



## Full Length Article

# Release and transformation behavior of Cl during pyrolysis of torrefied rice straw



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## HIGHLIGHTS

- Torrefaction at 250 and 300 °C inhibits the total release of Cl at 1000–1200 °C.
- BET surface area of pyrolysis char of torrefied straw at 250 and 300 °C is smaller.
- Removed volatiles during torrefaction reduce the release of Cl.
- Enrichment of Cl on surface for torrefied straw accelerates the release of Cl.
- Generated organochlorine during torrefaction doesn't decompose completely.

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## ABSTRACT

Pyrolysis experiments in a fixed-bed reactor at 800–1200 °C were carried out to compare the release and transformation behavior of Cl between raw and torrefied rice straw. The impact of torrefaction pretreatment on total release of Cl during rice straw high temperature pyrolysis has also been assessed. The influence factors, including volatile matter, particle structure, surface elements enrichment and occurrence forms of Cl, which are different between raw and torrefied rice straw, have been studied. The results show that Cl release ratios of torrefied rice straw at 250 and 300 °C are lower than that of raw rice straw during pyrolysis at 800–1200 °C. At 900–1200 °C, release ratio of Cl of torrefied rice straw decreases with the torrefaction severity. Torrefaction pretreatment at 250 and 300 °C inhibits the total release of Cl during rice straw pyrolysis at 1000–1200 °C. Enrichment of Cl on surface for torrefied rice straw accelerates the release of Cl. The removed volatiles during torrefaction would reduce the release of Cl during pyrolysis, and generated organochlorine (or C–Cl) during torrefaction has the same inhibiting effect on the release of Cl. Surface morphology and specific surface area of pyrolysis char are different between raw and torrefied rice straw. Less specific surface area for pyrolysis char of torrefied rice straw at 250 and 300 °C would restrict the release of Cl.

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## 1. Introduction

Biomass is an important renewable energy source, which is CO<sub>2</sub> neutral and abundant. Great attention has been given to the utilization of biomass. Clean and efficient gasification is a very promising method for utilizing biomass. However, the properties of raw biomass like high moisture content, low energy density, low bulk density and poor grindability are severe challenges during

biomass gasification. Torrefaction is a thermal pretreatment to upgrade biomass properties at 200–300 °C under an inert environment. During torrefaction, biomass would be dried and some part of fibrous structures would also be destroyed, effectively increasing the heating value, decreasing the ratio of O/C and H/C, and improving grindability [1–5]. Simultaneously, torrefied biomass fuels have better storability as compared to raw biomass. In the research of [6–9], torrefaction has a positive effect on the subsequent pyrolysis and gasification processes. Straw biomass usually contains a lot of Cl, part of which would release to the gas phase during thermochemical conversion. It would bring about some equipment operation problems and even environmental problems [10–13]. Besides, it is generally recognized that concentration and

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forms of Cl have a significant effect on release and transformation of the alkali and alkali earth metals [14,15]. Thus, release and transformation behaviors of Cl during biomass thermochemical conversion have been given serious attentions. Previous researches mainly focused on the behaviors during biomass torrefaction below 300 °C [16–19] and pyrolysis or gasification at 500–1000 °C [14,15,20–24].

During torrefaction, some part of Cl would release to the gas phase and organochlorine (C–Cl) is formed. In the study of Saleh [17], 60–70% Cl, most as form of methyl chloride, would be released to the gas phase at 350 °C. During birch wood torrefaction [19], most of Cl was released at 280 °C as well. The research about Cl release of several biomass fuels during pyrolysis investigated by Björkman [25] shows that 20–50% Cl released below 400 °C due to the reaction of KCl with the organic structures instead of SiO<sub>2</sub>. During pyrolysis of NaCl-loaded cellulose, the amount of organically bound Cl in solid residues, part of which was water-insoluble, increased at temperatures from 150 °C to 300 °C [26]. The organochlorine (C–Cl) was also observed by X-ray photoelectron spectroscopy (XPS) during straw torrefaction [16]. During straw pyrolysis, Jensen [24] found that Cl was released in two steps. About 60% released below 400 °C and most of residual Cl released at 700–900 °C [24]. Johansen [14] summarized the possible reaction path and release mechanisms of Cl during biomass pyrolysis and combustion. Release of Cl above 700 °C may be mainly due to the sublimation of metal chlorides [14,22,27]. Release of Cl and distribution among pyrolysis char were also influenced prominently by second reactions [24,28–31].

In our previous research [16] on torrefaction of rice straw, the contents of Cl in torrefied products are different from that in raw rice straw and organochlorine (C–Cl) is also formed. It would potentially influence the release and transformation characteristics of Cl during torrefied rice straw pyrolysis at high temperature. In addition, the effects of organic functional groups, volatile content and particle structure changed during torrefaction need to be considered. To our knowledge, little research has focused on the release and transformation behaviors of Cl during pyrolysis of torrefied biomass. In this work, pyrolysis experiments of raw and torrefied rice straw were carried out in a high-frequency furnace reactor at 800–1200 °C. The effect of torrefaction on release behavior of Cl during high temperature pyrolysis was studied. The influence factors, including volatile matter, particle structure development, surface element enrichment and occurrence modes of Cl, which are different between raw and torrefied straw, have been investigated.

## 2. Materials and methods

### 2.1. Materials

Rice straw (RS) collected from the suburb of Shanghai in china was used as raw material. Through pulverizing and screening, 178–420 μm straw was selected. Straw particle was dried at 105 °C for 24 h prior to use. Proximate and ultimate analysis was measured by Industrial Analyzer (5E-MAG6700) according to GB/T212-2008 and Elemental Analyzer (Vario MACRO Cube) respectively, and results are shown in Table 1. Relative deviations of proximate and ultimate analysis were less than 5%. Raw straw was also ashed below 200 °C in a low temperature asher (EMITECH K1050X) with plasma power 75 W. The yield of low temperature ash was 14.34% and ash chemical composition measured by X-ray Fluorescence (XRF, Thermo Scientific ARL Advant'XIntellipower™ 3600X) was also shown in Table 1.

Hydrofluoric acid washed straw was chosen as raw material to investigate the influence of volatile matter on release of Cl during

**Table 1**  
Raw straw analysis.

Proximate analysis (dry basis, wt%)	Ash	9.93
	VM	75.76
	FC	14.31
Ultimate analysis (dry basis, wt%)	C	44.23
	H	5.11
	O (by difference)	39.57
	N	0.89
	S	0.27
Low temperature ash composition	SiO <sub>2</sub>	55.08
	Al <sub>2</sub> O <sub>3</sub>	0.10
	CaO	3.17
	MgO	2.07
	Na <sub>2</sub> O	1.57
	K <sub>2</sub> O	20.92
	SO <sub>3</sub>	1.81
	Cl	12.55
	P <sub>2</sub> O <sub>5</sub>	2.35
	Others	0.38

high temperature pyrolysis eliminating the affecting of ash composition. 10 g straw was washed with 300 ml HF (40 wt%, AR) for 48 h to remove inherent ash. Then, the sample was rinsed by ultrapure water ( $\geq 18.2$  MΩ cm) and filtered repeatedly to obtain HF washed straw (HFS). HFS was torrefied at 300 °C for 60 min, to obtain torrefied HF washed straw (THFS). KCl-loaded HFS (HFSK) and KCl-loaded THFS (THFSK) were prepared by wet impregnation. Firstly, 1.00 g of KCl was accurately weighted and dissolved into 200 ml ultrapure water; then about 20 g HFS or THFS was dipped into the solution; thirdly, the mixtures were stirred and dried at 45 °C; at last, the samples were dried at 105 °C before pyrolysis. 10 g straw was also washed with 500 ml 0.5 M H<sub>2</sub>SO<sub>4</sub> to obtain acid washed straw, which was denoted as HSW. The yield of low temperature ash of HSW was 6.70%. Mass fraction of SiO<sub>2</sub> measured by XRF was 99.27%. KCl-loaded HSW (HSWK) was obtained according to the same method mentioned above. HSW was torrefied at 300 °C for 60 min, to obtain torrefied H<sub>2</sub>SO<sub>4</sub> washed straw (THSW) and KCl-loaded THSW was denoted as THSWK.

### 2.2. Torrefaction process

Torrefaction experiment was conducted in a fixed-bed reactor. Detailed setup of fixed bed reactor has been described elsewhere [16,32]. Accurate weighted 10 (±0.10) g raw straw was loaded into sample basket and the basket was hung in the setting position of reactor. A high-purity N<sub>2</sub> ( $\geq 99.999\%$ ) stream as carrier gas was inlet into the top of reactor with flow rate of 0.50 NL/min. After N<sub>2</sub> swept 5 min, the heating procedure started with heating rate 5 °C/min and the reactor temperature increased from ambient temperature to selected temperature of 200, 250 and 300 °C. When pre-selected holding time of 60 min at desired temperature reached, the basket would be pulled out to cooling zone and the flow of carrier gas was cut off after sample basket cooling down. Torrefied straw at 200, 250 and 300 °C was denoted as TS200, TS250 and TS300 respectively. For HFS and HSW, the initial weight of sample was 5 (±0.05) g. Each condition was carried out three times and maximum relative deviations of solid yield were less than 3%.

### 2.3. High temperature pyrolysis process

High temperature pyrolysis experiments of raw and torrefied straw were carried out in a high-frequency furnace, as shown in Fig. 1. Molybdenum crucible was heated by high frequency alternating magnetic field generated by induction coil [33]. S-type thermocouple inserted into a hole drilled in the bottom of

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