Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation

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Abstract

The behaviour of gaseous chlorine and alkali metals of three sorts of biomass (Danish straw, Swedish wood, and sewage sludge) in combustion or gasification is investigated by the chemical equilibrium calculating tool. The ranges of temperature, air-to-fuel ratio, and pressure are varied widely in the calculations (T = 400–1800 K, l = 0–1.8, and P = 0.1–2.0 MPa). Results show that the air excess coefficient only has less significant influence on the release of gaseous chlorine and potassium or sodium during combustion. However, in biomass gasification, the influence of the air excess coefficient is very significant. Increasing air excess coefficient enhances the release of HCl(g), KOH(g), or NaOH(g) as well as it reduces the formation of KCl(g), NaCl(g), K(g), or Na(g). In biomass combustion or straw and sludge gasification, increasing pressure enhances the release of HCl(g) and reduces the amount of KCl(g), NaCl(g), KCl(g), or NaOH(g) at high temperatures. However, during wood gasification, the pressure enhances the formation of KOH(g) and KCl(g) and reduces the release of K(g) and HCl(g) at high temperatures. During wood and sewage sludge pyrolysis, nitrogen addition enhances the formation of KCN(g) and NaCN(g) and reduces the release of K(g) and Na(g). Kaolin addition in straw combustion may enhance the formation of potassium aluminosilicate in ash and significantly reduces the release of KCl(g) and KOH(g) and increases the formation of HCl(g).

Keywords: Chlorine; Alkali metals; Behaviour; Biomass utilization

1. Introduction

The thermal utilisation of biomass can contribute to the reduction of CO₂ emissions. Compared with coal, biomass has a high amount of potassium, chlorine, and silicon as well as minor amounts of Ca, Mg, Al, Fe, Na, and S, etc. During combustion or gasification (i.e. air–fuel ratio l > 1 or < 1) of biomass, significant amounts of chlorine and alkali metals are released into the gas phase, such as HCl(g), KCl(g), KOH(g), and NaCl(g), etc. They are very harmful in terms of causing fouling, slagging, and high temperature corrosion in the furnace [1–10]. For direct fired combined cycles, the alkali species in the gas phase can result in serious corrosive problems at gas turbines [11–13]. Hydrogen chloride may also tend to produce unacceptably high emissions of HCl and dioxins [14–20]. In addition, HCl, SO₂, and released alkali species are likely to form aerosols in the flue gas [13,21–23].

It is found that the major ash forming elements (Al, Si) and the composition of gas phase (O₂, N₂, and H₂O, etc.) have significant influence on the behaviour of chlorine and alkali metals [24–31]. In fact, it may be affected by many factors, such as composition of the fuel, combustion or gasification conditions, and low or high pressure. However, few studies have been carried out to analyse the influence of fuel minerals on this behaviour considering all of the mineral elements (Al, Si, K, Na, Ca, Mg, Fe, Ti, Mn, S, Cl, and P, etc.). In addition, there are very limited results in this field for biomass gasification under pressurized conditions.

The aim of this work is to investigate the release of chlorine and alkali metals for three kinds of biomass during combustion or gasification under pressurized conditions by the equilibrium calculating tool FactSage (Table 1 shows
the composition of biomass). The ranges of temperature, air–fuel ratio, and pressure are varied widely, e.g. $T = 400$–1800 K, $\lambda = 0$–1.8, and $P = 0.1$–2.0 MPa.

### 2. Calculating method

The equilibrium analysis software FactSage was used to determine thermodynamic stable chemical and physical forms in the chemical system. When the parameters, such as the elementary composition of the fuel and air, temperature and pressure have been entered, FactSage will search the species including these elements from the database. In this paper, 611 species (143 gas, 94 liquid, and 374 solid species) are selected to conduct the thermodynamic equilibrium calculation for the chemical system including the elements C, H, O, N, S, Cl, Si, P, Ca, K, Na, Mg, Al, Fe, Ti, and Mn between 800 and 1800 K. Table 2 gives the moles of biomass composition based on 1000 kg fuels for equilibrium calculation.

Although the equilibrium analysis is a powerful tool to predict the stable species during the chemical process, there are some disadvantages of this method applied to the combustion case [32]. Either the temperature must be high enough or the species residence time should be long enough to reach the thermodynamic equilibrium. The difficulty will arise when the results of the equilibrium calculation are compared with those of real combustion systems. In general, the chemical equilibrium analysis may be used to give the equilibrium distribution of elements and the reaction mechanism of various species.

### 3. Results and discussion

Fig. 1 describes the transformation of alkali metals (e.g. potassium) during biomass thermal utilisation. In biomass gasification or combustion, some of potassium and chlorine will be released into gas, such as HCl(g), KCl(g), (KCl)2(g), K2SO4(g), KOH(g), and K(g), etc. And the others may be retained in ash, forming potassium silicate, aluminosilicate or sulphate. During the cooling process, the gaseous potassium may condense on the coarse fly ash as KCl(s) or K2SO4(s). Some of gaseous potassium directly forms aerosols or fine fly ash because of condensation, sulfation and carbonization. A part of these aerosols may also attach on the coarse fly ash. The enrichment of potassium, sulphur and chlorine in ash is very harmful because of causing fouling, slagging, and high temperature corrosion in the furnace. In addition, if aerosols are not collected in the ash separator, they may cause air pollution.

Fig. 2 shows the equilibrium results of potassium behaviour for Danish straw and Swedish wood combustion. At high temperatures (>1100 K), the main potassium containing species are K2Si4O9(liq), KCl(g), and KOH(g) for straw combustion, and KCl(g), K2SO4(g), and KOH(g) for wood combustion. Because of the higher content of

### Table 1

<table>
<thead>
<tr>
<th>Chemical analysis (%)</th>
<th>Danish straw</th>
<th>Swedish wood</th>
<th>Sewage sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>11.71</td>
<td>7.80</td>
<td>5.86</td>
</tr>
<tr>
<td>Volatile dry</td>
<td>71.32</td>
<td>84.10</td>
<td>48.45</td>
</tr>
<tr>
<td>Ash dry</td>
<td>13.42</td>
<td>0.20</td>
<td>48.06</td>
</tr>
<tr>
<td>Fixed C dry</td>
<td>15.26</td>
<td>15.70</td>
<td>3.65</td>
</tr>
<tr>
<td>C dry</td>
<td>41.43</td>
<td>49.57</td>
<td>25.77</td>
</tr>
<tr>
<td>N dry</td>
<td>1.09</td>
<td>0.07</td>
<td>3.02</td>
</tr>
<tr>
<td>S dry</td>
<td>0.10</td>
<td>0.06</td>
<td>0.81</td>
</tr>
<tr>
<td>H dry</td>
<td>4.18</td>
<td>6.05</td>
<td>4.31</td>
</tr>
<tr>
<td>O (diff.) dry</td>
<td>39.25</td>
<td>44.04</td>
<td>17.99</td>
</tr>
<tr>
<td>Cl dry</td>
<td>0.53</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>LHV (MJ/kg) dry</td>
<td>16.01</td>
<td>18.52</td>
<td>10.72</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Danish straw</th>
<th>Swedish wood</th>
<th>Sewage sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main elements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>30,457</td>
<td>38,055</td>
<td>20,200</td>
</tr>
<tr>
<td>H</td>
<td>49,612</td>
<td>63,997</td>
<td>46,758</td>
</tr>
<tr>
<td>O</td>
<td>30,737</td>
<td>29,737</td>
<td>24,335</td>
</tr>
<tr>
<td>N</td>
<td>686.91</td>
<td>46.07</td>
<td>2029.30</td>
</tr>
<tr>
<td>S</td>
<td>27.54</td>
<td>17.26</td>
<td>237.85</td>
</tr>
<tr>
<td>Cl</td>
<td>328.49</td>
<td>3.41</td>
<td>236.87</td>
</tr>
<tr>
<td><strong>Minor elements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>80.96</td>
<td>8.24</td>
<td>924.20</td>
</tr>
<tr>
<td>P</td>
<td>73.49</td>
<td>3.41</td>
<td>84.10</td>
</tr>
<tr>
<td>Fe</td>
<td>1.18</td>
<td>1.18</td>
<td>296.67</td>
</tr>
<tr>
<td>Ti</td>
<td>22.58</td>
<td>2.50</td>
<td>216.61</td>
</tr>
<tr>
<td>Mn</td>
<td>7.39</td>
<td>1.56</td>
<td>863.88</td>
</tr>
<tr>
<td>Mg</td>
<td>3.41</td>
<td>0.57</td>
<td>951.06</td>
</tr>
<tr>
<td>Na</td>
<td>2.62</td>
<td>0.21</td>
<td>39.98</td>
</tr>
<tr>
<td>Ca</td>
<td>1.90</td>
<td>1.43</td>
<td>7.75</td>
</tr>
</tbody>
</table>
silicon in straw, a higher amount of K₂Si₄O₉(liq) is formed, which may cause slagging and fouling in the furnace. The gaseous potassium species, e.g. KCl(g) and KOH(g), may form aerosols in the gas cooling process. At mid-temperatures (800–1100 K), the main species are potassium silicate and sulphate (i.e. K₂Si₄O₉(s,s₂) and K₂SO₄(s₂)) for straw combustion. Obviously, K₂Si₄O₉(s,s₂) is transformed by the liquid silicate K₂Si₄O₉(liq) under high temperature. For wood combustion, the main species are potassium aluminosilicate and sulphate (i.e. K₂Al₂Si₂O₇(s,s₂) and K₂SO₄(s₂)). At low temperatures (400–900 K), the main species are potassium chloride and sulphate (i.e. KCl(s), K₂SO₄(s), and K₂Si₂O₅(s)) for straw combustion. Because of the higher content of chlorine than sulphur in straw, a higher amount of chloride is formed than sulphate. For wood combustion, the main species are K₂SO₄(s) and K₂Al₃(SO₄)₂(s). Because of the relatively higher content of sulphur than chlorine in wood, potassium sulphate and aluminosilicate becomes important in ash.

Fig. 3 gives the release behaviour of chlorine and alkali metals in combustion with various air excess coefficients. For straw combustion in Fig. 3(a), increasing temperature from 800 to 1000 K significantly increases the amount of released HCl(g). This indicates that the gaseous HCl concentration attains maximum at 1000 K. The reason of this might be that most of chlorine in gaseous HCl comes from decomposing KCl(s) in the mid-temperature range. Then increasing temperature from 1000 to 1800 K reduces the amount of released HCl(g), thereby KCl(g) begins to form and gradually increases. At high temperatures (> 1400 K), a small amount of KOH(g) also occurs.

For wood combustion in Fig. 3(b), all of the chlorine is released as HCl(g) in the temperature range of 800–1000 K. With increasing temperature, KCl(g) and K₂SO₄(g) begins to form and causes HCl(g) to decrease. At 1350 K, KCl(g) attains maximum and HCl(g) attains minimum. In addition, from 1200 K, the release of KOH(g) significantly increases. Because of the low content of chlorine in wood
and relatively high content of hydrogen (meaning that more hydroxyl radical may be produced), increasing temperature from 1300 to 1800 K might induce the conversion of KCl(g) to KOH(g) via the reaction:

\[
\text{KCl}(g) + \text{H}_2\text{O} \rightarrow \text{KOH}(g) + \text{HCl}(g)
\]  

Therefore, at 1350 K, KCl(g) begins to reduce and HCl(g) and KOH(g) to increase.

Due to the higher sodium content than potassium in sewage sludge, Fig. 3(c) shows the release behaviour of sodium and chlorine in sewage sludge combustion. Similar with the results in Fig. 3(b), all of the chlorine is released as HCl(g) in the temperature range of 800–1200 K. Then increasing temperature from 1200 to 1800 K reduces the amount of released HCl(g), whereas NaCl(g) begins to form and gradually increases. At high temperature (>1500 K), NaOH(g) also occurs and significantly increases with increasing temperature.

Under combustion conditions shown in Fig. 3, the air excess coefficient (\(\lambda\)) has less significant influence on the released amount of chlorine and potassium or sodium. For straw or sludge (except wood) combustion in Fig. 3(a) or (c), increasing air excess coefficient reduces the release of HCl(g) and increases the amount of KCl(g) or NaCl(g) in the high temperature range. Obviously, a lot of alkali metals may release from the condensed phase (e.g. liquid alkali silicate or solid aluminosilicate) and produce gaseous alkali chloride at high temperatures. Increasing the oxygen concentration in the flue gas might promote the reaction (\(K^*\) denotes the radical potassium from the condensed phase):

\[
K^* + \text{HCl}(g) + O \rightarrow \text{KCl}(g) + \text{OH}
\]  

This increases the release of KCl(g). In addition, KOH(g) or NaOH(g) also increase with increasing air excess coefficient because of higher oxygen concentration in the gas phase.

Fig. 4 gives the release behaviour of chlorine and alkali metals in gasification with various air excess coefficients. Compared with Fig. 3, the air excess coefficient has significant influence on the released amount of chlorine, potassium or sodium under gasification conditions. For straw gasification in Fig. 4(a), increasing air excess coefficient from 0.2 to 0.8 increases the release of HCl(g) and reduces the formation of KCl(g).

For wood gasification in Fig. 4(b), KCl(s) directly vaporizes as KCl(g) in the temperature range of
800–1100 K and KCl(g) attains maximum at 1100 K. Increasing temperature from 1000 to 1800 K enhances the release of KOH(g) and K(g). HCl(g) begins to occur at high temperatures (>1100 K) and increases sharply with temperature. At high temperatures (>1100 K), increasing air excess coefficient increases the release of HCl(g) and KOH(g) and reduces the formation of KCl(g) and K(g).

Under gasification conditions, increasing air excess coefficient increases the concentration of H2O and radical OH in the gas, and the reaction (1) is likely to promote the conversion of KCl(g) to HCl(g) and KOH(g). With increasing air excess coefficient, the decrease of K(g) and increase of KOH(g) might be explained by the reaction:

\[ \text{K(g)} + \text{OH} \rightarrow \text{KOH(g)} \quad (3) \]

For sludge gasification, due to the higher sodium content than potassium, Fig. 4(c) shows the release behaviour of sodium and chlorine. Because the content of silicon and aluminium is high in sludge, sodium may retain in ash as aluminosilicate and is only likely to release at high temperatures (>1300 K). Increasing air excess coefficient increases the release of HCl(g) and NaOH(g) and reduces the formation of NaCl(g) and Na(g). This might be explained by the reactions:

\[ \text{NaCl(g)} + \text{H}_2\text{O} \rightarrow \text{NaOH(g)} + \text{HCl(g)} \quad (4) \]
\[ \text{Na(g)} + \text{OH(g)} \rightarrow \text{NaOH(g)} \quad (5) \]

Fig. 5 describes the effect of pressure on the release of chlorine and alkali metals during biomass combustion. For straw combustion in Fig. 5(a), at mid-temperatures
increasing pressure postpones the release of HCl(g), but the maximum amount of HCl(g) increases. At high temperatures (>1100 K), increasing pressure significantly enhances the release of HCl(g), and thus reduces the formation of KCl(g) and KOH(g). For wood combustion in Fig. 5(b), it is interesting that the pressure only has an influence in the temperature range between 1100 and 1500 K, thereby the pressure enhances the release of HCl(g) and decreases the formation of KCl(g) and KOH(g). For sludge combustion in Fig. 5(c), the influence of pressure only occurs in the temperature range above 1300 K. Similar with the results of straw and wood combustion, the pressure enhances the release of HCl(g) and reduces the formation of NaCl(g) and NaOH(g).

Fig. 6 gives the effect of pressure on the release of chlorine and alkali metals during biomass gasification.

Results of straw or sludge gasification in Fig. 6(a) or (c) are similar with those in Fig. 5(a) or (c). At high temperatures (>1200 K), increasing pressure enhances the release of HCl(g), and thus reduces the formation of KCl(g), NaCl(g), KOH(g), or NaOH(g). In addition, the release of K(g) or Na(g) also decreases with increasing pressure. For wood gasification in Fig. 6(b), at mid-temperatures (800–1200 K), the pressure reduces the formation of KCl(g) and KOH(g). However, at high temperatures (>1200 K), the pressure enhances the formation of KOH(g) and KCl(g) and reduces the release of K(g) and HCl(g).

Figs. 7 and 8 indicate the effect of additional nitrogen on the release of chlorine and alkali metals during wood and sewage sludge pyrolysis. In the pyrolysis reactor, high temperature nitrogen is often used to heat the biomass and carry the pyrolysis gas, and thus it may have influence on the release of chlorine and alkali metals. At high temperatures (>1200 K), Fig. 7 shows that nitrogen enhances the release of HCl(g) and reduces the amount of KCl(g) and NaCl(g). Increasing temperature significantly enhances the release of K(g) and Na(g). Nitrogen addition reduces the release of K(g) and Na(g), but causes a sharp increase of KCN(g) and NaCN(g). Due to the limited content of chlorine in sludge, Fig. 8 shows that nitrogen has less significant influence on the release of HCl(g), KCl(g), and NaCl(g). However, at very high temperatures (>1500 K), the amount of K(g), Na(g), KCN(g), and NaCN(g) significantly increases during
sludge pyrolysis. Nitrogen addition also enhances the formation of KCN(g) and NaCN(g) and reduces the release of K(g) and Na(g).

In Fig. 9, kaolin is mixed with biomass to investigate the influence of aluminosilicate addition on the release of chlorine and alkali metals during straw combustion. In the fluidized bed reactor, kaolin may be contacted very well with biomass particle and thus lead to the decrease of the release of alkali metals [8]. Obviously, kaolin may enhance the formation of potassium aluminosilicate and retain potassium in ash. Increasing kaolin dosage significantly reduces the formation of KCl(g) and KOH(g) and increases the release of HCl(g).

4. Conclusions

The chemical equilibrium calculation was used to investigate the release of chlorine and alkali metals during three sorts of biomass combustion or gasification under atmospheric or pressurized conditions. Results show that the main alkali containing species are K₂Si₄O₁₀(liq), KCl(g), and KOH(g) in straw combustion, and KCl(g), K₂SO₄(g), and KOH(g) in wood combustion, as well as NaCl(g) and NaOH(g) in sewage sludge combustion. Under combustion conditions, the air excess coefficient only has a limited influence on the release of chlorine and potassium or sodium. For straw or sludge combustion, increasing air excess coefficient reduces the release of HCl(g) and increases the formation of KCl(g) or NaCl(g) in the high temperature range.

Compared with the results in combustion, the air excess coefficient has significant influence on the release of chlorine, potassium or sodium during biomass gasification. At high temperatures (>1100 K), increasing air excess coefficient increases the release of HCl(g), KOH(g) or NaOH(g) as well as it reduces the formation of KCl(g), NaCl(g), K(g) or Na(g). Increasing air excess coefficient increases the concentration of H₂O and radical OH in the gas, and this is likely to promote the following reactions:

\[ \text{KCl} (g) + \text{H}_2\text{O} \rightarrow \text{KOH} (g) + \text{HCl} (g) \]  
\[ \text{K} (g) + \text{OH} \rightarrow \text{KOH} (g) \]

During biomass combustion, the pressure may enhance the release of HCl(g) and reduces the formation of KCl(g), NaCl(g), KCl(g), and NaOH(g) at high temperatures. During straw or sludge gasification, the pressure also enhances the release of HCl(g) and reduces the formation of KCl(g), NaCl(g), KCl(g), and NaOH(g) as well as K(g) and Na(g) at high temperatures. During wood gasification, at mid-temperatures (800–1200 K), the pressure reduces the formation of KCl(g) and KOH(g). However, the pressure enhances the formation of KOH(g) and KCl(g) and reduces the release of K(g) and HCl(g) at high temperatures (> 1200 K).

During wood and sewage sludge pyrolysis, nitrogen addition enhances the formation of KCN(g) and NaCN(g) and reduces the release of K(g) and Na(g). Kaolin addition in straw combustion may enhance the formation of potassium aluminosilicate in ash. Increasing kaolin dosage significantly reduces the formation of KCl(g) and KOH(g) and increases the release of HCl(g).

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