

Evaluation of the effects and interactions of initial chlorine and sulphur contents on the release of potassium compounds during biomass combustion

Wenhan Cao^{*}, Jun Li^{**}, Xiaolei Zhang

Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, G1 1XJ, UK

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ABSTRACT

In biomass combustion, understanding the effects of chlorine and sulphur release on the release of potassium compounds can help improve and predict the potassium release mechanisms. In this work, a kinetic model is applied to investigate the influences of S and Cl contents on the release of major potassium compounds during combustion. The results indicated that increasing the initial Cl from 3.8×10^{-5} mol/g biomass to 1.5×10^{-4} mol/g biomass promotes the maximum release of HCl and KCl by 518% and 273%, respectively, while inhibits the maximum release of KOH and K_2SO_4 by 99% and 68%, respectively. Cl in the biomass has directly influence the release of HCl, but indirectly impact the release of KCl; while its existence inhibits the formations of KOH and K_2SO_4 by adapting the contents of moisture, KO and KSO_3 . Raising the initial S from 2.7×10^{-5} mol/g biomass to 1.1×10^{-4} mol/g biomass only significantly affects the release of KOH and K_2SO_4 when temperature exceeds 1300 K, the maximum release of K_2SO_4 increased by 117%, while the release of KOH shifts from raise to decline. During combustion, S affects the formation and evaporation of K_2SO_4 by controlling the formations of intermediate S species. The results showed the model can accurately predict the major potassium compounds in various scenarios, and support the improvement of ash control technologies.

1. Introduction

Biomass is one of the indispensable renewable energy sources to ease the dual pressures we are facing of: 1) the energy crisis caused by the depletion of traditional fossil fuels; 2) the global climate change that mainly caused by the generation of greenhouse gases from fossil fuels [1]. Currently, biomass contributes ca. 13% of the global energy supply [2]. Biomass combustion is acknowledged as a mature means of biomass energy utilisation [3]. But the unique features of biomass as fuel still challenge the operation of combustion process, particularly ash-related problems (e.g., slagging, corrosion, agglomeration) during biomass combustion process remain the most challenging problem for the comprehensive use of biomass source [4].

The severity of ash-related problems largely depends on the fractions of alkali metals, especially K, and other inorganic elements (i.e. Cl and S) in the virgin biomass, which are transferred to the vapour when being heated [5]. These issues become particularly extreme when utilising herbaceous and agricultural residues, fast-growing non-food crops and

wood species, which often contain high concentrations of alkali metals [6,7]. During the combustion process of biomass, elemental alkali metals are vaporised and experience various chemical reactions to form aerosols [8]. This promotes the formation of deposits on internal surfaces of biomass boilers [9,10] and is widely known as the main cause of induced active corrosion during the biomass combustion [11–13]. As explored in our previous research [4], KCl, KOH and K_2SO_4 are the three main K-species released during the combustion of wheat straw. The release mechanism of K has been summarised as: (i) loosely bonded K and partial organic-K are released at the devolatilisation stage (473–773 K), mainly in the forms of KCl and KOH [4,14] (ii) a large amount of char-K and inorganic-K (i.e. K_2O , KOH and K_2SO_4); are released associated with the process of char oxidation (>973 K) [15,16].

As Cl and S are the most important ash-induced elements [17,18] that are known potentially affect the release of potassium, it is crucial to understand their release behaviours during biomass combustion in order to support the development of potassium release mechanisms for processing challenging Cl- and/or S-rich feedstock [19]. According to

* Corresponding author.

** Corresponding author.

E-mail addresses: wenca@kt.dtu.dk (W. Cao), jun.li@strath.ac.uk (J. Li).

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Johansen et al. [20], HCl and KCl are the most abundant Cl-containing species released during the combustion process of biomass. At low temperatures (<573 K), about 20–50% of the initial Cl (mainly organically associated Cl) content will be released [14], this Cl release process [21,22] is independent to that of K [20], mainly in the form of CH₃Cl and HCl [23]; with temperature further increases up to 973 K, inorganic Cl starts to release in the form of HCl that can be partially recaptured in the char via secondary reactions with available alkali metals to form KCl, then sublimated in abundant when temperature is above 973 K [24]. Moreover, Clery et al. [25] illustrated that a high Cl content in the biomass could facilitate the release of KCl to the gas phase during the combustion process. Similarly, the major release of S is occurring associated to the devolatilisation of biomass, mainly from organically-bounded S in forms of SO₂ and SO₃. The release of S at low temperatures (<773 K) composes up to 50% of the initial S content in the biomass. Once being released, SO₂ and SO₃ can be partially recaptured and react with char matrix and other inorganic elements, alongside the remaining inorganically bonded S that is retained in the solid, i. e. K₂SO₄, and they are eventually sublimated or/and dissociated at temperatures above 1173 K [8,26,27]. As reported by Glarborg et al. [28], the oxidation of SO₂ to SO₃ is the initial step of the KCl sulfation process, which controls the generation of K₂SO₄ and thus affect the generation and release of K during the combustion process. Afterwards, happens the secondary release which is the re-release of the recaptured S at the early stage.

Therefore, the release of K, Cl and S are closely associated to each other during the biomass combustion. This indicates the Cl and S contents in the virgin biomass can significantly affect the release of K. In fact, knowing that to what extent the different K compounds are released corresponding to Cl and S can help understand the release mechanisms of these interlinked ash-forming elements. However, due to lack of detective methods, it is difficult to experimentally provide detailed release profiles of K compounds in associated with the release of S and Cl species during biomass combustion. Modelling could be a useful tool to carry out this challenging investigation. Wan et al. [29] numerically studied the impact of HCl and SO₂ on the K emissions in pulverized-biomass combustion using Computational Fluid Dynamics (CFD) method, and revealed that HCl has a stronger influence on the K species than SO₂. Michella et al. [30] conducted CFD study on the SO₂ oxidation and the sulfation of KOH and KCl during biomass combustion and concluded that KOH is readily converted to K₂SO₄ in the presence of SO₂ at temperatures below 1500 K and gaseous K₂SO₄ nucleates at temperatures below 1100 K. Nevertheless, none of the research has been focused on the systematic studies predicting the effects of S and Cl contents on the potassium release mechanism during biomass combustion. A two-step kinetic model developed in our previous work [31] allows to estimate the release of K compounds under different operating conditions, which uses major chemical components (cellulose, hemicellulose and lignin) and inorganic elements as initial inputs to simulate different biomass feedstock. This work will further develop the model for accurate predictions of the influences of initial Cl and S contents on the release of different K compounds in biomass combustion. This work aims to obtain detailed release profiles of major K/Cl/S compounds when burning wheat straw, and provide a better understanding of the interlinked transition among K, Cl and S during biomass combustion process.

2. Theory and method

2.1. Description of the model

The model, for the estimation of the release of potassium compounds, was developed in Python with Cantera 2.4.0 package installed, which includes two steps: (1) decomposition reaction of biomass and (2) reactions of released species in gas phase. The decomposition step uses a mixture of cellulose, hemicellulose and lignin at given proportions to represent the wheat straw sample. It is assumed that the decomposition

of these major components is independent through a multistep, branched mechanism followed first-order reactions [32,33], the lumped reaction mechanisms (given as [supplementary material](#)) were taken from reference [34]. The kinetically-controlled release of elemental K, S and Cl were integrated into the decomposition step. The release kinetics of K, S and Cl from wheat straw were determined from the experimental results reported by Knudsen et al. [27], by minimizing the difference between experimental and modelling data using least-squares fitting with assumption of first order reactions of the release of K, S and Cl. The subsequent combustion in gas phase involves 420 reactions of 77 species, in which, 325 reactions of hydrocarbon species that are originally from GRI30. mech; the rest 95 reactions of K, S and Cl species that were extracted from the work of Peter et al [28], Cerru et al. [35] and Sliger et al. [36] are given as [supplementary material](#). Through the devolatilisation and combustion steps, the yields of all possible gaseous products are acquired, as well as the possible reaction pathways for the formations of K compounds and the corresponding reaction rates (the results of reaction pathways from this study are provided as [supplementary material](#)). A schematic of the modelling network is depicted in Fig. 1.

2.2. Model setup

In this study, wheat straw was studied as the raw material, its properties are summarised in Table 1. The fitting method developed by Teresa et al. [37] has been used to calculate the mole fractions of cellulose, hemicellulose and lignin in the raw biomass, while the initial fractions of moisture and potassium were taken from the literature [27]. Six cases were considered in this study to reflect different initial contents of chlorine and sulphur in biomass: Cl-lean, Cl-standard, Cl-rich, S-lean, S-standard and S-rich. The changes of Cl and S contents were calculated based on the standard amount of initial contents of Cl and S as summarised in our previous study [31]. Then, the contents of Cl and S in the Cl/S-lean case were calculated as half of their standard contents and that in the Cl/S-rich case were calculated as double of their standard contents, the initial setups are shown in Table 2. In this work, stoichiometric combustion was considered, the air fuel mass ratio is 5.38 g air/g biomass. The biomass samples are heated starting from 300 K at a heating rate of 20 K/min till the designated final temperatures, ranged from 600 K to 1400 K with an interval of 100 K. To ensure a complete combustion, a holding time of 600s is applied at each final temperature.

3. Results and discussion

3.1. Model validation

Due to the lack of analytical methods to directly measure the released gaseous K compounds during the biomass thermal conversions, the model is validated by comparing the predicted the released total amount of the elemental K, Cl and S against the experimental data extracted from various sources [5,16,20,26,27,38–44], which summarises the release of total amounts of K, Cl and S from the thermal conversions of different kinds of herbaceous and woody biomass and presented as dot-maps in the figures below, mapping out a general scale of the total released amount of K, Cl and S elements from biomass in corresponding to the final temperature. The predicted trends in this work agree well with the referenced data. As shown in Fig. 2, the predicted released total amounts of K, S and Cl are all increased with the raising of the final temperature; the released amount of Cl becomes flat after 1000 K, while the release of K and S in larger amounts occur at higher temperatures. Besides, the predicted results are all located within the dot maps, indicates the reasonableness and reliability of the predicted results in this work.

Fig. 2 also shows the predicted released total amounts of K, Cl and S are all relatively lower than that obtained from experiments. Due to the lack of relative reaction mechanisms, this model did not include organically associated K/S/Cl related and solid phase K and S (i.e. char-

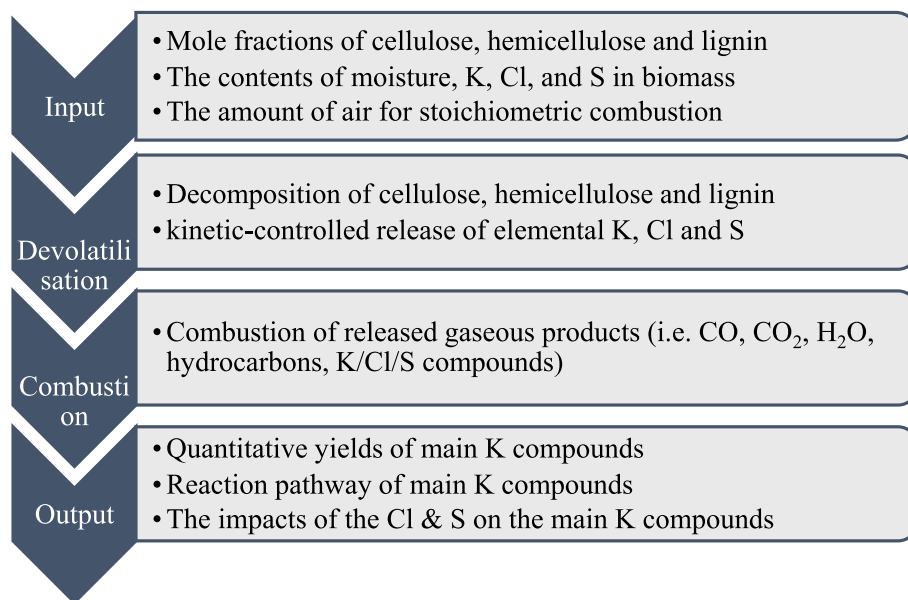


Fig. 1. Schematic of the modelling network.

Table 1
Fuel properties of wheat straw.

Compositions	Moisture ^{ar}	Volatile matter ^{db}	Ash ^{db}	C ^{db}	H ^{db}	O ^{db}	K ^{db}	S ^{db}	Cl ^{db}
Fraction, wt%	9.0	74.8	5.0	45.20	5.25	41.20	1.20	0.17	0.27

ar: as received; db: dry base.

Table 2
Summary of the initial inputs of the model.

Biomass						Atmosphere
	Cellulose	Hemicellulose	Lignin	H ₂ O	K	O ₂
Mol/g biomass	2.5×10^{-3}	2.1×10^{-3}	8.3×10^{-4}	5.0×10^{-2}	3.1×10^{-4}	3.9×10^{-2}
	Cl content (mol/g biomass)			S content (mol/g biomass)		
Case	Cl-lean	Cl-standard	Cl-rich	S-lean	S-standard	S-rich
	3.8×10^{-5}	7.6×10^{-5}	1.5×10^{-4}	2.7×10^{-5}	5.3×10^{-5}	1.1×10^{-4}

K and char-S) related reactions. As during the experiments, it would happen the dissociation of organic-K/S/Cl at lower temperatures and the release of K and S from solid char matrix at higher temperatures, which could add up to a higher released total amount of K/S/Cl. Therefore, relatively lower predictions on the released total amounts of these elements from the model are anticipated. In addition, the initial K, S and Cl contents in the tested biomass samples in the reference are different, which might also lead to the variations of the total released amount of elemental K, S and Cl from their experiments.

3.2. Sensitivity analysis

Due to the high number of reactions composing the detailed mechanism in this model, a sensitivity analysis was performed to identify those reactions that bear more potential to influence the release profiles of major potassium compounds (KCl, KOH and K₂SO₄) by the uncertainties under simulation conditions in this study. According to the analysis, the most sensitive reactions in combustion with respect to the KCl, KOH and K₂SO₄ are summarised in Fig. 3.

As depicted in Fig. 3, it is seen that the most sensitivity reactions for K₂SO₄ have the highest sensitivity values, while the most sensitivity reactions for KCl have the lowest sensitivity values. The most K/Cl/S

relevant sensitive reaction for KCl, KOH and K₂SO₄ generation is $\text{Cl} + \text{K} \rightleftharpoons \text{KCl}$, $\text{CO} + \text{KO} \rightleftharpoons \text{CO}_2 + \text{K}$ and $\text{KO} + \text{SO}_2 \rightleftharpoons \text{KSO}_3$, respectively. Besides, according to the results, free radical involved reactions are greatly dominant the KCl, KOH and K₂SO₄ generation. This indicates that intermediate species and reactions are largely involved in the formation process of potassium compounds and thus important in terms of the accurate prediction of release profiles of potassium compounds.

Moreover, as we can see in Fig. 3, several organic reactions are important for all mechanisms, however, they all involve the consumption and generation of OH radicals and H₂O, especially in the results with respect to K₂SO₄, the sensitivity values for the OH and H₂O related reactions can go up to 1.5. This implies that the generation of potassium compounds are highly sensitive to the moisture content and the available OxHy radicals in the reaction system.

3.3. Effects of initial Cl content

This work studied the effects of initial Cl content on the release of potassium compounds under different operating temperatures, with 3 scenarios of the initial content of chlorine in biomass: Cl-lean, Cl-standard, Cl-rich. The changes of amounts of the HCl and potassium compounds (i.e. KCl, KOH and K₂SO₄) with various initial Cl contents in the

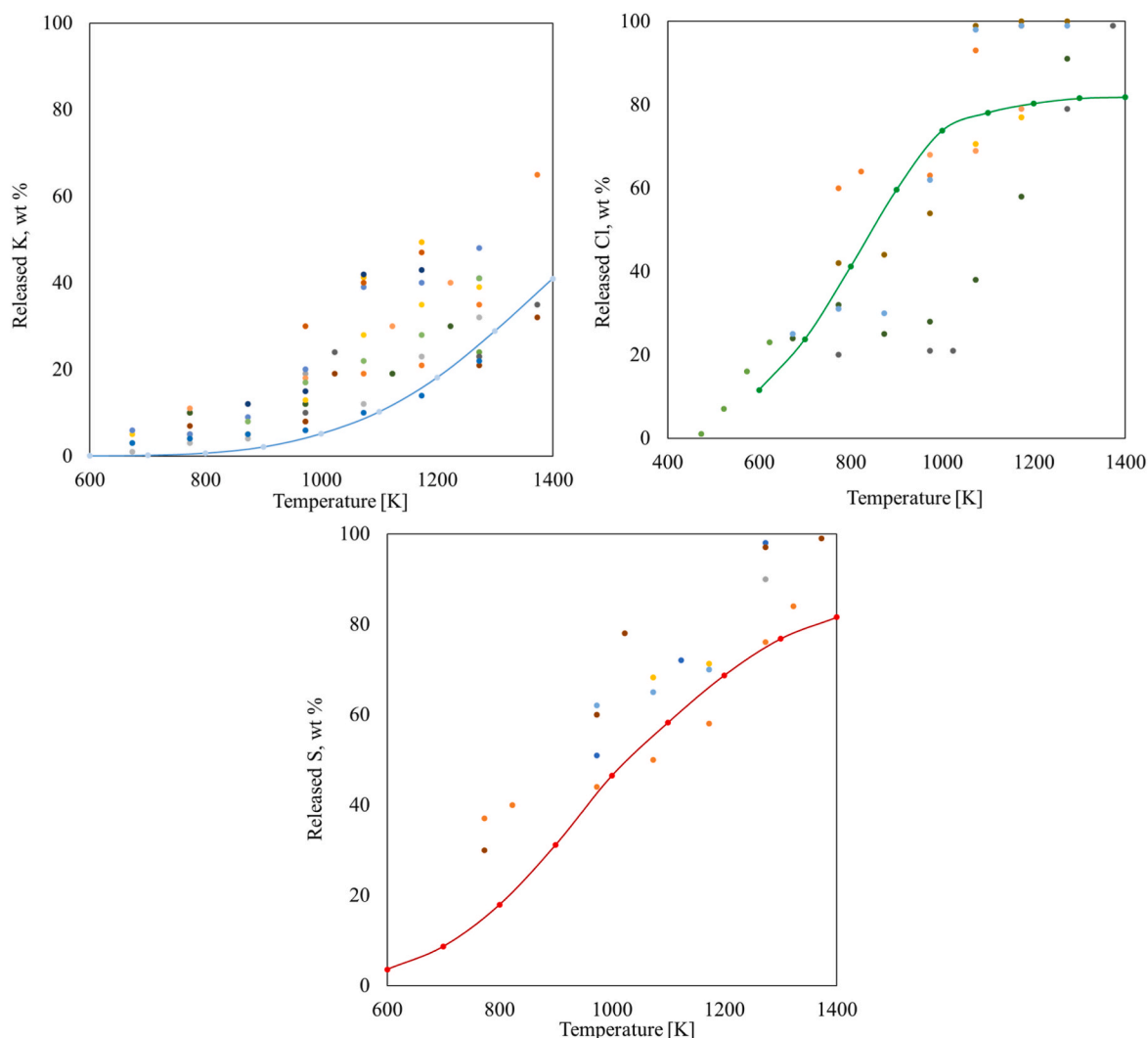


Fig. 2. Comparison of results between this work (solid lines) and Ref. [5,16,20,26,27,38–44] (dots map).

biomass are presented in Fig. 4. It shows significant variations of the released amounts of these compounds.

The release of HCl (Fig. 4 (a)) starts at 700 K and reaches its peak before 1000 K, the higher the initial Cl content, the more amount of HCl released. The peaks of HCl release shift for Cl-lean, Cl-standard and Cl-rich cases, corresponding to the operating temperature varying from 900 K, 950 K and 1000 K, with the peak released amount of HCl as 3.4×10^{-4} mol/g biomass, 8.5×10^{-4} mol/g biomass and 2.1×10^{-3} mol/g biomass, respectively; as we can see, the increasing of initial Cl from 3.8×10^{-5} mol/g biomass to 1.5×10^{-4} mol/g biomass promotes the maximum release of HCl by 518%. Subsequently, the release of HCl starts to decline, and it shows that the higher the initial Cl content, the higher final temperature is needed to terminate the release of HCl. In fact, during the biomass combustion, Cl starts to release at relatively low temperatures (700 K–800 K) [14], majority in the form of HCl [20]. The other dominant Cl species in the biomass is KCl, which remains stable in the solid phase until the final temperature exceeds 1000 K [12,45]. Moreover, the peak of released HCl is more than doubled when doubling the initial input of Cl content. This reveals that the release of Cl is not only via the directly evaporation of HCl, but also through Cl-related intermediate reactions such as: $\text{Cl} + \text{H}_2\text{O}_2 = \text{HCl} + \text{HO}_2$ (R1) and $\text{Cl} + \text{HO}_2 = \text{HCl} + \text{O}_2$ (R2) [36]; increasing of initial Cl concentration would facilitate these reactions to occur.

The profile of KCl release is shown in Fig. 4 (b). It shows that the initial Cl content significantly promotes the release of KCl when the final

temperature surpasses 1100 K. The curve in Cl-lean case becomes flat after 1100 K, and the amount reaches its peak as 6.7×10^{-4} mol/g biomass at 1400 K and remains constant; the release of KCl in Cl-standard case shows a similar trend and reaches its final amount, 1.3×10^{-3} mol/g biomass, at 1400 K. While the release of KCl in the case of Cl-rich steeply increases with increasing of temperature up to the final temperature (1400 K), and thus a delayed peak. According to the results, raising the initial Cl from 3.8×10^{-5} mol/g biomass to 1.5×10^{-4} mol/g biomass can result in 273% more maximum release of KCl. Along with the decline of HCl, KCl starts to release in large amount due to its sublimation when temperature exceeds 1000 K [46] and becomes the major route to release Cl and K contents at the later stage of combustion. As a result, the influence of initial content of Cl becomes distinguishable. Besides, the large amount of release of HCl at an early stage could react with KOH to generate KCl, therefore as the final temperature increased it occurs the raise of the release amount of KCl. In addition, the more HCl exists in gas phase, the higher possibility of completion of the reaction with KOH, indicating more KCl would be generated.

The release profile of KOH is demonstrated in Fig. 4 (c). It shows that, in the same reaction condition, the release amount of KOH decreases with the increase of initial Cl content. The release of KOH become noticeable from 1100 K to 1200 K in the cases of Cl-lean and Cl-standard, respectively. Then the release of KOH steeply increases and reaches its peak at 1300 K, with 1.5×10^{-3} mol/g biomass in Cl-lean case and 8.0×10^{-4} mol/g biomass in Cl-standard case. Subsequently, the release of

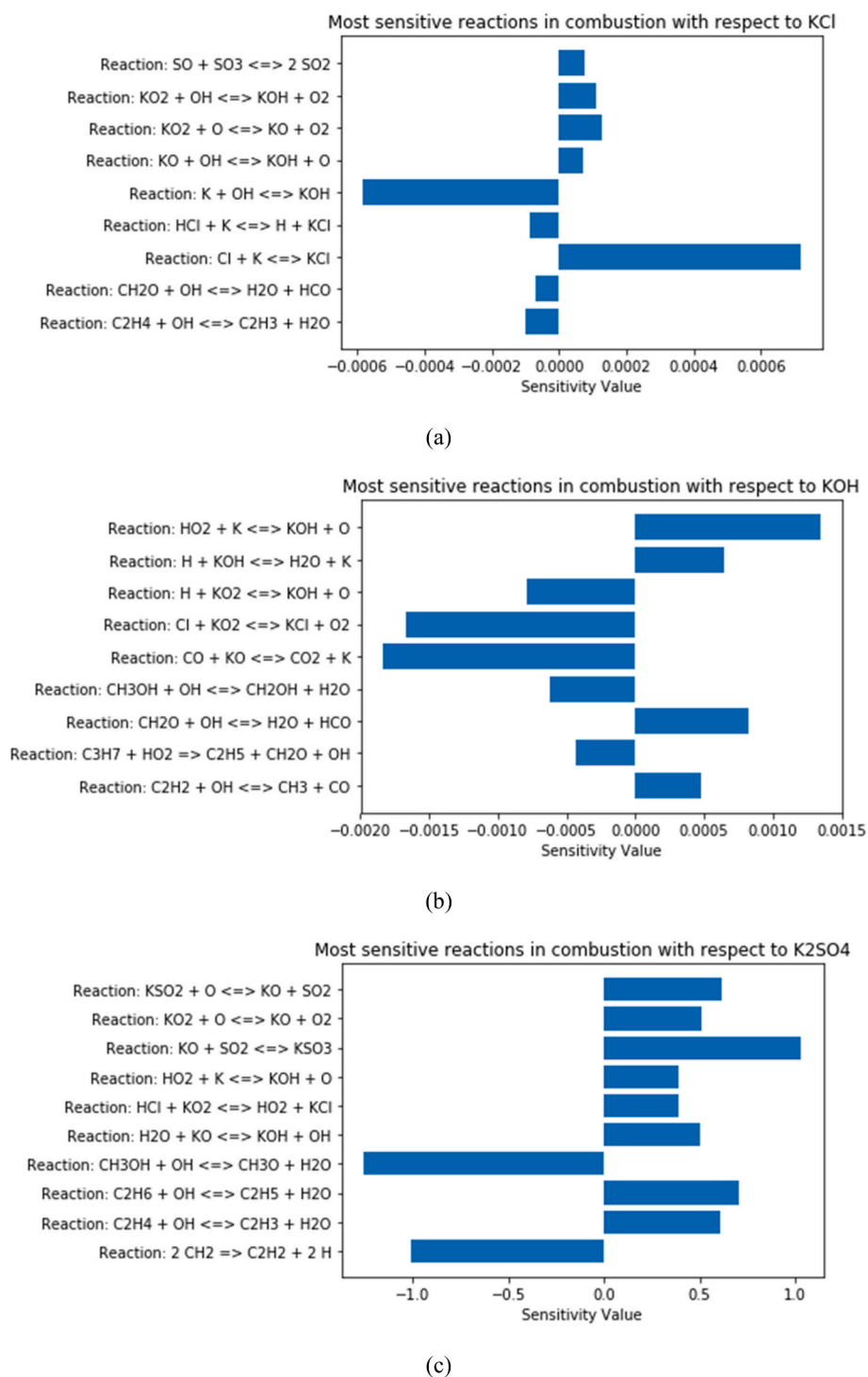


Fig. 3. Sensitivity analysis for KCl (a), KOH (b) and K_2SO_4 (c) in combustion.

KOH starts to decline, until the final amount with 1.0×10^{-3} mol/g biomass and 5.9×10^{-4} mol/g biomass in cases of Cl-lean and Cl-standard, respectively. Interestingly, the release of KOH is negligible in Cl-rich case when compared with that in other two cases. The increase of release of KOH is only minor as observed from 1300 K to 1400 K, and its final amount is 1.1×10^{-4} mol/g biomass. The results showed that the release of KOH is highly sensible to the initial Cl content. A high initial Cl content leads to more gaseous Cl-species, which would readily consume KOH. Moreover, as indicated in Ref. [25], the formation of KOH at the early stage of the combustion relies on the K and moisture content. Nevertheless, the increased Cl concentration in the reaction

system might facilitate the reaction between Cl and moisture to generate HCl, resulting in a less generation of KOH at the early stage of the combustion.

Fig. 4 (d) illustrates the release profile of K_2SO_4 . It shows the release of K_2SO_4 at temperature below 1300 K is negligible. Once the final temperature exceeds 1300 K, there is a sharply-increased release of K_2SO_4 and highly depending on the initial Cl content. The release of K_2SO_4 reaches its highest amount at 1400 K, with 5.9×10^{-4} mol/g biomass, 7.0×10^{-4} mol/g biomass and 1.9×10^{-4} mol/g biomass in Cl-lean, Cl-standard and Cl-rich cases, respectively. According to the reaction mechanism [31], $KHSO_4$ is an essential intermediate species to

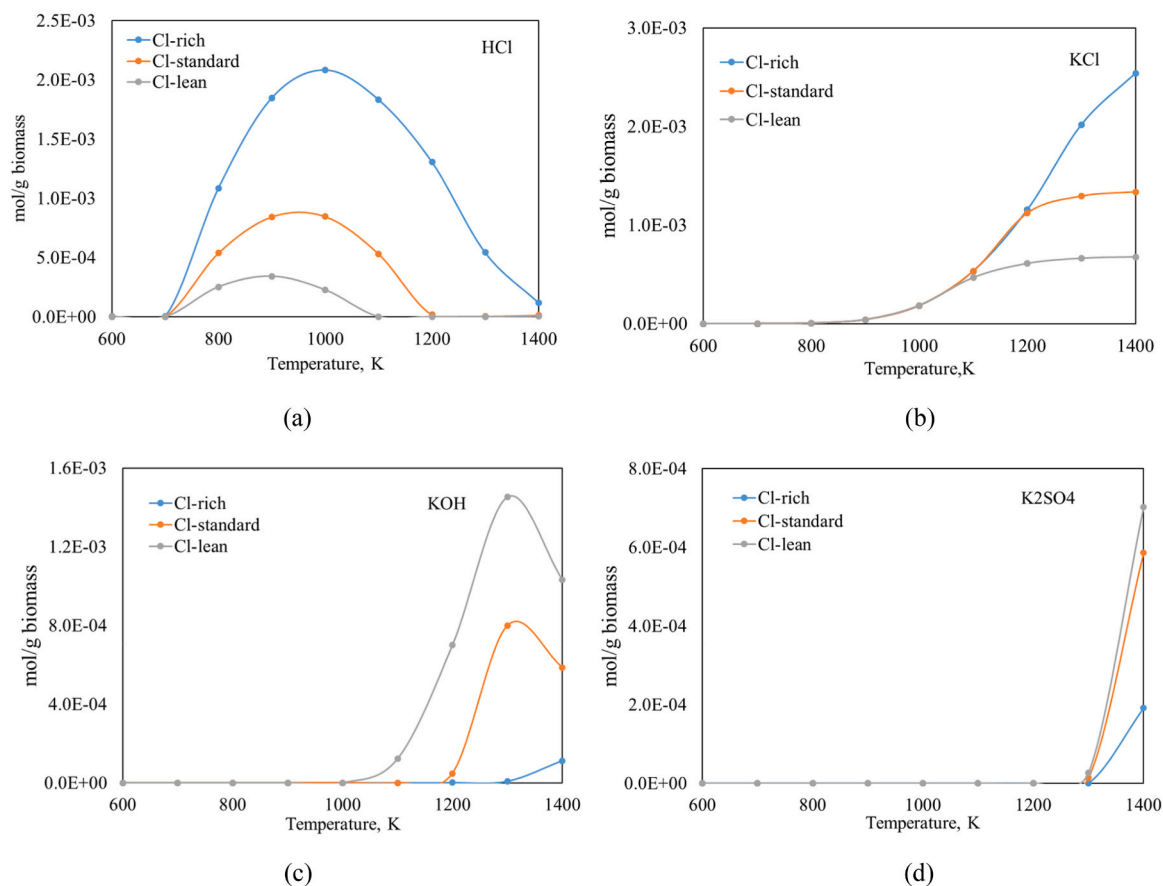


Fig. 4. The change of HCl and potassium compounds with the change of initial Cl content.

form K_2SO_4 during the combustion process, and $KHSO_4$ can be generated from the reaction of SO_3 with KOH [28]. While as illustrated in Fig. 3 (c), the higher the initial Cl concentration, the lower the release amount of KOH . This potentially leads to inhibition of $KHSO_4$ formation, via the only reaction pathway $KHSO_4 + KOH = K_2SO_4 + H_2O$ (R3) [28]. The release profile of K_2SO_4 reveals that the high initial Cl content can significantly inhibit the release of K_2SO_4 , and the effect becomes more obvious at high temperatures.

3.4. Effects of initial S content

Fig. 5 shows the release profiles of the major potassium compounds (i.e. KCl , KOH and K_2SO_4) with the change of initial S contents at various temperatures. As indicated in the results, the change of initial S content has no noticeable influence on the release of KCl , but its influences are getting significant on KOH and K_2SO_4 at temperatures higher than 1200 K.

Fig. 5 (a) shows no obvious difference among the release profiles of KCl in three cases. The release of KCl in large amount starts after 800 K and then sharply increase to 1.1×10^{-3} mol/g biomass at 1200 K before becoming constant. At low temperatures, the released S mainly exists in the form of SO_2 , which is the most stable form of S [47] and unlikely to react with other species. Therefore, the change of initial S content does not affect the transition and release of Cl-related species, i.e. KCl . As indicated in the previous studies [8,26,27,46], the release of abundant inorganically associated S happens only at temperatures above 1150 K; Once the final temperature exceeds 1200 K, the high S content would facilitate the reaction $KCl + SO_3 = KSO_3Cl$ (R4) [28] to form intermediate species KSO_3Cl , which could further react with KOH via the reaction $KSO_3Cl + KOH = K_2SO_4 + HCl$ (R5) [28]. Thus, causes the minor decreasing of the release of KCl at 1400 K when increasing the initial S

content.

Fig. 5 (b) presents the release profile of KOH . It shows that the release of KOH is minor compared to those of KCl at temperatures below 1200 K. Hence, the change of initial S content has negligible influence on the release of KOH . When final temperature exceeds 1200 K, the release amount of KOH sharply increases, which are overlapping in all three cases at temperatures below 1300 K. In S-standard case and S-rich case, the amount of KOH reaches its peak at 1300 K, with 8.0×10^{-4} mol/g biomass and 7.8×10^{-4} mol/g biomass, respectively. Subsequently, KOH starts to decrease. In S-lean case, however, after the released KOH sharply increased to 8.1×10^{-4} mol/g biomass at 1300 K, the amount of KOH continues to raise mildly, and reaches 1.0×10^{-3} mol/g biomass at 1400 K. It is known that, at relatively low temperatures, moisture is more likely to react with available K to form KOH [48]; while only at high temperatures the reactions between S and moisture could take place [49]. In consequence, the initial S content has less impact on the formation of KOH . At high temperatures (>1300 K), with the raise of initial S content, more SO_2/SO_3 can be generated during the combustion, which consume KOH via the reaction pathways: $KOH + SO_3 = KHSO_3$ (R6) and $KHSO_3 + KOH = K_2SO_4 + H_2O$ (R7). This leads to a decline of KOH release at temperatures over 1300 K.

The release profile of K_2SO_4 with the change of initial S content is presented in Fig. 5 (c). It shows the release of K_2SO_4 is negligible at low temperatures, as K_2SO_4 is the most stable form for K and S elements [47], which is not evaporated until temperature reaches 1250 K [27]. When final temperature exceeds 1300 K, the release steeply increases, up to 3.6×10^{-4} mol/g biomass, 5.9×10^{-4} mol/g biomass and 7.8×10^{-4} mol/g biomass at 1400 K in S-lean, S-standard and S-rich cases, respectively. As stated in Ref. [50], the inorganic sulphate can be transformed into other solid inorganic sulphur compounds during the thermal conversion process, which means, the initial S content can affect

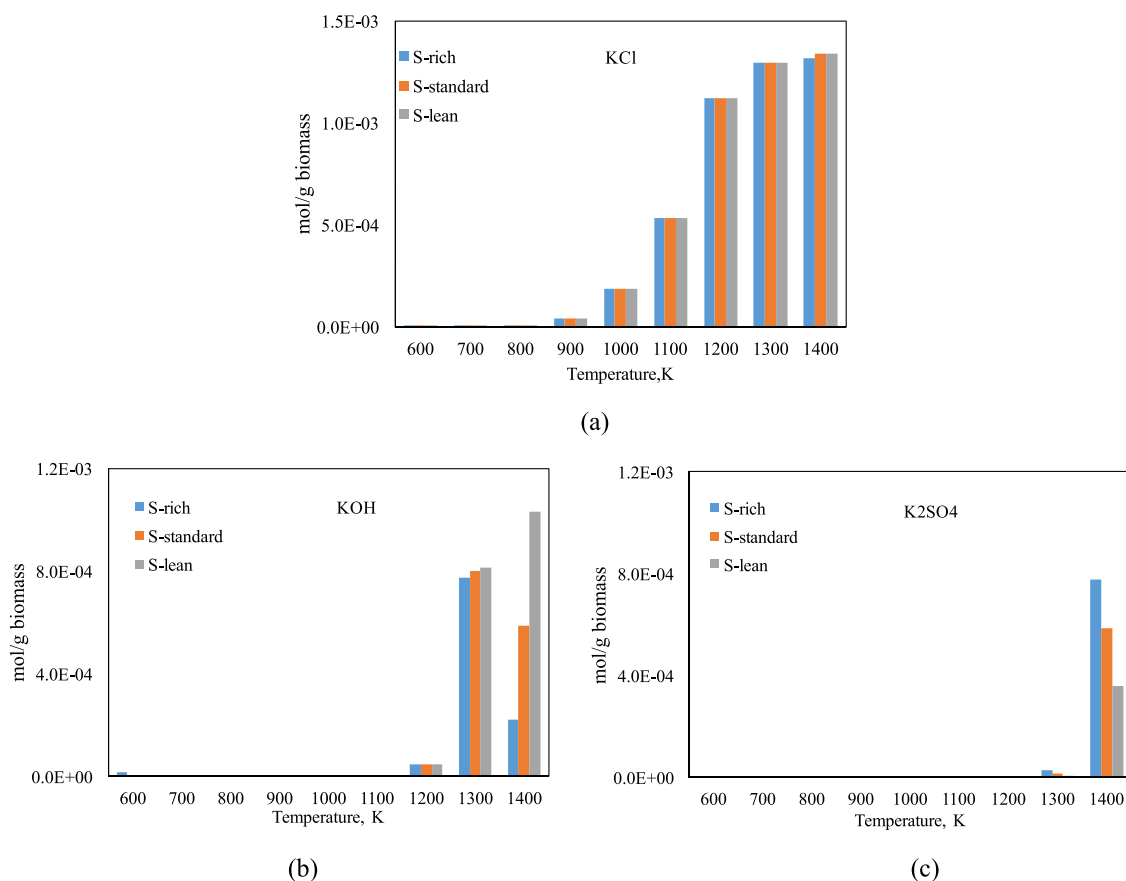


Fig. 5. The change of major potassium compounds with the change of initial S content.

the release of K₂SO₄ by influencing the formation of intermediate K–S species, such as KSO₂ and KSO₃Cl. And the higher the initial S content, the more generation of intermediate species. Then those intermediate species would further react to generate K₂SO₄ via the possible reactions R8–R11 as indicated in Table 3.

3.5. Distribution of the released KCl–KOH–K₂SO₄

By summarising the results on the effects of S and Cl, the distribution of the released potassium compounds (i.e., KOH, KCl and K₂SO₄) in combustion have been analysed, as shown in Fig. 6. To normalise the impacts of Cl and S on various scenarios with different initial S and Cl contents in biomass, mole ratios of K/Cl and K/S were applied. The resulting data presented in these diagrams have been focused on the results obtained at temperatures above 1000 K, as according to the aforementioned results and discussions, key potassium compounds KCl–KOH–K₂SO₄ are released in identifiable amounts at high temperatures for comparisons.

Table 3
Summary of potential reactions.

Cl + H ₂ O ₂ = HCl + HO ₂	R1
Cl + HO ₂ = HCl + O ₂	R2
KHSO ₄ + KOH = K ₂ SO ₄ + H ₂ O	R3
KCl + SO ₃ = KSO ₃ Cl	R4
KSO ₃ Cl + KOH = K ₂ SO ₄ + HCl	R5
KOH + SO ₃ = KHSO ₃	R6
KHSO ₃ + KOH = K ₂ SO ₄ + H ₂ O	R7
KO ₂ + KSO ₂ = K ₂ SO ₄	R8
KO ₂ + KSO ₂ = K ₂ SO ₄	R9
KCl + SO ₃ = KSO ₃ Cl	R10
KSO ₃ Cl + KOH = K ₂ SO ₄	R11

As we can see from the diagrams, K/Cl and K/S ratios can significantly affect the distribution of K compounds at temperature higher than 1200 K. The higher the K/Cl ratio, the more evenly distributed of KCl, KOH and K₂SO₄ in the gas-phase products; The KCl % decreased dramatically, and the dominate K compound shift from KCl to KOH. Similarly, raising the K/S ratio leads to an even distribution of KCl, KOH and K₂SO₄. However, KCl dominates the K compounds all the time.

In Fig. 6, different colours indicate the different key potassium compounds, and their distributions are presented according to their mass fractions. As we can see, the distributions are varied with the change of final temperature and K/Cl and K/S ratios. The higher the final temperature, the distribution tends to shift towards KOH + K₂SO₄ in both situations. Meanwhile, with the increasing of K/Cl ratio, the distribution shifts from KCl + K₂SO₄ to KOH + K₂SO₄; while raising the K/S ratio, the distribution of key potassium compounds shifts from KCl + KOH towards KCl + K₂SO₄.

Based on the summary, it can be expected that at lower temperatures, K/Cl and K/S has insignificant influence on the distribution of key potassium compounds, KCl remain as the major released potassium compound and occupies the most of the released K content. At higher temperatures, K/Cl ratio has more effect on the distribution, and the higher the ratio, the more KOH and K₂SO₄ will be anticipated; while increasing the K/S ratio, the released amount of KOH will exceed the released amount KCl, and the release of K₂SO₄ will become neglectable eventually.

4. Conclusions

This paper used a two-step model to predict the release of major K compounds from biomass combustion, and investigated the impacts of the S and Cl contents in the virgin biomass.

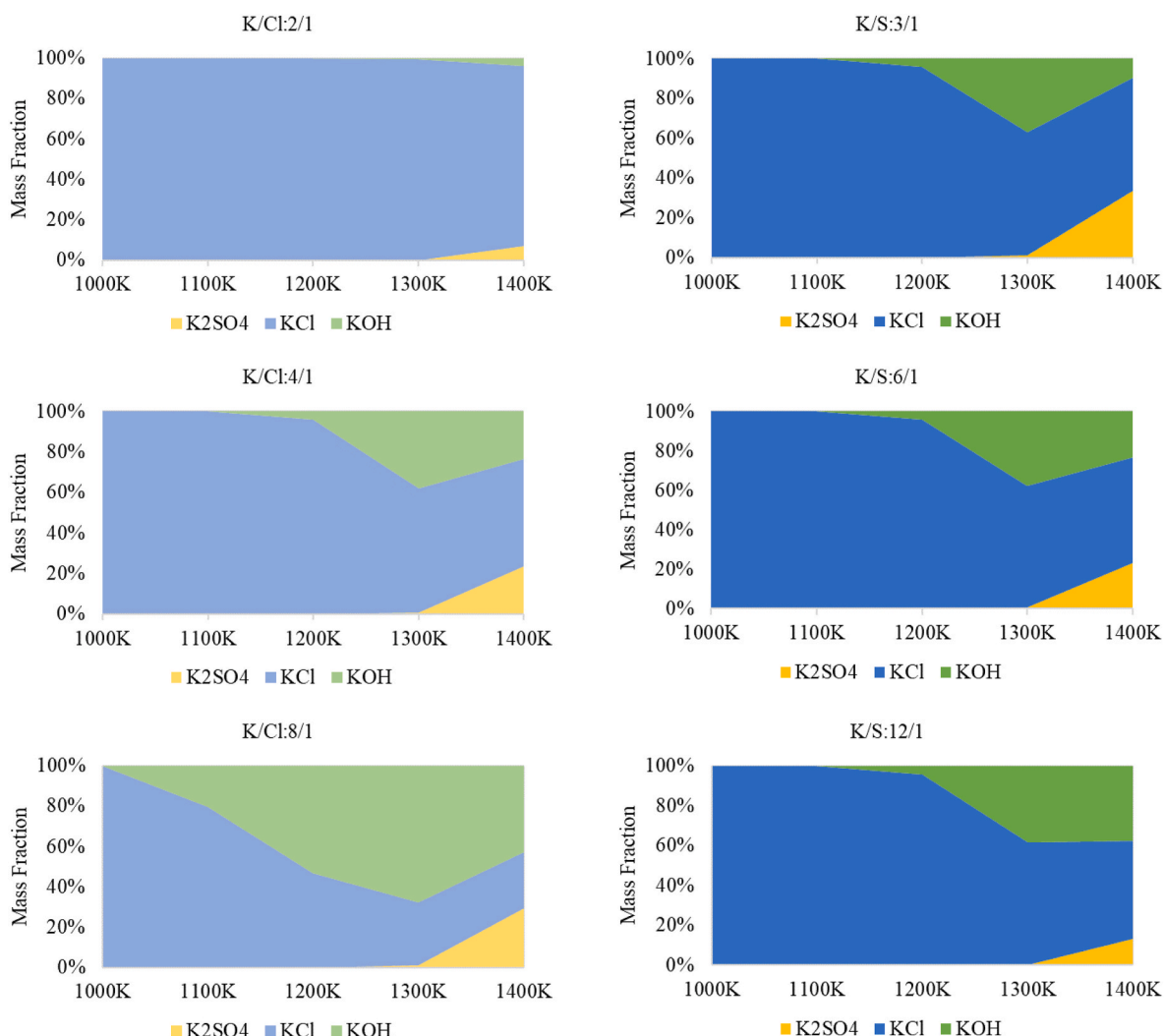


Fig. 6. Distribution of KOH–KCl–K₂SO₄ with the change of K/Cl and K/S ratio in combustion.

The modelling results showed that during the combustion process, increasing the initial Cl concentration in the biomass favours the release of HCl and KCl. It directly affects the formation of HCl, however, the release of KCl is less depending on the initial Cl content. Nevertheless, a higher Cl content could significantly inhibit the formations of KOH and K₂SO₄. This influences the release of KOH by controlling the available moisture content for K to react with and by consuming the formed KOH with large amount of Cl compounds; while it controls the formation of KO and KSO₃ to prevent the generation and release of K₂SO₄.

Whereas, the initial S content has less influences on the release of HCl and KCl, and could only affect the release of KOH and K₂SO₄ at high temperatures above 1300 K. At high temperatures, the higher content of initial S, the larger amount of K₂SO₄ released. A high S content could directly increase the formation of intermediate species: KSO₂ and KSO₃ so to indirectly affect the generation of K₂SO₄ which can be greatly sublimated and evaporated afterwards.

The main findings of this paper could help better understand the release behaviour of K compounds with different S and Cl contents in the biomass. It can provide insightful information about the K, S and Cl reaction chemistry inside the boiler, and the formation of corrosive ash deposit during the combustion process, and thus, help us to develop more detailed kinetic mechanisms of K–S–Cl related ash compounds. This could be beneficial to biomass processing industry to guide the selection and preparation of raw materials and enhance the apparatus design and modification.

The model will be further developed to be robust for applications of the different types of biomass materials; reaction mechanisms of organic-K and more inorganic-K compounds will be investigated and integrated into the model. The phase change of released K compounds would also be introduced to further predict the condensation and deposition of the ash when burning biomass materials. In this way, we can better predict the release and deposit behaviour of K compounds during the thermal conversion process, and then mitigate the ash-related problems that they are caused.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.joei.2022.01.014>.

References

- [1] H. Long, et al., Biomass resources and their bioenergy potential estimation: a review, *Renew. Sustain. Energy Rev.* 26 (2013) 344–352.
- [2] Radiation, U.N.S.C.E.A., Sources and Effects of Ionizing Radiation Sources, vol. 1, United Nations Publications, 2000.
- [3] A. Demirbas, Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues, *Prog. Energy Combust. Sci.* 31 (2) (2005) 171–192.
- [4] W. Cao, et al., Release of alkali metals during biomass thermal conversion, *Arch. Ind. Biotechnol.* 1 (1) (2016) 1–3.
- [5] P.A. Tchhoffor, K.O. Davidsson, H. Thunman, Transformation and release of potassium, chlorine, and sulfur from wheat straw under conditions relevant to dual fluidized bed gasification, *Energy Fuels* 27 (12) (2013) 7510–7520.
- [6] P. Sommersacher, et al., Application of novel and advanced fuel characterization tools for the combustion related characterization of different wood/kaolin and straw/kaolin mixtures, *Energy Fuels* 27 (9) (2013) 5192–5206.
- [7] Y. Wang, et al., Release and transformation of chlorine and potassium during pyrolysis of KCl doped biomass, *Fuel* 197 (2017) 422–432.
- [8] S.C. Van Lith, et al., Release to the gas phase of inorganic elements during wood combustion. Part 1: development and evaluation of quantification methods, *Energy Fuels* 20 (3) (2006) 964–978.
- [9] H. Nielsen, et al., The implications of chlorine-associated corrosion on the operation of biomass-fired boilers, *Prog. Energy Combust. Sci.* 26 (3) (2000) 283–298.
- [10] L.A. Hansen, et al., Influence of deposit formation on corrosion at a straw-fired boiler, *Fuel Process. Technol.* 64 (1–3) (2000) 189–209.
- [11] F.J. Frandsen, Ash Formation, Deposition and Corrosion when Utilizing Straw for Heat and Power Production, DTU, 2010.
- [12] H.P. Michelsen, et al., Deposition and high temperature corrosion in a 10 MW straw fired boiler, *Fuel Process. Technol.* 54 (1–3) (1998) 95–108.
- [13] J. Werther, et al., Combustion of agricultural residues, *Prog. Energy Combust. Sci.* 26 (1) (2000) 1–27.
- [14] E. Björkman, B. Strömberg, Release of chlorine from biomass at pyrolysis and gasification conditions, *Energy Fuels* 11 (5) (1997) 1026–1032.
- [15] H. Zhao, et al., In situ measurement of potassium release during biomass combustion using laser-induced breakdown spectroscopy: effect of silicate on potassium release, *Energy Fuels* 34 (3) (2020) 3262–3271.
- [16] H.-b. Zhao, et al., Study on the transformation of inherent potassium during the fast-pyrolysis process of rice straw, *Energy Fuels* 29 (10) (2015) 6404–6411.
- [17] T. Brunner, et al., Behaviour of ash forming compounds in biomass furnaces—measurement and analyses of aerosols formed during fixed-bed biomass combustion, in: Proc. of the International IEA Seminar “Aerosols in Biomass Combustion”, 2001. Zurich, Switzerland.
- [18] J. Dahl, et al., Results and evaluation of a new heavy metal fractionation technology in grate-fired biomass combustion plants as a basis for an improved ash utilisation, in: 12th European Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection, 2002.
- [19] T. Ma, et al., Biomass ash induced agglomeration in fluidized bed. Part 2: effect of potassium salts in different gas composition, *Fuel Process. Technol.* 180 (2018) 130–139.
- [20] J.M. Johansen, et al., Release of K, Cl, and S during combustion and co-combustion with wood of high-chlorine biomass in bench and pilot scale fuel beds, *Proc. Combust. Inst.* 34 (2) (2013) 2363–2372.
- [21] J.T. Hamilton, et al., Chloride methylation by plant pectin: an efficient environmentally significant process, *Science* 301 (5630) (2003) 206–209.
- [22] H. Egsgaard, J. Ahrenfeldt, U.B. Henriksen, On the significance of methyl chloride in gasification processes, in: 18th European Biomass Conference and Exhibition, 2010.
- [23] S.B. Saleh, et al., Release of chlorine and sulfur during biomass torrefaction and pyrolysis, *Energy Fuels* 28 (6) (2014) 3738–3746.
- [24] P. Sommersacher, et al., Simultaneous online determination of S, Cl, K, Na, Zn, and Pb release from a single particle during biomass combustion. Part 2: results from test runs with spruce and straw pellets, *Energy Fuels* 30 (4) (2016) 3428–3440.
- [25] D.S. Clery, et al., The effects of an additive on the release of potassium in biomass combustion, *Fuel* 214 (2018) 647–655.
- [26] S.C. Van Lith, et al., Release to the gas phase of inorganic elements during wood combustion. Part 2: influence of fuel composition, *Energy Fuels* 22 (3) (2008) 1598–1609.
- [27] J.N. Knudsen, P.A. Jensen, K. Dam-Johansen, Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass, *Energy Fuels* 18 (5) (2004) 1385–1399.
- [28] P. Glarborg, P. Marshall, Mechanism and modeling of the formation of gaseous alkali sulfates, *Combust. Flame* 141 (1–2) (2005) 22–39.
- [29] K. Wan, et al., Numerical study of HCl and SO₂ impact on potassium emissions in pulverized-biomass combustion, *Fuel Process. Technol.* 193 (2019) 19–30.
- [30] M.R. Mortensen, et al., Modeling post-flame sulfation of KCl and KOH in bio-dust combustion with full and simplified mechanisms, *Fuel* 258 (2019), 116147.
- [31] W. Cao, et al., Prediction of potassium compounds released from biomass during combustion, *Appl. Energy* 250 (2019) 1696–1705.
- [32] E. Ranzi, et al., Chemical kinetics of biomass pyrolysis, *Energy Fuels* 22 (6) (2008) 4292–4300.
- [33] A.D. Lewis, T.H. Fletcher, Prediction of sawdust pyrolysis yields from a flat-flame burner using the CPD model, *Energy Fuels* 27 (2) (2013) 942–953.
- [34] E. Ranzi, P.E.A. Debiagi, A. Frassoldati, Mathematical modeling of fast biomass pyrolysis and bio-oil formation. Note I: kinetic mechanism of biomass pyrolysis, *ACS Sustain. Chem. Eng.* 5 (4) (2017) 2867–2881.
- [35] F. Cerru, A. Kronenburg, R. Lindstedt, Systematically reduced chemical mechanisms for sulfur oxidation and pyrolysis, *Combust. Flame* 146 (3) (2006) 437–455.
- [36] R.N. Sliker, J.C. Kramlich, N.M. Marinov, Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species, *Fuel Process. Technol.* 65 (2000) 423–438.
- [37] T. Martf-Rosselló, J. Li, L. Lue, Quantitatively modelling kinetics through a visual analysis of the derivative thermogravimetric curves: application to biomass pyrolysis, *Energy Convers. Manag.* 172 (2018) 296–305.
- [38] J. Fagerström, et al., Alkali transformation during single pellet combustion of soft wood and wheat straw, *Fuel Process. Technol.* 143 (2016) 204–212.
- [39] P.A. Tchhoffor, K.O. Davidsson, H. Thunman, Effects of steam on the release of potassium, chlorine, and sulfur during char conversion, investigated under dual-fluidized-bed gasification conditions, *Energy Fuels* 28 (11) (2014) 6953–6965.
- [40] A. Anca-Couce, et al., Multi-stage model for the release of potassium in single particle biomass combustion, *Fuel* 280 (2020), 118569.
- [41] T. Okuno, et al., Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass, *Energy Fuels* 19 (5) (2005) 2164–2171.
- [42] H. Chen, et al., Release and transformation characteristics of K and Cl during straw torrefaction and mild pyrolysis, *Fuel* 167 (2016) 31–39.
- [43] D.J. Lane, et al., Release of Cl, S, P, K, and Na during thermal conversion of algal biomass, *Energy Fuels* 29 (4) (2015) 2542–2554.
- [44] L. Deng, et al., Transformation and release of potassium during fixed-bed pyrolysis of biomass, *J. Energy Inst.* 91 (4) (2018) 630–637.
- [45] S.C. Van Lith, Release of Inorganic Elements during Wood-Firing on a Grate, Technical University of Denmark Lyngby, Denmark, 2005.
- [46] J.M. Johansen, et al., Release of K, Cl, and S during pyrolysis and combustion of high-chlorine biomass, *Energy Fuels* 25 (11) (2011) 4961–4971.
- [47] F. Miller, G. Young, M. Von Seebach, Formation and techniques for control of sulfur dioxide and other sulfur compounds in Portland cement kiln systems, *R&D Serial* (2460) (2001) 56.
- [48] H. Fatehi, et al., LIBS measurements and numerical studies of potassium release during biomass gasification, *Proc. Combust. Inst.* 35 (2) (2015) 2389–2396.
- [49] Features of the interaction of sulfur and water. MEL Science. <https://melscience.com/US-en/articles/features-interaction-sulfur-and-water/>.
- [50] J.N. Knudsen, et al., Sulfur transformations during thermal conversion of herbaceous biomass, *Energy Fuels* 18 (3) (2004) 810–819.