

Article

Chlorine Release from Co-Pyrolysis of Corn Straw and Lignite in Nitrogen and Oxidative Pyrolysis

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Abstract: Elevated emissions of hydrogen chloride (HCl) from the combustion of biomass in utility boilers are a major issue because they can cause corrosion problems and deposit molten alkali chloride salts on boilers' water tubes, resulting in further corrosion. Pyrolysis is a good pre-treatment for solving this problem. This work conducted pyrolysis and co-pyrolysis of pulverized corn straw and lignite coal in a horizontal muffle furnace, with compositions typical of power plant combustion effluents (5% O₂, 15% CO₂, 80% N₂) at different temperatures. Cl compounds were monitored in fuel, flue gas, and solid production of pyrolysis. The co-pyrolysis significantly affected Cl release from fuel. Cl release from corn straw into fuel gas was reduced during biomass co-pyrolysis with lignite. Co-pyrolysis had little influence on the release of organic Cl and KCl. Furthermore, at moderate-temperature pyrolysis, O₂ promoted HCl release, when compared with pyrolysis under a N₂ atmosphere.

Keywords: biomass; lignite coal; co-pyrolysis; Cl release; oxidative pyrolysis



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1. Introduction

Renewable energy, as the fastest growing source of energy, has experienced a growth of 7.1% per year and contributes to around half of the increase in global energy, with its share in primary energy increasing from 4% in 2019 to around 15% by 2040 [1]. In 2018, in the United States, the renewable energy ratio was 11% of the total primary energy consumption, and bioenergy (wood, biofuels, biomass waste) accounted for 45% of renewable energy consumption [2]. In Germany, renewable energy shared 14.0% in primary energy consumption, and biomass accounted for more than half of that [3]. In the United Kingdom and China, the corresponding renewable energy shares in total primary energy were 12% and 4.4%, respectively, in 2018 [4].

As a renewable energy source, biomass is abundant on Earth and could be defined as a nearly CO₂-neutral energy source. For many years, biomass has been widely used via direct combustion [5–8] to generate power and electricity. Moreover, renewable biomass co-fired with coal in existing power plants is applied worldwide [9–13]. However, biomass has disadvantages that limit the widespread utilization of raw biomass as fuel, including its high moisture content, low energy density, low combustion efficiency, resistance to pulverization, high price of transportation per unit of energy content, and short shelf life [14,15]. Additionally, surface deposition by slagging and fouling, as well as corrosion associated with biomass combustion, are critical problems which have not yet been solved [16]. Therefore, some researchers [17–21] advise that pyrolysis or moderate-temperature pyrolysis are good methods used to give biomass more stability, higher energy density, friability, and grindability.

Scholars have focused on co-pyrolysis behaviors (such as product distribution, product characteristics, and the possibility of existing synergetic effects) of different fuels (such as sawdust, legume straw, lignite, and bituminous coal) with different reactors (such as thermogravimetry, fluidized bed reactors, fixed bed reactors, vacuum reactors, etc.), under various operating parameters (such as temperature, heating rate, blending ratio, particle size, and contacting method of particles) [22]. Vuthaluru [23], Kastanaki et al. [24], and Pan et al. [25] reported the lack of synergistic effect or interaction during co-pyrolysis of biomass and coal. However, recent research [26–36] shows significant interactions and synergistic effects on the yields of major pyrolysis products, gaseous components, and tar components, and the reactivity of char during co-pyrolysis of coal and biomass. Moreover, Yuan et al. [37] pointed out that remarkable synergy can occur when coal and biomass are in close contact, while increasing proportions of biomass will weaken the synergy due to the lower packing density and thermal conductivity of biomass compared with coal. Wu et al. [38] found that cellulose had a positive synergistic effect on the thermal decomposition of bituminous coal with lower char yield, while hemicellulose and lignin, whether there was a positive or negative synergistic effect, were related to the mixed ratio and temperature range.

Chlorine is one of the most important micronutrients of vascular plants, and it exists mainly in the form of water-soluble chloride and ion-exchange in plants. The chloride ion is considered as one of the main mineral anions in the plant cell [39,40]. However, the content of chlorine in fuel remarkably affects the likelihood of slagging and corrosion [41–43]. Therefore, measures have focused on solving the issues caused by chlorine in biomass, such as fuel washing [17,44], limiting the amount of biomass blending to low percentages [45,46], and implementing a sorbent injection into the furnace to address the slagging and corrosion problems caused by chlorine [47–49]. Herein, literature reports show that pyrolysis or torrefaction could reduce the chlorine content in fuel. In low-temperature pyrolysis, 20–50% of the chlorine in biomass is released at 400 °C [50]. In some experiments, pyrolysis reduced the chlorine content by at least 50% [51]. For chlorine compounds, pyrolysis could release a great amount of HCl and other chlorine compounds [52]. Methyl chloride (CH₃Cl) was detected in volatile pyrolysis products [53]. Ren et al. [54] investigated corn straw pyrolysis and found that more than half of its original mass of chlorine was composed of CH₃Cl and HCl. Jensen et al. [55] found that about 60% of chlorine was released during low-temperature pyrolysis (200 °C to 400 °C), and most of the residual chlorine was released between pyrolysis at 700 °C and 900 °C. The initial release of potassium to the gas phase at approximately 700 °C was caused by the evaporation of deposited KCl particles. Hence, the release of Cl to the gas phase was strongly affected by temperature, heating rate, and alkali content.

Based on a literature review, few works focus on Cl release during the co-pyrolysis of coal and biomass, especially at different temperatures and atmospheric conditions (oxygen and oxygen-free atmosphere). Therefore, this work investigated the comparative emissions of HCl from the pyrolysis of coal, biomass, and a mixture of coal and biomass at different temperatures and atmospheres.

2. Experimental Apparatus and Procedure

This study complements previous work, in which corn straw and lignite were co-pyrolyzed in an oxygen atmosphere and an oxygen-free atmosphere, in a horizontal furnace, under similar conditions [16]. Corn straw, as a widely used biomass with high chlorine content, was selected for the experiments and supplied by Harbin. The lignite used was Zhundong coal, obtained from Xinjiang Province (China). All of the fuels were dried, chopped, or ground in a household blender and then sieved to obtain an amount of 75–150 µm. The experimental system was described in previous research from this laboratory [56,57]. The pyrolysis of all samples was carried out in a horizontal furnace (Figure 1) in the N₂ atmosphere and the simulated gas atmosphere, at different temperatures for 10 min, and the flowmeters controlled the mass flow rate of each gas.

The compositions of the fuels are presented on an air-dry basis after proximate analysis, and a dry ash-free basis on ultimate analysis (Table 1). The proximate analysis of the fuels was carried out based on GB/T 212-2008 Chinese standards in an electric oven (5E-DHG) and a muffle furnace (5E-MF6000). Ultimate analysis of the fuels was performed by an elemental analyzer (CHN2200, standard deviation is $\pm 2\%$, $\pm 5\%$ and $\pm 10\%$ for C, H and N, respectively) according to GB/T 30733-2014 standards. The heating values of the biomass fuels were measured with a calorimeter (5E-AC/PL) according to GB/T 213-2008. The chlorine in the coal was detected based on GB/T 3558-1996. The coal sample was mixed with an Eschka reagent and placed into the muffle furnace for melting to convert chlorine into chloride, which was leached with boiling water. Excess silver nitrate solution was added to the acidic medium and titrated with potassium thiocyanate solution, with ammonium ferric sulfate as the indicator. The chlorine content in the coal was calculated based on the actual consumption of the silver nitrate solution.

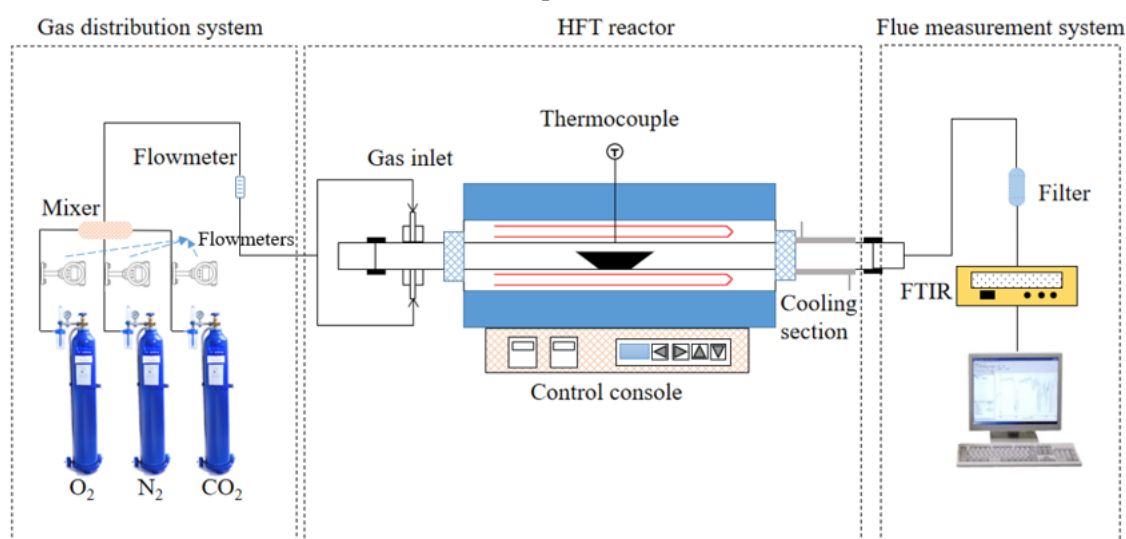


Figure 1. Schematic of the laboratory setup for pyrolysis of pulverized coal and biomass samples [56].

Table 1. Proximate and ultimate analysis of raw biomass, lignite, and mixture.

Samples	Proximate Analysis (wt%)				Ultimate Analysis (wt%, daf)				
	M _{ad}	V _{ad}	A _{ad}	FC _{ad}	C	H	S	N	Cl
Lignite	3.01	34.90	3.31	58.78	73.30	4.10	0.18	1.19	0.06
Corn straw	7.40	80.92	2.52	9.16	42.86	6.66	0.32	0.83	0.75
Mixture	5.21	57.91	2.92	33.97	58.08	5.38	0.25	1.01	0.41

M—Moisture, V—Volatile matter, A—Ash, FC—Fixed carbon, ad—air dried, daf—dry ash-free.

Lignite and corn straw were pyrolyzed in an atmospheric-pressure horizontal flowtube (HFT) reactor for 10 min (Figure 1). Two atmospheric conditions were conducted. One experiment was conducted in a N₂ atmosphere at a flow rate of 3 NL/min. Other carrier gases containing blends of N₂, CO₂, and O₂ were used to simulate the dried effluents of thermal power plants known as flue gas. The volume flow rate of nitrogen was constant in every experiment at about 2.4 NL/min to keep the nitrogen concentration close to 80%. The oxygen flow rate was set to 0.15 NL/min (5%), and the corresponding CO₂ flow rate was set at 0.45 NL/min (15%), which kept the total gas flow rate at about 3 NL/min in every experiment. The results were compared with experiments conducted in neat nitrogen to compare the combined effects of oxygen and carbon dioxide on Cl release during pyrolysis. Seven process temperatures within 300 °C–900 °C were selected for this experiment, and coal, biomass, and coal/biomass blends were successively fed into the horizontal flow tube reactor. The pyrolysis effluent gas was heated to 180 °C to avoid the condensation of water vapor and ensure that the sample remained in gaseous phase, even

with high concentrations of H₂O or corrosive gases, such as HCl (EPA method 321 [58]). Thereafter, the effluent gas was passed through a fiber filter to collect particles, and the emissions were monitored and analyzed by Fourier-transform infrared (FTIR) spectroscopy (with a GASMET DX4000 instrument) [54]. All experiments were repeated in at least triplicate, mean values of which and standard deviation for each case are presented in the Results section.

3. Experimental Results and Discussion

3.1. Biomass Pyrolysis-Induced Composition Changes

In the temperature range of 300 °C–900 °C, mass loss occurred in all pyrolysis processes (Table 2). Under the N₂ environment, the corn straw lost more than half of its mass, from 57.51% to 72.94%, with increasing temperature. Similarly, with the flue gas case, the corn straw's mass reduced from 48.69% to 85.91% with increasing temperature. At low temperature pyrolysis, such as 300 °C, O₂ may generate more Char-COOH, resulting in the inhibition of partial devolatilization. Therefore, the mass loss during oxygen pyrolysis is lower than that during nitrogen pyrolysis at 300 °C. The lignite had mass loss from 4.43% to 34.52% under the N₂ environment, and from 8.09% to 44.39% under the flue gas environment. The mass loss of lignite is significantly smaller than that of corn straw during pyrolysis at different temperatures, because the volatile of lignite is less than that of corn straw (30.49% and 80.92%, respectively, Table 2). The mass loss of lignite in the flue gas case is slightly higher than in the N₂ case, with values of 3.66% and 9.87%. The pyrolysis reaction was accelerated by O₂ in the flue gas. The mixture of coal and biomass lost mass from about 29% in N₂ and the flue gas environment and reached 54.94% and 62.11%, respectively. As shown in Figure 2, the mass loss of the mixture is related to the composition rate of lignite and corn straw. The estimated lines calculated, based on the single pyrolysis process of lignite and corn straw, show the same results as the lines of the mixture cases, both in the N₂ and flue gas atmospheres.

Table 2. Mass loss during fuel pyrolysis under different atmospheres at different temperatures (wt%).

Fuel Type	Atmosphere	Temperature						
		300 °C	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
Corn straw	N ₂	57.51	63.62	66.18	69.49	71.14	71.88	72.94
	5% O ₂	48.69	58.88	72.13	76.68	77.66	82.00	85.91
Lignite	N ₂	4.43	18.04	22.03	27.23	30.74	33.24	34.52
	5% O ₂	8.09	23.82	29.13	32.78	35.37	37.20	44.39
Coal and biomass	N ₂	29.50	41.68	46.02	47.90	51.20	53.33	54.94
	5% O ₂	29.75	41.55	46.89	51.35	52.58	55.51	62.11

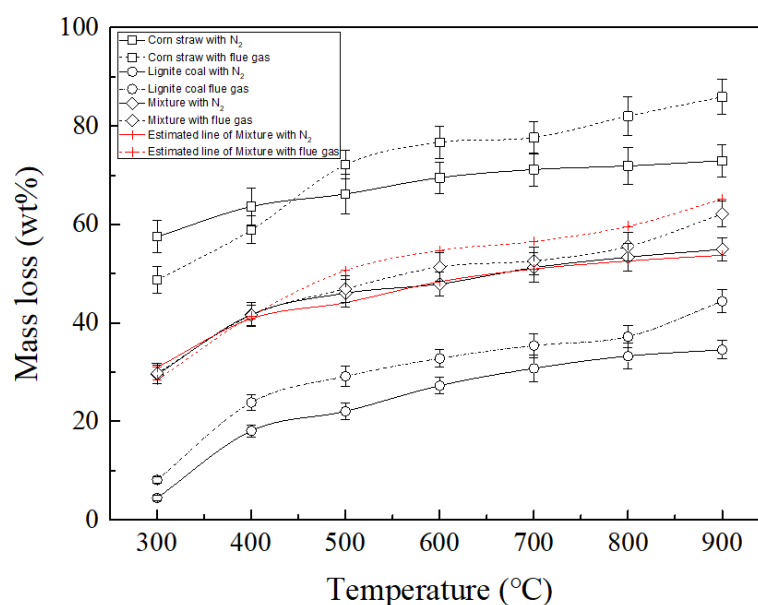


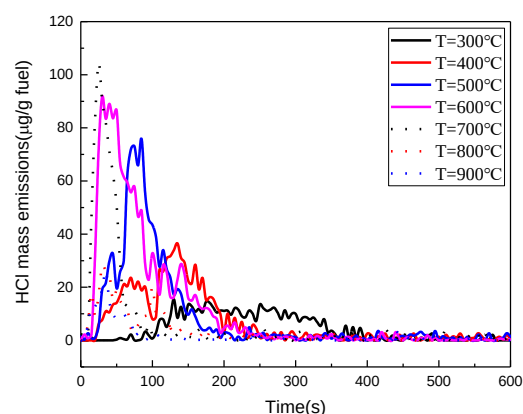
Figure 2. Mass loss variation during fuel pyrolysis under different atmospheres at different temperatures.

3.2. Cl Emissions from the Pyrolysis with N_2 Atmosphere

In the pyrolysis process of the biomass, HCl is one of the major Cl products in the gas phase. During pyrolysis, chlorine in metal chlorides may react with carboxylic groups to generate HCl, as shown in Equation (1) [59,60].

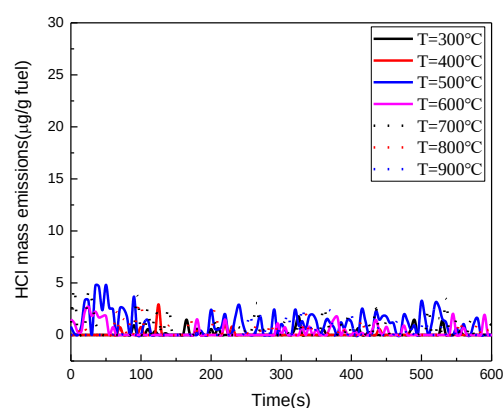


where M represents metals, such as potassium or sodium. Therefore, quantitative measurement of HCl is a practicable approach used to comprehend the migration of Cl during pyrolysis. Time-resolved emissions from the pyrolysis of 0.3 g of samples in different cases were analyzed by FTIR. The evolutions of HCl in corn straw, lignite, and their mixture under the N_2 atmosphere, are shown in Figure 3a–c, respectively.

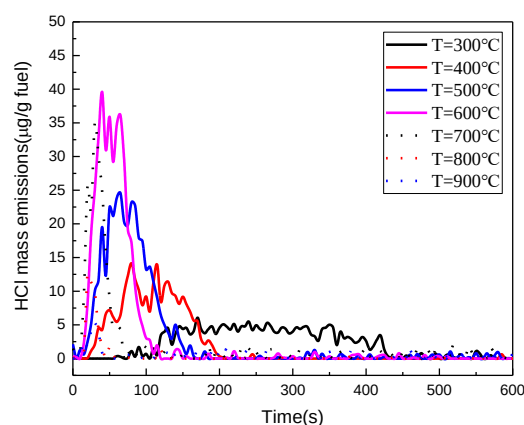


(a) Corn straw

Figure 3. Cont.



(b) Lignite



(c) Mixture

Figure 3. HCl mass emissions during pyrolysis at different temperatures with N₂ atmosphere.

In Figure 3a, the HCl emissions of corn straw occurred within 600 s, and most cases within 200 s. The peak mass emissions appeared in the 700 °C case as 104.35 µg/g fuel. When the pyrolysis temperature was less than 400 °C or greater than 800 °C, the mass emissions of HCl were smaller than 20 µg/g fuel. Hence, with the appropriate pyrolysis temperature (around 500 °C–700 °C), the corn straw would release HCl quickly and generously. By contrast, the lignite rarely released HCl (less than 5 µg/g) fuel during pyrolysis at all selected temperatures (Figure 3b). The mixture of corn straw and lignite (Figure 3c) showed similar HCl mass-emission patterns as corn straw but lower values. In detail, the peak mass emissions appeared at 600 °C (39.62 µg/g fuel). When the pyrolysis temperature was less than 400 °C or greater than 800 °C, the mass emissions of HCl were smaller than 15 µg/g fuel, and Cl would be released as other Cl compounds. The comparison among plots shows that the mixture of corn straw and lignite could restrain the HCl release in pyrolysis at different temperatures.

Furthermore, the HCl mass-emission integrations were calculated with time. The Cl (%) in fuel released as HCl during pyrolysis was calculated based on the detected HCl, as shown in Equation (2).

$$Cl_{HCl}/Cl_{total} = \frac{\text{mass of Cl in HCl}}{\text{mass of Cl in raw sample}} \quad (2)$$

The HCl mass emissions (µg/g fuel) and the Cl conversion rate to HCl are shown in Figure 4. For corn straw, the HCl mass emissions increased first and then decreased with increasing pyrolysis temperature, changing from 537 µg/g fuel to the maximum of

1432 $\mu\text{g/g}$ fuel at 600 $^{\circ}\text{C}$, and then decreasing to 210 $\mu\text{g/g}$ fuel. The Cl conversion rate to HCl (Figure 4b) was within 9.10% and 61.91%. At 600 $^{\circ}\text{C}$, 61.91% Cl was released as HCl, indicating that HCl was the main product of Cl during pyrolysis.

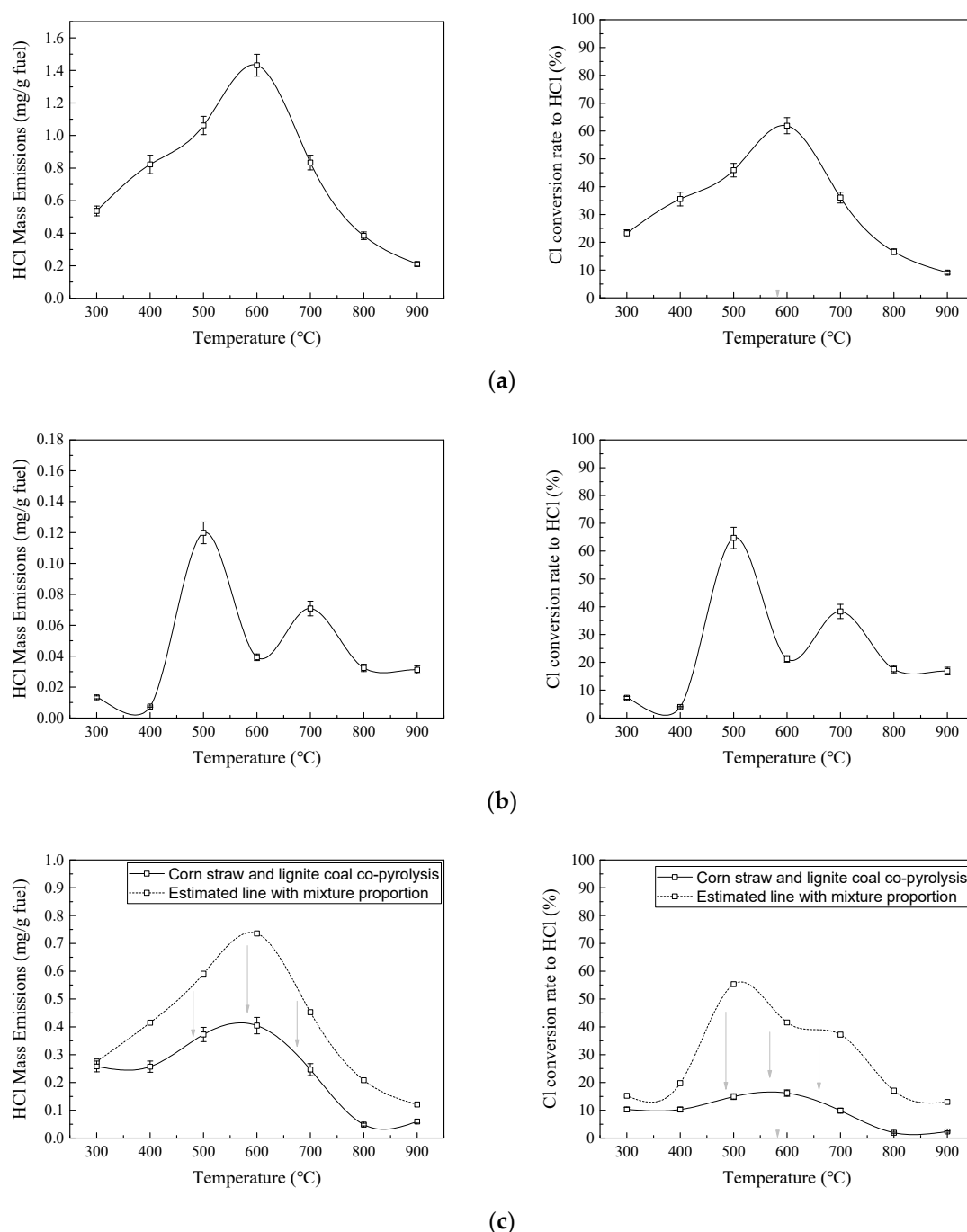


Figure 4. HCl detected in the effluent of corn straw, lignite, and corn straw and lignite co-pyrolysis at different temperatures under N_2 atmosphere for 10 min. (a) Corn straw; (b) lignite; (c) corn straw and lignite co-pyrolysis.

For lignite, HCl mass emissions (7–120 $\mu\text{g/g}$ fuel) were lower than for the corn straw case. Accordingly, the Cl conversion rate to HCl changed by 7.23–64.76%. Although the HCl mass emissions were low due to the small amount of Cl in lignite, the maximum value of the Cl conversion rate to HCl could also reach 64.76%.

For the co-pyrolysis process of corn straw and lignite (Figure 4c), the HCl mass emissions were less than the estimated values with the mixture proportion in all cases, varying from 258 $\mu\text{g/g}$ fuel to 404 $\mu\text{g/g}$ fuel (maximum value at 600 $^{\circ}\text{C}$) and decreasing

to 60 µg/g fuel. The Cl conversion rate to HCl was also lower than the estimated values, which was less than 15% in each case.

The route of the main Cl migration was investigated to explain the phenomenon of Cl release. The two main routes are as follows: (a) Cl emission as another gas with Cl compounds, and (b) Cl staying in solid productions. Other than HCl, many kinds of Cl compounds could be released during pyrolysis. Chlorine could be presented in hydrocarbon chlorides, such as CH₃Cl [53,59], or in alkali salts. Through PY-GC/MS (pyrolysis—gas chromatography/mass spectroscopy), Cl may be released as C₁₀H₁₁ClO, C₁₀H₁₆ClNO, C₁₀H₉ClO₃, C₁₉H₃₆Cl₂O₂, etc. Monitoring every hydrocarbon chloride in the pyrolysis process with such abundant varieties and small amounts is difficult. Therefore, the sum of hydrocarbon chlorides was calculated as Cl released, except HCl, during pyrolysis (Cl_{rest,gas}/Cl_{total}):

$$Cl_{rest,gas}/Cl_{total} = 1 - Cl_{ash}/Cl_{total} - Cl_{HCl}/Cl_{total} \quad (3)$$

Cl (%) that stayed in the bottom ash:

$$Cl_{ash}/Cl_{total} = \frac{\text{mass of ash} * \text{Cl content in ash}}{\text{mass of Cl in raw sample}} \quad (4)$$

Cl obtained during pyrolysis with the N₂ atmosphere is listed in Table 3.

Table 3. Chlorine accounting in pyrolysis with N₂ atmosphere.

Fuel Type	Temperature	Cl Content in Sample (%)	Cl _{HCl} /Cl _{total} (%)	Cl _{ash} /Cl _{total} (%)	Cl _{rest,gas} /Cl _{total} (%)
Corn straw	Original	0.75	-	-	-
	300 °C	0.28	23.22	15.64	61.14
	500 °C	0.19	45.91	8.53	45.56
	700 °C	0.16	36.06	6.23	57.71
Lignite	Original	0.06	-	-	-
	300 °C	0.04	7.23	71.36	21.41
	500 °C	0.01	64.76	10.87	24.37
	700 °C	0.01	38.31	13.46	48.23
Mixture of corn straw and lignite	Original	0.41	-	-	-
	300 °C	0.34	10.32	59.31	30.37
	500 °C	0.32	14.91	43.26	41.83
	700 °C	0.31	9.86	37.16	52.98

First, Cl was released in significant amounts in the pyrolysis of corn straw, and the content decreased from 0.75% before pyrolysis to 0.28%, 0.19% and 0.16% at 300 °C, 500 °C, 700 °C, respectively, as did the content variation in the pyrolysis of the lignite and in the mixture of corn straw and lignite. The concentration of HCl and the content of Cl in the ash were tested to determine the route of Cl during pyrolysis (Table 3).

At all temperatures, the co-pyrolysis of corn straw and lignite could depress Cl, resulting in more Cl remaining in the solid production of pyrolysis. Lignite restrains both the HCl and other Cl compounds. For example, at 300 °C, the HCl conversion rate was 10.32% instead of 15.22% (the estimated value was based on the composition with the proportion relationship), and the rate of the other Cl compounds was 30.37% instead of 41.28%. After comparison of the cases among different temperatures, at the lower pyrolysis temperatures, less Cl was released during the pyrolysis. The main reasons were listed as follows: the pyrolysis atmosphere, pyrolysis volatile production, CHN compounds in the lignite, and metallic compounds from the lignite. It is hard to distinguish which one could promote the reduction in Cl release directly. However, some deductions could

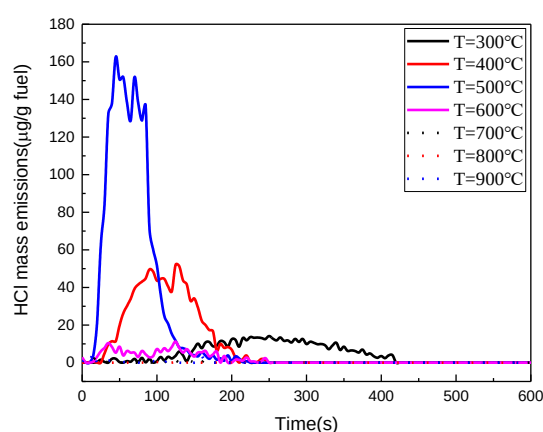
be made according to the series of tests conducted. It would be analyzed with flue gas atmosphere cases.

Within a low temperature range of 300 °C–500 °C, the major Cl compound was organic chlorine [54,61]; with increasing temperature, the major Cl compound would be HCl [54], and further would be KCl [62,63]. Due to the alkali ash in co-pyrolysis, the HCl was adsorbed and stayed in the solid phase. Within 500 °C–700 °C, the HCl emissions, as the major Cl compound in gas productions, were reduced significantly in the corn straw and lignite co-pyrolysis process, as demonstrated in Figure 4c and Table 3.

3.3. Cl Emissions from the Pyrolysis with Flue Gas Atmosphere

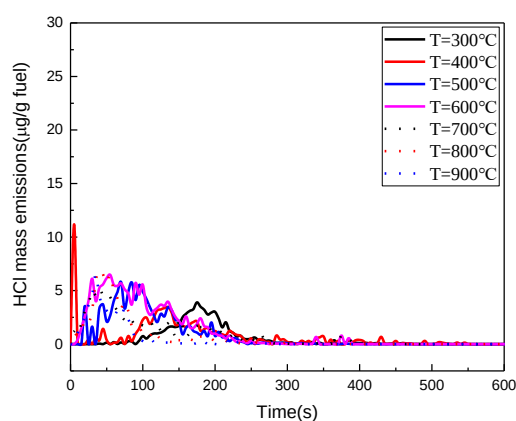
The evolutions of HCl in the corn straw, the lignite, and the mixture of both under the flue gas atmosphere are shown in Figure 6a–c respectively.

In Figure 5a, the HCl emissions of corn straw occurred within 600 s, and in most cases within 200 s. The peak mass emissions appeared in the 500 °C case as 162.71 µg/g fuel, which occurred with lower temperature and higher mass emissions compared with the N₂ atmosphere. At a pyrolysis temperature within 400 °C and 500 °C, abundant HCl was released during the corn straw pyrolysis process. When the pyrolysis temperature was less than 400 °C or greater than 500 °C, the mass emission of HCl was 20 µg/g fuel or even less. By contrast, the lignite rarely released HCl, with less than 15 µg/g fuel released during the pyrolysis process at all selected temperatures (Figure 5b). The mixture of corn straw and lignite (Figure 5c) showed similar HCl mass-emission patterns as corn straw, but the total amounts were less. In detail, the peak HCl mass emission appeared at 500 °C as 60.15 µg/g fuel, which was higher than corn straw. When the pyrolysis temperature was less than 400 °C or greater than 500 °C, the mass emissions of HCl were 15 µg/g fuel or even less. The flue gas atmosphere with O₂ promoted the release of HCl. The mixture of corn straw and lignite could restrain the HCl release in pyrolysis at different temperatures. One probable reason is that the ash in coal may react with HCl, which is produced during biomass pyrolysis. Produced HCl may be captured by ash in coal again to retain char. Therefore, the fraction of Cl released during co-pyrolysis is less when compared with the separate pyrolysis of coal and biomass.

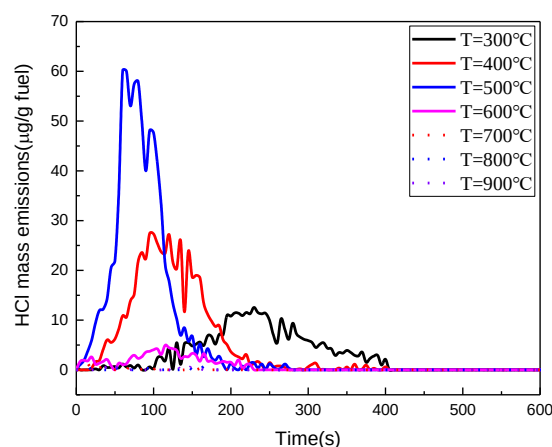


(a) Corn straw

Figure 5. Cont.



(b) Lignite



(c) Mixture

Figure 5. HCl mass emissions during pyrolysis process at different temperatures with flue gas atmosphere.

The HCl mass emissions (μg/g fuel) and the Cl conversion rate to HCl are shown in Figure 6. For corn straw, the HCl mass emissions increased firstly from 549 μg/g fuel to 2090 μg/g fuel (maximum at 500 °C) and then dropped to 19 μg/g fuel, with the pyrolysis temperature increasing. Similarly, the Cl conversion rate to HCl, shown in Figure 6b, increased from 23.72% to 90.33% then dropped to less than 0.82% when the temperature was higher than 700 °C. Under the flue gas atmosphere, the Cl conversion rate to HCl of corn straw reached a peak value of 90.33% at 500 °C, which was significantly higher than other cases under the N₂ and flue gas conditions.

For lignite, the HCl mass emissions increased at first from 62 μg/g fuel to 144 μg/g fuel at 600 °C, then went down to 55 μg/g fuel. Accordingly, the Cl conversion rate to HCl changed in the range of 31.86 to 83.54%. Under the flue gas atmosphere, the HCl mass emissions were low due to the small amount of Cl in lignite, but the Cl conversion rate to HCl could also reach 83.53% at 600 °C. For both corn straw and lignite, the flue gas (5% O₂) atmosphere was a positive factor in the HCl release.

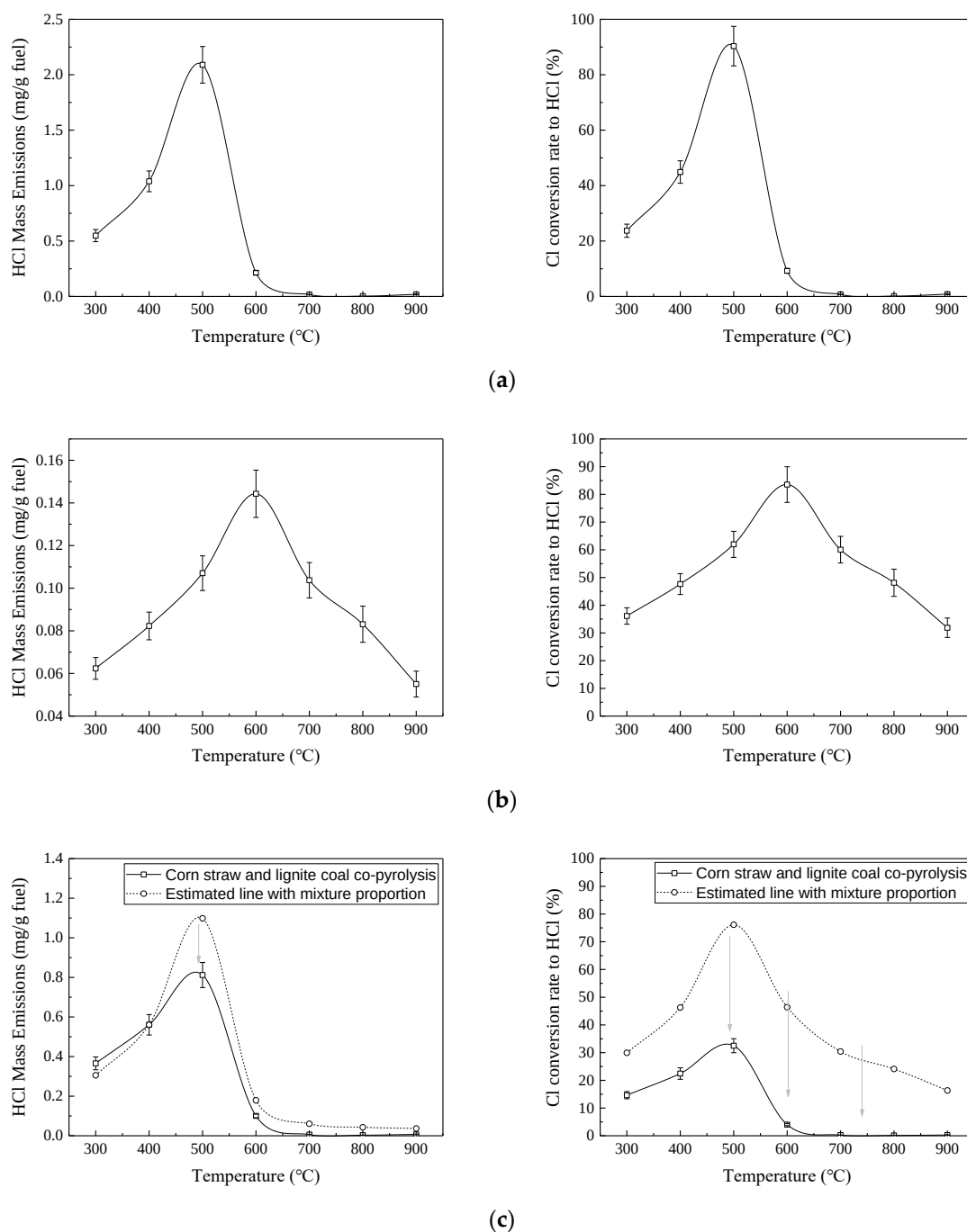


Figure 6. HCl detected in the effluent of corn straw and lignite co-pyrolysis at different temperatures under flue gas atmosphere for 10 min. (a) HCl release during corn straw pyrolysis; (b) HCl release during lignite pyrolysis; (c) HCl release during coal co-pyrolysis with corn straw.

For the co-pyrolysis process of corn straw and lignite (Figure 6c), the HCl mass emissions were less than the estimated values with the mixture proportion in all cases, varying from 366 $\mu\text{g/g}$ fuel to 100 $\mu\text{g/g}$ fuel (maximum at 600 °C) and then decreasing to lower than 100 $\mu\text{g/g}$ fuel.

Furthermore, the Cl accounting in pyrolysis with the N_2 atmosphere are listed in Table 4. Generally, the Cl distribution of fuels with the flue gas atmosphere was similar to the N_2 atmosphere, but the Cl release values were higher.

Table 4. Chlorine accounting in pyrolysis with flue gas atmosphere.

Fuel Type	Temperature	Cl Content in Ash (%)	Cl (%) Released as HCl	Cl (%) Retained in Ash	Rest Cl (%) in Gas
Corn straw	Original	0.75	-	-	-
	300 °C	0.15	23.72	10.22	66.06
	500 °C	0.09	90.33	3.51	6.16
	700 °C	0.12	0.75	3.69	95.56
Lignite	Original	0.06	-	-	-
	300 °C	0.03	36.12	44.75	19.13
	500 °C	0.01	61.97	8.29	29.74
	700 °C	0.01	60.05	11.05	28.90
Coal and biomass	Original	0.41	-	-	-
	300 °C	0.32	14.64	55.28	30.08
	500 °C	0.27	32.50	35.29	32.21
	700 °C	0.25	0.24	29.43	70.33

3.4. Chlorine Distribution after Pyrolysis

The concentrations of HCl and Cl in ash were tested to determine where the Cl goes during pyrolysis (Table 4). In all temperature situations, the co-pyrolysis of corn straw and lignite could depress the release of Cl, which means more Cl remained in the solid production of pyrolysis. Lignite restrained both the HCl and other Cl compounds, except with a high pyrolysis temperature of 700 °C. At 700 °C, the HCl rate was only 0.24% instead of 30.40% (the estimated value was based on the composition with the proportion relationship), but the rate of the other Cl compounds could reach 70.33% instead of 62.23%.

As mentioned in Part (b), several aspects could cause the phenomenon: the pyrolysis atmosphere, pyrolysis volatile productions, CHN compounds in lignite, metallic compounds from lignite and so on. First of all, neither the N₂ nor the O₂ (flue gas) atmosphere was the main reason, since in both cases, the phenomenon existed. The O₂ (flue gas) could help more Cl release from the samples, comparing Table 3 with Table 4, as well as HCl in the low temperature range. At a higher pyrolysis temperature, the HCl emissions reduced obviously, resulting from the O₂ (flue gas) restraining the conversion of Cl into HCl at high temperatures.

Under flue gas conditions (5% O₂), organic chlorine would be the major Cl compound, especially at low temperatures, such as 300 °C. During the 500 °C pyrolysis, HCl replaced the organic chlorine to become the main Cl compound released [62]. At higher pyrolysis temperatures, the major Cl compound may be KCl. Due to the alkali ash in co-pyrolysis, HCl emissions were adsorbed and remained in the solid phase. At 300 °C–600 °C, the HCl emissions, as the major Cl compound in gas productions, were reduced significantly in corn straw and lignite co-pyrolysis (Figure 6). At higher temperatures, few HCl emissions were detected in the corn straw pyrolysis, and the alkaline ash in co-pyrolysis even adsorbed partial HCl, derived from lignite pyrolysis.

4. Conclusions

This work conducted pyrolysis and co-pyrolysis of pulverized corn straw and lignite coal in a horizontal furnace in N₂ and with compositions typical of power plant combustion effluents (5% O₂, 15% CO₂, 80% N₂) at different temperatures. Cl release was detected. In low-temperature pyrolysis, Cl is released mainly as organic chlorine; during moderate-temperature pyrolysis, Cl is released mainly as HCl; and during high-temperature pyrolysis, Cl is probably released mainly as KCl. Moreover, during moderate-temperature pyrolysis, O₂ will promote HCl release when compared with pyrolysis under the N₂ atmosphere. Co-

pyrolysis of lignite coal and corn straw will cause the inhibition of HCl release. However, co-pyrolysis has little influence on the release of organic chlorine and KCl.

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