



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.

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