3067

Received 28th February 2023  
Accepted 29th May 2023

DOI: 10.1039/d3se00263b

rs.c.li/sustainable-energy

## Characterization of sulfur and chlorine behavior during pyrolysis of biomass and waste

Hala Braidy,<sup>ab</sup> Sylvie Valin<sup>\*a</sup> and Fabrice Patisson<sup>b</sup>

The aim of this study is to characterize the behavior of sulfur and chlorine during the pyrolysis of biomasses (agricultural residues: corn residues and colza straw) and waste components (cardboard, wool, and PVC), selected for their different compositions and ash contents. Pyrolysis experiments were performed between 365 and 850 °C. The major parts of S for wool and cardboard, and Cl for PVC, initially present in organic forms, are easily released into the gas phase, even below 550 °C, with no interaction with ash-forming elements. For the agricultural residues, both the organically and inorganically associated S contribute to its release. Cl, initially mainly present in inorganic chloride salts (KCl, KClO<sub>4</sub>...), is only partly released. In the remaining char for colza straw, sulfur is associated with calcium as CaSO<sub>4</sub>, reduced to CaS above 800 °C; for corn residues, sulfur and chlorine are found as K<sub>2</sub>SO<sub>4</sub>, KCl and MgCl<sub>2</sub>.

### 1. Introduction

To reduce the dependence on fossil fuels and to push forward a circular economy, the gasification of renewable or non-valorized carbonaceous resources (biomass, waste) allows to produce a synthesis gas (mainly composed of H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>), which can then be used as a form of energy or transformed by catalytic synthesis into fuel or other chemical raw materials. However, volatile inorganic elements (S, Cl, N) found in carbonaceous resources are often released in the gas phase during gasification; these may be harmful to the post-gasification processes due to their corrosive nature (HCl, KCl, NaCl...) and their poisoning effect on catalysts (H<sub>2</sub>S, COS).

In recent years, there has been an uptake in experimental and thermodynamic studies on the gasification of biomass and/or waste rich in inorganic elements, with a particular focus on characterizing gaseous inorganic pollutant emissions (H<sub>2</sub>S, COS, HCl, NaCl, NH<sub>3</sub>...). Various parameters related to the feedstock and the operating conditions (temperature, type of oxidant, equivalence ratio) during the gasification process influence the behavior of these emissions and their release mechanism.<sup>1–5</sup> Moreover, different quantities and chemical forms of inorganic elements have been identified in carbonaceous resources correlating with the type of material of origin and making the link with their release under thermal treatment. Investigating the association of ash-forming elements in the fuel structure seemed an important aspect to understand their release behavior. Studies in the literature have investigated the relationship between the different chemical forms of

sulfur in coal and their behavior during pyrolysis.<sup>6,7</sup> Moreover, other studies focused on the release of sulfur during thermal conversion of biomass feedstock and showed that it is released through two mechanisms related to its chemical form: an initial release of organic S at low temperatures (<500 °C), followed by a decomposition of inorganic S at higher temperatures.<sup>2,3,5</sup>

Other studies<sup>1,3,4,8,9</sup> were conducted to characterize the transformation of chlorine, alkali and alkaline earth metals in biomass feedstock, where they exist primarily in inorganic salt forms. These chloride salts may vaporize as alkali chlorides (KCl(g), NaCl(g)) at temperatures above 700 °C or may decompose and release Cl, which is rapidly converted into HCl(g) at lower temperatures. Below 700 °C, organic and inorganic chlorine partially transforms into HCl. In solid recovered fuels (SRF), where Cl exists in its two different forms, the distinction between inorganic and organic Cl did not correlate with the differentiation between volatile and non-volatile chlorine after pyrolysis.<sup>10</sup>

On the other hand, in our previous study,<sup>11</sup> thermodynamic equilibrium calculations have shown that the major elements of ash (mainly Ca and Si) can influence the S distribution in gaseous and solid products. The reaction of calcium with other elements, particularly silicon, inhibits its ability to retain sulfur in the condensed solid phase and thus increases the release of sulfur in the gas phase. This influence of ash-forming elements was experimentally observed in<sup>12</sup> for biochars generated from pyrolysis and gasification of oak and corn stover; silicon-poor oak biochar was found to retain a higher fraction of sulfur compared to the biochar of the silicon-rich corn stover. In bagasse gasification, the release of alkali metals present as water-soluble salts (KCl, K<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>) and ion-exchangeable ions bound to the organic matrix (K<sup>+</sup>) was reduced by the presence of aluminosilicates in the feedstock.<sup>13</sup>

<sup>a</sup>Univ. Grenoble Alpes, CEA, LITEN, DTCH, 38000 Grenoble, France. E-mail: sylvie.valin@cea.fr

<sup>b</sup>Université de Lorraine, Institut Jean Lamour, Labex DAMAS, Nancy, 54011, France

However, in another study on biomass gasification, the ash composition had a marginal effect on the release of S and Cl, but was relevant for the release of K.<sup>5</sup>

In biomass-derived feedstock such as paper and cardboard, or materials derived from fossil resources such as textiles, to our knowledge, there is less information available on the sulfur and chlorine nature in such types of resources and their resulting release mechanisms.

Therefore, the transformation of inorganic volatile elements (S, Cl, K...) during pyrolysis and gasification and their distribution between solid and volatile phases still need experimental investigation, considering their initial chemical forms, the characteristics of the resource, and its chemical composition, especially its ash content and composition. This study focuses on the sulfur and chlorine transformation during the pyrolysis of biomass and waste from different types and origins, pyrolysis being considered as the first step of gasification. It investigates a previously unexplored relationship between the type and composition of such feedstocks and the behavior of sulfur and chlorine. Two agricultural residues with different ash content and composition and three waste components were selected as feedstock. A leaching technique was applied to the selected resources to quantify the different initial chemical forms of sulfur and chlorine (organic/inorganic). Analytical experiments were conducted using a lab-scale induction heated reactor. Various analytical techniques were employed to quantitatively and qualitatively assess the behavior of sulfur and chlorine during pyrolysis. This innovative approach enables a more precise and comprehensive evaluation of the impact of the resource's chemical composition, especially the composition of ash, as well as the chemical forms of S and Cl associated with the type of raw material.

## 2. Experimental

### 2.1. Feedstock and its characterization

Five feedstocks were selected among agricultural residues and materials present in waste to investigate a large variety of composition, ash, sulfur and chlorine content:

- Colza straw and corn residues (leaf, husk, stalk) are post-harvesting crops and residues deriving from agriculture.
- Cardboard, PVC, and wool (textile) are urban post-consumer residues deriving from industries or households.

To obtain the most homogeneous and representative samples possible, starting from agricultural residues batches of a few kg, quartering followed by grinding to mm size using a hammer mill was performed to obtain particles between 1 and 1.5 mm. The waste components were shredded up to particles between 3 and 10 mm (Fig. 1).

The elemental composition of the samples was determined according to the standards:

- ISO 18122 for the determination of the ash content.
- EN ISO 21663 for the determination of the total content of C, H, and N using a micro-analyzer.
- EN 15408 and EN ISO 10304-1 for the determination of the total content of S and Cl. This method is carried out in two steps; the sample is first oxidized by combustion with O<sub>2</sub> in



Fig. 1 Pictures of the feedstocks selected for this study.

a bomb calorimeter (Parr 6200 Isoperibol Calorimeter) where sulfur and chlorine are transformed respectively into chlorides and sulfates, which are dissolved and/or absorbed in a 5 M NaOH solution. Then, the bomb is washed out and the recovered solution is analyzed by ion chromatography.

- ASTM D6349 for the determination of major inorganic element contents (Si, Ca, K, Na, Mg, Fe, Al, and P) by Inductively Coupled Plasma (ICP) Spectrometry.

A chemical fractionation method was applied to four of the selected feedstock: the two agricultural residues, cardboard, and wool, to investigate in which chemical form inorganic elements are present and how they are associated in the fuel structure. This method was originally developed for coal<sup>14</sup> and then modified and applied for biomass fuels.<sup>15,16</sup> It is based on selective leaching by increasingly aggressive solvents, *i.e.*, water, 1 M ammonium acetate, and 1 M hydrochloric acid. The different types of ash-forming elements are distinguished according to their solubility in the different solvents.

In our study, the chemical fractionation method was limited to consecutive leaching in two solvents, *i.e.*, pure water and 1 M ammonium acetate (NH<sub>4</sub>Ac) solution. First, an excess of Milli-Q water (15 mL g<sup>-1</sup> of the solid sample) was used to leach out 10 g of solid fuel with agitation for 24 hours at ambient temperature. After this period, the solution was filtered and the water leachate was collected. The remaining solid was then leached out in a 1 M NH<sub>4</sub>Ac solution (pH = 7.45) (5 mL g<sup>-1</sup> of solid) with agitation for 24 hours at ambient temperature. The suspension was filtered and the acetate leachate was collected. Water and acetate leachates were analyzed by ICP-OES for S quantification and by ionic chromatography for Cl<sup>-</sup> and cations (K<sup>+</sup>, Na<sup>+</sup>, and Ca<sup>2+</sup>) quantification. In addition, the content of S and Cl in the dried residual solid was determined with the same method as that used for the raw feedstock, in an attempt to complete the elemental balance of S and Cl in the fractionation method.

### 2.2. Pyrolysis experimental setup and procedure

Experiments were performed in a lab-scale setup that was described in detail in a previous study<sup>17</sup> and was adapted for this study. It consists in an induction-heated set-up, in which the reaction takes place, followed by a condensable and gas products collection system (Fig. 2). The reactor is a quartz tube



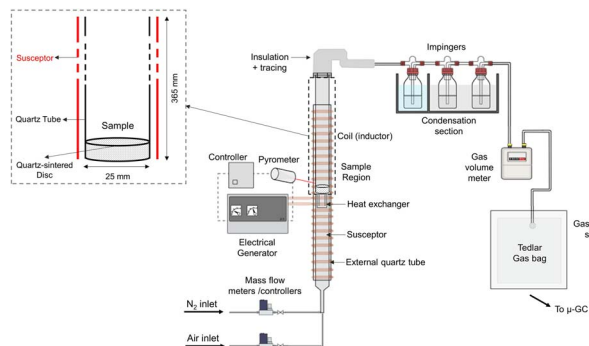


Fig. 2 Schematic representation of the lab-scale setup and details of the reaction zone.

(365 mm in height, 22 mm in internal diameter, 3 mm in thickness) fixed to a porous quartz-sintered disc (25 mm in diameter, 4 mm in thickness, grade 0 in porosity with maximum pore size from 160 to 250  $\mu\text{m}$ ) that can withstand temperatures up to 900  $^{\circ}\text{C}$ . Quartz was selected as the reactor's material to avoid any adsorption or interaction with the released inorganic species.<sup>18</sup> The reactor is placed inside a susceptor that consists in a 316L stainless-steel tube (560 mm in height, 30.15 mm in internal diameter). Inside the susceptor and under the quartz tube reactor, a metallic heat exchanger helps to preheat the entering gas ( $\text{N}_2$  continuously fed at a flow rate of 0.5  $\text{NL min}^{-1}$  in order to flush the system and carry the volatile products). The susceptor is surrounded by a water-cooled copper coil inductor (420 mm long), which is connected to a 12 kW electrical generator that supplies energy to the induction circuit. An external quartz tube is placed between the coil and the susceptor to avoid any contact between them and to center the setup. Set point temperature is adjusted with a PID controller connected to a two-color optical pyrometer, which aims at the susceptor wall at the sample level, so that the susceptor reaches the set point value with a heating rate of approximately 85  $^{\circ}\text{C s}^{-1}$ . However, the quartz reactor takes a longer time to reach the set point with a heating rate of 10  $^{\circ}\text{C s}^{-1}$  measured in its center. The temperature is homogeneous in the sample region, between the sintered disc and 32 mm above, with a maximum temperature difference of 10  $^{\circ}\text{C}$ .

For each experiment, the reactor was filled up to 40 mm of its height with 2 to 4 g of dried feedstock. To determine the real temperature of the samples during each experiment, the temperature profile inside the sample was measured using three thermocouples at different axial positions ( $z = 2, 17, 32$  mm above the quartz disc) inside the sample. The average of the measurements at the three axial positions was considered. Two types of experiments were performed.

- Experiments in which the reactor was heated up and kept at the desired temperature for 20 minutes. Tests were performed at two different set point temperature levels: 800  $^{\circ}\text{C}$  and 850  $^{\circ}\text{C}$  for all feedstocks.

- Experiments in which the heating was interrupted at different times and in which each sample therefore reached a different maximum temperature. These tests were intended to

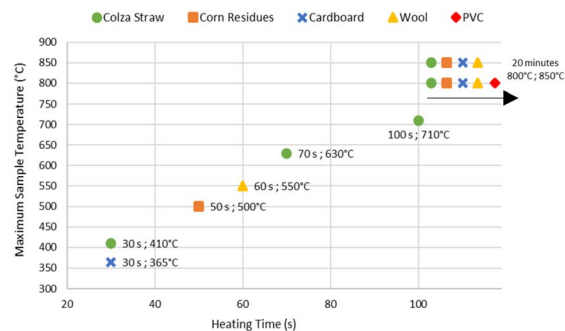


Fig. 3 Maximum temperature reached in the sample versus heating time for each experiment.

have a more comprehensive understanding of the transformation of S and Cl during heating.

Each experiment is shown in Fig. 3 as a function of its heating time, where it is referred to according to the maximum average temperature reached inside the sample.

The remaining solid product in the sample holder, referred to as the char, is collected for further analyses once the reactor has cooled down. The mass yield of the char (in %) is calculated as the ratio of the mass of the char to that of the dried feedstock.

### 2.3. Char characterization

The elemental composition of the char was analyzed according to the same methods as that used for the feedstocks. The retention of an inorganic element in the char is defined as the ratio of the mass of the element in the char to that of the element in the dried feedstock.

The crystalline phase analysis of the char samples was conducted with a powder X-ray diffractometer. XRD patterns were evaluated using the DIFFRAC.EVA software with ICDD RDB databases (PDF-2 and PDF-4).

The chars' morphology and local surface elemental composition were studied using a scanning electron microscope (Philips XL30 with a 15 kV electron beam) coupled to an energy dispersive X-ray spectroscopy (SEM-EDX).

## 3. Results and discussion

### 3.1. Feedstock characteristics

**3.1.1. Elementary composition.** Table 1 presents the moisture, ash content, and elemental composition of the feedstock. Corn residues have an ash content of 3.5 wt% while colza straw has a higher ash content of 10.1 wt%. As usually found in agricultural residues, the main ash-forming elements are silicon, calcium, and potassium. The presence in soils of fertilizers containing sulfates explains their significant sulfur content (0.11–0.33 wt%). In the plant, a part of the sulfur remains in sulfate form, and the other part is reduced for its incorporation as a macronutrient into amino acids, proteins, and coenzymes. Chlorine along with potassium are associated with the nutrient cycle and plant growth processes, they remain in ionic form and are not metabolized by the plant. The chlorine



**Table 1** Composition and characteristics of feedstock (all values on a dry basis, except moisture on a raw basis)<sup>a</sup>

	Unit	Colza straw	Corn residues	Cardboard	Wool	PVC
Moisture	wt%	11.3	9.7	7.5	11.7	—
Ash at 550 °C	wt%	10.1	3.5	12.8	1.2	3.5
C	wt%	43.9	45.8	42.3	49.1	39.5
H	wt%	5.47	6.02	5.36	6.54	5.23
N	wt%	0.96	1.24	0.28	14.47	0.09
O by difference	wt%	38.6	43.5	42.2	25.19	2.25
S	wt%	0.33	0.11	0.1	2.66	0.06
Cl	wt%	0.15	0.36	0.07	0.09	49.4
K	wt%	0.77	0.73	0.11	0.1	<0.04
Si	wt%	0.54	0.27	2.0	0.6	0.39
Ca	wt%	3.74	0.45	4.17	0.78	0.29
Na	wt%	0.01	0.003	0.19	0.15	<0.04
Mg	wt%	0.12	0.21	0.18	0.06	<0.03
Al	wt%	0.04	0.01	0.77	0.11	0.12
Fe	wt%	0.03	0.01	0.74	0.11	0.09
P	wt%	0.13	0.15	0.03	0.04	0.008
Pb	wt%	na	na	na	na	1.1

<sup>a</sup> na: not analyzed.

content is 0.15 and 0.36 wt% respectively for colza straw and corn residues. It depends on several factors such as the use of fertilizers, the proximity of biomass to the sea, the leaching of soils by rain, the harvesting techniques, and the treatment and storage methods. Cardboard is a biomass-derived feedstock, coming from wood or recycled fiber manufactured in the pulp and paper industry. It has a relatively high ash content of 12.8 wt%. The main ash-forming elements are Ca and Si with 4.2 and 2 wt% respectively. Besides existing already in wood or recycled fibers, these elements can be found in the additives and mineral fillers that are used in the manufacturing process to change or enhance the cardboard properties. Chemical pulping and bleaching involve the use of chemicals, such as sodium sulfide Na<sub>2</sub>S and chlorine, which are responsible for the presence of sulfur and chlorine in the cardboard composition (around 0.1 wt%).

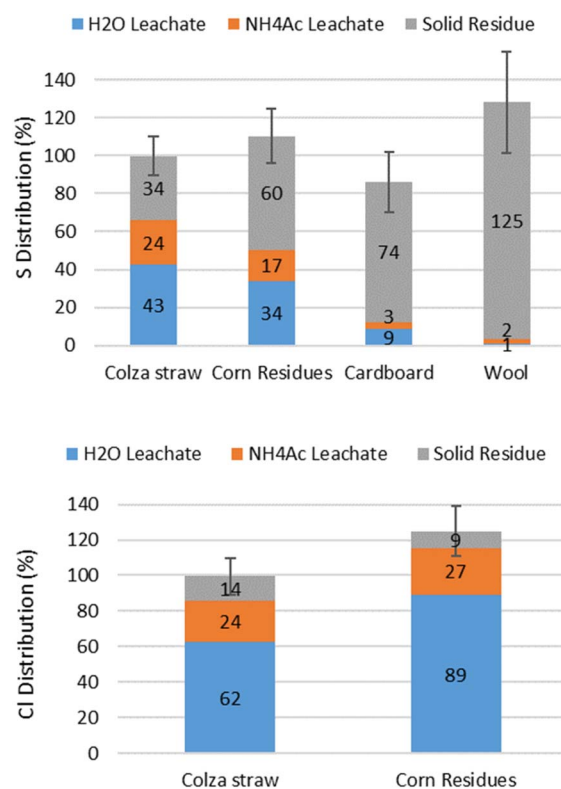
Wool is a natural fiber of animal origin, and thus presents a high protein content (keratin), which has a polypeptide chain with amino acid side chains (cystine, cysteine, cysteic acid, and methionine).<sup>19</sup> Among the selected feedstock, wool has the highest sulfur content (2.7 wt%) and the lowest ash content (1.2 wt%).

PVC is a fossil-based resource and one of the most widely-used types of plastics, it has a very high chlorine content of 49.4 wt%. It contains approximately 1 wt% of lead, which can be attributed to the usage of lead stabilizers during the manufacturing process. These stabilizers are commonly employed to enhance the stability and durability of PVC products.<sup>20</sup>

**3.1.2. Chemical fractionation results.** The distribution of sulfur and chlorine obtained after chemical fractionation analysis is presented in Fig. 4. Note that only the cases for which the initial S or Cl content is higher than 0.1 wt% were investigated. To ensure the repeatability, the leaching test for each feedstock was performed in duplicate. The results shown are averages of the two replicates. Error bars show the relative

uncertainty of the total mass balance calculated by the propagation of uncertainties. The mass balances over the fractionation experiment are satisfactory (closing to 100%, considering the uncertainties).

According to,<sup>8</sup> cations (K<sup>+</sup>, Na<sup>+</sup>, and Ca<sup>2+</sup>), anions (Cl<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), and Si(OH)<sub>3</sub>O<sup>-</sup>, found in the water and NH<sub>4</sub>Ac leachates, come from inorganic forms of dissolved

**Fig. 4** Sulfur and chlorine distribution in recovered leachates and solid residue of the feedstocks (chemical fractionation results).



salts in plant fluids or precipitated soluble salts in dried biomass. S, Cl and P that are insoluble and thus found in the solid residue are included in organic covalent forms. In addition, metal cations bound to anionic organic groups in the organic molecules constituting the biomass (ex:  $\text{COO}^-$ ), typically,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Al}^{3+}$  are soluble in  $\text{NH}_4\text{Ac}$  where they undergo ion exchange and are replaced with ammonium ions and thus released to the liquid phase. Other minerals such as calcium salts and silicon compounds that are precipitated naturally in the biomass and are closely embedded in carbonaceous material remain insoluble.

Significant differences can be noted in the distribution of sulfur and chlorine in the leachates and the solid residue between the agricultural residues, cardboard, and wool, which means, as mentioned before, differences in the relative quantities of their two chemical forms (organic and inorganic).

For the colza straw and corn residues, 67% and 51% of S, respectively, and more than 85% of Cl were found in the water (predominantly) and  $\text{NH}_4\text{Ac}$  leachates. Thus, more than half of the sulfur and almost all the chlorine are present in the inorganic form of soluble salts in the agricultural residues. To get more information on the association of S and Cl with other key inorganic elements, Table 2 presents the fraction of major ash elements (K, Ca, and Si) measured in the water leachates where they could be associated to S or Cl. A high fraction (>75%) of the potassium is recovered in water where, similarly to S and Cl, it is present in an inorganic form of soluble salts. The molar ratios K/Cl and K/(S + Cl) in the initial feedstock and in the water leachates are higher than 1. This indicates that the number of moles of potassium is sufficiently high to be able to bond with chlorine and with sulfur. Possible forms of salts made of these elements are potassium chlorides KCl and  $\text{KClO}_4$ .<sup>9</sup> The molar ratio K/S is higher than 2 only for the corn residues for which S could thus be present in the form of potassium sulfates  $\text{K}_2\text{SO}_4$ .<sup>21</sup> K can also be present in other soluble forms such as carbonates ( $\text{K}_2\text{CO}_3$ )<sup>5</sup> and phosphates  $\text{K}_2\text{HPO}_4$ .<sup>22</sup> For colza straw and corn residues, 20% and 50% of the calcium is recovered in the water, respectively. It can be present in the form of sulfates such as  $\text{CaSO}_4$ ,<sup>23</sup> or even as calcium oxalates ( $\text{CaC}_2\text{O}_4$ ).<sup>24</sup> The insoluble part of Ca can be organically associated into the biomass (Ca-COO) or in carbonates ( $\text{CaCO}_3$ ).<sup>24</sup> Silicon is only slightly leached in water, which shows that it mainly remains in the solid residue. It can be present as included minerals (silica  $\text{SiO}_2$ ) or excluded minerals coming from soil sand and clay ( $\text{SiO}_2$  and aluminosilicates often with some K, Na, or Ca).

For cardboard, less than 15% of sulfur is recovered in the leachates as inorganic sulfur, while 74% of sulfur is measured in the solid residue, indicating that S is mainly in an organic form in the cardboard. In the Kraft pulping process, sodium

sulfide  $\text{Na}_2\text{S}$  is used to dissolve the lignin that binds the cellulose fibers together in the lignocellulosic biomass. Therefore, at the end of the process, remainder of the sulfur additives could be found as minerals or be included in the lignin structure (organically associated).

For wool, all the sulfur is in the solid residue, which shows that S is mainly in an insoluble organic form. This is in agreement with what was expected, with sulfur mostly present in amino acids in this type of feedstock.

Lixiviation is not adapted to solid plastic materials. However, it is well known that the organic form of chlorine is dominant in PVC that contains organically chlorinated compounds.

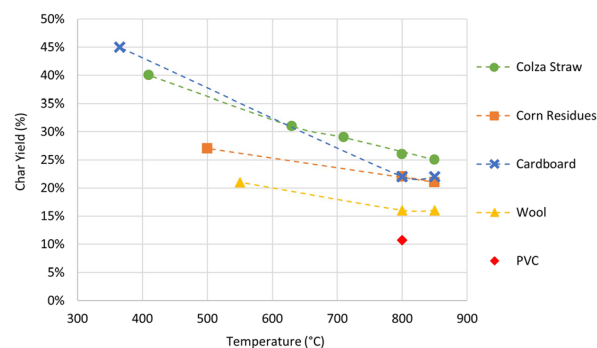
### 3.2. Sulfur and chlorine behavior in pyrolysis

**3.2.1. Inorganic elements retention in char.** The char yields of the different feedstocks are shown in Fig. 5 as a function of maximum pyrolysis temperature. For all feedstocks, the char yield decreases with the increase of pyrolysis temperature from 365 °C to 850 °C. The devolatilization occurs during the whole temperature rise until 800 °C. However, between 800 °C and 850 °C, the char yield only slightly changes for most feedstock, which shows a low influence of the temperature on this range. At 800 °C, PVC has the lowest char yield (11 wt%) among the five feedstocks, which is linked to its higher volatile content.<sup>25</sup> Subsequently, the characterization of the PVC char was not possible due to its low recovered mass.

Fig. 6 illustrates the sulfur and chlorine retention in the chars as a function of maximum pyrolysis temperature. Error bars show the relative uncertainty calculated by the propagation method. For colza straw, 46% of the initial sulfur is retained in the char produced at the pyrolysis temperature of 410 °C. The sulfur retention decreases to about 35% in the chars produced at higher temperatures (630 °C, 710 °C, 800 °C and 850 °C). For corn residues, the sulfur retention in the char is between 24 and 30% in the pyrolysis experiments performed at 500 °C, 800 °C and 850 °C. For cardboard, 35% of the initial sulfur is found in the char produced at a pyrolysis temperature of 365 °C. However, at 800 °C and 850 °C, the sulfur retention decreases to 15%. On the other hand, only 5% to 7% of the initial sulfur is retained in the chars of wool produced at 550 °C, 800 °C and 850 °C.

**Table 2** Fraction of K, Ca, and Si measured in the water leachates of the feedstocks

	K	Ca	Si
Colza straw	77%	20%	3%
Corn residues	77%	50%	0.25%



**Fig. 5** Char yield as a function of maximum pyrolysis temperature.



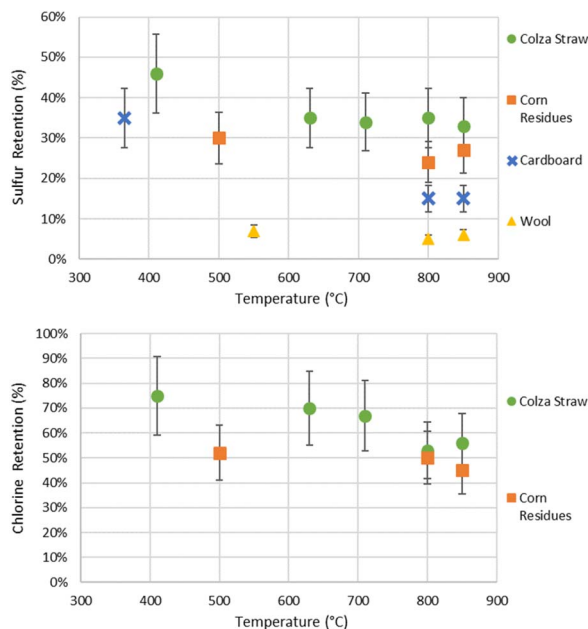


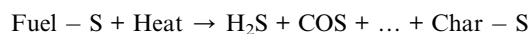
Fig. 6 S and Cl retention in the char as a function of maximum pyrolysis temperature.

These experimental results show a low influence of the final pyrolysis temperature between 500 and 850 °C for agricultural residues. This is in agreement with other studies that found a slight decrease of the total sulfur content of the char<sup>4</sup> or a constant release of sulfur<sup>2</sup> with increasing temperature from 550 °C to 900 °C during pyrolysis of wheat straw. Temperature increase from 550 to 850 °C has also a low influence on the retention of sulfur in the char for wool. Nonetheless, it is not the case for cardboard when comparing between pyrolysis temperatures of 365 °C and 800–850 °C.

To explain the different results seen among the four feedstocks, the sulfur retention in the char after pyrolysis can be related to the initial chemical form of sulfur in the feedstock. According to studies found in the literature,<sup>2,3</sup> organic forms of sulfur are more volatile and easily released into the gas phase even at low temperatures below 500 °C, compared to inorganic forms. For wool, the fraction (5–7%) of the initial sulfur retained in the solid residue is close to the inorganic fraction (3%) of sulfur measured in the original resource. This shows that the dominating organic form of S in wool is probably completely released in the gas phase before reaching 550 °C. Moreover, for cardboard in which S is mainly in organic forms, S retention decreases as temperature increases, until it reaches 15% at 800 °C and 850 °C, which could correspond to its initial inorganic fraction. If S is considered to be included in the lignin structure in cardboard, the lignin decomposition on a wide temperature range of about 250 to 600 °C (ref. 26) could explain why S continues to be released above 365 °C.

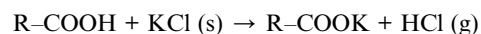
For the agricultural residues, the fraction of S retained in the chars (24–35%) is lower than the fraction of inorganic S (51–67%) quantified by lixiviation. This shows that besides the organic S initially released at low temperatures below 500 °C,

a part of inorganic S is also released. Indeed, pyrolysis studies<sup>1–3,5</sup> showed that, during the devolatilization process, the organically associated S is released *via* the formation of highly reactive SH radicals that either remain in the char or extract H, C, or O from the char, to form later H<sub>2</sub>S, COS, or SO<sub>2</sub>:



As for inorganic sulfur, at temperatures below 1000 °C, the evaporation rates of inorganic sulfates are low. However, previous authors<sup>2,27</sup> showed that a part of these sulfates can be transformed to char-bound S and thus be released to the gas phase. This could explain why the fraction of S retained in the chars is lower than the fraction of inorganic S in our results and could confirm that both the organically and the inorganically associated S contribute to the amount of S released.

There is no significant evolution of the chlorine retention in the chars for the agricultural residues, considering the uncertainties. About 50% of the initial chlorine is retained in the char between 500 °C and 850 °C for the corn residues. In the colza straw, 67–75% of the chlorine remains in the char between 410 °C and 710 °C, while only 55% is retained in the char at 800 and 850 °C. In the case of the PVC pyrolysis experiment at 800 °C, two impingers filled with deionized water were placed downstream of the reactor, to collect the chlorinated species (HCl, KCl, NaCl) released in the gas phase. Around 90% of the initial chlorine was measured in the impingers, and therefore released in the gas phase. This allows us to consider that less than 10% of the initial chlorine is retained in the char in the case of PVC. The difference in the retention of chlorine between the agricultural residues and PVC chars can be related to its initial chemical form in the resource. PVC, having the totality of Cl in an organic form, undergoes three steps (dehydrochlorination, condensation and fragmentation) during the devolatilization stage, in the temperature range 150–500 °C, which results in the complete release of Cl as HCl.<sup>28,29</sup> Furthermore, it has been reported that, at molar ratio Cl/Pb = 3,<sup>30</sup> the hydrogen chloride (HCl) produced from the decomposition of PVC during pyrolysis can potentially reacts with lead oxide (PbO) to form lead(II) chloride (PbCl<sub>2</sub>) that subsequently melts and volatilizes at temperatures exceeding 501 °C.<sup>30,31</sup> In our case, despite the presence of a notable quantity of lead in our PVC sample originating from lead stabilizers used in PVC manufacturing, the molar ratio of Cl to Pb is considerably higher, making it challenging to confirm any significant interaction between the two elements. On the other hand, more than 85% of chlorine is present in an inorganic form of soluble salts in the agricultural residues (Fig. 4). According to previous studies,<sup>1,3,4</sup> under pyrolysis conditions, at temperatures under 700 °C, the release of a significant fraction of the Cl (40–60%) in the fuel as HCl is attributed to an ion-exchange reaction of KCl and oxygen-containing functional groups that are either present in the fuel or formed during the devolatilization step:



Above 700 °C, the evaporation of KCl is considered to be the main pathway for the release of Cl. According to our results, only a part of inorganic chlorine is released in the gas phase in pyrolysis experiments.

According to literature (Section 1), the behavior of inorganic forms of S and Cl can depend on the ash composition of the feedstock. To have a deeper understanding of the influence of the ash-forming elements on the sulfur and chlorine behavior during pyrolysis, the chars were analyzed for their inorganic composition. Fig. 7 presents the retention in the char of the major inorganic elements (K, Ca, Si) after pyrolysis for the two agricultural residues. Error bars show the relative uncertainty calculated by the propagation method.

K totally remains in the char below 700 °C for both agricultural residues. In the original feedstock, K is mainly present in soluble inorganic salts (KCl, KClO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>...). Under 700 °C, the evaporation rates of these inorganic salts are low and as said in the preceding paragraph, K can combine with volatile organic compounds and transform into organic K (R-COOK). This could explain its total retention in the char at temperatures below 700 °C. At 800 °C and 850 °C, a low release is observed. By comparing with Fig. 6, the retentions of K and Cl follow a similar profile, which could suggest that the release of metal chlorides, particularly KCl, can start occurring at temperatures above 800 °C. This is in agreement with previous studies that have shown that only a small amount (5–10%) of K is released at temperatures below 700 °C,<sup>3–5</sup> and that the release of alkali metals and chlorine is closely related to one another.<sup>3</sup>

All the silicon is retained in the chars at the different temperatures. As expected, Si is not volatile and remains in the silicate matrix.<sup>8</sup>

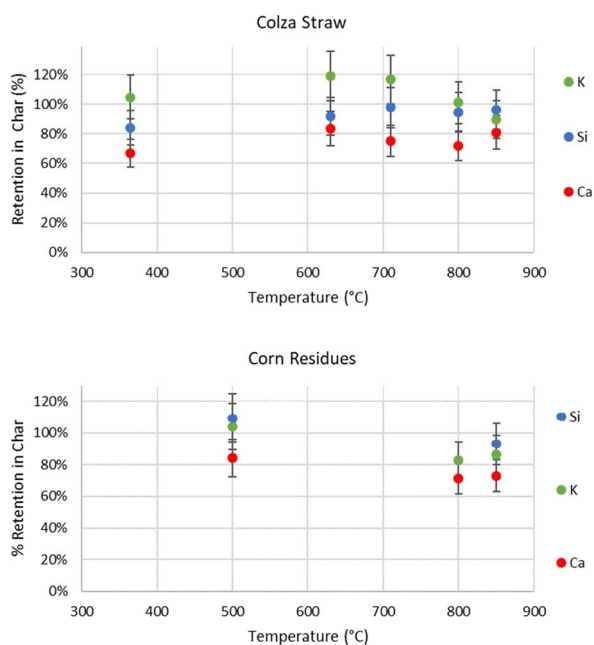


Fig. 7 Major ash-forming elements retention in the char as a function of maximum pyrolysis temperature.

67 to 83% of the Ca is retained in the char between 365 and 850 °C for colza straw, while 71% to 84% of Ca remains in the corn residue char between 500 and 850 °C. Even at temperatures as low as 365 °C, there is a fraction of Ca released in the gas that is not negligible (15–35%). The temperature has no significant influence on the Ca retention considering the uncertainties. As mentioned before, 80% and 50% of the total Ca is organically bound or present as carbonates for colza straw and corn residues, respectively. Literature reports that significant fractions of Ca are volatilized during cane bagasse and cane trash pyrolysis at 500 °C,<sup>32</sup> and cane bagasse gasification between 650 and 1170 °C.<sup>13</sup> The reduction in Ca bound to the organic phase after gasification and the observation of acetate ions in the syngas indicated that during gasification, organically bound Ca (COO–Ca) was volatilized releasing Ca<sup>2+</sup>, and COO<sup>–</sup> ions. The thermal breakdown of carboxylates (COO) in the biomass from large molecular mass structures and the subsequent release of light carboxylates might be an important mechanism for the release of Ca that is organically bound (Ca–COO) from the pyrolysis of biomass at low temperatures. This provides an explanation for the release of Ca in our experiments.

**3.2.2. XRD and SEM-EDX analysis of the chars.** To precise the interactions between sulfur, chlorine and the ash-forming elements, more experimental investigations are needed to characterize the forms in which sulfur and chlorine are retained in the char at different pyrolysis temperatures. Therefore, XRD and SEM-EDX analyses were carried out on the char samples. The XRD analysis indicated the qualitative presence of crystalline minerals in the char samples. Fig. 8 reports the XRD patterns for the chars of the agricultural residues and cardboard at the different maximum pyrolysis temperatures. The SEM-EDX analysis was used to study the surface elemental composition, which may give information on the non-crystalline forms present in the chars. Fig. 9 presents the SEM observations of the chars at 800 °C, together with indications on locally distributed inorganic compounds, derived from EDX elemental composition measurement.

Since wool samples have a very low ash content, their chars showed no clear mineral phases and therefore their XRD results are not presented. The main part of wool chars consists in a carbonaceous matrix containing some inorganic elements, which may explain their amorphous nature seen in the XRD analysis. The SEM-EDX analysis showed the presence of sulfur along with calcium in the carbonaceous matrix.

For colza straw, in the samples pyrolyzed between 410 and 710 °C, peaks are observed at  $2\theta = 28.2^\circ$ ,  $2\theta = 40.3^\circ$  and  $2\theta = 50^\circ$  and are attributed to sylvite (KCl). In the SEM-EDX analysis, Cl is found in a phase at 710 °C containing high K content, which could correspond to KCl. However, for the chars produced at higher pyrolysis temperatures, 800 °C and 850 °C, no presence of sylvite is found in XRD. These observations could confirm that above 800 °C there is a release of Cl and K due to the metal chlorides volatilization. In the SEM-EDX analysis, at 800 °C and 850 °C, the carbonaceous matrix mainly contains Ca, with some K, Mg, S, P and Cl.

The SEM-EDX analysis shows the presence of sulfur with the carbonaceous matrix along with high amount of Ca and some K,





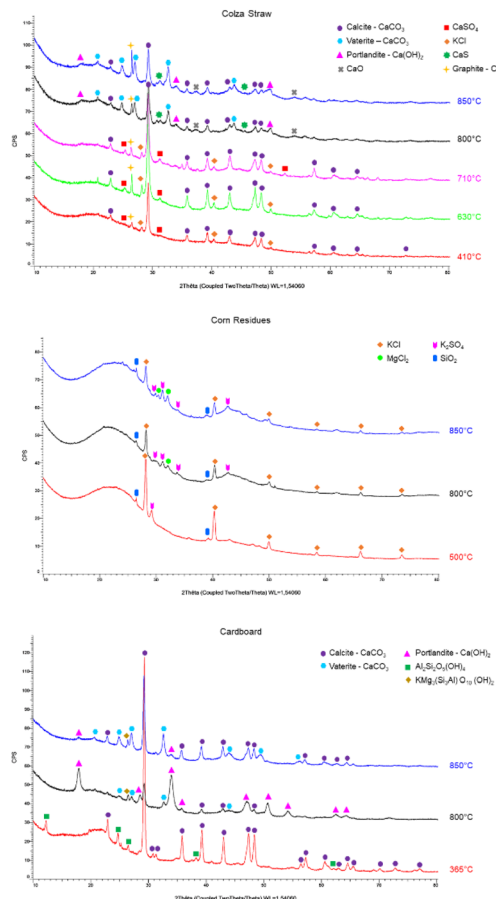


Fig. 8 XRD diffractograms of colza straw, corn residues and cardboard chars at their different pyrolysis temperatures.

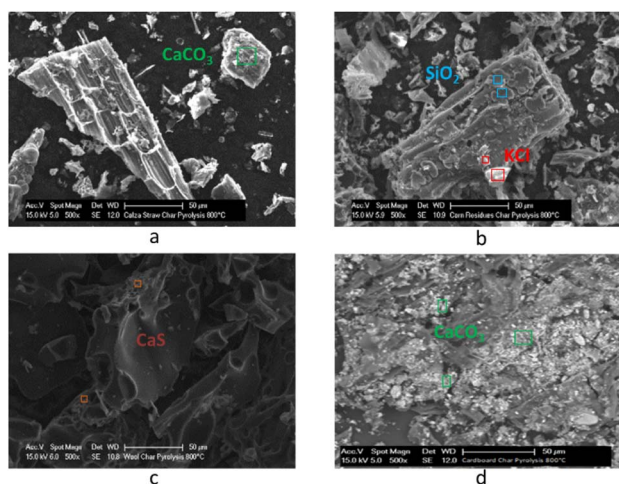


Fig. 9 SEM observations of colza straw (a), corn residues (b), wool (c) and cardboard (d) chars at 800 °C.

P and Mg. In the XRD results, calcium sulfate  $\text{CaSO}_4$  ( $2\theta = 25.3^\circ$  and  $2\theta = 31.3^\circ$ ) is identified in the chars produced at 410 °C, 630 °C, and 710 °C. At 710 °C, the intensity of the two peaks is the highest, with a third additional peak present at  $2\theta = 52.3^\circ$ ;

this can be due to the larger devolatilization of the carbon matrix at higher temperatures, inducing a higher concentration of  $\text{CaSO}_4$ . No peaks corresponding to  $\text{CaSO}_4$  are found for the chars produced at 800 °C and 850 °C. On the other hand, the presence of calcium sulfide  $\text{CaS}$  is confirmed by the peaks at  $2\theta = 31.3^\circ$  and  $2\theta = 45.5^\circ$  in these chars. This could show that the inorganic sulfates, besides being partially transformed to organic S bound to the char and released in the gas as discussed previously, can also be reduced to inorganic sulfide at temperatures above 700 °C, as seen in previous studies.<sup>2</sup> The main crystalline phase detected in the chars produced under 740 °C is calcite ( $\text{CaCO}_3$ ). However, for the chars produced at higher temperatures (800 °C and 850 °C), calcite and vaterite, two polymorphs of calcium carbonate, are the major predominant crystalline phases. Additional peaks are then observed at  $2\theta = 18^\circ$ ,  $28.5^\circ$ , and  $34^\circ$  and at  $2\theta = 37.5^\circ$  which are attributed to the presence of portlandite ( $\text{Ca(OH)}_2$ ) and lime ( $\text{CaO}$ ) respectively.

For the corn residues char at 500 °C, the SEM-EDX analysis show phases containing K and Cl appearing as fine particles attached to the char, which could correspond to KCl. As temperature rises to 800 °C and 850 °C, the concentration of these particles decrease. In addition, grains containing Si and O, which may correspond to silicon oxide  $\text{SiO}_2$ , are found dispersed on the matrix in the different chars. These observations are consistent with the XRD results. Indeed, for all temperatures, silica ( $\text{SiO}_2$ ) is detected in the corn residue chars by XRD. Sylvite (KCl) is the major crystalline phase detected with several peaks. Their intensity decreases with the increase of the temperature above 500 °C, which can be explained by the partial release of KCl at these temperatures. Contrary to colza straw char, KCl is still detected in the chars produced at 800 and 850 °C. On the other hand, for the chars produced at 800 °C and 850 °C, magnesium chloride ( $\text{MgCl}_2$ ) is present with a peak at  $2\theta = 32^\circ$  and two peaks ( $2\theta = 30.3^\circ$  and  $2\theta = 32^\circ$ ) at 850 °C. According to,<sup>32</sup> while Cl may be bonded into the char organic matrix, it may also react with Mg and Ca to form refractory  $\text{MgCl}_2$  or  $\text{CaCl}_2$ . Moreover, additional peaks appear at  $2\theta = 30^\circ$ ,  $2\theta = 31.2^\circ$ ,  $2\theta = 34^\circ$  and  $2\theta = 43^\circ$  corresponding to potassium sulfate  $\text{K}_2\text{SO}_4$ , the only sulfur-containing phase for this feedstock.

No crystalline structures containing S or Cl are identified in the diffractograms of the cardboard char samples pyrolyzed at the three different temperatures (365 °C, 800 °C and 850 °C). Moreover, in the SEM-EDX analysis, neither S nor Cl are observed in the chars at the different temperatures. This could be due to the very low content of S and Cl remaining in the char samples (under 0.1 wt%). The main crystalline phase detected in the char produced at 365 °C is calcite  $\text{CaCO}_3$ . In addition, three peaks are identified at  $2\theta = 12.2^\circ$ ,  $2\theta = 24.6^\circ$  and  $2\theta = 26.5^\circ$  attributed to kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). Both calcite and kaolin (clay) are inorganic minerals used in the paper industry as fillers and as surface coatings.<sup>33</sup> For the chars produced at 800 °C and 850 °C,  $\text{CaCO}_3$  is present in two of its polymorphs: calcite and vaterite. In addition, a silicate of formula  $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$  is found. Portlandite  $\text{Ca(OH)}_2$  also appears to be present especially in the char at 800 °C.





**3.2.3. Result synthesis.** As shown by the XRD and SEM-EDX analyses as well as S and Cl retention measurements, the release of the dominating organic forms of S and Cl in the waste components (S for wool and cardboard, Cl for PVC) seems to happen without interaction with ash-forming elements. This is remarkable for cardboard which presents a high ash content (12.8 wt%), and especially a high calcium content (4.3 wt%), which could have been expected to react with sulfur. For the agricultural residues, both the organically and the inorganically associated S contributed to the amount of S released. Inorganic sulfates have negligible evaporation rates below 1000 °C; however, they may partially transform to organic S and be released in the gas. In the Ca-rich colza straw, the sulfur remaining in the char was found to be associated with calcium, especially in sulfates  $\text{CaSO}_4$ , that were reduced to calcium sulfide CaS above 800 °C. On the other hand, for the K-rich corn residues, the sulfur remaining in the char was associated with potassium in sulfates  $\text{K}_2\text{SO}_4$ , which could be detected up to 850 °C. The dominating inorganic Cl is partially released, probably as HCl at temperatures below 700 °C, and by partial evaporation of metal chlorides above 700 °C. In the K-rich biomass, Cl was still detected in the char in crystallized phases (KCl and  $\text{MgCl}_2$  even above 800 °C), while it was not the case in the Ca-rich biomass.

## 4. Conclusions

The objective of this study was to characterize the sulfur and chlorine release during pyrolysis of biomass and waste and to evaluate the effect of the chemical forms of S and Cl, the chemical composition of the feedstock, and the temperature on this release. A leaching technique was applied to the selected resources to determine the repartition of initial sulfur and chlorine into organic and inorganic forms. In the two agricultural residues, S was found in its two chemical forms as organically bonded to the carbon matrix and as inorganic soluble sulfates ( $\text{CaSO}_4$  in the Ca-rich colza straw and  $\text{K}_2\text{SO}_4$  in the K-rich corn residues). Cl is mainly in the form of inorganic salts (KCl,  $\text{KClO}_4$ ...). However, in the waste components wool and cardboard, sulfur was mainly found in an organic form, while in PVC Cl is known to be organically bonded in the polymer structure. Pyrolysis tests performed at variable temperatures between 420 and 850 °C show a resource-dependent retention of S and Cl in the char. For wool and cardboard, approximately 100% and 65% of S is released in the gas respectively, which corresponds to the fraction of S initially present in organic form. For PVC initially containing organically chlorinated compounds, more than 90% of the Cl is released into the gas as HCl. Thus, the organic forms of S and Cl are volatile and easily released into the gas phase even at low temperatures without interacting with other inorganic elements, even in high ash content resources. For agricultural residues, Cl is mainly in the form of inorganic salts (KCl,  $\text{KClO}_4$ ...), while about half of the S is in an organic form bound to the C matrix and the other half is in inorganic form (sulfates:  $\text{K}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ...). In pyrolysis, the release of inorganic forms in the gas is partial. Different crystallized S containing forms are

identified in the chars ( $\text{CaSO}_4$  or CaS for colza straw,  $\text{K}_2\text{SO}_4$  for corn residues...), which depend on the pyrolysis temperature and the ash composition. These results constitute a basis for further study on *in situ* cleaning methods based on interactions between inorganic elements to limit the release of inorganic volatile pollutants.

## Author contributions

Hala Braidy – investigation, visualization, writing – original draft; Sylvie Valin – writing – review & editing, supervision; Fabrice Patisson – writing – review & editing, supervision.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We thank Maguelone GRATEAU, Maria Antonia MAROTTA and Sebastien THIERY for their contribution during this paper preparation.

## Notes and references

- 1 J. N. Knudsen, P. A. Jensen and K. Dam-Johansen, *Energy Fuels*, 2004, **18**, 1385–1399.
- 2 J. N. Knudsen, P. A. Jensen, W. Lin, F. J. Frandsen and K. Dam-Johansen, *Energy Fuels*, 2004, **18**, 810–819.
- 3 J. M. Johansen, J. G. Jakobsen, F. J. Frandsen and P. Glarborg, *Energy Fuels*, 2011, **25**, 4961–4971.
- 4 P. A. Tchoffor, K. O. Davidsson and H. Thunman, *Energy Fuels*, 2013, **27**, 7510–7520.
- 5 P. A. Tchoffor, F. Moradian, A. Pettersson, K. O. Davidsson and H. Thunman, *Energy Fuels*, 2016, **30**, 10435–10442.
- 6 M. Wang, Y. Hu, J. Wang, L. Chang and H. Wang, *J. Anal. Appl. Pyrolysis*, 2013, **104**, 585–592.
- 7 Y. Gu, J. Yperman, J. Vandewijngaarden, G. Reggers and R. Carleer, *Fuel*, 2017, **202**, 494–502.
- 8 M. Zevenhoven, P. Yrjas, B.-J. Skrifvars and M. Hupa, *Energy Fuels*, 2012, **26**, 6366–6386.
- 9 L. Deng, X. Huang, Y. Tie, J. Jiang, K. Zhang, S. Ma and D. Che, *J. Energy Inst.*, 2022, **103**, 117–127.
- 10 E. Daouk, R. Sani, D. Pham Minh and A. Nzihou, *Fuel*, 2018, **225**, 54–61.
- 11 H. Braidy, S. Valin and F. Patisson, *30th European Biomass Conference and Exhibition*.
- 12 S. Cheah, S. C. Malone and C. J. Feik, *Environ. Sci. Technol.*, 2014, **48**, 8474–8480.
- 13 C. Andrea Jordan and G. Akay, *Fuel*, 2012, **91**, 253–263.
- 14 S. A. Benson and P. L. Holm, *Ind. Eng. Chem. Prod. Res. Dev.*, 1985, **24**, 145–149.
- 15 L. L. Baxter, T. R. Miles, T. R. Miles, B. M. Jenkins, T. Milne, D. Dayton, R. W. Bryers and L. L. Oden, *Fuel Process. Technol.*, 1998, **54**, 47–78.
- 16 M. Zevenhoven-Onderwater, PhD thesis, Aabo Akademi, 2001.



- 17 O. Sosa Sabogal, S. Valin, S. Thiery and S. Salvador, *Chem. Eng. Res. Des.*, 2021, **173**, 206–214.
- 18 V. F. de Almeida, A. Gómez-Barea, J. Arroyo-Caire and I. Pardo, *Waste Biomass Valorization*, 2020, **11**, 6869–6884.
- 19 A. C. Pina, N. Tancredi, C. O. Ania and A. Amaya, *J. Mater. Sci. Eng. B*, 2021, **268**, 115115.
- 20 A. CHABROL and S. GIROIS, *Tech. Ing., Plast. Compos.*, 2013, am3233.
- 21 S. V. Vassilev, D. Baxter, L. K. Andersen, C. G. Vassileva and T. J. Morgan, *Fuel*, 2012, **94**, 1–33.
- 22 P. Piotrowska, M. Zevenhoven, K. Davidsson, M. Hupa, L.-E. Åmand, V. Barišić and E. Coda Zabetta, *Energy Fuels*, 2010, **24**, 333–345.
- 23 F. Suárez-García, A. Martínez-Alonso, M. Fernández Llorente and J. M. D. Tascón, *Fuel*, 2002, **81**, 1161–1169.
- 24 A. Pettersson, M. Zevenhoven, B.-M. Steenari and L.-E. Åmand, *Fuel*, 2008, **87**, 3183–3193.
- 25 M.-H. Cho, Y.-K. Choi and J.-S. Kim, *Energy*, 2015, **87**, 586–593.
- 26 P. de Wild, PhD thesis, Rijksuniversiteit Groningen, 2011.
- 27 P. A. Tchoffor, K. O. Davidsson and H. Thunman, *Energy Fuels*, 2014, **28**, 6953–6965.
- 28 M. Bläsing, M. Weigand, J. Fassenacht and M. Müller, *Fuel Process. Technol.*, 2015, **134**, 85–91.
- 29 A. Casazza, E. Spennati, A. Converti and G. Busca, *Chem. Eng. Trans.*, 2019, **74**, 1141–1146.
- 30 S.-J. Wang, H. Zhang, L.-M. Shao, S.-M. Liu and P.-J. He, *Chemosphere*, 2014, **117**, 353–359.
- 31 W. Xu, G. Song, Q. Song and Q. Yao, *Fuel Process. Technol.*, 2022, **227**, 107089.
- 32 D. M. Keown, G. Favas, J. Hayashi and C.-Z. Li, *Bioresour. Technol.*, 2005, **96**, 1570–1577.
- 33 M. A. Hubbe and R. A. Gill, *Bioresources*, 2016, **11**, 2886–2963.

