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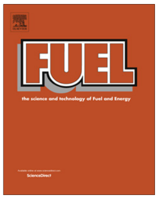

Release and transformation characteristics of K and Cl during straw torrefaction and mild pyrolysis

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HIGHLIGHTS

- Release of Cl was synchronous with devolatilization at 200–350 °C.
- Particle size influenced the release ratio of Cl obviously.
- Secondary reactions had a limited influence on speciation transformation of K.
- The reaction intensities of KCl with four macromolecules were different.

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ABSTRACT

The release and transformation characteristics of K and Cl during straw torrefaction and mild pyrolysis under different conditions were investigated. The results show that release ratio of Cl increased continuously with temperature and holding time and the release of Cl was linearly proportional to devolatilization. The particle size was one of most important factors influencing Cl release. The release ratio for 74–124 μm straw particle was 60.78%, which was much higher than 27.25% for 250–420 μm at 350 °C. The influence of sample weight, particle size and heating rate was mainly due to secondary reactions of once-released Cl and pyrolysis char (the AAEMs and carbon active sites) during the diffusion process of volatiles. The influence of secondary reactions on K release and transformation behavior was not significant. The reaction intensities of KCl and macromolecules (cellulose, lignin, xylan and pectin) were different. The release of Cl was not generally equal to the fractions of K transformed into ion-exchanged species and released to the gas phase during KCl-loaded macromolecules torrefaction and mild pyrolysis, mainly due to different intensities of their secondary reactions.

1. Introduction

Biomass, one of the most promising renewable energy sources, would realize zero CO_2 emission over its whole life cycle and produce less pollution comparing with the fossil fuels. Torrefaction is a mild pyrolysis process to improve the biomass properties at the temperature range of 200–300 °C under an inert environment. By means of torrefaction, most of the moisture in biomass would be removed and fibrous structure would also be destroyed, effectively increasing heating value and improving grindability and uniformity. The torrefied biomass is more suitable for combustion and gasification than raw materials. Currently, the study on biomass torrefaction was getting more and more attention [1–4].

Biomass generally contains a number of inorganic elements, such as the alkali and alkaline earth metals (AAEMs), Si, Cl and S, whose influence on the biomass gasification or co-gasification of coal and biomass can't be ignored. During biomass thermochemical conversion, part of inorganic elements (especially the alkali metals and Cl) will be released to the gas phase, bringing about some serious problems of fouling, slagging, particle agglomeration, corrosion [5,7]. On the other hand, K has a catalytic effect on gasification of biomass char and also has a significant impact on the compositions of pyrolysis and gasification products, which may be one of the main causes of synergistic effect in co-gasification of coal and biomass. The previous researches on release and transformation behavior of K and Cl were mainly carried out at

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the temperature over 500 °C [8–12] and the study during torrefaction was limited. The release and transformation characteristics of K and Cl during pyrolysis and gasification of torrefied products may be different from that of origin biomass fuels, due to the variation of contents and chemical forms.

In the research of Olsson et al. [13] and Davidsson et al. [14], alkali release was clearly detected at 300–400 °C during pyrolysis of different biomasses, and it probably concerned with the decomposition of organic structure. Torrefaction of birch wood at 280 °C resulted in a transformation from water soluble K to ion-exchangeable K, which due to the destruction of carboxylic acid groups [15]. The release and transformation of Na during the kitchen waste torrefaction was investigated by Shuai Liu [16]. The results show that about 10% Na was released at 300 °C and some part of water-soluble Na transformed into CH_3COONH_4-soluble (ion-exchangeable) Na. The further studies on torrefaction of Na_2CO_3, $NaHCO_3$ and CH_3COONa loaded samples indicated an interconersion between water soluble and CH_3COONH_4-soluble forms.

Björkman et al. [17] investigated the Cl release behaviors of several biomass fuels during pyrolysis. The results showed that 20–50% Cl released already at 400 °C and it was connected with the organic structures instead of SiO_2 at low temperature. About 60% Cl released at 400 °C during straw pyrolysis, but the release ratio increased little at 400–700 °C [12]. During birch wood torrefaction, most of Cl was released at 280 °C as well [15]. Some researchers hold the point that Cl may release in the form of CH_3Cl besides HCl. Hamilton et al. [18] measured the release contents of CH_3Cl in the pyrolysis processes of leaf and woody tissues at 150–350 °C and the contents reached the maximum at about 300 °C. The release of CH_3Cl at low temperature may be the reaction product of Cl and CH_3 from methyl-esterified carboxyl groups in pectin. The studies of quantification of Cl found that not all Cl was released in form of HCl which can be caught by Eschka flux (sodium and carbonate and magnesium oxide) [19,20]. The contact between the released Cl from torrefaction and biomass being torrefied would influence the release behavior of Cl beside temperature. In the research of Saleh [21], increasing the straw content in the reactor led to a lower fractional release of Cl, probably due to secondary binding of Cl to the solid product.

In the present study, the release and transformation behavior of Cl and K was investigated during straw torrefaction at 200-300 °C and mild pyrolysis at 350 °C. The influence of temperature, holding time at selected temperature, particle size and sample weight on release ratio of Cl and K were studied. The speciation transformation of K was also investigated by Chemical fractionation analysis (CFA). KCl-loaded model compounds were torrefied to understand different rules of macromolecules (cellulose, lignin and xylan, etc.) played in the release and transformation behavior of Cl and K. At the same time, the release and transformation path of Cl and K was also discussed.

2. Materials and methods

2.1. Materials

Rice straw obtained from the suburb of Shanghai in china was chosen as raw material. Straw was pulverized and sized into a range 178–420 μm (if not specified). The selected particles were dried at 105 °C for 24 h and sealed prior to use. Proximate and ultimate analysis results, measured by Industrial Analyzer of 5E-MAG6700 (GB/T212-2008) and Elemental Analyzer of Vario MACRO CHNS respectively, were shown in Table 1.

Table 1
Proximate and ultimate analysis of straw.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.%)				
	Ash[b]	Volatile matter[b]	Fixed carbon[b]	C[b]	H[b]	O[a]	N[b]	S[b]
Straw	9.93	75.76	14.31	44.23	5.11	39.57	0.89	0.27
Cellulose	\	85.08	14.92	43.37	6.11	50.52	\	\
Lignin	3.67	63.63	32.70	64.74	5.49	24.36	1.00	0.74
Xylan	3.55	83.02	13.43	41.92	7.47	46.81	0.07	0.18
Pectin	0.54	83.31	16.15	38.08	7.15	53.82	0.19	0.22

[a] Oxygen calculated by difference.
[b] Dry basis.

KCl-loaded cellulose, KCl-loaded lignin, KCl-loaded xylan and KCl-loaded pectin were also employed as model compounds. The CAS numbers of cellulose, lignin, xylan and pectin were 9004-34-6, 8068-05-1, 9014-63-5 and 9000-69-5 respectively. KCl-loaded model compounds were prepared according to following methods. Firstly, about 1.5 g of KCl was weighted and dissolved into 300 ml ultrapure water; then about 30.0 g cellulose, lignin, xylan or pectin were dipped into the solution; thirdly, the mixtures were stirred and dried at 45 °C; at last, the model compounds were dried at 105 °C in drying oven when most of the mixture had evaporated. All model samples were ground and the particle was smaller than 420 μm.

Raw straw, lignin and xylan were ashed at the temperature lower than 200 °C in the low temperature asher (EMITECH K1050X) with plasma power 75 w, in order to prevent the loss of ash elements. The yields of low temperature ash of straw, lignin and xylan were 14.34%, 4.74% and 4.58% respectively. The ash chemical composition was analyzed by X-Ray Fluorescence (XRF, Thermo Scientific ARL Advant'XIntellipower^{TM} 3600X) with the result shown in Table 2.

2.2. Torrefaction and mild pyrolysis process

The torrefaction and mild pyrolysis experiment was conducted in a fixed-bed reactor, as shown in Fig. 1. The inner diameter of the stainless steel tube reactor was 50 mm. The diameter of sample basket was 40 mm and the height of wire-mesh was 50 mm. The thermocouple inserted into the reactor tube from bottom was used to measure the reaction temperature.

Accurate weighted 10 (±0.10) g (if not specified) raw material was loaded into the basket and the basket was hung in the setting position of reactor with a steel wire. A high-purity N_2 ($\geqslant$99.999%) stream was inlet into the top of reactor with the flow rate of 500 ml/min to provide an inert atmosphere. After carrier gas N_2 swept 5 min, a certain heating procedure started with heating rate 5 °C/min and the reactor temperature increased from ambient temperature to the selected temperature of 200, 250, 300 and 350 °C. When the pre-selected holding time (15, 30, 60 min) at the desired temperature reached, the basket would be pulled out from the reactor zone to cooling zone and the flow rate of carrier gas remained constant until the sample basket cooling down. At the same time, non-isothermal heat treatment was carried out. In this condition, the experiment was stopped when the selected temperature just reached and the condition was denoted as NIHT. Each condition was carried out three times and the relative standard deviations of char yield were less than 3%. Torrefaction of 1 (±0.01) g raw straw was also carried out with the same experiment step mentioned above. The heating rate was 5 °C/min and holding time in the isothermal stage was 60 min. The stack height was about 45 mm when the initial raw straw weight was 10 g and the stack height was below 5 mm for 1 g.

Four different particle sizes of rice straw were torrefied and the initial mass before torrefaction was 1 (±0.01) g. The particle sizes were 250–420 μm, 178–250 μm, 124–178 μm and 74–124 μm.