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Release and transformation of chlorine and potassium during pyrolysis of KCl doped biomass

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A B S T R A C T

The formation of CH_3Cl and the transformation of chlorine and potassium during pyrolysis of biomass were investigated. Model biomass compounds (cellulose, xylan, lignin and pectin) and pine wood doped with KCl were pyrolysed in a TGA at different heating rates (10–1000 °C/min), temperatures (300–850 °C), and KCl contents (0–5 wt%). The volatiles were collected and analyzed for CH_3Cl concentration by GC–MS. The solid residue was analyzed by ICP-OES for the contents of total and water soluble K and Cl. Considerable amounts of CH_3Cl, corresponding to 20–50% of the fuel chlorine, were formed in pyrolysis of KCl doped pine wood, lignin and pectin samples, suggesting a methylation ability of these biomass on KCl by their methoxyl groups. Lignin and pine wood could supply methoxyl groups for reaction with as much as about 2% KCl doping, and pectin had an even greater capacity. Organic K was found in the solid residue of all samples, further supporting the occurrence of reactions between KCl and the organic matrix in biomass. With a holding temperature of 500 °C, an increase of heating rate from 10 °C/min to 500 °C/min significantly reduced the yield of CH_3Cl from KCl doped wood/lignin/pectin, while no further reduction effect was observed at 1000 °C/min. For a heating rate of 500 °C/min, an increase of holding temperature from 300 °C to 850 °C caused a decreased yield of CH_3Cl.

1. Introduction

Biomass is becoming important in heat and power production because of its renewable and CO_2-neutral characteristics. However, utilization of biomass in high temperature processes is challenged by ash-related problems, such as deposition and corrosion [1–4]. The release of Cl and K is a main concern due to the relatively high content of Cl and K in biomass (especially in annual biomass) and their adverse effect on biomass combustion and gasification processes, such as deposition [5,6], corrosion [7], deactivation of SCR catalysts [8], and emission of HCl and CH_3Cl [9–12]. To minimize these operational problems, a good understanding of the Cl and K release and transformation during high temperature utilizations of biomass is required.

The concentration and association of Cl and K vary in different biomass [13,14]. In woody biomass, the concentration of Cl is typically very low (<0.01%) and more than 90% of the Cl is water soluble [15]. In annual biomass like rice and wheat straw, the concentration of Cl is much higher (0.1–0.6%), and the water soluble Cl constitutes an important part of the total Cl (typically above 50%) [16]. Potassium normally has the second largest concentration among all inorganic elements in biomass (lower than Si or Ca depending on fuel type), ranging from 0.02% to 1.5% depending on fuel type (low in woody biomass and high in annual biomass) [13–16]. More than 50% of the total K in biomass may exist in a form of water soluble K [16]. Water soluble Cl and K are largely present as KCl, which is proposed as a major inorganic constituent in biomass [17]. Therefore, understanding the interactions between KCl and biomass during thermochemical conversion processes is of importance.

In biomass thermochemical conversion processes, Cl is primarily released during the devolatilization stage. Van Lith et al. [18,19] investigated the Cl release of several woody biomass in a fixed bed reactor at a heating rate of about 30 °C/min and reactor temperatures of 500–800 °C. They found that 60–80% of the Cl release took place during the devolatilization phase. Rahim et al. [20] observed that little Cl was retained in char during pyrolysis of bark at a temperature of 400 °C. For annual biomass with a high Cl content, Johansen et al. [21,22], Knudsen et al. [23] and Jensen et al. [24] found a release of 40–60% of the Cl during pyrolysis at 500–800 °C. Since KCl is considered as main Cl species in biomass, it

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Table 1
Inorganic elemental composition of the model biomass compounds and pine wood (dry basis).

Parameter	Unit	Cellulose	Xylan	Lignin	Pectin	Pine wood
Al	mg/kg	<10	50 ± 4	150 ± 12	18 ± 1	32 ± 12
Ca	mg/kg	<10	5800 ± 460	160 ± 13	1400 ± 110	950 ± 60
Cl	mg/kg	<100	<100	<100	<100	160 ± 20
Fe	mg/kg	<10	80 ± 6	43 ± 3	12 ± 1	26 ± 5
K	mg/kg	<150	180 ± 14	950 ± 76	1200 ± 96	480 ± 30
Mg	mg/kg	<10	79 ± 6	170 ± 12	380 ± 30	140 ± 10
Na	mg/kg	13 ± 1	19,000 ± 1500	6500 ± 520	20,000 ± 1600	95 ± 10
P	mg/kg	<20	160 ± 13	<20	110 ± 9	52 ± 8
S	mg/kg	<20	160 ± 13	16,000 ± 1280	470 ± 38	70 ± 30
Si	mg/kg	<100	200 ± 16	300 ± 24	<100	<200
Ti	mg/kg	<3	<4	<3	<3	<5

Table 2
Experimental conditions and samples.

Experiment condition	Content of doped KCl
(1): Temperature: 500 °C Heating rate: 10 °C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl
(2): Temperature: 500 °C Heating rate: 100 °C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl
(3): Temperature: 500 °C Heating rate: 500 °C/min	Pine wood: 0%, 0.5%, 1%, 2%, 3%, 4%, 5%, 6% KCl, Cellulose: 2% KCl, Xylan: 2% KCl, Lignin:0%, 1%, 2%, 5% KCl, Pectin:0%, 1%, 2%, 5% KCl
(4): Temperature: 500 °C Heating rate: 1000 °C/min	Pine wood: 2% KCl, Lignin: 2% KCl
(5): Temperature: 300 °C Heating rate: 500 °C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl
(6): Temperature: 850 °C Heating rate: 500 °C/min	Pine wood: 2% KCl, Cellulose: 2% KCl, Xylan: 2% KCl Lignin: 2% KCl, Pectin: 2% KCl

is hypothesized that the KCl in biomass reacts with organic groups during devolatilization, releasing Cl to gas phase and fixing K in the char [18,19]. The hypothesis is supported by the observation that a relatively smaller amount of K is released during pyrolysis compared to Cl in the temperature range of 200–700 °C [18,19,21–24]. The difference in Cl release during pyrolysis of different biomasses is presumably caused by the speciation and availability of organic functional groups in the biomass that can react with KCl [18]. For biomass with a low Cl content, a large fraction of Cl has the opportunity to react with the organic matrix, thus resulting in the release of a larger fraction of Cl [18,19].

HCl and CH_3Cl are the two main gas phase chlorine species released during devolatilization. Dayton et al. [25] observed HCl release with molecular beam mass spectrometry (MBMS) in switchgrass combustion at 1100 °C. Strömberg et al. [26] suggested that KCl can react with chain-bonded carboxylic groups in the temperature range of 200–700 °C and yield HCl. They also studied the reactions between KCl and other functional groups [9], and found that ester, acetal, hemiactal and hydroxymethyl also reacted with KCl and released HCl. Hamilton et al. [10] reported a significant CH_3Cl release in biomass combustion at temperatures of 150–350 °C and ascribed it to the methylation of Cl^- by lignin and pectin. Saleh et al. [27] found that CH_3Cl is the predominant form of gaseous chlorine released in straw pyrolysis at 250–500 °C, and the release of CH_3Cl decreases with increasing pyrolysis temperature. Sailaukhanuly et al. [28] and Czegeny et al. [29] identified methylation ability of Cl^- in pectin and lignin, respectively, in the temperature range of 200–300 °C.

In spite of the progress, there are still some unresolved issues about the reaction between biomass and KCl, such as the influences of heating rate and different biomass components on the release of chlorine and the formation of CH_3Cl. To address these issues, four model compounds of biomass (cellulose, xylan, lignin and pectin) and a pine wood, were chosen in this work to investigate their reactions with KCl during pyrolysis. The experiments were carried out in a TGA under well-controlled heating rate (10–1000 °C/min) and temperature (300–850 °C) conditions that are relevant for gasification/combustion of biomass in fluidized bed and fixed bed systems. The focuses have been on the impacts of heating rate, temperature and KCl concentration in biomass on the release of chlorine and the formation of CH_3Cl.

2. Experimental

2.1. Reactants

Cellulose (CAS No. 9004-34-6), xylan (CAS No. 9014-63-5), lignin (CAS No. 8068-05-1) and pectin (apple) (CAS No. 9000-69-5) were obtained from Sigma Aldrich (Germany). The model biomass compounds and the pine wood particles were prepared and analyzed according to CEN/TS 14780 and CEN/TS 15290 respectively. The inorganic elemental compositions are shown in Table 1. The Cl content in all fuels was negligible (<0.01%). The K content was slightly higher, taking up 0.095% and 0.12% for lignin and pectin respectively.

2.2. Sample preparation

The KCl doping procedure used in [30] was chosen to produce KCl doped biomass. As an example, cellulose doped with 2% KCl was prepared in the following way: 3.92 g cellulose and 0.08 g KCl were weighted separately and put into a dry empty beaker. The mixed sample was then dissolved in 100 ml distilled water and stirred for 12 h before being dried in a muffle furnace at 105 °C.