



Releasing behavior of chlorine and fluorine during agricultural waste pyrolysis



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ABSTRACT

The releasing behavior of chlorine (Cl) and fluorine (F) during agricultural waste pyrolysis was investigated using a fixed-bed pyrolysis system with pyrohydrolytic-ion chromatography and thermodynamic equilibrium calculation. Agricultural waste contains a large amount of Cl-bearing species, among which approximately 30% is easily released with biomass drying. During biomass pyrolysis, Cl-bearing species evolve out rapidly to the gas phase, and higher temperature is favorable for the releasing. The releasing process can be divided into two ranges: the fast evaporating range (200–600 °C) and slow evaporating range (600–1000 °C). F shows similar transforming behavior. However, higher temperature is preferred for the release. Thermodynamic simulation shows that Cl mainly exists as KCl(g) at higher temperatures (>600 °C) with some HCl(g) and K₂Cl₂(g) as intermediate species at lower temperatures (<600 °C), whereas F mainly releases as SiF₄ at higher temperatures (>500 °C) with SF₅Cl being the dominant F-bearing species at lower temperatures (<500 °C).

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1. Introduction

The replacement of fossil fuels by various renewable energy sources is one of the most important issues confronting sustainable energy development strategies [1]. Biomass offers environmental advantages over fossil fuels for being a renewable energy source with low sulfur and nitrogen content as well as for being CO₂-neutral [2]. As a life cycle requirement, agricultural wastes show a high amount of chlorine (Cl)-bearing species (100–7000 mg/kg) [3,4]. Agricultural waste mainly exists in Cl[−], which easily evaporates and transforms into the gas phase as acid or alkali chloride during the thermal conversion of biomass [5,6]. Cl is harmful to downstream equipment because it causes high-temperature corrosion, fouling, and slagging; moreover, Cl may even affect the normal operation of biomass conversion units [7–12]. HCl is the third most important pollutant to global acidification after SO₂ and NO_x. Simultaneously, Cl release from solid wastes may enhance the formation of dioxin and aerosols [5]. Thus, the control of Cl-bearing species release is crucial for the utilization of biomass resources.

A number of studies have been conducted to investigate the properties of Cl release during the thermal conversion process through experiment and simulation [13–20]. Nearly all Cl species in biomass are in the form of water-soluble chlorides [13].

Thermodynamic equilibrium calculation shows that Cl is preferably combined with K and Na as alkali chlorides, which show high volatility. Such combination is the main pathway for Cl release as alkali chlorides evaporate to the gas phase as the temperature becomes higher than 600 °C [14,15]. Dayton et al. emphasized that Cl evolved out as HCl and KCl at 800 °C during biomass gasification, and the evolution covered the entire process of volatile release and char combustion [16]. At lower temperatures (in reducing atmosphere), Cl is released as HCl, and the evolving rate reached the maximum at 400 °C. At higher temperatures, Cl evolved as alkali chlorides during biomass combustion. Some Cl reacted with inorganic species in the gaseous phase to form alkali chlorides at temperatures higher than 600 °C [13]. Bjorkman et al. found that 30–50% of Cl evolved out at 400–600 °C during sawdust pyrolysis with KCl addition [18]. The existence of Cl facilitates the mobility of many inorganic salts, particularly potassium, which dictates that in most cases, the release of alkali salts is determined primarily by Cl concentration instead of the amount of alkali salts in the fuel [17]. High Cl content has been found to enhance the alkali metal emission from ash above 500 °C [19]. Wei et al. simulated the releasing behavior of Cl-bearing species at even higher temperature (approximately 1500 °C) [20], but it is difficult to prove the conclusions using experimental data. Rahim et al. studied the release of Cl during fast pyrolysis and found that a considerable proportion of Cl evolved out from the solid product [13]. The current research mainly focuses on the combustion process for its significant

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influences on boilers while rarely involving the pyrolysis process, let alone the moderate pyrolysis process.

The fluorine (F) content in biomass samples is slightly low (10–100 mg/kg) but shows similar properties as those of Cl for being volatilized with strong corrosiveness and toxicity [21,22]. The current research on the releasing property of F is mainly focused on the thermal conversion of coal, and only a few publications have been reported on F releasing behavior and its in-depth mechanism. With the development of biomass thermal utilization technology, the problems related to F and Cl releasing restrict their demonstration and commercialization. However, the online measurement of the release of F/Cl-bearing species is extremely difficult, and previous studies were mainly conducted based on simulation with thermodynamic equilibrium. Pyrolysis, the first step of thermal conversion, is the most important process to obtain value-added products. The contents of F and Cl in char, bio-oil, and gas products have important influences on the utilization of the products and the control of pollutants. However, the releasing properties of F and Cl as well as their distribution in products containing matters during biomass pyrolysis with experiment trials, particularly F/Cl concentration in liquid products, have rarely been reported. Thus, the releasing behavior of F and Cl from typical Chinese agricultural waste pyrolysis was investigated in a fixed-bed reactor combined with thermodynamic equilibrium calculation in this paper to understand the releasing and transforming mechanism of F and Cl during biomass thermal conversion. This research is helpful for the environment-friendly utilization of biomass resources.

2. Materials and experimental method

2.1. Materials

Wheat straw and rice husk were selected as typical agricultural waste samples with a forest waste sample, sawdust, as a comparison. The proximate and ultimate analyses results are summarized in Table 1. Ash contents are significantly higher in wheat straw and rice husk (over 10%) than that in sawdust (approximately 1%). This finding might be related to the growing requirement and harvest environments of agricultural plants. The lower heating value of the biomass sample is approximately 14 MJ/kg, with significantly low N and S contents (<1%), which indicates that biomass can be used as an environment-friendly renewable resource. Inorganic matter analysis is performed with X-ray fluorescence spectroscopy, and the results are shown in Table 2. The dominant inorganic matters in wheat straw and sawdust ashes are Si, K and Ca, which account for more than 80%, whereas the predominant component in rice husk ash is Si, which comprises approximately 90%.

Among the different test methods for F and Cl, such as spectral photometer [23] and microwave digestion combined with ion chromatography, this paper selected pyrohydrolytic-ion chromatography (PIC) to analyze F and Cl contents in biomass samples as such elements contained in biomass samples can be converted to F and Cl ionic components, which are dissolvable in a water solution and can be directly detected using ion chromatography (USA, ICS-

Table 2

Contents of inorganic matters in biomass ash (wt.%, based on ash).

Samples	Al	Si	K	Ca	Mn	Fe
Wheat straw	4.87	45.70	18.12	23.24	—	1.60
Rice husk	1.41	89.01	6.58	2.09	0.48	0.43
Sawdust	4.71	11.36	16.96	49.09	0.77	6.56

90) [24,25]. Meanwhile, the results are verified using the oxygen-flask combustion (OFC) method [26]. The results are listed in Table 3. Although the value observed by PIC is slightly lower than that obtained by OFC, the relative error between the two methods is quite acceptable (significantly less than 5%). This finding indicates that the PIC method is feasible for the determination of F and Cl contents. Being more convenient than the OFC method, the PIC method is used for the latter experiments. As shown in Table 3, the F contents of all studied samples are very low at approximately 30 mg/kg. Agricultural waste samples show significantly higher Cl contents (over 1800 mg/kg) than forest waste samples, particularly for rice husk (approximately 2600 mg/kg). This finding might be associated with the nutrient cycle and the living portion of biomass materials [11].

2.2. Experimental apparatus and methods

The pyrolysis experiments were conducted with a fixed-bed biomass pyrolysis system, as shown in Fig. 1. The system mainly includes a horizontal quartz tube reactor, an electric furnace, bio-oil condensing containers, and a gas cleaning and collection system. Temperatures are measured by two thermocouples. The sample (approximately 4 g) placed in a crucible was first loaded in a water-cooled chamber, and then the reactor was heated to the preset temperature by the electric furnace and maintained for approximately 10 min to achieve a stable condition. The crucible was then placed into the center of the reactor and maintained for 20 min. Thereafter, the furnace was rapidly cooled down, and the pyrolysis experiment was completed. During the whole process, pure N₂ was employed as the carrier gas with a flow rate of 1 L/min. The solid residue left in the crucible was collected as bio-char. The condensing tube and gas line was washed with acetone (15 mL), and the solution was collected and dried at 78 °C. The weight was taken as the amount of liquid oil. The yield of gas product was calculated based on the difference of the original biomass sample to solid char and liquid oil. To analyze the influence of pyrolysis temperature, the final furnace temperature was set at 200, 400, 600, 800, and 1000 °C.

During biomass pyrolysis process, F and Cl matters evolved out and transformed into gas products and liquid oil with some left in solid chars. The contents of F and Cl in solid char and liquid oil were analyzed using PIC, whereas the part of F and Cl that evaporated to the gas phase was determined by difference. The reproducibility of the results was verified by duplicating some experiments. The largest difference found in the Cl release between two identical experiments was less than 5%.

Table 1

Proximate and ultimate analyses of biomass samples.

Samples	Proximate analysis (wt.%)				Ultimate analysis (wt.%)					LHV (MJ/kg)
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}^*	
Wheat straw	5.08	68.28	10.51	16.14	40.45	8.07	0.71	0.38	34.82	13.04
Rice husk	5.92	61.83	15.03	17.22	36.26	9.33	0.55	0.47	32.43	14.52
Sawdust	5.99	75.39	1.23	17.40	43.69	6.75	0.09	0.23	42.03	14.31

M: moisture; V: volatile; A: ash; FC: fixed carbon; O^{*}: determined by difference; ad: air dried basis; and LHV: lower heating value.

Table 3
Contents of F and Cl in biomass samples determined by two methods.

Samples	F			Cl		
	PIC (mg/kg)	OFC (mg/kg)	RE (%)	PIC (mg/kg)	OFC (mg/kg)	RE (%)
Wheat straw	26.29	26.51	0.84	1890.12	1921.21	1.64
Rice husk	33.24	34.78	4.63	2589.57	2623.87	1.32
Sawdust	31.15	31.59	1.41	1592.56	1599.61	0.44

RE: relative error.

2.3. Thermodynamic equilibrium calculation of F and Cl compounds transformation

The thermodynamic equilibrium calculation of F and Cl compound transformation behavior during biomass pyrolysis was performed using the equilibrium analysis software HSC-Chemistry 5.11 to determine thermodynamic stable chemical and physical forms in the chemical system based on the minimization of the Gibbs free energy of the system. In this study, 1030 species (including gas, liquid, and solid products) are selected to conduct the thermodynamic equilibrium calculation for the chemical system, including the elements C, H, O, N, S, Cl, F, Si, Al, Ca, K, Fe, and Mn, between 200 and 1000 °C at 1 atm. The inputs are given in moles of biomass compositions based on 1000 kg samples.

Although the equilibrium analysis is a powerful tool to predict stable species during the chemical process, thus method has some disadvantages when applied to the pyrolysis case because the HSC-Chemistry calculations do not consider the kinetics (rates) of the chemical reactions and the non-ideality of solutions. The difficulty will arise when comparing the results of the equilibrium calculation with those of real pyrolysis system. However, the chemical equilibrium analysis in this work was adopted to determine the equilibrium distribution of elements (F, Cl) and the reaction mechanism of various species.

3. Results and discussion

3.1. Transformation property of Cl contained matters

The transformation property of Cl during biomass pyrolysis is shown in Fig. 2 as a percentage of the original content. At 200 °C, approximately 40% of Cl evolved out from solid biomass samples

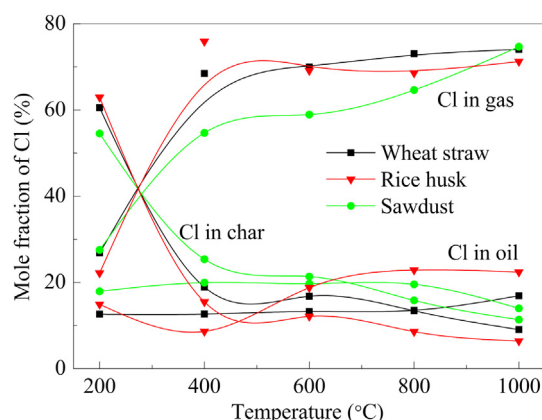


Fig. 2. Transformation property of Cl during biomass pyrolysis.

with approximately 25% evaporated to the gas phase and 15% released to the liquid phase. This finding indicates that Cl easily dissolved in water, and left coupled with steam; the dominating Cl-containing compound was HCl [27] as biomass was in drying process with water evaporating in the temperature range (<200 °C) [28]. With pyrolysis temperature increasing (200–600 °C), Cl in biomass samples rapidly evaporated. Consequently, the Cl content remained in bio-char was reduced from 60% to 15%, whereas that in gas products increased accordingly. At higher temperatures (>600 °C), the influence of temperature on Cl transformation became very limited, and the release of Cl increased slightly with increasing pyrolysis temperature. At 1000 °C, most of the Cl was released from solid samples, and only 7–10% Cl remained in the solid char residue. The amount of Cl in liquid bio-oil was quite low, accounting for approximately 15–20% of total Cl. From the transforming profiles of Cl during biomass pyrolysis, we can derive that the release of Cl can be divided into two ranges, i.e., lower temperature range (200–600 °C) and higher temperature range (>600 °C), which is consistent with previous literature [6,29]. Furthermore, volatile releasing also showed a similar trend [28]. This finding suggests that most Cl-containing matters might release Cl combined with the organic volatile evolution process during biomass pyrolysis.

With respect to the releasing mechanism, at lower temperatures, the release of Cl was mainly caused by the following reaction: $2\text{KCl} + n\text{SiO}_2 + \text{H}_2\text{O} \Rightarrow \text{K}_2\text{O}(\text{SiO}_2)_n + 2\text{HCl}$, as KCl and SiO₂ in biomass inorganic matters react with water contained in biomass and result in the formation of silicate and HCl. When the temperature is higher than 600 °C, the direct evaporation of alkali chlorides to the gas phase is the main pathway for Cl release [30]. As shown in Fig. 2, the evaporated proportion of Cl from saw dust is lower than that from rice husk and wheat straw because of the capture of HCl by CaO for the high Ca content in saw dust ash [31]. However, the conversion mechanism would be analyzed in detail with Cl-containing species measured online in the future.

From the perspective of different biomass types, the releasing properties of Cl compounds varied slightly. First, the releasing amount of Cl from sawdust pyrolysis (at 200 °C) was higher than that from wheat straw and rice husk, as sawdust showed higher moisture content and O element (the potential component for H₂O formation) with more water-soluble Cl-containing matters, which were mainly released with H₂O evaporation. However, the release (200–600 °C) of Cl from sawdust pyrolysis is significantly lower than that from two agricultural waste samples, and only ~50% Cl was converted to the gas phase at 400 °C. At higher temperatures (>600 °C), the release of Cl from saw dust was significantly enhanced by increasing temperature. This condition might be

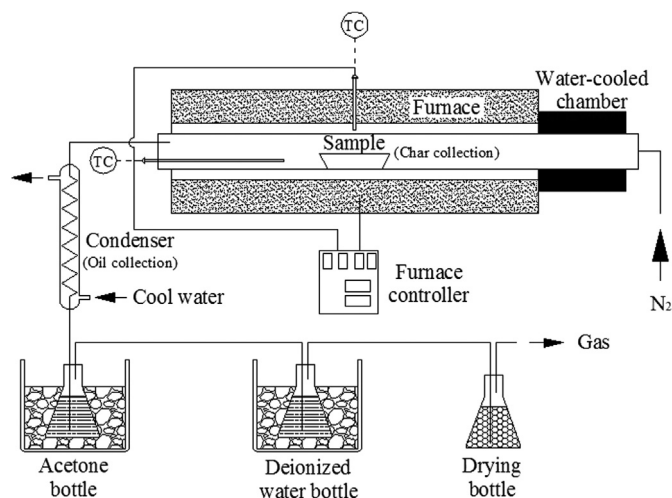


Fig. 1. Test rig of biomass pyrolysis system.

attributed to the structure difference between forest waste and agricultural waste samples, as more Cl compounds coupled with volatile organics in agricultural wastes evolved with volatile release, whereas the Cl released from sawdust was mainly caused by the evaporation of KCl at higher temperatures (>600 °C). Meanwhile, for rice husk, the release of Cl to bio-oil was increased significantly with increasing temperature (>400 °C), whereas no evident effect of temperature on the release of Cl to the gas phase was found over 600 °C. This finding indicates that Cl might be combined with organic compounds to form organic Cl compounds, which will evaporate at higher temperatures and condense with liquid bio-oil ($\sim 20\%$), given that lower alkali matter content was found in the rice husk sample. A possible reason for the difference in Cl release among the three samples is that the contents of three main components (cellulose, hemi-cellulose, and lignin) varied in different biomass samples. The trapping of Cl-bearing species by the char matrix is also an important factor in the release of Cl [32]. Owing to the relatively high char yield under moderate reaction conditions, the proportion of Cl in char is slightly higher in this work than in previous works [13]. The functional groups of char derived from different components differ, such that the interaction between the functional groups of the char surface and Cl-bearing species mainly affect the release of Cl. However, the in-depth mechanism of the interaction has not been reported elsewhere, thus making this topic a very interesting work for future research.

The Cl in liquid product can be mainly attributed to the solubility of chlorides in water-rich bio-oil rather than the condensation of organic Cl-bearing species because few publications have reported on Cl-bearing organic components in bio-oil.

3.2. Transformation and distribution property of F

The transformation property of F during biomass pyrolysis is shown in Fig. 3. At 200 °C, approximately 25% of F is released and might exist as HF. This fraction can easily dissolve in water and evaporate to the gas phase with steam during the drying process. This condition is largely caused by the release of the fluoride covalently bonded in the biomass macromolecule, given that organically associated fluorine in the form of anion fluorine is adsorbed on the biomass organic surface in pores and is surrounded by moisture. This finding suggests that water leaching can remove some F-containing matters in biomass.

During the thermal conversion process, F evaporated to the gas phase gradually, and temperature showed a significant influence on the transformation property. With increasing temperature, the

amount of F in the gas phase significantly increased. The releasing process can also be divided into two ranges: 200–800 °C and 800–1000 °C. The release of F was almost completed at 800 °C, and approximately 90% of F-bearing matters shifted to the gas phase. Previous studies showed that F mainly exists as inorganic salt in coal samples and then evolves as HF and SiF_4 [22,33]. We can deduce that the release of F was mainly caused by the thermal cracking of F-containing inorganic matters in biomass samples combined with a series of complex reactions, such as $\text{SiO}_2 + 4\text{HF} \Rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ [22].

At higher temperatures (>800 °C), the amount of F in solid char decreased slowly, particularly for the two agricultural waste samples. Different mechanisms of F matter evolution were compared with that at lower temperatures. As the melting point of alkali fluoride (NaF and KF) is quite high (>900 °C), such material might melt and evaporate to the gas phase at higher temperatures. However, the mechanism should be confirmed with experimental data in the near future.

3.3. Thermodynamic simulation of F and Cl compounds transformation

The profiles of Cl- and F-containing matter transformation based on thermodynamic equilibrium calculation are shown in Figs. 4 and 5 based on 1000 kg biomass samples. Rice husk was selected as the representative sample in this case because it shows the highest Cl and F contents among the raw biomass samples involved, and similar profiles were found for the other two samples.

From Fig. 4, we can observe that at lower temperatures (<300 °C), Cl is mostly coupled with alkali and alkaline earth metals as solid inorganic matters $\text{KCl} \cdot \text{CaCl}_2$ with a trace amount of SF_5Cl . With increasing temperature (300–425 °C), some potassium chloride dimers [$\text{K}_2\text{Cl}_2(\text{g})$] were formed, and the amount was significantly enhanced with the diminishing of $\text{KCl} \cdot \text{CaCl}_2$. Accordingly, some $\text{HCl}(\text{g})$ in gas phase was formed and reached the maximum value at ~ 450 °C. However, the thermodynamic equilibrium state is difficult to achieve at lower temperatures, making the results differ from those of the experiment as Cl preferably evolves in hydrochloride, but not $\text{K}_2\text{Cl}_2(\text{g})$, during biomass pyrolysis [20]. At a temperature between 425 and 475 °C, no evident change was noted, and HCl and K_2Cl_2 remained thermally stable. Thereafter, HCl diminished quickly, whereas $\text{K}_2\text{Cl}_2(\text{g})$ began to increase continuously with increasing temperature (475–500 °C). However, $\text{K}_2\text{Cl}_2(\text{g})$ is not thermodynamically stable and easily cracks into $\text{KCl}(\text{g})$ at higher temperatures (>600 °C). Thus, the amount of

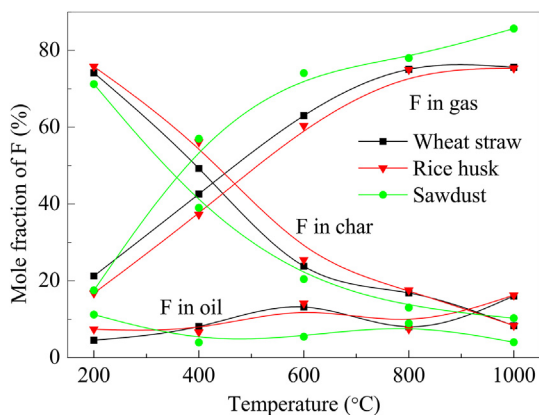


Fig. 3. Transformation property of F during biomass pyrolysis.

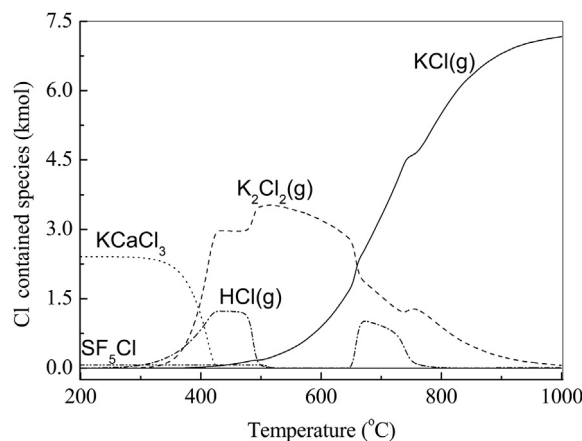


Fig. 4. Transforming profiles of Cl-bearing matters during the pyrolysis of rice husk.

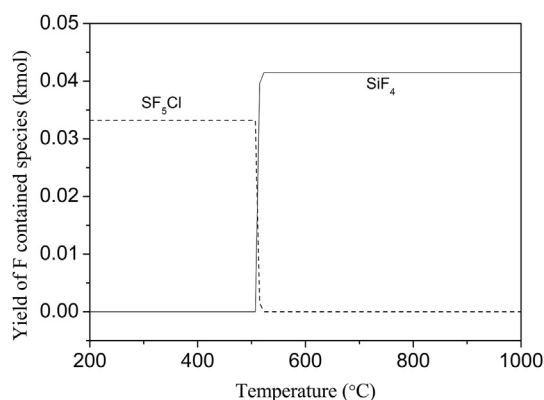


Fig. 5. Transforming profiles of F-bearing matters during the pyrolysis of rice husk.

KCl(g) increased considerably with a further increase in temperature (>600 °C), and most of the Cl was converted to KCl(g) at 1000 °C. This finding is consistent with the experimental result that Cl evolved the gas phase rapidly with increasing temperature. Simultaneously, we confirmed that the evaporation of KCl was the main pathway for Cl evolution at higher temperatures (>600 °C). However, at 650–750 °C, some HCl was released, which might be attributed to the fact that $K_2Cl_2(g)$ dissolved in steam, which was formed from the secondary cracking of biomass volatiles. Meanwhile, trace KOH and $K_2O \cdot 2SiO_2$ was found. In general, the transformation of Cl can be divided into two steps: conversion to $K_2Cl_2(g)$ and HCl(g) at lower temperatures (<600 °C) and then transformation to KCl(g) at higher temperatures (>600 °C).

From the conversion profile of F-bearing matters shown in Fig. 5, we can observe that F mainly existed in SF_5Cl at lower temperatures (<500 °C), after which SF_5Cl vanished sharply and resulted in the formation of a large amount of SiF_4 with increasing temperature. This condition might be attributed to the fact that F is easily combined with inorganic matters, such as SiO_2 [33]. The process can be described as follows: SF_5Cl was dissolved in water at higher temperatures to form hydrogen fluoride, which would react with SiO_2 to form SiF_4 ($SiO_2 + 4HF \Rightarrow SiF_4 + 2H_2O$). Threshold was observed at ~ 500 °C, and SF_5Cl was the main F-containing matter as the temperature became lower than 500 °C. SiF_4 was the only F-bearing species as the temperature became higher than 500 °C. This finding proves that F largely evolved as SiF_4 (<800 °C). However, as alkali metal content was limited for rice husk and might be mainly combined with Cl (refer to Fig. 4), no alkali fluoride (NaF and KF) was formed. The thermodynamic simulation results agreed to a large extent with the experimental results, which showed that at high temperatures (>500 °C), most F was released to the gas phase, whereas the discrepancy might result from the limitation of the simulation method.

4. Conclusions

Three typical agricultural waste samples were investigated to determine the releasing behavior of Cl and F during biomass pyrolysis process. Thermodynamic equilibrium calculation was performed to gain a better understanding of the release mechanism of Cl and F. Some conclusions were drawn as follows.

Cl- and F-containing matters are water soluble, such that the elements easily evolve as chloride acid with water steam during biomass drying. During agricultural waste pyrolysis, Cl was feasibly shifted to the gas phase, and the evolution involved the rapid release of HCl (200–600 °C) and slow evaporation (>600 °C) of KCl. F-containing matters displayed similar properties. However, the

release is slightly slower, and the threshold temperature increased to 800 °C. The thermodynamic equilibrium simulation results showed that SF_5Cl was the dominant F-containing species at lower temperatures (<500 °C), whereas SiF_4 was the major F-containing species at higher temperatures (>500 °C).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.energy.2014.01.012>.

References

- [1] Lund H. Renewable energy strategies for sustainable development. *Energy* 2007;32(6):912–9.
- [2] Wu CZ, Yin XL, Yuan ZH, Zhou ZQ, Zhuang XS. The development of bioenergy technology in China. *Energy* 2010;35(11):4445–50.
- [3] Coda B, Aho M, Berger R, Hein KRG. Behavior of chlorine and enrichment of risky elements in bubbling fluidized bed combustion of biomass and waste assisted by additives. *Energy Fuels* 2001;15(3):680–90.
- [4] Diaz-Ramirez M, Sebastian F, Royo J, Rezeau A. Combustion requirements for conversion of ash-rich novel energy crops in a 250 kWth multifuel grate fired system. *Energy* 2012;46(1):636–43.
- [5] Davidsson KO, Amand LE, Leckner B, Kovacevic B, Svane M, Hagstrom M, et al. Potassium, chlorine, and sulfur in ash, particles, deposits, and corrosion during wood combustion in a circulating fluidized-bed boiler. *Energy Fuels* 2007;21(1):71–81.
- [6] Knudsen JN, Jensen PA, Dam-Johansen K. Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy Fuels* 2004;18(5):1385–99.
- [7] Niu YQ, Liu YY, Tan HZ, Xiong YY, Xu TM. Origination and formation of NH_4Cl in biomass-fired furnace. *Fuel Process Technol* 2013;106:262–6.
- [8] Demirbas A. Sustainable cofiring of biomass with coal. *Energy Convers Manage* 2003;44(9):1465–79.
- [9] Schofield K. A new method to minimize high-temperature corrosion resulting from alkali sulfate and chloride deposition in combustion systems. I. Tungsten salts. *Energy Fuels* 2003;17(1):191–203.
- [10] Kassman H, Pettersson J, Steenari BM, Amand LE. Two strategies to reduce gaseous KCl and chlorine in deposits during biomass combustion – injection of ammonium sulphate and co-combustion with peat. *Fuel Process Technol* 2013;105:170–80.
- [11] Tillman DA, Duong D, Miller B. Chlorine in solid fuels fired in pulverized fuel boilers – sources, forms, reactions, and consequences: a literature review. *Energy Fuels* 2009;23(7):3379–91.
- [12] Frandsen FJ, van Lith SC, Korbbe R, Yrjas P, Backman R, Obernberger I, et al. Quantification of the release of inorganic elements from biofuels. *Fuel Process Technol* 2007;88(11–12):1118–28.
- [13] Rahim MU, Gao XP, Garcia-Perez M, Li Y, Wu HW. Release of chlorine during Mallee Bark pyrolysis. *Energy Fuel* 2013;27(1):310–7.
- [14] Ah Chen, Xn Yang, Wg Lin. Thermodynamic equilibrium analysis on release characteristics of chlorine and alkali metals during combustion of biomass residues. *Chin J Process Eng* 2007;7(5):989–98.
- [15] Turn SQ. Chemical equilibrium prediction of potassium, sodium, and chlorine concentrations in the product gas from biomass gasification. *Ind Eng Chem Res* 2007;46(26):8928–37.
- [16] Dayton DC, French RJ, Milne TA. Direct observation of alkali vapor release during biomass combustion and gasification. 1. Application of molecular beam/mass spectrometry to switchgrass combustion. *Energy Fuels* 1995;9(5):855–65.
- [17] Baxter LL, Miles TR, Jenkins BM, Milne T, Dayton D, Bryers RW, et al. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Process Technol* 1998;54(1–3):47–78.
- [18] Bjorkman E, Stromberg B. Release of chlorine from biomass at pyrolysis and gasification conditions. *Energy Fuels* 1997;11(5):1026–32.
- [19] Olsson JC, Jaglid U, Pettersson JBC, Hald P. Alkali metal emission during pyrolysis of biomass. *Energy Fuels* 1997;11(4):779–84.
- [20] Wei X-L, Schnell U, Hein KRG. Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation. *Fuel* 2005;84(7–8):841–8.
- [21] Bauer CF, Andren AW. Emissions of vapor-phase fluorine and ammonia from the Columbia coal-fired power plant. *Environ Sci Technol* 1985;19(11):1099–103.

- [22] Li W, Lu H, Chen H, Li B. Volatilization behavior of fluorine in coal during fluidized-bed pyrolysis and CO₂-gasification. *Fuel* 2005;84(4):353–7.
- [23] Wang WF, Qin Y, Wang JY, Li J, Weiss DJ. A preliminary method for determining acceptable trace element levels in coal. *Energy* 2010;35(1):70–6.
- [24] Doolan KJ. A pyrohydrolytic method for the determination of low fluorine concentrations in coal and minerals. *Anal Chim Acta* 1987;202:61–73.
- [25] Jeyakumar S, Raut VV, Ramakumar KL. Simultaneous determination of trace amounts of borate, chloride and fluoride in nuclear fuels employing ion chromatography (IC) after their extraction by pyrohydrolysis. *Talanta* 2008;76(5):1246–51.
- [26] Geng W, Nakajima T, Takanashi H, Ohki A. Determination of total fluorine in coal by use of oxygen flask combustion method with catalyst. *Fuel* 2007;86(5–6):715–21.
- [27] Dayton DC, Jenkins BM, Turn SQ, Bakker RR, Williams RB, Belle-Oudry D, et al. Release of inorganic constituents from leached biomass during thermal conversion. *Energy Fuels* 1999;13(4):860–70.
- [28] Yang HP, Yan R, Chen HP, Lee DH, Liang DT, Zheng CG. Mechanism of palm oil waste pyrolysis in a packed bed. *Energy Fuels* 2006;20(3):1321–8.
- [29] Jensen PA, Frandsen FJ, Dam-Johansen K, Sander B. Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. *Energy Fuels* 2000;14(6):1280–5.
- [30] Mojtahedi W, Backman R. The fate of sodium and potassium in the pressurized fluidized-bed combustion and gasification of peat. *J Inst Energy* 1989;62(453):189–96.
- [31] Lee JM, Kim DW, Kim JS, Na JG, Lee SH. Co-combustion of refuse derived fuel with Korean anthracite in a commercial circulating fluidized bed boiler. *Energy* 2010;35(7):2814–8.
- [32] Jensen PA, Frandsen FJ, Dam-Johansen K, Sander B. Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. *Energy Fuels* 2000;14(7):1280–5.
- [33] Qi Q, Liu J, Cao X, Zhou J, Cen k. Fluorine emission characteristics and kinetic mechanism during coal combustion. *J Fuel Chem Technol* 2003;31(5):400–4 (in Chinese).