Full Length Article

Migration and speciation transformation of K and Cl caused by interaction of KCl with organics during devolatilization of KCl-loaded model biomass compounds

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GRAPHICAL ABSTRACT
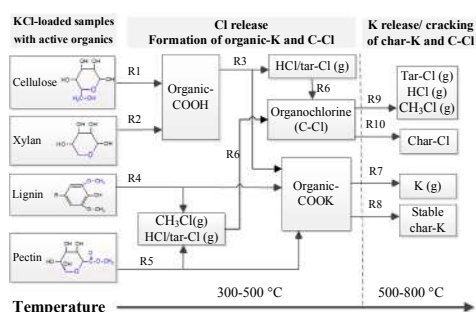
ARTICLE INFO

ABSTRACT

To better understand migration of K and Cl caused by interaction of KCl with organics, KCl-loaded model compounds (cellulose, xylan, lignin and pectin) were pyrolyzed within 300–800 °C using a fixed-bed apparatus. The amounts of different chemical occurrences of K and Cl in chars were quantitatively determined by sequential chemical fraction analysis combined with ICP-OES and IC. Morphologies and occurrence modes of Cl and K were further examined via XPS and SEM-EDS. Big differences in K and Cl migration were observed among four samples, and the distinction was closely related to types of organic functional groups. At temperature of below 500 °C, a low proportion of K was released from four samples, while amounts of water-soluble K was transformed into organically-bounded form via different ion-exchange reaction mechanisms, thereby promoting Cl release. About 46.93–53.31% and 32.47–41.75% of organic-K, presumably formed by reaction of KCl and methoxyls, were detected in lignin and pectin chars, apparently higher than that in xylan and cellulose chars. At the same time, amounts (71.98–81.83%) of Cl was released from doped pectin, followed sequentially by lignin (35.12–52.34%), cellulose (18.56–35.68%), and xylan (10.67–18.65%). Part of released Cl was recaptured by active carbon sites, thereby forming organochlorine, and C-Cl generation followed a sequence of lignin > xylan > cellulose > pectin. As pyrolysis proceeded, cellulose exhibited highest K release due to decomposition of organic-K, while a considerable of char-K with high thermal stability still retained in other samples. Mechanism on migration of K and Cl caused by reaction of KCl with organics was proposed.

1. Introduction

Biomass is becoming a promising substitute for fossil fuel due to its renewable and CO_2-netural characteristics. In China, about 0.68 billion tons of agricultural straw is produced annually [1], and these agricultural wastes were usually used to supply heat and power through gasification or combustion. However, utilization of agricultural biomass during thermochemical conversion process has been challenged by serious issues with fouling, corrosion and slagging. Agricultural straw usually has high concentrations of potassium (K) and chlorine (Cl), which will easily migrate and cause ash-related problems [2,3]. Hence, to solve these K- and Cl-induced issues, understanding of release and transformation characteristics of K and Cl during thermochemical conversion process of agricultural biomass is of great importance.

The concentration and occurrence forms of K and Cl vary in different biomass. Generally, agricultural biomass has remarkably higher concentrations of K (0.2–2.3 wt%) and Cl (0.1–1.5 wt%) than woody biomass (K: 0.05–0.4 wt%; Cl: < 0.1 wt%) [4–6]. The K and Cl can exist in biomass as inorganic salts and organic-bonded forms. In agricultural straw, about 60–90% of K and almost all of Cl exist as water-soluble forms, and the water-soluble K and Cl were mainly present as KCl [5,7]. Therefore, a comprehensive study on interaction between KCl and biomass is important to better understanding of K and Cl migration.

The water-soluble KCl salt might react with organics in biomass under heat treatment, thereby giving rise to migration and speciation transformation of K and Cl. The speculation was strongly supported by the observation that a large fraction of Cl was released into gaseous phase while amounts of K were bounded in solid char at temperature of below 700 °C [8–10]. Plenty of work [10–13] has indicated that K and Cl exhibited total different migration behaviors. Jensen et al. [10] found about 60% of Cl was released from wheat straw at 200–400 °C, while no significant K release was observed. Wang et al. [11] conducted pyrolysis experiments on KCl-loaded pine wood, and found that Cl release amount (~58%) at 500 °C was remarkably higher than K (~5%), at the same time, amounts of organic-associated K (char-K) and a low proportion of organochlorine (C-Cl) were detected in solid char. The Cl release and organic-K formation were usually ascribed to reaction of KCl with organics as described in Eq. (1) [10,14].

$$KCl + Organics \rightarrow Organic - K + HCl/CH_3Cl/Tar - Cl(g, l) \qquad (1)$$

Biomass is an organically-associated macromolecular polymer and owns amounts of organic functional groups, which significantly affect migration and transformation of K and Cl through reaction with KCl. As described in Eq. (1), the Cl might be released in forms of HCl, CH_3Cl or tar-Cl, mainly depending on the types of functional groups [15–18]. Björkman et al. [15] reported that KCl might react with carboxylic acids in biomass at 200–700 °C and release Cl in form of HCl. Bläsing et al. [17] also identified HCl release from herbaceous fuels by online molecular beam mass spectrometry (MBMS). Besides, the methoxyl groups

in biomass would also promote Cl release [11,18]. Hamilton et al. [18] conducted low-temperature (150–350 °C) combustion experiments on several woody biomass, and detected amounts of CH_3Cl releasing. They hold the point that the formation of CH_3Cl was mainly ascribed to methylation of Cl by methoxyl groups. Besides, other organic functional groups, such as ester, acetal and hemiacetal might also react with KCl and promote Cl release and char-K formation [19].

The migration and transformation of K and Cl caused by reaction of KCl with organics vary for different biomasses. Suriyati et al. [20] compared Cl release from six biomass with different chemical components (i.e., two herbaceous and four woody biomasses). They obtained that about 64% of Cl in straw were released at 350 °C while almost all of Cl in woody biomasses were volatilized. Deng et al. [21] conducted repaid pyrolysis experiments on wheat straw, cornstalk and rice hull within 400–1000 °C, and found that corn stalk had the lowest K release ratio among three materials at 400–800 °C. As temperature increased from 800 °C to 1000 °C, K release fraction from corn stalk began to exceed that from rice hull but still be lower than that from wheat straw. Huang et al. [7] found about 9% of organic-associated K were formed during pyrolysis of wheat straw at 500 °C, remarkably lower than that (25%) for KCl-loaded pine wood [11]. The significant difference in migration of K and Cl among different biomasses was closely related to types of organic functional groups in biomass. However, owning to complexity of macromolecular structure and diversity of organic functional groups in biomass, mechanism on migration and transformation of K and Cl from KCl has not been well addressed.

Owing to their relatively simple macromolecular structure, cellulose, xylan, lignin and pectin were chosen as model compounds of biomass. Hence, migration and speciation transformation of K and Cl caused by interaction of organics with KCl can be thoroughly explored by using KCl-loaded model compounds. In recent, a few research on K and Cl release from model compounds were conducted [11,22–24]. Rahim et al. [23] and Chen et al. [24] paid special attention on Cl or K release during mild pyrolysis of KCl-doped samples at temperature of below 400 °C. Zhao et al. [22] focused effect of KCl concentrations on release of K and Cl through loading different contents of KCl into cellulose. Wang et al. [11] concentrated on the difference in Cl forms releasing from KCl-loaded samples at 500 °C and 850 °C, respectively. Despite progress above, mechanism on migration of K and Cl has not been extensively discussed, and an important prerequisite for that is to deeply understand of interaction between KCl and organics.

In this work, K and Cl migration during devolatilization of KCl-loaded model compounds was quantitatively investigated on a self-designed fixed-bed apparatus. The amounts of different chemical occurrences of K and Cl in solid char were quantitatively determined by sequential chemical fraction analysis combined with ICP-OES and IC. Morphologies and occurrence modes of Cl and K in char were further examined via XPS and SEM-EDS. Based on this, the possible mechanism on migration and transformation of K and Cl caused by interaction of

Table 1
Ultimate and proximate analyzes of biomass model compounds (wt %, dry basis).

Samples	Ultimate analysis					Proximate analysis			Inorganic elements			
	C	H	O*	N	S	V	FC*	Ash	K	Cl	S	Na
Xylan	41.46	6.61	50.94	0.00	0.18	95.01	4.18	0.81	–	–	–	–
Cellulose	42.44	6.48	49.71	0.00	0.00	95.27	3.36	1.37	–	–	–	–
Alkali lignin	52.14	4.88	27.07	0.00	0.74	45.76	39.07	15.17	0.03	0.03	3.76	3.91
Pectin	37.66	5.77	51.81	0.29	0.22	78.13	17.62	4.25	0.09	0.08	0.04	0.16
The K and Cl concentrations in KCl-loaded model compounds (mg/g)												
	xylan			cellulose			lignin			pectin		
K	14.88			14.76			15.94			15.45		
Cl	13.67			14.19			14.37			14.32		
Mole ratio (K/Cl)	0.99			0.95			1.01			0.98		

*O = 100-C-H-N-S-Ash; FC = 100-V-Ash.

KCl with organics was proposed.

2. Experimental

2.1. Materials

The model biomass compounds, cellulose (CAS No. 9004-34-6), xylan (CAS No. 9014-63-5), lignin (CAS No. 8068-05-1) and pectin (CAS No. 9000-69-5) were purchased from Macklin Biochemical Co., Ltd (China). The elemental compositions of these samples was determined using an elemental analyzer (Vario EL III, Elementar, Germany), and contents of volatile and ash were measured according to ASTM E872 and E1755, respectively. The major inorganic species (K, Na, Cl, S) were identified by ICP-OES. Table 1 lists ultimate and proximate analyses of the samples.

According to amounts of K and Cl in agricultural straw, the KCl-loaded concentration of was set as 3.0%. 2.40 ± 0.01 g of KCl was dissolved into 400 mL ultrapure water, and 77.60 ± 0.01 g of samples was added into the solution. After being stirred for 12 h, the mixture was freeze-dried for 72 h. The contents of K and Cl in KCl-loaded samples were measured by ICP-OES and IC as described in Section 2.3, and listed in Table 1. It can be seen that the mole ratios of K/Cl for four samples were almost 1.0.

2.2. Experimental apparatus and procedures

A laboratory-scale fixed-bed reactor was employed to conduct pyrolysis of KCl-loaded samples. Detailed description of pyrolysis procedure was listed in our previous work [7]. In brief, 2.00 ± 0.005 g of KCl-loaded samples were dropped into reactor basket and then placed into isothermal reaction zone. After the air was purged out, the sample was heated from room temperature to a designated temperature at a heating rate of 10 °C/min with a high-purity N_2 stream of 600 mL/min, and then kept for about 15 min. After heat treatment, the reactor basket was placed into the cooling section under inert atmosphere. At last, the obtained char was collected and weighed. Each condition was carried out three times and the relative standard deviations of char yields were < 3%.

The release fractions of volatiles (x_i, %) were calculated using Eq. (2).

$$x_i = \frac{m_0 - m_i}{m_0} \times 100 \tag{2}$$

where m_0 and m_i were mass weights of raw samples and solid char on a dry basis (g), respectively.

2.3. Analysis methods

2.3.1. Quantification of K by CFA combined with ICP-OES

Chemical fractionation analysis (CFA) was employed to identify occurrence forms of K in solid chars, and detailed procedure of the CFA was described in our previous publication [7]. Briefly, the water-soluble K and organically bounded K in samples were sequentially extracted with ultrapure water and 1.0 mol/L ammonium acetate (NH_4AC). Then, the solid residue after NH_4AC extraction was dissolved by microwave-assisted acid digestion with a combination of H_2O_2, HNO_3, and HF (1:5:0.4, volume ratio) according to Swedish standards CEN/TS 14780 and CEN/TS 15290, followed by H_3BO_3 addition to remove extra HF [7]. The contents of K in abstraction solutions and digestion liquid were analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer 8000DV).

All the data were calculated on the basis of the total K and Cl in original dry samples. The release ratio of total K ($R_{K\,total,i}$, %) was calculated using Eq. (3).

$$R_{K\,total,i} = \frac{C_{K\,total,0} - C_{K\,total,i}(1 - x_i/100)}{C_{K\,total,\,0}} \times 100 \tag{3}$$

where $C_{K\,total,\,0}$ and $C_{K\,total,i}$ were total K concentrations of raw materials and residue chars on a dry basis (mg/g), respectively.

For convenience, the above-mentioned K fractions were subsequently designated as water-soluble K, NH_4AC-soluble K and insoluble K in this work. The fraction of various K species ($w_{K\,j,i}$, %) in char was calculated using Eq. (4).

$$w_{K\,j,i} = \frac{C_{K\,j,i}(1 - x_i/100)}{C_{K\,total,\,0}} \times 100 \tag{4}$$

where $C_{K\,j,i}$ was the concentration of various K species in char on a dry basis (mg/g).

2.3.2. Quantification of Cl by IC

The total concentrations of Cl in virgin samples and solid chars were determined using oxygen bomb combustion method according to ASTM D4208-13. About 400 ± 1 mg of virgin samples or 50 ± 1 mg of chars were used for each measurement. The water-soluble Cl was extracted by ultrapure water during CFA process. The solution was filtered and analyzed using ion chromatography (IC; Metrohm761, Switzerland).

The release ratio of total Cl ($R_{Cl\,total,i}$, %) was calculated using Eq. (5).

$$R_{Cl\,total,i} = \frac{C_{Cl\,total,0} - C_{Cl\,total,i}(1 - x_i/100)}{C_{Cl\,total,\,0}} \times 100 \tag{5}$$

where $C_{Cl\,total,\,0}$ and $C_{Cl\,total,i}$ were the total Cl concentration in virgin sample and chars on a dry basis (mg/g), respectively.

The fraction of above-mentioned water-soluble Cl and insoluble Cl ($w_{Cl\,j,i}$, %) in char was calculated using Eq. (6).

$$w_{Cl\,j,i} = \frac{C_{Cl\,j,i} \times (1 - x_i/100)}{C_{Cl\,total,\,0}} \times 100 \tag{6}$$

where $C_{Cl\,j,i}$ was the concentration of different Cl species in chars on a dry basis (mg/g).

2.3.3. XPS analysis

The X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi) was used to investigate chemical forms of Cl in char samples. High-resolution scanning of the Cl 2p region was conducted in 0.05 eV steps with a pass energy of 50 eV. All binding energies were calibrated using C 1 s peak with reference energy of 284.6 eV. The Cl 2p spectra were curve-fitted with a Gaussian/Lorentzian function using binding energies of 198–199 eV for KCl and 200–201 eV for char-Cl. The difference of the binding energy and the peak area ratio of 2p 3/2 and 2p 1/2 for both KCl and char-Cl were 1.5 eV and 2.0, respectively.

2.3.4. SEM-EDS analysis

Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS; Hitachi SU-70) was used to investigate morphology of solid char and association of K and Cl. For EDS analysis, an accelerating voltage of 5 kV was used and the diameter of the measured spot was about 100 nm.

3. Results and discussion

3.1. Volatile release of KCl-loaded model biomass compounds

Fig. 1 shows more volatiles were released from all the four samples with temperature increasing from 300 °C to 800 °C, while the releases amounts displayed a big difference among them. The loaded cellulose showed the highest volatile release (61.51–79.13%) within 300–800 °C, whereas doped lignin exhibited the lowest one (17.98–43.28%). The big difference might be ascribed to the lowest volatile (45.76%) and
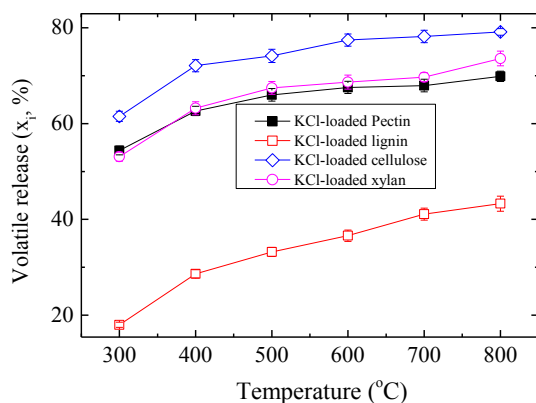
**Fig. 1.** volatile release during pyrolysis of KCl-loaded model compounds within 300–800 °C.

highest fixed carbon (39.07%) contents in lignin (Table 1). For the other two samples, about 53.09–73.58% of volatiles escaped away from loaded xylan, close to that from pectin with a minor difference. Furthermore, in spite of their similar volatile and fixed carbon contents, the doped cellulose displayed apparently higher weight loss than xylan. Similar results were also reported by wang et al.[11], and the difference might be mainly ascribed to distinct organic functional groups between them.

3.2. Variation behavior of K and Cl during pyrolysis of doped model compounds

3.2.1. KCl-loaded cellulose

As shown in Fig. 2a, a small amount of (2.52–5.9%) of K was released at 300–500 °C, which was consistent with other observations [11,22]. At the same time, amounts of organic-K (i.e., NH$_4$AC-soluble K), with a gradual increase from 24.92% at 300 °C to 26.32% at 500 °C, were detected in cellulose chars. The organic-K was mainly generated by interaction of KCl with oxygen-containing active functional groups, thereby forming coordination bonds between K with oxygen under heat treatment. The occurrence of organic-K was also confirmed by SEM-EDS analysis due to high mole ratio of K/Cl (Area 2, in Fig. 7b–d). As pyrolysis proceeded, more K was released and about 35.99% of K escaped away at 700 °C, while the fraction of organic-K was significantly decreased to 4.98%. Given little variation in water-soluble K proportion, it might be reasonably deduced that the increase of K release was mainly resulted from decomposition of organic-K as described in Eq. (7). As temperature further increased to 800 °C, about 69.92% of K was released with an apparent decrement of water-soluble K. Hence, part of K

was sublimated as KCl (g) due to increase of vapor pressure. Few KCl (< 0.5%) was transformed into NH$_4$AC-insobule K due to low ash content in cellulose.

$$Char - COOK \rightarrow Char + CO_2 + K(g)\uparrow \qquad (7)$$
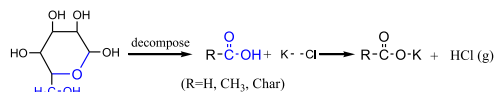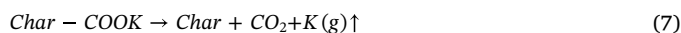
$$(R=H, CH_3, Char) \qquad (8)$$

Fig. 2b shows that Cl exhibited totally different variation behavior from K. A considerable fraction (18.56–35.68%) of Cl escaped away from cellulose at 300–500 °C. Cellulose is an unbranched polysaccharide composed primarily of β-D-glucopyranose units connected by (1–4) glycosidic linkages[25], and contains amounts of active functional groups, such as hemiacetal, exocyclic hydroxymethyl, and so on. Strömberg et al. [19] revealed that both hemiacetal and hydroxymethyl attached on rings (–CH$_2$OH) contributed to Cl release. They hold the point that these active functional groups were chemical precursors for carboxylic acids. Under heat treatment, part of them were decomposed into organics with free carboxyl acids [26], and would react with KCl via ion-exchange reaction as show in Eq. (8). Cl was then released mainly in form of HCl (g) or Tar-Cl (g) other than CH$_3$Cl (g) due to the absent of CH$_3$ donor in cellulose. Rahim et al.[23] conducted pyrolysis experiments on NaCl-loaded cellulose within 150–400 °C, and confirmed HCl (g) was the only released Cl-containing gas besides tar-Cl (g). It should be noted that a considerable fraction (19.46%) of organochlorine (i.e., waste-insoluble Cl) was formed at 300 °C. The formation of C-Cl was also detected during pyrolysis of coal [27,28] and biomass [24,29]. Based on previous reports [23,24,27], it can be deduced that part of primary released Cl was recaptured by decomposition fragments from cellulose, such as, aldehydes, furans, anhydrosugars, and so on [30], thereby forming C-Cl. With temperature increasing from 300 °C to 400 °C, the Cl release abruptly increased from 18.56% to 32.48% with a significant decrease of C-Cl from 19.46% to 5.02%. Given little variation in water-soluble Cl, it might be deduced that a great part of C-Cl was decomposed and was released as tar-Cl or HCl at 400 °C. As pyrolysis proceeded, a slight reduction of C-Cl and a slow increase in Cl release were observed within 400–700 °C, followed by a significant growth of Cl release at 800 °C due to sublimation of KCl.

3.2.2. KCl-loaded xylan

Fig. 3a shows about 3.87–8.58% of K was released from doped xylan within 300–500 °C, slightly higher than that from cellulose. As pyrolysis proceeded, more K was released, and the release fraction (17.38–45.55%) at 600–800 °C was obviously lower than that from cellulose. The lower release amount from xylan might be partly related to its smooth and compact char surface (Fig. 8), implying larger
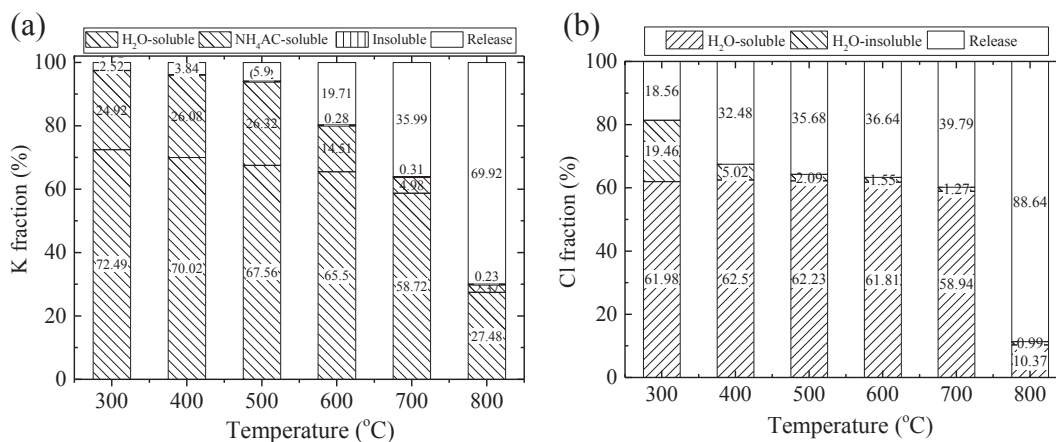

Fig. 2. migration of (a) K and (b) Cl during pyrolysis of KCl-loaded cellulose at 300–800 °C.
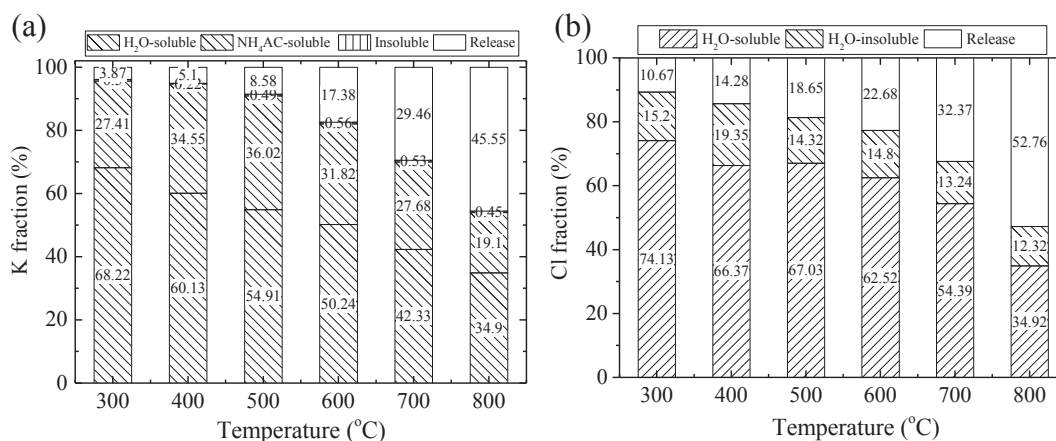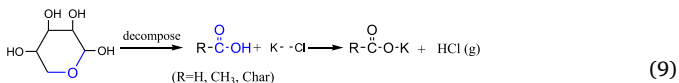
Fig. 3. migration of (a) K and (b) Cl during pyrolysis of KCl-loaded xylan at 300–800 °C.

diffusion resistance for K releasing. Besides the released K, a considerable proportion of water-soluble K was transformed into organically-bounded form, and the high mole ratio of K/Cl (Area 2 in Fig. 8b–d) also indicated occurrence of organic-K. The formation of organic-K was generally caused by interaction of KCl with reaction intermediates with free carboxyl acids, and the reaction was enhanced within 300–500 °C. About 27.41%-36.02% of organic-K, with a gradual increase, were detected at 300 °C-500 °C. Furthermore, it should be pointed out that the amount of organic-K in xylan char was apparently higher than that in cellulose char, and this might be partly ascribed to that more water-soluble organic-K (i.e., CH_3COOK) was formed during pyrolysis of loaded cellulose [11,22]. As temperature exceeded 500 °C, the amount of organic-K started to decrease due to thermal decomposition under intensive conditions, and about 19.1% of char-K was retained at 800 °C.

$$\text{(structure)} \xrightarrow{\text{decompose}} R\text{-}\overset{O}{\underset{\|}{C}}\text{-OH} + K\cdot\ \cdot Cl \longrightarrow R\text{-}\overset{O}{\underset{\|}{C}}\text{-O·K} + HCl\,(g) \quad (9)$$
$$\text{(R=H, CH}_3\text{, Char)}$$

As shown in Fig. 3b, about 10.67–18.65% of Cl was released from doped xylan at 300–500 °C. Xylan is a homopolymer composed primarily of D-xylose units connected by (1–4) linkages [31], containing abundant of hemiacetal groups. As reported by Strömberg et al. [19], the active hemiacetals might be decomposed into compounds with free carboxyl acid groups, which would react with KCl and effectively promote Cl release in form of HCl as shown in Eq. (9), at the same time, part of Cl would escape away together with volatiles and released as tar-Cl. About 15.2–19.32% of C-Cl detected in solid char at 300–400 °C, followed by a slight decrease with increasing temperature. The formation of C-Cl at low temperature might be mainly ascribed to interaction

with primary-released Cl with xylan cracking fragments (i.e., ketones, aldehydes) [30]. Besides, amounts of molten reaction intermediates generated from xylan, would recapture once-released HCl before leaving char particle beds, thereby forming C-Cl. Furthermore, SEM morphologies of xylan char (Fig. 8) exhibited smooth surfaces without visible pores, indicating larger diffusion resistances for Cl-containing gas escaping out of xylan char.

3.2.2.1. KCl-loaded lignin. Fig. 4(a) shows that, comparing with that from other three samples, a remarkably smaller fraction of K was released from KCl-loaded lignin within 300–800 °C. No more than 5% of K was volatized at below 500 °C. As pyrolysis proceeded, the K release increased slightly, and only 15.84% of K was released at 800 °C. The limitation of K vaporization from lignin might be related to its smooth structure (Fig. 9). In contrast with low K release, amounts of NH_4AC-soluble K, with a variation tendency of increasing initially followed by a sudden decrease, was detected. About 46.93% of NH_4AC-soluble K was formed at 300 °C due to reaction of KCl with abundant methoxyl (-O-CH$_3$) groups in lignin [18], and the interaction was enhanced within 300–500 °C, leading to more organic-K formation. As temperature further increased to 600 °C, a few of organic-K was decomposed and presumably formed water-soluble K_2SO_4 salt by combining with the SO_4^- in lignin (Table 1, Fig. 9). Hence, a slight increase of water-soluble K was detected in lignin char at above 500 °C. In general, lignin showed the highest fraction of organic-K during whole pyrolysis, possibly due to high thermal stability of aromatic-K.
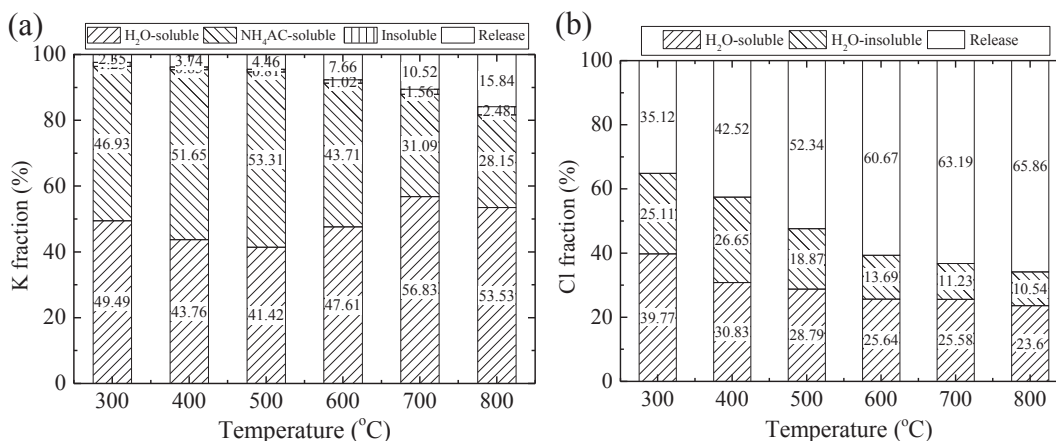

Fig. 4. migration of (a) K and (b) Cl during pyrolysis of KCl-loaded lignin at 300–800 °C.
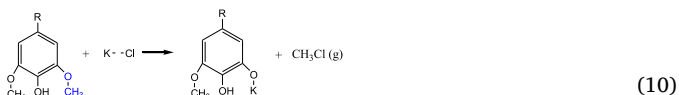
$$\text{(10)}$$

Fig. 4(b) displays about 35.12% of Cl was released from doped lignin at 300 °C, significantly higher than that from cellulose and xylan. Lignin contains abundant methoxyl (-O-CH3) groups [32], producing amounts of ·CH3 radicals under heat treatment. These ·CH3 radicals would combine with Cl, promoting Cl release in form of CH3Cl as described in Eq. (10). Czegeny et al. [26] pyrolyzed lignin under HCl atmosphere and detected release of CH3Cl. They proposed that the CH3 group was disrupted from lignin moiety by HCl and thereby forming CH3Cl. Wang et al. [11] conducted pyrolysis on lignin and found CH3Cl was mainly formed at 200–350 °C. They deduced that KCl could react with lignin and release CH3Cl. As pyrolysis proceeded, other Cl-containing volatiles (i.e., HCl, tar-Cl) were also produced, and the Cl release kept increasing and reached the maximum of 71.86% at 800 °C. The Cl release from lignin was generally higher than that from both xylan and cellulose at below 800 °C. Besides, the organochlorine (i.e., C-Cl) was also detected in lignin char. About 25.11–26.65% of C-Cl were formed at 300–400 °C with an abrupt decrease at 500 °C due to thermal decomposition. The amount of C-Cl almost kept stable at above 600 °C, indicating formation of char-Cl with high thermal stability due to aromatic structure in lignin char.

3.2.3. KCl-loaded pectin

As shown in Fig. 5a, a slightly higher fraction (3.83–10.08%) of K was released from doped pectin within 300–500 °C comparing with other samples. However, with temperature further increasing, the released K became lower than these from cellulose and xylan but still obviously higher than that from lignin. Simultaneously, about 32.47–41.75% of NH4AC-soluble K with a gradual increase, was detected in pectin char at 300–500 °C. The formation of organic-K was mainly ascribed to interaction of KCl with active oxygen-containing functional groups (i.e., free carboxyl acid, ester, and hemiacetal) in pectin. As temperature was elevated from 500 °C to 600 °C, a considerable fraction of organic-K was decomposed due to its weak thermal stability, while a slight increase in K volatilization was detected. At the same time, the water-soluble K in char was obviously increased, hence, it might be deduced that part of organically-bounded K was decomposed into water-soluble organic-K (such as, CH3COOK). Similar results were also reported by other researchers [33]. As pyrolysis further proceeded, the NH4AC-soluble K almost kept stable and about 20.7% of char-K was retained at 800 °C.

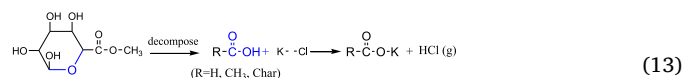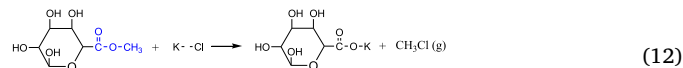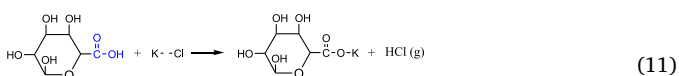$$\text{(11)}$$

$$\text{(12)}$$

$$\text{(13)}$$

Fig. 5b shows huge amounts (71.98–86.25%) of Cl was released from pectin, significantly higher than these from other three samples. Pectin is a polysaccharide composed primarily of α- galacturonic acid units polymerized with (1–4) linkages [18], containing abundance of active functional groups, such as ester (−C═O−O−), methoxyl (−OCH3), free carboxyl acid (−COOH) and hemiacetal, and so on. These active groups would contribute to Cl release via different reaction mechanisms. The free carboxylic acids would directly react with KCl, setting free HCl via an ion-exchange reaction as described in Eq. (11) [15]. The esters and methoxyls provided ·CH3 radicals and caused Cl releasing as CH3Cl. Hamilton et al. [18] conducted pyrolysis experiments on leaves and pectin, and detected amounts of CH3Cl were released. They deduced methoxyls (−OCH3) in pectin played a key role on CH3Cl formation. Sailaukhanuly et al. [34] focused on thermal solid state reaction between pectin and alkali chlorides (KCl, NaCl), and proposed reaction mechanism as in Eq. (12). Besides, part of hemiacetals might be decomposed into light organics with free carboxyl acids, and then reacted with KCl as described in Eq. (13). Strömberg et al. [19] compared contribution of several functional groups on Cl release, and found that free carboxylic acid played the most important role in Cl volatilization, followed by ester in lactone ring and hemiacetal. Considering Cl release behavior, pretreatment of biomass at low temperature might be an effective way for Cl removing. A low proportion (5.94%) of C-Cl was formed at 300 °C, and most of them was released together with volatiles at elevated temperatures.

3.3. Structure analysis of char matrix pyrolyzed from KCl-loaded samples

3.3.1. XPS analysis

Fig. 6 displays XPS spectra of Cl (2p) in solid chars obtained at 500 °C with curve-fitted results. The appearance of C-Cl in chars confirmed the formation of C-Cl during pyrolysis of doped model compounds. The C-Cl was presumably formed by secondary reaction of once-released Cl with active carbon sites (such as, cracking fragments, molten reaction intermediates, and so on) [23,27]. Tsubouchi et al. [27] explored HCl evolution from coal pyrolysis and the change in Cl functionality, and confirmed the reaction of HCl with active carbon sites, thereby forming C-Cl. Furthermore, the relative proportions of C-Cl in four solid chars exhibited a big difference among them. The chars from lignin (9%) and xylan (5.4%) owned relatively higher fraction of C-Cl than these from pectin (3.1%) and cellulose (1%), and the
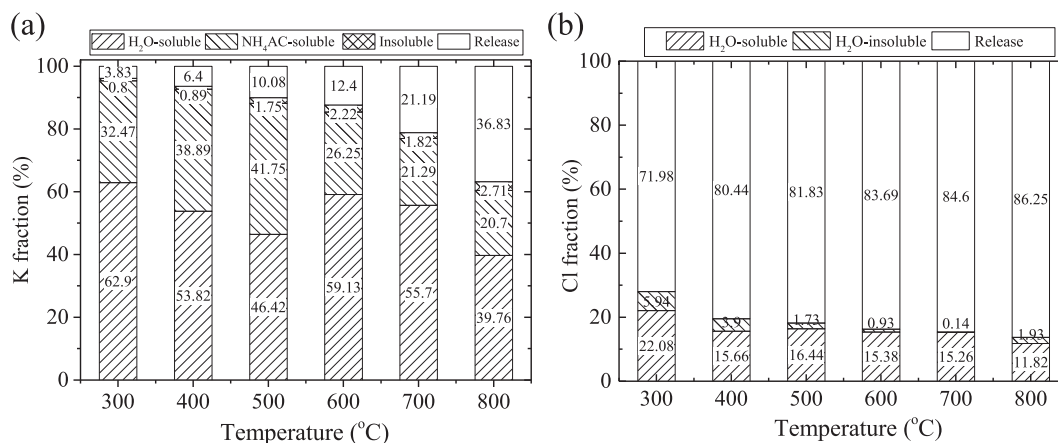

Fig. 5. migration behavior of K and Cl during pyrolysis of KCl-loaded pectin at 300–800 °C.
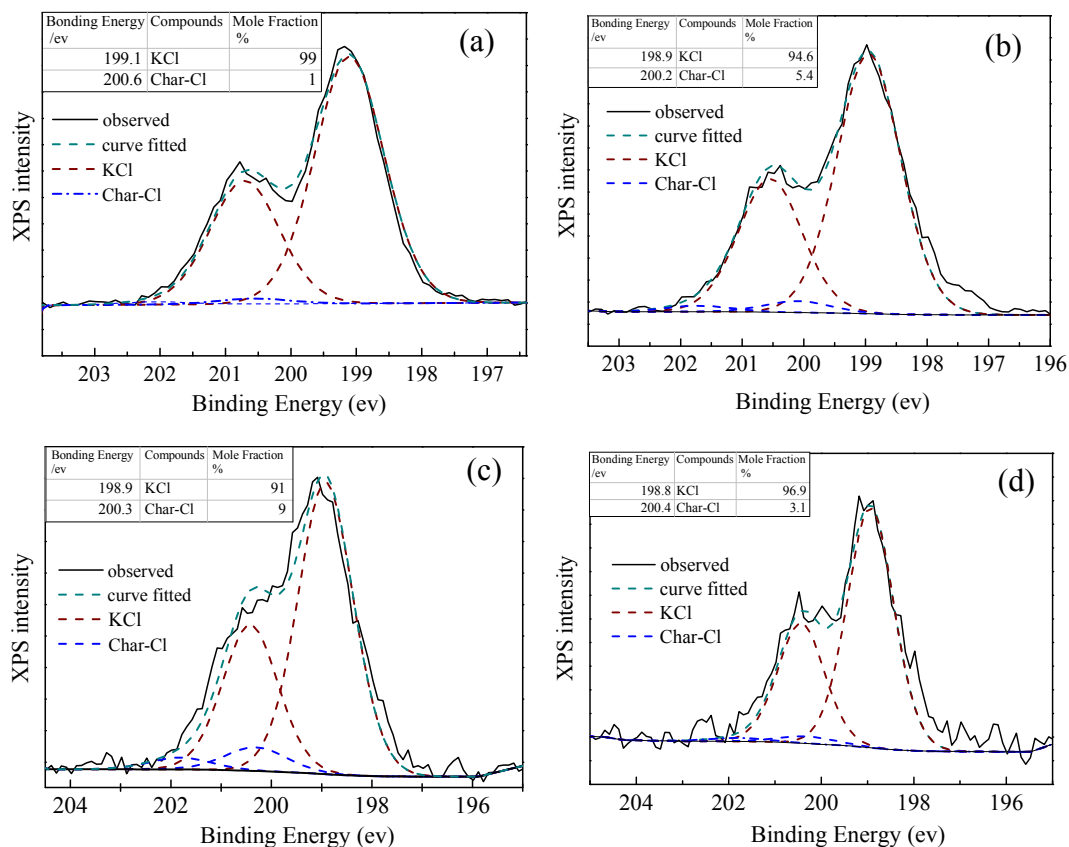
Fig. 6. XPS spectra of Cl in char matrix obtained from pyrolysis of KCl-loaded (a) cellulose, (b) xylan, (c) lignin and (d) pectin at 500 °C.

difference might be related to different functional groups and char structure. It should be noted that the relative C-Cl fractions in lignin and xylan chars analyzed by XPS were significantly lower than these obtained by the water-leaching method. The reason was that XPS mainly examined apparent surfaces of char particles, while most of C-Cl might be incorporated into the inner of particles, resulting in lower proportions of C-Cl by XPS.

3.3.1.1. SEM-EDS analysis. The morphologies of KCl-loaded samples before and after pyrolysis were shown in Figs. 7–10, and EDS compositions of spots and areas on samples were also listed. No observable KCl particle was found on surfaces of doped cellulose and pectin before pyrolysis, and composition of Area 1 in Figs. 7a and 10a suggested most of KCl was uniformly dispersed in the samples. While big particles were examined on surfaces of doped xylan and lignin, and
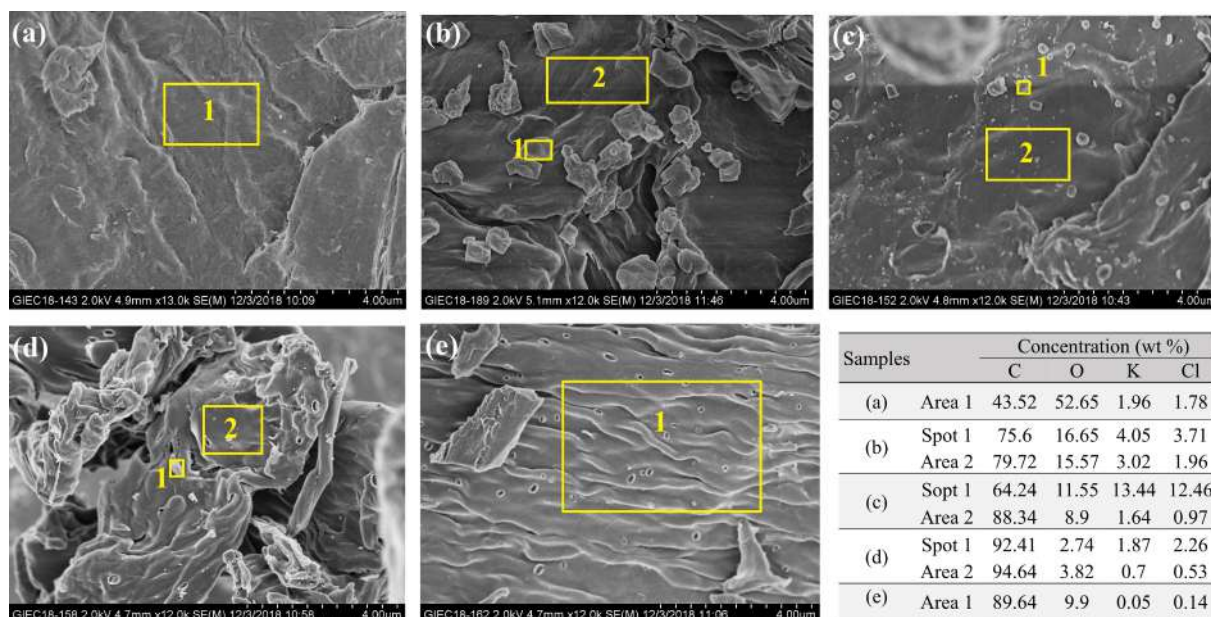

Samples		Concentration (wt %)			
		C	O	K	Cl
(a)	Area 1	43.52	52.65	1.96	1.78
(b)	Spot 1	75.6	16.65	4.05	3.71
	Area 2	79.72	15.57	3.02	1.96
(c)	Sopt 1	64.24	11.55	13.44	12.46
	Area 2	88.34	8.9	1.64	0.97
(d)	Spot 1	92.41	2.74	1.87	2.26
	Area 2	94.64	3.82	0.7	0.53
(e)	Area 1	89.64	9.9	0.05	0.14

Fig. 7. morphologies and compositions of (a) KCl-loaded cellulose, and its chars pyrolyzed at (b) 300 °C, (c) 500 °C, (d) 800 °C, and (e) the char-500 °C after NH₄AC leaching.
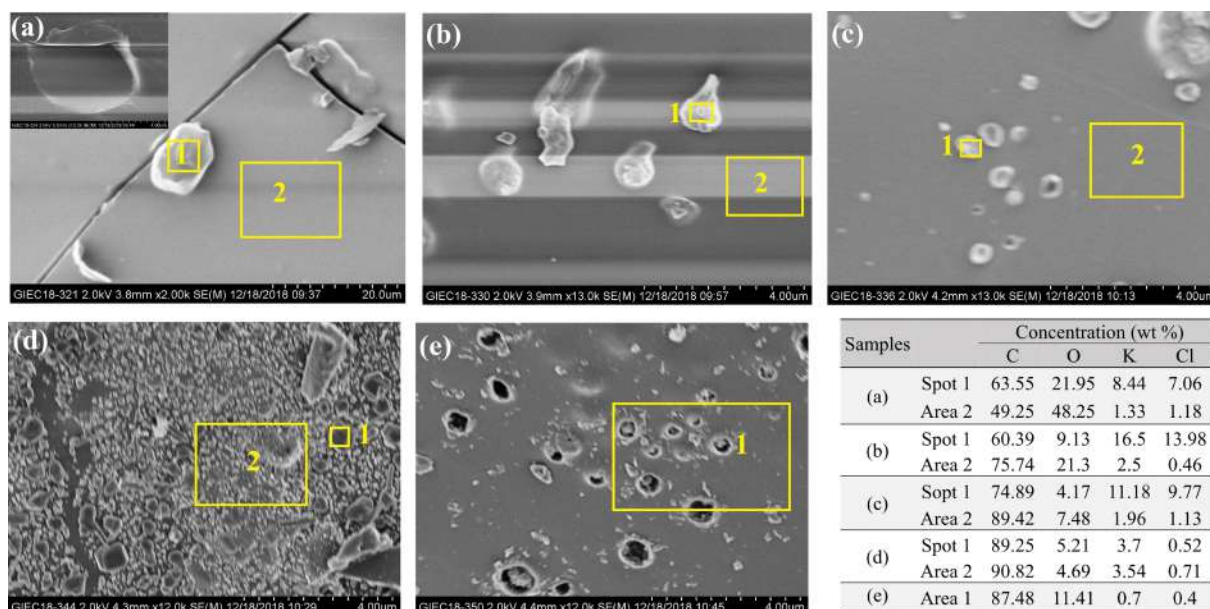
Fig. 8. morphologies and compositions of (a) KCl-loaded xylan, and its pyrolyzed chars at (b) 300 °C, (c) 500 °C, (d) 800 °C, and (e) the char-500 °C after NH$_4$AC leaching.

the K/Cl ratio of Spot 1 in Fig. 8a suggested it was KCl indeed, while Spot 1 in Fig. 9a might be mainly composed of KCl, Na and S. Besides, composition analysis of Area 2 in Figs. 8 and 9a suggested that part of the loaded KCl was distributed evenly in xylan and lignin. After pyrolysis, KCl particles (Spot 1 in Figs. 7–9b–d) were observed in chars from cellulose, xylan and lignin, and the EDS analysis of Area 2 in Figs. 7–9(b)–(d) indicated that the chars contained organically-bounded K. For pectin, no visible KCl particles were observed in solid char as most of Cl was released even at low temperature of 300 °C (Fig. 5b), thereby resulting in higher mole ratio of K/Cl (spots and areas in Fig. 10b–d), which was consistent with that in Section 3.2.4. Besides, it should be noted that the protrusions or visible pores in cellulose char and loose flat structure in pectin char might be beneficial for K and Cl escaping out of char particles, resulting in relatively higher release fractions as displayed in Figs. 2 and 5. However, the compact and

smooth surfaces of xylan and lignin chars increased diffusion resistances for K and Cl releasing. The chars after washing by NH$_4$AC solution (Figs. 7–10e) shows abundant pores with different sizes in cellulose, xylan and pectin except lignin, which would affect migration of K and Cl. The composition of Areas 1 in Figs. 7–10(e) indicated few NH$_4$AC-insoluble K were detected, consistent with that in Section 3.2.

3.4. Mechanism on migration of K and Cl caused by interaction of KCl with organics

The possible mechanism on migration and speciation transformation of K and Cl caused by interaction of KCl with organics are summarized in Fig. 11. Cellulose and xylan with active oxygen-containing groups (i.e., hemiacetals, hydromethyls) were decomposed into organics with free carboxyl acids (R1 and R2). These carboxyls promoted
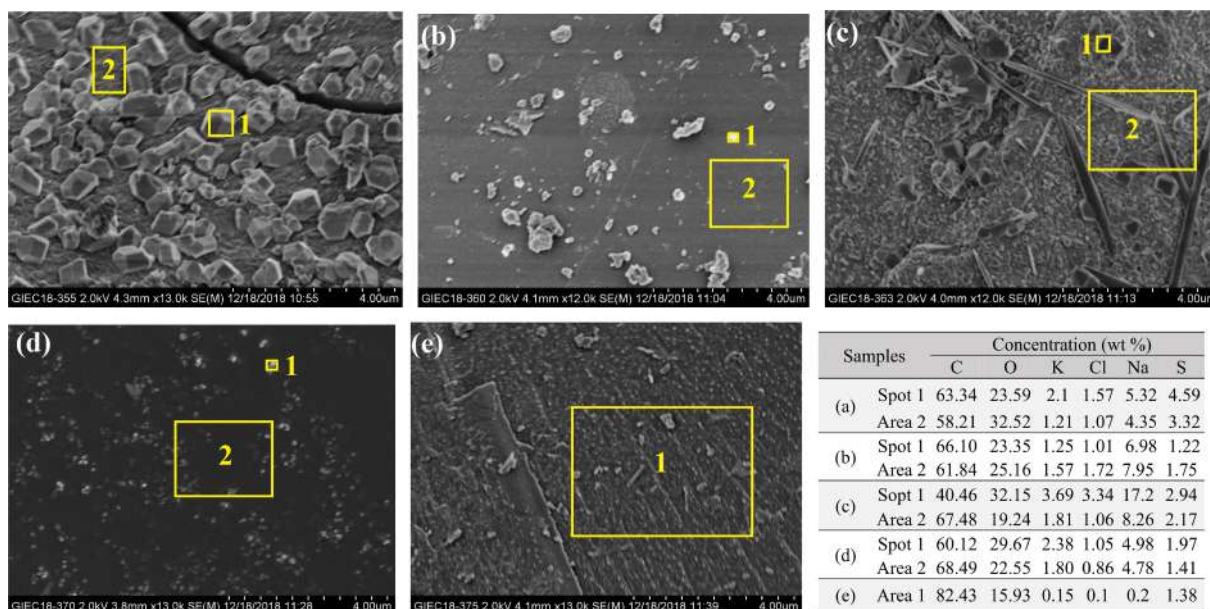

Fig. 9. morphologies and compositions of (a) KCl-loaded lignin, and its pyrolyzed chars at (b) 300 °C, (c) 500 °C, (d) 800 °C, and (e) the char-500 °C after NH$_4$AC leaching.

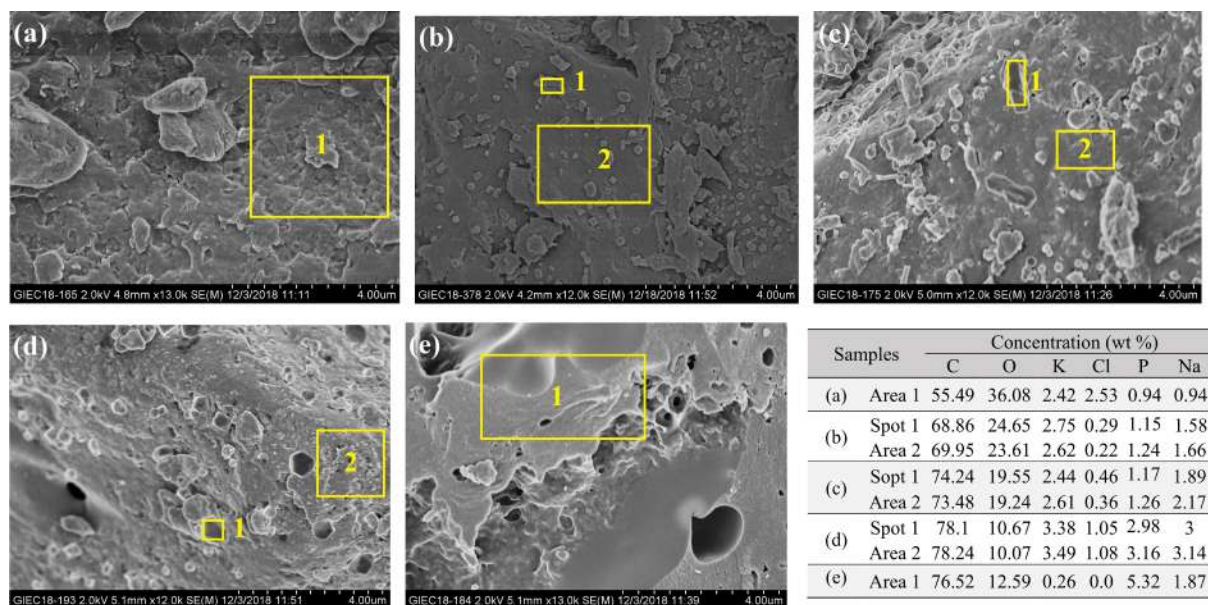| Samples		Concentration (wt %)					
		C	O	K	Cl	P	Na
(a)	Area 1	55.49	36.08	2.42	2.53	0.94	0.94
(b)	Spot 1	68.86	24.65	2.75	0.29	1.15	1.58
	Area 2	69.95	23.61	2.62	0.22	1.24	1.66
(c)	Sopt 1	74.24	19.55	2.44	0.46	1.17	1.89
	Area 2	73.48	19.24	2.61	0.36	1.26	2.17
(d)	Spot 1	78.1	10.67	3.38	1.05	2.98	3
	Area 2	78.24	10.07	3.49	1.08	3.16	3.14
(e)	Area 1	76.52	12.59	0.26	0.0	5.32	1.87

Fig. 10. morphologies and compositions of (a) KCl-loaded pectin, and its pyrolyzed chars at (b) 300 °C, (c) 500 °C, (d) 800 °C, and (e) the char-500 °C after NH$_4$AC leaching.
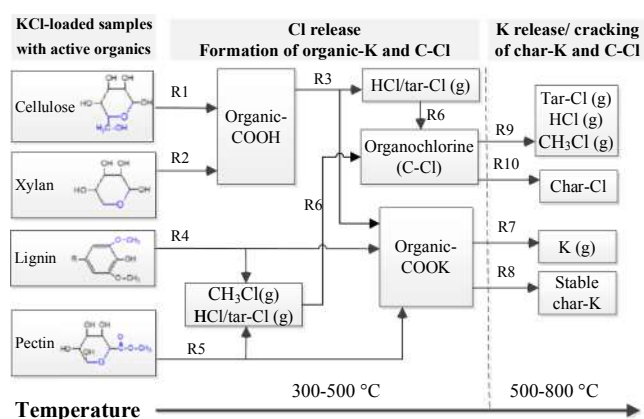

Fig. 11. Possible mechanism on K and Cl migration caused by interaction of KCl with organics.

water-soluble K transforming into organic-K via ion-exchange reaction (R3), at the same time, the water-soluble Cl combined with ·H radicals and release as HCl (g) (R3). Amounts of methoxyls and esters in lignin and pectin were significantly benefited for water-soluble K transformation, thereby forming organic-K (R4 and R5). The cleavage of methoxyl (-O-CH$_3$) provided ·CH$_3$ radical and promoting Cl releasing as CH$_3$Cl (R4 and R5). Besides, part of Cl might also be released together with tar in form of tar-Cl (R3-R5). The once-released HCl (g) and CH$_3$Cl (g) was captured by active carbon sites via secondary reaction and formed organochlorine (R6). As pyrolysis proceeded, part of organic-K was decomposed into K (g) (R7), while part of organic-K retained in chars to form stable char-K (R8). The amount of char-K was closely related to chemical structure. As discussed in Section 3.2, few of char-K were detected in cellulose char at temperature of above 500 °C, whereas a considerable fraction of char-K remained in other chars. Part of C-Cl was released together with volatiles in form of tar-Cl (g), HCl (g) or CH$_3$Cl (g) (R9), and a few of C-Cl remained in solid char to form char-Cl (R10).

4. Conclusion

To better understand migration and speciation transformation of K

and Cl caused by interaction of KCl with organics, KCl-doped model compounds (i.e., cellulose, xylan, lignin and pectin) were employed owning to their relatively simple structure comparing with real biomass. Pyrolysis of doped samples were conducted within 300–800 °C, and migration of K and Cl were quantitatively investigated. Big difference in K and Cl migration were observed among four samples, and the distinction was closely related to types of organics. In general, a low proportion of K was released from all the four samples at 300–500 °C, while amount of organic-K were formed via different ion-exchange reaction mechanisms, thereby promoting Cl release. Comparing with that cellulose and xylan, more organic-K were formed during pyrolysis of both doped lignin and pectin due to intensive reaction of KCl with methoxyls, esters or free carboxyl acids. At the same time, huge amounts of Cl were released from pectin and lignin, providing a possible way for Cl removing. Organochlorine were also formed via secondary reaction of released Cl with carbon active sites. As pyrolysis proceeded, Cellulose exhibited highest K release due to decomposition of organic-K, while a considerable of char-K with high thermal stability still retained in other samples. Results of this work will supply practical information for gas cleaning during biomass gasification and combustion.

CRediT authorship contribution statement

Yanqin Huang: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Huacai Liu:** Analysis, Writing - review & editing, Investigation. **Hongyou Yuan:** Validation, Investigation. **Xianchao Lv:** Analysis, Investigation. **Bin Xu:** Analysis, Investigation. **Weizhen Li:** Resources, Investigation. **Jenjira Uttaruean:** Validation, Investigation. **Xiuli Yin:** Supervision. **Chuangzhi Wu:** Supervision.

Declaration of Competing Interest

Acknowledgements

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