

Thesis for the Degree of Doctor of Philosophy in Energy Engineering

**Release to the Gas Phase of Potassium, Chlorine, and Sulfur from  
Biomass Fuels under Dual Fluidized Bed Gasification Conditions**

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## Abstract

The transformation and release of ash-forming elements during the thermal conversion of biomass are conducive to ash-related problems, for example, agglomeration of the bed material in fluidized beds. The occurrence and severity of ash-related problems largely depend on the extents to which potassium (K), chlorine (Cl), and sulfur (S) are released from biomass fuels to the gas phase during thermal conversion processes. To predict and better mitigate these problems, knowledge of the extent, and the mechanism by which of each of these elements is released from the fuel to the gas phase under relevant operational conditions is required. As K is also a catalyst for char and tar conversion, understanding its transformation and release is also important, as it could be deactivated by other ash-forming elements, such as silicon and phosphorus.

In the present work, the transformation and release of K, Cl, and S from biomass under conditions relevant to dual fluidized bed gasification were investigated. The main aim was to assess the influences of operational conditions and fuel ash characteristics on the extents to which these elements are released to the gas phase during the main stages of fuel conversion, i.e., devolatilization, char gasification, and char combustion. The obtained information is relevant for: 1) the optimization of operational conditions towards the minimization of ash-related problems; and 2) the maximization of the beneficial effects of ash transformation during thermal conversion.

The study was carried out using a laboratory-scale bubbling fluidized bed reactor operated in the temperature range of 550°–900°C. The release of K, Cl, and S from biomass fuels during devolatilization, char gasification, and char combustion were quantified using a mass balance that linked the mass of each element in the virgin fuel to that in the solid residue obtained at the end of each experiment. To gain further insights into the release mechanisms, chemical fractionation, Brunauer-Emmett-Teller (BET) surface area measurements, and chemical thermodynamic equilibrium modeling were carried out.

For a typical temperature range within which the gasification chamber of dual fluidized bed gasifiers is operated (800°–900°C), most of the Cl and virtually all of the S in the virgin biomass follow the raw gas out of the gasification chamber, while most of the K follows the char and bed material to the combustion chamber. During char combustion, further release of K occurs; this K would follow the flue gas out of the combustion chamber unless retained on the bed materials. Furthermore, the complete conversion of the organic matrix of the char increases the risk of K reacting with other ash-forming elements, such as Si in the fuel or in the bed material, which may render the K inactive for char and tar conversion. Therefore, unless measures are taken to capture and maintain the K in a catalytically active form in the combustion chamber with subsequent recirculation to the gasification chamber, catalytic char and tar conversion may be hindered. The transformation and release of K, Cl, and S as functions of temperature, retention time, atmosphere, and fuel ash characteristics are also discussed.

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Special thanks to my family for their love, prayers and moral support. I dedicate this thesis to the memories of my father Michael Chi Tawambeng and my brother Protus Fontaku Atongka. Their words of encouragement and perseverance in the pursuit of excellence will linger forever.

Finally, I would like to thank Almighty God for the grace of life that He gives me to carry out my daily activities.

## List of appended publications

The following publications are included in this thesis:

- I. Tchoffor, P. A.; Davidsson, K.O.; Thunman, H.; Transforming and Release of Potassium, Chlorine, and Sulfur from Wheat Straw under Conditions Relevant for Dual Fluidized Bed Gasification. *Energy and Fuels*, 2013, 27(12), 7510–7520.
- II. Tchoffor, P. A.; Davidsson, K. O.; Thunman, H.; Effects of Steam on the Release of Potassium, Chlorine, and Sulfur during Char Conversion Investigated under Conditions Relevant for Dual Fluidized Gasification. *Energy and Fuels*, 2013, 28(11), 6953–6965
- III. Tchoffor, P. A.; Davidsson, K. O.; Thunman, H. Production of Activated Carbon within the Dual Fluidized Bed Gasification Process. *Industrial & Engineering Chemistry Research*, 2015, 54 (15) 3761–3766.
- IV. Lundberg, L.; Tchoffor, P. A.; Pallares, D.; Johansson, R.; Thunman, H.; Davidsson, K.O. Influence of Surrounding Conditions and Fuel Size on the Gasification Rate of Biomass Char in a Fluidized Bed. *Fuel Processing Technology*, 2016, 144, 323–333
- V. Tchoffor, P. A.; Moradian, F.; Pettersson, A.; Davidsson, K. O.; Thunman, H. Influence of Fuel Ash Characteristics on the Release of Potassium, Chlorine, and Sulfur from Biomass Fuels under Steam Fluidized Bed Gasification Conditions. Submitted to *Energy and Fuels*, June 2016
- VI. Moradian, F.; Tchoffor, P. A.; Davidsson K. O.; Pettersson, A.; Backman, R. Thermodynamic Equilibrium Prediction of Bed Agglomeration Tendency in Dual Fluidized Bed Gasification of Forest Residues. *Fuel Processing Technology*, 2016

## Other works by the author not included in this thesis

- i. Hjörnhede, A.; Hermansson, S.; Seemann, M.; Alamia, A.; Larsson, A.; Niklasson, F.; Davidsson, K.O.; Tchoffor, P.A.; Jones, F. Two-stage Combustion, a New Concept in Reducing Alkali Operational Problems. *Waste Refinery report (WR-44)*, 2012.
- ii. Davidsson, K.O.; Tchoffor, P.A.; Haraldsson, C.; Kunemuth, D.; Richards, T.; Sahlin, E.; Thunman, H. Fuel Analysis for Gasification. Göteborg Energi Forskningsstiftelsen (11-02), 2013.
- iii. Lundberg, L.; Tchoffor, P. A.; Pallares, D.; Johansson, R.; Thunman, H. Determination of Kinetic Parameters for the Gasification of Biomass Char Using a Bubbling Fluidised Bed Reactor. *22nd International Conference on Fluidized Bed Conversion*, 2015.
- iv. Davidsson, K.O.; Tchoffor, P.A.; Folkesson, B.; Moradian, F.; Pettersson, A.; Richards, A. Ash and Bed Materials Effects During Dual Fluidized Bed Gasification. *EnergiForsk report (284)*, 2016.

## **Contributions of the author to the appended publications**

Papers I–III: I planned and carried out the experiments. The evaluation of the results and writing of the manuscript were performed in collaboration with my co-authors.

Paper IV: I contributed to the experiments, analyses, and writing of the manuscript.

Papers V and VI: I carried out the experiments. The analyses, evaluation of the results, and writing of the manuscript were performed in collaboration with my co-authors.

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# 1 Introduction

Dual fluidized bed gasification (DFBG) of biomass is an emerging technology for the conversion of biomass to an energy-rich gas, from which transportation fuels, electricity, heat, or high-value chemicals can be produced. This high-temperature process is carried out in two interconnected fluidized bed reactors (see the *Theory* section). In Sweden, where the government has the goal of sustaining the entire vehicle fleet exclusively with fossil-free fuels by Year 2030, a demonstration plant to produce biomethane from woody biomass *via* DFBG was constructed in Year 2010. The plant, which is called GoBiGas, is currently operational.

In similarity to other thermal conversion processes for biomass in fluidized bed reactors, the ash in biomass fuels may exert negative or positive effects on the DFBG process. Some of the negative effects include the agglomeration of bed materials,<sup>1, 2</sup> corrosion<sup>3, 4</sup> and fouling<sup>5</sup> of heat transfer surfaces, and poisoning<sup>6, 7</sup> of the catalysts used in processes downstream of the gasifiers. These problems could result in high maintenance costs, costly unscheduled shutdowns, or a decrease in the overall efficiency of the plant. Most of these ash-related problems are related to the transformation and release of ash-forming matter, which consists mainly of K, Cl, and S.<sup>8</sup> Catalytic tar and char conversion by K and Ca are some of the positive effects of fuel ash. For example, K has been observed to enhance the conversion of char<sup>9</sup> and tar.<sup>9-11</sup> The ash contents and the concentrations of these elements vary for the different types of biomass fuels.<sup>12</sup> Fuels obtained from stem wood, such as wood pellets/chips, typically have lower ash contents and lower concentrations of K, Cl, and S than other biomass fuels.<sup>12, 13</sup> These fuels are hereinafter referred to as ‘ash-lean’ fuels. Bark, forest residues, and wheat straw are examples of fuels that have higher contents of ash and/or higher concentrations of K, Cl, and S than the ash-lean fuels.<sup>12, 13</sup> These fuels are hereinafter referred to as ‘ash-rich fuels’. One of the best primary measures to minimize the severity of the aforementioned ash-related problems is to select ash-lean fuels as the feedstock for thermal conversion.<sup>14, 15</sup> Thus, ash-lean fuels, such as wood pellets/chips, are typically applied in DFBG processes.<sup>16, 17</sup> However, the application of these fuels could be disadvantageous in terms of the economic viability of the gasification plant, as these fuels are typically far more expensive than ash-rich fuels,<sup>18</sup> so their application could increase significantly the operational cost of the gasification plant. Furthermore, the low concentrations of K in ash-lean fuels may reduce the chemical efficiency of the gasification processes, as K is a catalyst for both tar and char conversion. Therefore, if the ash-related problems associated with ash-rich fuels can be predicted and effectively mitigated during thermal conversion, one can envisage that their lower cost and high concentrations of K would improve the economic and chemical efficiencies of gasification plants.

According to literature, the occurrence and magnitude of ash-related problems during thermal conversion depend significantly on the extents to which K, Cl, and S are released from the applied biomass fuels to the gas phase.<sup>8, 14</sup> Therefore, quantifying the release of these elements from biomass fuels and elucidating the mechanisms through which they are released under

relevant operational conditions could be helpful in predicting and effectively mitigating any problems that they may cause during thermal conversion. Furthermore, knowledge of the release and transformation of K as a catalyst is important, as it may be deactivated in the fuel matrix during reactions with other ash-forming elements (e.g., Si<sup>19</sup>). Previous studies on the release of K, Cl, and S from biomass fuels, which were carried out for the most part under fixed bed pyrolysis and combustion conditions, revealed that operational conditions affect the release of these elements to the gas phase.<sup>8, 20</sup> These operational conditions include temperature, fuel particle retention time and heating rate, and the atmosphere in the reactor. For a given thermal conversion process, the fuel particle heating rate and retention time depend heavily on the type of reactor used. The heating rate of the fuel particles during devolatilization is established by the heat transfer coefficient of the applied reactor.<sup>21</sup> For a given fuel particle size, the heat transfer coefficient in a fluidized bed reactor is generally much higher [up to 1000 W/(m<sup>2</sup>/K)]<sup>22</sup> than that in a fixed bed reactor [up to 100 W/(m<sup>2</sup>/K)].<sup>22</sup> Furthermore, the fuel retention time is significantly lower in fluidized beds than in fixed beds.<sup>23</sup> Therefore, significant differences in the extents to which K, Cl, and S are released to the gas phase may arise when biomass fuels are thermally converted within different types of reactors. While the release of K, Cl, and S have been extensively quantified in fixed bed reactors, similar studies using fluidized bed reactors are scarce, especially under DFBG conditions.

## 1.1 Aim

The central aim of the present work is to characterize the transformation and release of K, Cl, and S from biomass under conditions relevant to dual fluidized bed gasification of biomass. More specifically, the objectives are to:

- 1) Quantify the influences of various operational parameters (temperature, fuel particle retention time, and atmosphere) on the release of K, Cl, and S to the gas phase;
- 2) Quantify the influences of the ash characteristics (ash composition, and the speciation of K, Cl, and S in the fuel matrix) on the release of K, Cl, and S to the gas phase; and
- 3) Identify the mechanisms/pathways through which K, Cl, and S are released to the gas phase.

The information acquired through the pursuit of these objectives would be relevant for the optimization of operational conditions with respect to the mitigation of ash-related problems and the maximization of beneficial effects related to the transformation and release of K, Cl, and S from biomass during DFBG. The mitigation of these problems enhances the overall efficiency and lifetime of the DFBG plant, which in turn contributes to limiting dependence on fossil-based fuels.

## 1.2 Structure of the thesis

Chapter 1 introduces the aim of the research conducted as part of this thesis. Chapter 2 provides basic information as to the compositions of biomass fuels, the pathways for the release of K, Cl, and S from biomass during thermal conversion processes, and the operational conditions for DFBG. In Chapter 3, the materials and methods applied to meet the aim of the research topic are presented. The main results and conclusions from the experiments are summarized in

Chapters 4 and 5. The publications related to the work of this thesis are appended at the end of the thesis.

## 2 Theory

### 2.1 Biomass

The rapid depletion, harmful environmental effects, and rising prices of fossil fuels are some of the factors motivating the search for sustainable and environmentally friendly sources of energy. One of the renewable sources of energy that could significantly contribute to replace fossil fuels is biomass.<sup>24</sup> In the context of energy conversion, biomass is widely considered to be any non-fossilized organic material that originates from plants.<sup>24, 25</sup> Plants produce biomass using CO<sub>2</sub> and water together with sunlight energy in the process of photosynthesis.<sup>24, 25</sup> Biomass can be roughly divided into a few groups according to biological diversity and source (Table 1).

Table 1. Biomass varieties as solid-fuel resources grouped according to biological diversity, source, and origin.<sup>12</sup>

Biomass group	Biomass sub-groups, Varieties, and Species
Wood and woody biomass	Coniferous or deciduous; angiospermous or gymnospermous plants; soft or hard woods; stems, branches, bark, chips, pellets, briquettes, sawdust
Herbaceous and agricultural biomass	Perennial or annual, and field-based or processed-based including: <ul style="list-style-type: none"><li>• Grasses and flowers. e.g., miscanthus, and switch grass</li><li>• Straws, e.g., wheat, oats, and rice</li><li>• Other residues, e.g., Bagasse, husks, and kernels</li></ul>
Aquatic biomass	Freshwater or marine algae; macroalgae or microalgae, others
Animal and human biomass waste	Bones, meat-bone meal, chicken litter, various types of manure, others
Contaminated biomass and industrial biomass wastes	Municipal solid waste, demolition wood, sewage sludge, paper-pulp sludge, others
Biomass mixtures	Blends of the above varieties

The initial and most important steps during the investigation and application of a given solid fuel are the identification and characterization of the chemical and phase compositions of the fuel.<sup>25</sup> These compositions determine the properties and potential applications of the fuel, as well as the environmental challenges that may occur when the fuel is applied in energy conversion processes.<sup>12, 25</sup> For convenience, the composition of a biomass can be separated into the: structural composition; ultimate composition; and proximate composition.

#### 2.1.1 Structural composition

From a structural point-of-view, biomass consists mainly of varying amounts of cellulose, hemicellulose, and lignin.<sup>26 25</sup> Collectively, they are referred to as lignocellulose, which

represents the most abundant renewable material on earth.<sup>25</sup> Cellulose is a linear polysaccharide that consists of  $\beta$ -D glucopyranose units connected by glycosidic bonds (1–4).<sup>26, 27</sup> Hemicellulose is a polysaccharide, the building blocks of which consist of different monosaccharides.<sup>26, 27</sup> Lignin is an aromatic polymer derived from phenylpropanoid precursors.<sup>25, 26</sup> In addition to the major constituents, biomass also contains low levels of lipids, proteins, simple sugars, and starches, as well as water and inorganic matter.<sup>25</sup> The structural composition of biomass is important for assessing its heating value.<sup>25</sup>

### 2.1.2 Ultimate composition

Ultimate analysis of biomass gives the concentrations of C, H, O, N, S, and Cl in the fuel.<sup>28</sup> C, H, and O are important for assessing the heating value of the fuel.<sup>25</sup> The concentrations of N, S, and Cl in biomass are relevant in estimating the environmental impact associated with emissions of NO<sub>x</sub>, HCl, and SO<sub>x</sub> when the biomass fuel is completely combusted.<sup>25, 27</sup> The ultimate analysis for the various groups of biomass species are shown in Table 2.

Table 2. Chemical compositions of the various biomass groups based on the proximate and ultimate analyses of 86 varieties of plant biomass plus algae-based biomass.<sup>12</sup>

Biomass group		Proximate analysis (wt%, dry basis)			Ultimate analysis (wt%, dry and ash-free basis)					
		VM	FC	Ash	C	H	O	N	S	Cl*
Wood and woody biomass	Mean	78.0	18.5	3.5	52.1	6.2	41.2	0.4	0.08	0.02
	Minimum	69.5	12.3	0.1	48.7	5.4	32.0	0.1	0.01	0.01
	Maximum	86.3	26.3	16.5	57.0	10.2	45.3	0.7	0.42	0.05
Herbaceous and agricultural biomass	Mean	75.2	19.1	5.7	49.9	6.2	42.6	1.2	0.15	0.20
	Minimum	59.3	12.4	0.9	42.2	3.2	34.2	0.1	0.01	0.01
	Maximum	85.5	37.9	20.1	58.4	6.5	49.0	3.4	0.60	0.83

\* Values shown are wt%, dry basis.

VM, volatile matter; FC, fixed carbon.

### 2.1.3 Proximate composition

Proximate analysis assesses the moisture content, as well as the fixed carbon, volatile matter, and ash contents.<sup>24, 25</sup> This analysis is relevant for predicting the behavior of the fuel during thermal conversion.<sup>24, 25</sup> For example, the ash content and composition of the biomass are very important for predicting the formation of slag during thermal conversion processes.

The composition of biomass ash varies greatly and depends on the species, use of fertilizer, harvesting technique, and time of harvesting.<sup>25, 29</sup> With respect to the tendency to form molten oxides during thermal conversion processes, the composition of biomass ash can be divided into the following classes based on the concentrations of Ca, Si, and K in the ash:

- i. Biomass ash rich in Ca but lean in Si and K. The wood and woody biomass fuels generally fall into this group. Thermal conversion of these fuels is less likely to result in slag formation.

- ii. Biomass ash rich in K and Si but lean in Ca. Herbaceous and agricultural biomass can be placed in this group. Thermal conversion of these fuels is more likely to result in slag formation. This biomass type is also likely to contain higher concentrations of Cl, and S than the wood and woody biomass fuels as shown in Table 3.

Table 3. Selected ash-forming elements in the biomass groups based on high-temperature ash analyses of 86 varieties of plant biomass plus algae-based biomass.<sup>12</sup>

Biomass group		wt% in ash				wt% daf	wt% dry basis
		SiO <sub>2</sub>	CaO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	S	Cl
WWB	Mean	22.22	43.03	10.75	3.48	0.08	0.02
	Min	1.86	5.79	2.19	0.66	0.01	0.01
	Max	68.18	83.46	31.99	13.01	0.42	0.05
HAB	Mean	33.39	14.86	26.65	6.48	0.15	0.2
	Min	2.01	0.97	2.29	0.54	0.01	0.01
	Max	94.48	44.32	63.90	31.06	0.60	0.83

WWB, wood and woody biomass; HAB, herbaceous and agricultural biomass; Min, minimum; Max, maximum; daf, dry and ash-free basis.

#### 2.1.4 Speciation of ash-forming elements in biomass fuels

Speciation here refers to the various chemical forms of ash-forming elements in biomass fuels. Ash-forming elements can be present in biomass fuels in four general forms (see Figure 1).<sup>30</sup> These forms are: (1) water- and acid-soluble salts; (2) ash-forming elements that are associated with the organic fraction of the biomass; and (3) minerals. The minerals may be incorporated into the fuel structure or may be added during harvesting. The water-soluble and the organic forms of the elements are considered to be reactive or releasable during thermal conversion processes.<sup>31, 32</sup>

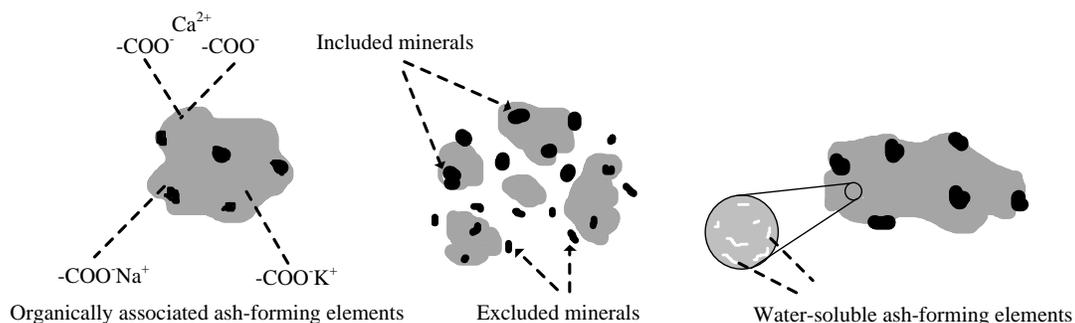


Figure 1. Speciation of ash-forming elements in biomass fuels.<sup>33</sup>

A widely used method to determine the speciation of ash-forming elements in biomass fuels is chemical fractionation.<sup>30, 32, 34</sup> In this technique, biomass is sequentially leached with solvents of increasing severity (i.e., water, 1 M ammonium acetate, and 1 M hydrochloric acid), as shown in Figure 2.<sup>14</sup> The various forms of the ash-forming elements are dissolved in these solvents

depending on their solubilities. The fractions of the ash-forming elements that dissolve in water are typically salts of alkali metals (e.g., alkali chlorides, carbonates, and sulfates). Chemical fractionation analyses of some biomass fuels have revealed that most of the Cl (>80%) and K (>50%), as well as a substantial fraction of the S (up to 60%) are water-soluble.<sup>30, 32, 34-36</sup>  $\text{NH}_4\text{Ac}(\text{aq})$  dissolves the exchangeable ions of some elements, such as Ca, K, Na, and Mg. This fraction is believed to be organically associated. Exceptions to this rule are Cl, P, and S, for which it has been observed that the fractions in the acetate leachate are present in the same chemical form as in the water leachate.<sup>34</sup> In some biomass fuels, a small fraction of K (<40%) and a small fraction of S (<20%) have been observed to dissolve in acetate.<sup>30</sup> The fraction leached out by  $\text{HCl}(\text{aq})$  mostly comprises carbonates, sulfates, and phosphates of alkaline earth metals. In a few studies, <10% of the K and <20% of the S in some biomass fuels were shown to dissolve in this step.<sup>30, 35</sup> Ash-forming matter that consists of silicates and other minerals is insoluble in any of these solvents. Furthermore, any fractions of S, P, and Cl that are insoluble in any of the aforementioned solvents can be assumed to be covalently bound to the organic substance of the fuel matrix.<sup>14, 30</sup> For some biomass fuels, chemical fractionation has indicated that a small fraction of the K (<30%) and a substantial fraction of the S (up to 70%) are insoluble in any of these solvents.<sup>30</sup>

The speciation of ash-forming elements in the fuel matrix is seldom carried out to assess the suitability of a given biomass fuel for thermal conversion in a fluidized bed reactor. However, studies have shown that similar to the chemical composition of the fuel ash, the speciation of ash-forming elements in the fuel matrix differs among biomass fuels,<sup>30</sup> and it may affect the extent to which these elements are released to the gas phase during thermal conversion processes.

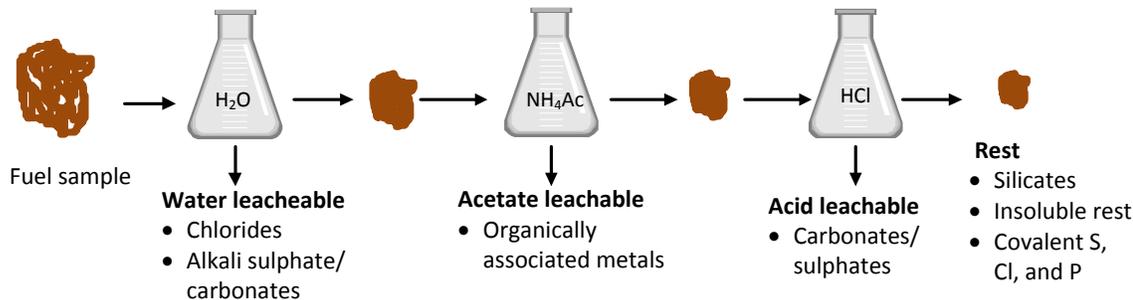


Figure 2. Chemical fractionation procedure.<sup>14</sup>

## 2.2 K, Cl, and S release pathways

The extents to which K, Cl, and S are released from biomass fuels during thermal conversion processes depend on factors related to the fuel and to the operational conditions. The most important fuel-related issues relate to how the ash-forming elements are associated in the fuel, the relative concentrations of the ash-forming elements, and the size and compactness of the fuel particles. Factors related to the operational conditions include the temperature of the reactor, the heat transfer coefficient, and the retention time.

### 2.2.1 Chlorine release pathways

Since Cl exists mainly as KCl in biomass, it is expected to be released at temperatures  $>700^{\circ}\text{C}$ , where the vapor pressure of KCl is significant for evaporation. However, it has been observed in some studies<sup>8, 37, 38</sup> that a substantial fraction of Cl (20%–60%) in some biomass fuels is released at temperatures in the range of  $300^{\circ}\text{C}$ – $500^{\circ}\text{C}$  under both oxidizing and reducing atmospheres. The release of Cl at these temperatures has been attributed to an ion exchange reaction between KCl and oxygen-containing groups formed during biomass devolatilization, in which Cl is released as HCl (see R1).<sup>8, 20, 39, 40</sup>



The release of Cl through this pathway is limited by the availability of oxygen-containing functional groups.<sup>20, 40</sup> Reaction 1 could be facilitated by a liquid tar phase in which KCl migrates and reacts with these groups.<sup>38</sup>

At temperatures  $>700^{\circ}\text{C}$ , the vapor pressure of KCl increases significantly and the evaporation of KCl becomes the primary pathway for the release of Cl from the biomass.<sup>8</sup> During devolatilization, the evaporation of KCl from the fuel can be limited by the diffusional resistance posed by the still-intact or compact fuel matrix.<sup>39</sup> After devolatilization, the obtained char is oxidized, making it less compact.<sup>8</sup> As a result, diffusional resistance to the evaporation of KCl from the char decreases, leading to the release of K and Cl.

### 2.2.2 Potassium release pathways

In addition to KCl mentioned in the preceding section, other possible K-based salts that are present in biomass, such as KOH and  $\text{K}_2\text{CO}_3$ , have vapor pressures that are too low to enable them to be released in significant quantities at temperatures  $<700^{\circ}\text{C}$ .<sup>8, 39</sup> However, at these temperatures, a small fraction of K ( $<20\%$ ) in some biomass fuels has been observed to be released under both oxidizing and reducing conditions during thermal conversion processes.<sup>8, 20, 38, 39</sup> The release of K at these temperatures has been attributed to the thermal decomposition of the organic fuel matrix during the initial devolatilization stage, whereby organically associated K is released,<sup>41, 42</sup> as  $\text{KOH}^{20}$  or combined with water-soluble and water-insoluble tars.<sup>43</sup>

In addition to the release of organically associated K after the devolatilization of biomass, the release of K from the char at temperatures in the range of  $700^{\circ}\text{C}$ – $900^{\circ}\text{C}$  can occur through the evaporation of KCl, decomposition of  $\text{K}_2\text{CO}_3$ , and the release of char-bound K.<sup>38, 44</sup> At temperatures approaching  $900^{\circ}\text{C}$ ,  $\text{K}_2\text{CO}_3$  decomposes, with the consequence that K is released as KOH (see R2 and R3).<sup>8</sup>



The decomposition of  $\text{K}_2\text{CO}_3$  (R2–4) is enhanced in the presence of water vapor:<sup>8, 44</sup>



Since water vapor enhances the decomposition of  $\text{K}_2\text{CO}_3$ , the release of K through this pathway is more likely to occur during steam gasification than during combustion. Char-bound K is either released or retained in the ash depending on the extent of char conversion and the concentration of Si in the char. During the early stage of char conversion, the organic matrix

hinders the formation of potassium silicates, so the retention of K in the ash is limited.<sup>8</sup> Consequently, for the fraction of the organic matrix of the char that is converted, the char-bound K in both the Si-rich char and Si-lean char is released,<sup>8</sup> most likely as KOH.<sup>8,45</sup> Towards the end of char conversion, at which point the organic matrix of the char is almost completely converted, the formation of K-silicates and thus, the retention of K, is favored.<sup>8,39</sup> Consequently, K is liable to be released in greater amounts from Si-lean char than from Si-rich char.<sup>8</sup> It has also been observed<sup>8</sup> that irrespective of the ash composition of the char, the release of K will be favored if a high level of Cl is present in the char.

### 2.2.3 Sulfur release pathways

In some pyrolysis studies,<sup>8,39</sup> 40%–55% of the S in various biomass fuels was released at temperatures <700°C. At these temperatures, 40%–80% of the S in various biomass fuels was released during combustion.<sup>8,20,42</sup> The released S was attributed to the thermal decomposition of the organic fuel matrix during devolatilization.<sup>8,46</sup> It has been suggested that the release of S through this pathway proceeds *via* the formation of SH radicals, which are generated during the thermal decomposition of organic compounds to which S is bound.<sup>47</sup> These highly reactive SH radicals are either retained in the char or extract H, C or O from the char, so as to form H<sub>2</sub>S, COS, or SO<sub>2</sub>.

Although the rate of evaporation of K<sub>2</sub>SO<sub>4</sub> is negligible at temperatures <1000°C,<sup>8,46,48</sup> the K<sub>2</sub>SO<sub>4</sub> may partially react with the char matrix during devolatilization, leading to the formation of metal sulfides and the bonding of S to the organic matrix.<sup>46</sup> This may occur if the formation of potassium- and calcium-silicates is hindered by organic components in the fuel matrix.<sup>46</sup> In a fixed bed pyrolysis study in which the release of inorganically and organically bound S in wheat straw was measured, it was found that the S present in the form of sulfate in the wheat straw was transformed to char-bound S (predominantly) and metal sulfides.<sup>46</sup> The char-bound S was either released or retained in the ash as the char was converted.

The release of S from various biomass fuels has been observed to increase slightly with increases in temperature within the range of 700°–900°C, during both pyrolysis<sup>46</sup> and combustion.<sup>8,46</sup> However, at temperatures >900°C, the release of S from some biomass fuels has been observed to increase dramatically during combustion.<sup>42</sup> At these temperatures, the release of S occurs as a result of the evaporation of K<sub>2</sub>SO<sub>4</sub> and/or the decreasing stability of condensed K<sub>2</sub>SO<sub>4</sub>.<sup>46</sup>

## 2.3 Dual fluidized bed gasification

DFBG of biomass is carried out in two interconnected fluidized bed reactors.<sup>17,49</sup> A schematic of the DFBG setup is shown in Figure 3. Biomass is introduced into one of the reactors, where it is dried and devolatilized. This reactor is henceforth referred to as the ‘gasification chamber’. The char that results from the devolatilization process is partially gasified with steam. The raw gas produced from the feedstock contains permanent gases and impurities. The impurities are removed downstream of the gasification chamber, and the clean gas can be used for electricity generation<sup>17</sup> or can be conditioned and used in the production of transportation fuels<sup>50</sup> and high-

value chemicals. The unconverted char together with the bed material from the gasification chamber are circulated to the second reactor, where the char is combusted with air. This reactor is henceforth referred to as the ‘combustion chamber’. The heat that is released from the combustion process heats the bed material, which is then recirculated to the gasification chamber to supply the heat needed for gasification. In some DFBGs, additional fuel can be fed into the combustion chamber.<sup>49</sup> By separating the gasification and combustion processes in these two reactors, the nitrogen in the air used for char combustion in the combustion chamber is prevented from diluting the raw gas exiting the gasification chamber.

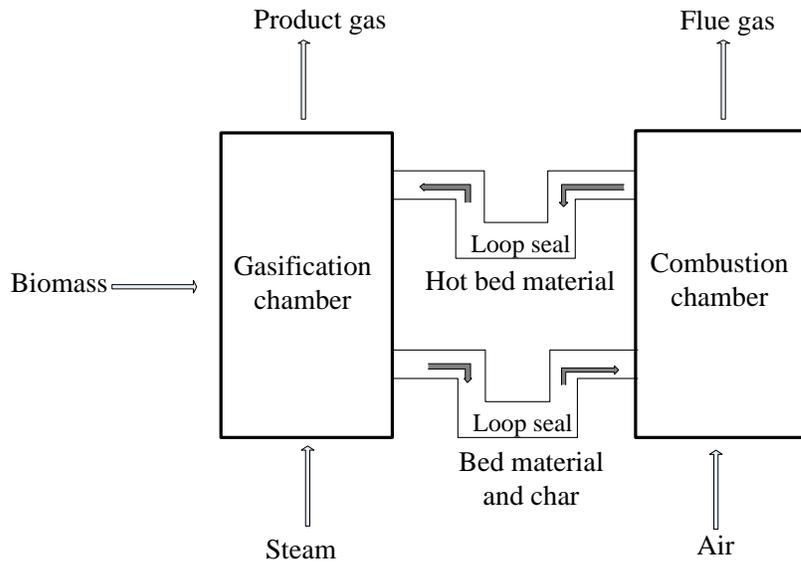


Figure 3. Schematic of the dual fluidized bed gasification system.

The operational temperature in the gasification chamber typically lies in the range of 800°–900°C.<sup>51, 52</sup> The difference in prevailing temperature between the gasification and combustion chambers depends on the heat demand for gasification and the rate of circulation of bed material between the two chambers.<sup>52</sup> The combustion chamber is operated at higher temperatures than the gasification chamber. Typical operational temperatures in the combustion chamber are in the range of 850°–930°C.<sup>51, 53</sup> The retention time of fuel particles in the gasification chamber is influenced by many factors, such as the circulation rate of the bed material between the two chambers,<sup>54, 55</sup> the location of fuel feeding, and the fluidization velocity.<sup>54</sup> Average retention times for the fuel particles in the gasification chamber in the range of 1–2 minutes have been reported.<sup>16, 55, 56</sup>

In contrast to DFBG, char gasification and char combustion are carried out in the same reactor during stand-alone fluidized bed gasification. Consequently, when air is used as gasification agent during stand-alone fluidized bed gasification, the product gas is diluted with nitrogen which lowers its heating value.<sup>21</sup>

In addition to fluidized bed reactors, the other main type of reactor used for biomass gasification is fixed bed reactors.<sup>23</sup> In fixed bed reactors the fuel flows down a grate in either a countercurrent, cocurrent or (seldom) crosscurrent manner with respect to the gasification agent.<sup>23</sup> Detailed descriptions of fixed bed gasifiers are available in literature.<sup>23, 57</sup> From a thermal conversion point of view, the main differences between fluidized bed reactors and fixed reactors include the heating rate of the fuel particles, and the retention time of fuel particles.<sup>23</sup> For a given fuel particle size, the heat transfer coefficient in a fluidized bed reactor is generally much higher [up to 1000 W/(m<sup>2</sup>/K)]<sup>22</sup> than that in a fixed bed reactor [up to 100 W/(m<sup>2</sup>/K)].<sup>22</sup> Fuel particle retention times in fixed bed reactors are generally much longer (hours to days)<sup>57</sup> than those in fluidized bed reactors (seconds to minutes).<sup>23</sup>

## 3 Materials and methods

### 3.1 Experimental section

#### 3.1.1 Fuels

In Papers I and II, Danish wheat straw (denoted as ‘WSI’) was used. The WSI was supplied in pelletized form (diameter, 8 mm). Various batches of stem wood (supplied in pelletized form; diameter, 8 mm) were used in the studies described in Papers III and IV. The wood pellets applied in Paper III are denoted as ‘WPI’, while those applied in Paper IV are denoted as ‘WPPII’. In addition to WPPII, wood chips (denoted as ‘WC’) were used in Paper IV. The WC particles were of various sizes (see Figure 3 in Paper IV). In Papers V and VI, Swedish wheat straw (denoted as ‘WSII’) and forest residues (FR) were applied. The WSII and FR were each milled, homogenized, and pelletized to obtain 8-mm pellets. The elemental compositions of all the fuels used are presented in Table 4. The Leco Truspec elemental analyzer was applied to determine the concentrations of C, H, and N. The Eltra CS-580A Helios sulfur analyzer was applied for determining the concentrations of S. Ion chromatography was used for assessing the levels of Cl. Total digestion followed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) were used to measure the levels of K, Na, Mg, Ca, P, Si, Al, and Fe.

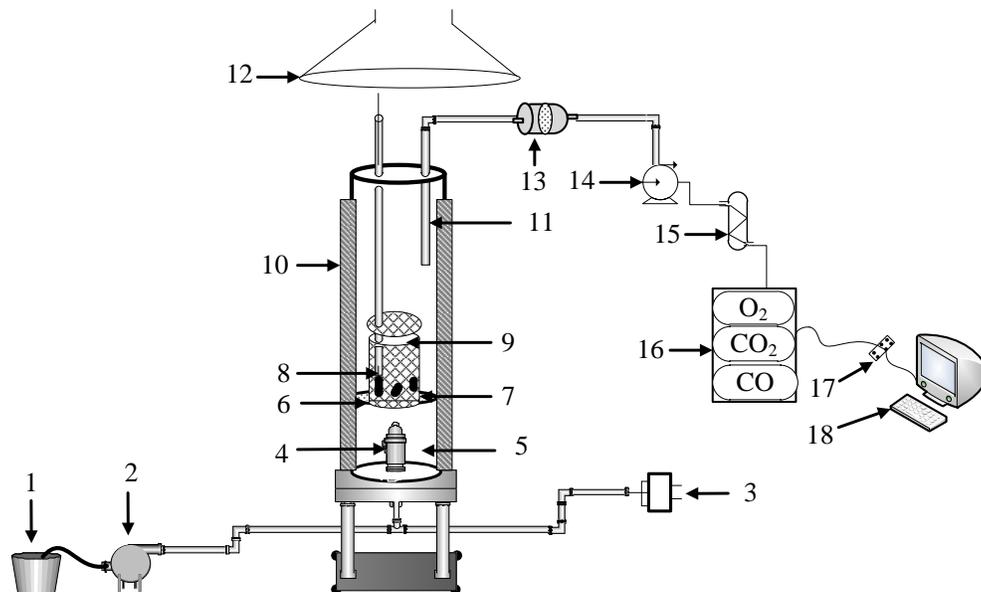
Table 4. Composition of the fuels applied in this work

Substance	Danish wheat straw (WSI)	Swedish wheat straw (WSII)	Wood pellets I (WPI)	Wood pellets II (WPPII)	Forest residues (FR)	Wood chips (WC)
Moisture (wt.%)	11.5	10.4	0.4	8.8	11.8	19.65
Ash (wt.%, d.b.)	4.8	4.3	0.4	0.4	1.8	0.5
C (wt.%, d.b.)	47.10	46.8	50.7	49.7	50.3	49.7
H (wt.%, d.b.)	5.80	5.8	6.2	6.2	6.1	5.9
N (wt.%, d.b.)	0.48	0.69	0.08	0.07	0.50	0.16
S (wt.%, d.b.)	0.09	0.07	<0.01	<0.02	0.03	<0.02
Cl (wt.%, d.b.)	0.55	0.2	<0.01	<0.01	0.01	<0.01
K (wt.%, d.b.)	1.21	0.96	0.04	0.05	0.19	0.088
Na (wt.%, d.b.)	0.02	0.045	<0.01	<0.01	0.013	<0.01
Mg (wt.%, d.b.)	0.08	0.097	0.02	0.017	0.053	0.23
Ca (wt.%, d.b.)	0.36	0.3	0.10	0.12	0.43	0.15
P (wt.%, d.b.)	0.06	0.07	<0.01	<0.01	0.04	0.015
Si (wt.%, d.b.)	0.85	0.87	0.02	0.021	0.12	<0.01
Al (wt.%, d.b.)	0.01	0.032	<0.01	<0.01	0.021	<0.01
Fe (wt.%, d.b.)	0.01	0.042	<0.01	<0.01	0.021	<0.01
Ca/S mol/mol	3.20	3.43	-	-	11.47	-
K/Si mol/mol	0.60	0.79	0.86	1.03	1.14	-
Cl/K mol/mol	0.85	0.23	-	-	0.06	-
(Ca + 0.5 K)/Si mol/mol	0.59	0.48	3.94	4.5	2.85	-

d.b., dry basis.

### 3.1.2 Experimental facility

Figure 4 shows a schematic of the experimental setup. A laboratory-scale bubbling fluidized bed reactor with a diameter of 7 cm and a height of 140 cm was used. A perforated metallic plate on which the bed material particles rest separates the upper section of the reactor from the lower section. The lower section of the reactor, which is 60 cm in length, functions as a gas preheater. The space above the bed material in the upper section of the reactor functions as the freeboard. The bed temperature is measured with a K-type thermocouple. A temperature regulator connected to heating elements (surrounding the reactor) maintain the temperature in the bed of the reactor within  $\pm 5$  °C of the desired temperature. In the experiments in which steam was used as the fluidization agent, the steam was generated by pumping distilled water at a controlled rate into an inbuilt steam generator located in the gas preheater (lower section of the reactor). The instantly generated steam was heated to the bed temperature in the gas preheater, after which it entered the bed of the reactor through the perforated metallic plate. CO/CO<sub>2</sub> and O<sub>2</sub> gas analyzers were used to measure the concentrations of CO, CO<sub>2</sub>, and O<sub>2</sub> in the gas that exited the reactor.



1-water tank, 2-water pump, 3-mass flow regulator 4-inbuilt steam generator, 5-gas preheater, 6-perforated ceramic plate, 7- sand bed, 8- thermocouple inserted into a pellet, 9-wire mesh basket, 10- heating elements, 11-gas probe, 12-exhaust hood, 13-particle filter, 14- gas pump, 15- condenser, 16-gas analyzers, 17- pc logger , 18- computer.

Figure 4. Schematic of the laboratory-scale bubbling fluidized bed reactor used in this work

### 3.1.3 Procedure

In this section, the experiments that were carried out in the appended papers are briefly described. For the sake of clarity, the experiments are described below according to the fluidization gas (or reactant gas) to which the fuel particles were exposed.

A. **Exposure of virgin fuel to nitrogen gas.** Virgin fuel was devolatilized (pyrolyzed). The main aims were to: (1) quantify the release of K, Cl, S during devolatilization; and (2) measure the char yield. An overview of these experiments is presented in Table 5. The experiments were carried out as follows:

- i. Sand (400–600 g) was placed in the reactor, and heated to the desired temperature (550°–900°C). The sand particles consisted mainly of SiO<sub>2</sub> (91%), K<sub>2</sub>O (2%, present as feldspar), and Al<sub>2</sub>O<sub>3</sub> (5%). They had a sauter diameter of 0.35 mm.
- ii. In Papers I, II, III, V, and VI, the virgin fuel was dried to a constant mass at 105°C prior to each experiment, while in paper IV, some of the experiments were carried out using the fuel as-received.
- iii. When the reactor reached the desired temperature, 5–15 g of fuel was placed in a wire-mesh basket and inserted into the reactor. The wire-mesh basket had openings of size 0.8 mm. These openings enabled the entry and exit of the bed material particles. Char particles of <0.8 mm in diameter (hereinafter referred to as ‘char fines’) could leave the basket while larger particles were retained in the basket.
- iv. After 1.5–3.0 minutes of residence in the reactor, the basket that contained the resulting char was removed from the reactor and rapidly cooled in a stream of nitrogen gas.
- v. Thereafter, the fluidization gas was switched from nitrogen to air (21% oxygen), to allow combustion of the char fines that passed through the basket mesh into the bed of the reactor.
- vi. The mass of carbon in the char fines was calculated from the measured concentrations of CO<sub>2</sub> and CO in the flue gas that exited the reactor using Eq. (1):

$$m_{\text{carbon}} = 12 \int_0^t n_g (V_{\text{CO}_2} + V_{\text{CO}}) dt, \quad (1)$$

where  $n_g$  is the molar flow rate of O<sub>2</sub> into the reactor,  $V_{\text{CO}_2}$  and  $V_{\text{CO}}$  are the concentrations of CO<sub>2</sub> and CO, respectively, in the flue gas that exits the reactor. From this mass and the concentration of carbon in the char recovered from the reactor in the basket, the mass of the combusted char fines was calculated using Eq. (2):

$$m_{\text{char fines}} = \frac{m_{\text{carbon}}}{X_{\text{carbon}}}, \quad (2)$$

where  $X_{\text{carbon}}$  is the concentration of carbon in the char recovered from the reactor in the basket. This mass was then added to the mass of the char recovered from the reactor using the basket to obtain the final mass of char from each experiment.

B. **Exposure to steam.** The virgin fuel was devolatilized in steam, followed by *in situ* char gasification. The main aims here were to: (1) estimate the release of K, Cl, and S during char gasification; and (2) study the pore development of the char. The experiments were carried out in a manner similar to that described for exposure to nitrogen gas above; except for the fact that steam (50–86 vol% in nitrogen) was applied instead of 100% nitrogen gas, and that the retention time applied was in the range of 2.5–6.0 minutes. An overview of these experiments is given in Table 5.

- C. **Exposure to nitrogen followed by steam.** In this case, the virgin fuel was first devolatilized in nitrogen gas, and thereafter subjected to either *in situ* or *ex situ* char gasification with steam. The main goal here was to study the char gasification rate. An overview of these experiments is presented in Table 6. The following procedure was used:
- i. Devolatilization as described for A above. The main exception was that some of the experiments were carried out without a basket (in Paper IV). In those experiments in which the basket was applied, the axial location of the fuel particles was controlled (for details, see Paper IV).
  - ii.
    - *In situ* char gasification. After 3 minutes of devolatilization, the fluidization gas was switched from nitrogen to a mixture of nitrogen and steam (50%–86% steam in nitrogen on volume basis).
    - *Ex situ* char gasification: Virgin fuel was placed in a basket, and inserted into the reactor. After 3 minutes of devolatilization in nitrogen gas, the basket was removed from the reactor and cooled in nitrogen gas. The cooled char was thereafter re-inserted into the reactor and exposed to steam. After 10–25 minutes of residence in the reactor, the wire mesh basket that contained the unconverted char was removed from the reactor and rapidly cooled in a stream of nitrogen gas.
  - iii. Thereafter, steps v–vi described in A above were applied.
- D. **Exposure to nitrogen/steam followed by exposure to oxygen (6% oxygen by volume).** The char that resulted from the exposure of the virgin fuel to either nitrogen or steam was partially combusted *in situ*. The main aim was to quantify the release of K, Cl, and S during char combustion. An overview of the settings used in these experiments is presented in Table 7. The procedure was as follows:
- i. Exposure of the virgin fuel to nitrogen gas, as described for A, or to steam, as described for B.
  - ii. After 3–6 minutes of exposure of the virgin fuel to nitrogen or steam, the fluidization gas was switch to a mixture of air and nitrogen (6% O<sub>2</sub> by volume).
  - iii. After 3–6 minutes of char combustion, the basket was removed from the reactor and cooled in a stream of nitrogen gas.
  - iv. Thereafter, steps v–vi described in A above were applied.
- E. **Exposure to steam followed by exposure to steam.** Virgin fuels were devolatilized in steam, after which the char was gasified with steam *ex situ*. The main aim was to study the pore development of the char during gasification. An overview of the settings used in these experiments is presented in Table 7. The procedure was as follows:
- i. Virgin fuel was exposed to steam (83% vol in nitrogen), as described in B.
  - ii. After 1.0–2.5 minutes of retention, the basket that contained the char was removed from the reactor and cooled in nitrogen gas, after which the char was removed and weighed.
  - iii. Thereafter, some of the char was placed in the basket and re-inserted into the reactor where the char was exposed to steam of a lower concentration (52% vol in nitrogen) than was used in the first step.

- iv. After 15–20 minutes in the reactor, the basket was removed and rapidly cooled in nitrogen gas.
- v. Thereafter, steps  $v-vi$  described in **A** were applied.

Table 5. Exposure of virgin biomass to either nitrogen gas (N<sub>2</sub>) or steam (H<sub>2</sub>O).

Fuel	Temperature, °C	Time, minutes	Exposure gas	Further details in Paper
WSI	550	3	N <sub>2</sub>	I
	700	3	N <sub>2</sub>	I, II
	700	3	H <sub>2</sub> O	II
	800	3	N <sub>2</sub>	I, II
	800	3	H <sub>2</sub> O	II
	800	6	H <sub>2</sub> O	II
	900	3	N <sub>2</sub>	I, II
	900	3	H <sub>2</sub> O	II
	900	6	H <sub>2</sub> O	II
WSII	550	1.5	N <sub>2</sub>	V
	850	1.5	N <sub>2</sub>	V
	850	5	H <sub>2</sub> O	V
FR	550	1.5	N <sub>2</sub>	V
	850	1.5	N <sub>2</sub>	V
	850	5	H <sub>2</sub> O	V
	850	2.5	H <sub>2</sub> O	V
WP1	800	1	H <sub>2</sub> O	III
	840	1	H <sub>2</sub> O	III
	840	2.5	H <sub>2</sub> O	III
WP2	840	3	N <sub>2</sub>	IV
	840	3	H <sub>2</sub> O	IV
	850	3	N <sub>2</sub>	IV
WC	840	3	N <sub>2</sub>	IV

Table 6. Exposure of virgin biomass to nitrogen gas followed by *in situ* or *ex situ* exposure of the char to steam.

Fuel	Step one			Char →	Step two		
	Temperature, °C	Time, min	Fluidization gas		Temperature, °C	Time, min	Fluidization gas
WP2	840	~3	N <sub>2</sub>		840	25	H <sub>2</sub> O
WC	840	~3	N <sub>2</sub>		840	25	H <sub>2</sub> O
WP2	850	~3	N <sub>2</sub>		850	25	H <sub>2</sub> O

Table 7. Exposure of virgin fuel to either nitrogen gas or steam, followed by exposure of the resulting char to steam or oxygen (6% vol. in nitrogen).

Fuel	Step one			Char →	Step two			
	Temperature, °C	Time, min	Fluidization gas		Temperature, °C	Time, min	Fluidization gas	Paper #
WSI	700	3	N <sub>2</sub>		700	3	O <sub>2</sub>	I

WSI	800	3	N <sub>2</sub>		800	3	O <sub>2</sub>	I, II
WSI	800	3	H <sub>2</sub> O		800	3	O <sub>2</sub>	
WSI	800	6	H <sub>2</sub> O		800	6	O <sub>2</sub>	
WSI	900	3	N <sub>2</sub>		900	3	O <sub>2</sub>	
WSI	900	3	H <sub>2</sub> O		900	3	O <sub>2</sub>	
WSI	900	6	H <sub>2</sub> O		900	6	O <sub>2</sub>	
WPI	800				850	15		
WPI	840	1	H <sub>2</sub> O <sup>a</sup>		850	15	H <sub>2</sub> O <sup>b</sup>	III
WPI	840				850	20		

<sup>a,b</sup> The steam concentration in **a** (83% vol in N<sub>2</sub>) was higher than that in **b** (52% vol in N<sub>2</sub>).

### 3.1.4 Chemical analysis

The concentrations of K in the char samples were determined by first digesting a test sample (0.2 g) of the char with a mixture of 7 ml of concentrated nitric acid and 2 ml of 30% hydrogen peroxide and with heating in a microwave. The digested char was filtered, and the potassium concentration was determined by ICP-OES. Cesium was added as an ionization buffer. For chlorine, 0.5–1.0 g of the sample in a crucible that contained 1 ml of deionized water as receiving solution was combusted in the presence of 30 bar of oxygen in a closed bomb calorimeter. The chlorine content of the receiving solution was then determined by ion chromatography. The concentrations of sulfur in the samples were determined by first combusting 0.2–0.3 g of the sample in a stream of oxygen at 1370°C. The generated sulfur oxides were then detected and measured by IR.

### 3.1.5 Calculation of fuel conversion and release of K, Cl, and S

Fuel conversion, and the release of K, Cl, and S were determined by setting up mass balances for the fuel, and the elements at each stage of fuel conversion. All the equations applied are summarized in Tables 2 and 3 of Paper II.

### 3.1.6 Pore characteristics of the char samples obtained from the experiments

As mentioned in the *Theory* section, the degree of compactness of the fuel matrix affects the ease of diffusion of volatile salts out of the fuel matrix. In the present work, the compactness of the fuel matrix was assessed in terms of its pore characteristics. The pore characteristics considered are the total pore volume and the Brunauer-Emmett-Teller (BET) surface area. These characteristics of the various char samples were determined using the automated adsorption instrument TriStar 3000 V6.04 A. Prior to the analysis, the samples were crushed and sieved. Particles of diameter 3 mm were selected for the analysis. The particles were dried to a constant mass in an oven that was maintained at 150°C. The BET surface area of each char sample was determined from the N<sub>2</sub> adsorption isotherm measured at 77 K. The total volume of the pores in each sample was estimated as the volume of liquid nitrogen at a relative pressure of 0.99.

### 3.1.7 Chemical fractionation

The speciation of ash-forming elements in the fuels (FR, and WSII) applied in Papers V and VI was determined by chemical fractionation. Samples of the fuels were milled to a particle size of <5 mm. The milled samples were then sequentially leached with water, 1 M NH<sub>4</sub>Ac, and 1 M

HCl. The mass ratio of solvent to fuel sample applied in each leaching step was 10. In the first step, 10–15 g of each sample were added to deionized water and shaken for 24 hours, after which the whole suspension was filtered. In the second step, the solid residue from the first step was added to a solution of 1 M NH<sub>4</sub>Ac and shaken for 24 hours, after which the entire suspension was filtered. This step was repeated twice, after which the solid residue was washed with deionized water. In the final step, the solid residue from the second step was added to a solution of 1 M HCl and shaken for 24 hours. This step was repeated, after which the whole suspension was filtered and the solid residue was dried at 105°C to constant mass. The leachate obtained at each leaching step and the final dried solid residues were subsequently analyzed using inductively coupled plasma-sector field mass spectrometry and inductively coupled plasma-atomic emission spectrometry.

The fractions of K, Cl, and S that were water-soluble in the fuel (WSI) and used in Papers I and II were determined according to the standard SIS-CEN/TS 15105:2006.<sup>58</sup> The procedure consisted in heating 1 g of each sample at 120°C for 1 hour in a closed container. The concentrations of Cl and S in the leachate were determined by ion chromatography, while ICP-OES was used to determine the concentration of K.

### 3.2 Chemical thermodynamic equilibrium modeling (CTEM)

CTEM was performed to facilitate the interpretation of the experimental results for the release of K, Cl, and S to the gas phase. Furthermore, the reactions of ash-forming elements in the fuel matrix and their reactions with bed materials were studied with CTEM. These analyses were carried out with the FactSage software version 6.2<sup>59</sup> (in Paper I), and version 7 (Paper II). This tool calculates the equilibrium concentrations and phase distribution of chemical species which minimizes the total Gibbs free energy of a system subject to the material balance of the system.<sup>60</sup> <sup>61</sup> The FT oxid-SLAGA, FT salt-KCO, FT salt-LCSO, FT salt-SALTF, and FTpulp-MELTA databases were employed. Further details of these databases are available in Papers I and VI. The temperatures applied were in the range of 400°–1200°C, and the pressure was fixed at 0.1 MPa. In Paper I, the entire amount of each element in the virgin fuel/char was used in the CTEM. However, in Paper VI, only the reactive fractions of each element in the virgin fuel/char were applied. Further details as to the compositions of the fuels applied are provided in Table 2 of Paper I and Table 1 of Paper VI.

The interpretation of the results of the CTEM was performed bearing in mind the limitations of global equilibrium analysis, which *inter alia* assumes infinite reaction times and perfect mixing.<sup>62</sup>

## 4 Main findings and implications

The main findings are summarized in the following sections. Further details are available in the appended papers.

### 4.1 Release of chlorine and potassium

#### 4.1.1 Devolatilization

Virtually all of the Cl and at least half of the K in the fuels were water-soluble (Figure 5), and thus likely present as salts, probably in the form of KCl (see Papers II and V). Similar findings have been reported in the literature.<sup>34</sup>

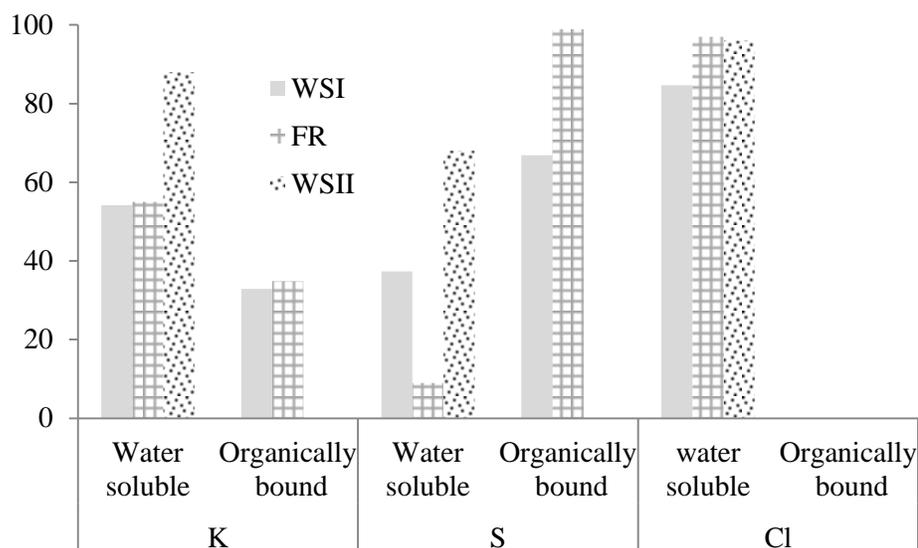


Figure 5. Water-soluble and organically bound fractions of K, Cl, and S in the virgin fuels

The vapor pressure of KCl is low at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ .<sup>8</sup> Therefore, the release of Cl to the gas phase through the evaporation of KCl from biomass fuels would be unlikely. This is also supported by the CTEM, which predicts that when biomass is devolatilized, the Cl is released to the gas phase only at temperatures  $\geq 700^{\circ}\text{C}$  (Figure 6). However, in contrast to the results of the CTEM, experimental data shows that when WSI was devolatilized (experiment A), a high release of Cl ( $\sim 75\%$ ) into the gas phase occurred at  $550^{\circ}\text{C}$  (Figure 7). Furthermore, the level of Cl released at this temperature was higher than that ( $\sim 58\%$ – $62\%$ ) released at  $700^{\circ}\text{--}900^{\circ}\text{C}$ . Further details are available in Paper I. The release of Cl at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$  from biomass fuels, including wheat straw, under fixed bed pyrolysis conditions has also been observed in previous studies.<sup>8, 38, 39</sup> However, in contrast to the present work, the levels of release of Cl in the referred studies were generally higher ( $\sim 57\%$ – $98\%$ ) at temperatures in the range of  $700^{\circ}\text{--}900^{\circ}\text{C}$  than at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$  ( $\sim 42\%$ – $60\%$ ). Furthermore, the release of Cl at  $550^{\circ}\text{C}$  in the present work ( $\sim 75\%$ ) was generally higher than the levels released ( $\sim 42\%$ – $60\%$ ) in the referred pyrolysis studies conducted at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ .

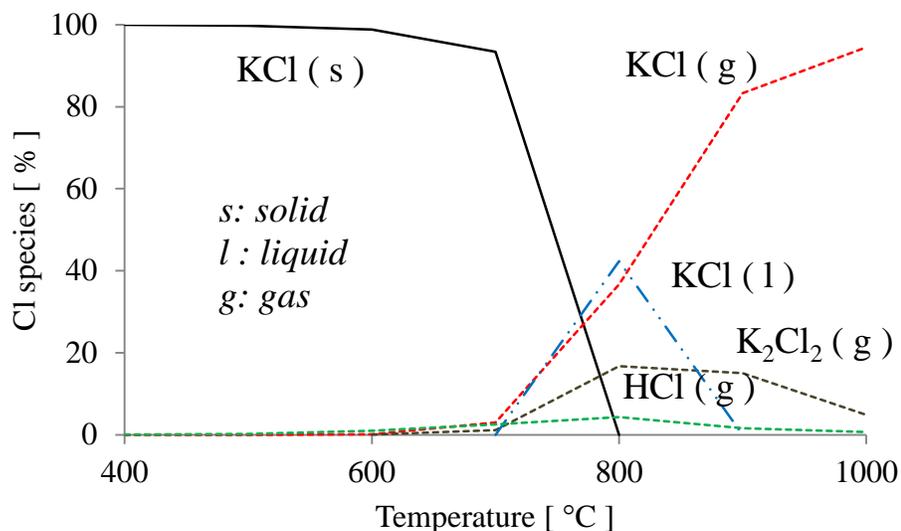


Figure 6. Predicted distributions of thermodynamically stable Cl species as a function of temperature when Danish wheat straw (WSI) was exposed to nitrogen.

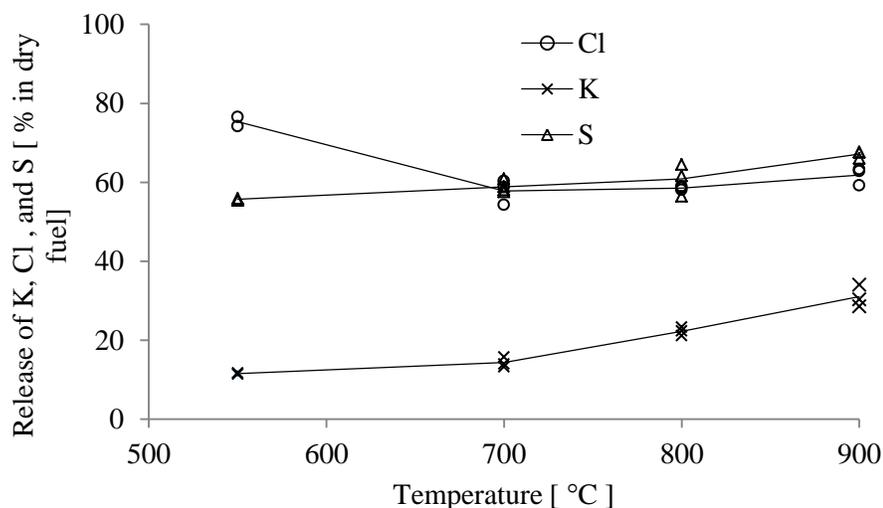


Figure 7. Release of K, Cl, and S from Danish wheat straw (WSI) as functions of temperature after exposure to nitrogen.

Given that the reactor type (fluidized bed) and the retention time (3 minutes) applied in the present work are different from the reactor type (fixed bed) and retention times (15–25 minutes) used in the referred works, it is plausible that the differences in the patterns of Cl release in the present and previous works are related to differences in the reactor types and retention times. In this light, information on how the applied operational conditions affect the pathways through which Cl is released under the investigated temperature range may be useful in explaining the differences in the extents of Cl release noted between the present work and the previous studies. Since virtually all the Cl is potentially present as KCl in the WSI, and since KCl has a low vapor

pressure to be in the gas phase at  $<600^{\circ}\text{C}$ , it can be inferred that the high level of Cl release at  $550^{\circ}\text{C}$  could only have occurred through transformation of KCl. As mentioned in the *Theory* section, the transformation of KCl involves an ion-exchange reaction in which KCl reacts with oxygen-containing functional groups (e.g., carboxylic acids and phenols) that are present in the fuel and/or generated during devolatilization of the fuel (see R1). On the one hand, this reaction may be limited by the amounts of these groups present during devolatilization.<sup>39, 42</sup> On the other hand, this reaction may be facilitated by a liquid tar phase.<sup>38</sup> Tar yields are generally higher when biomass is subjected to fast heating conditions, as compared to slow heating conditions.<sup>63, 64</sup> The fuel particles in fluidized bed reactors experience much higher heating rates than those in fixed bed reactors (see *Theory* section). Therefore, more tar is generated in a fluidized bed reactor than in a fixed bed reactor. On this basis, the finding in the present work that the level of Cl released at  $550^{\circ}\text{C}$  was generally higher than those observed for the aforementioned fixed bed pyrolysis studies is probably due to the higher heating rate of the fuel particles in fluidized beds, as compared to that the fixed beds.

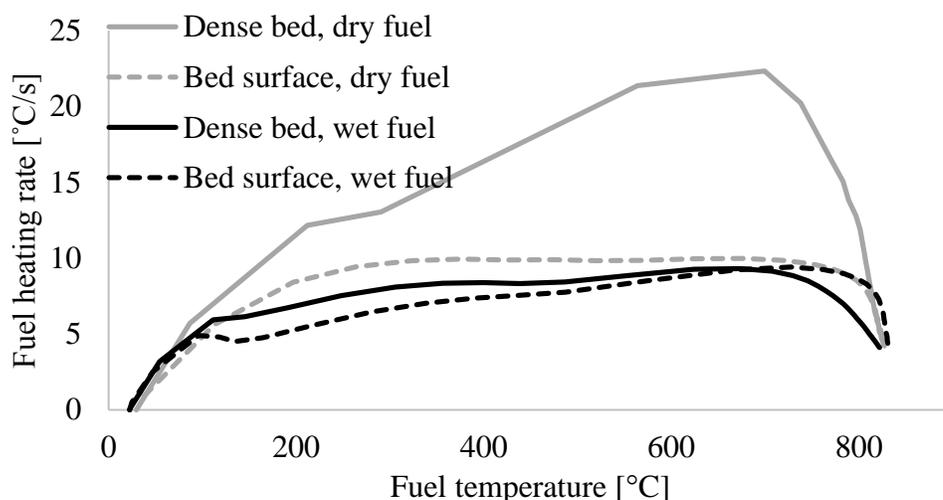


Figure 8. Heating rates for dry, and wet fuel particles placed in the dense bed or bed surface in a bubbling fluidized bed reactor.

Since the heating rate of fuel particles in the reactor appears to influence the release of Cl, it is important to know how the axial positions of the fuel particles in a fluidized bed reactor affect their heating rate. In Paper IV, the heating rates of fuel particles on the bed surface and in the dense bed of a fluidized bed reactor were estimated. It was observed that during devolatilization, the heating rate of the fuel particles was higher when they were located in the dense bed, as compared with the case in which they were located on the bed surface, especially when dry fuel particles were used (Figure 8). This suggests that the release of Cl from fuel particles is higher when the particles are located in the dense bed rather than being located on the bed surface. Therefore, controlling the axial location of dry fuel particles during devolatilization may provide a means to enhance or minimize the release of Cl at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ .

As mentioned earlier, KCl has a significant vapor pressure to be in the gas phase at temperatures  $\geq 700^{\circ}\text{C}$ . Therefore, when a fuel particle is dropped into a reactor that is operated at

temperatures  $\geq 700^{\circ}\text{C}$ , it can be envisaged that when the fuel particles heat up to temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ , a high release of Cl will occur through R1 (as discussed in the preceding paragraph), and this should be followed by additional release of Cl through the evaporation of KCl when the fuel particles reach temperatures  $\geq 700^{\circ}\text{C}$ . In other words, for the same retention time of fuel particles in the reactor, the release of Cl should be higher at temperatures  $\geq 700^{\circ}\text{C}$  than at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ . However, in the present work, it was observed that the level of Cl released at  $550^{\circ}\text{C}$  was higher than at  $700^{\circ}\text{--}900^{\circ}\text{C}$  (see Figure 7). This suggests that something limited the release of Cl through the transformation of KCl (R1). It is well known that both the tar yield and the levels of oxygenated tar components decrease with temperature.<sup>65, 66</sup> Therefore, the decrease in the release of Cl observed when the applied temperature was decreased from  $550^{\circ}\text{C}$  to  $700^{\circ}\text{C}$  in the present study may be attributable, at least in part, to a decrease in the levels of total tar and oxygenated tar generated with increasing temperature. An alternative explanation for the lower release of Cl through R1 is that heat transfer through the fuel particles occurred very rapidly. As a result, when the applied temperature was in the range of  $700^{\circ}\text{--}900^{\circ}\text{C}$ , the reaction time for R1 to go to completion was shorter than when the maximum temperature in the reactor was maintained at  $<600^{\circ}\text{--}700^{\circ}\text{C}$ . Since the release of Cl through R1 is limited at temperatures  $\geq 700^{\circ}\text{C}$ , evaporation of KCl would appear to be the main pathway for the release of Cl. One of the factors that influence the evaporation of KCl from biomass fuels is the retention time of the fuel particles in the reactor.<sup>8</sup> Therefore, the lower release of Cl at temperatures in the range of  $700^{\circ}\text{--}900^{\circ}\text{C}$ , as compared to the release of Cl at  $550^{\circ}\text{C}$  observed in the present work, is attributable in part to the short retention time applied, which limited the evaporation of KCl from the fuel matrix to the gas phase. As mentioned earlier, in fixed-bed pyrolysis studies in which significantly longer retention times were applied (compared to the present experiments), higher levels of Cl release were observed at temperatures in the range of  $700^{\circ}\text{--}900^{\circ}\text{C}$ , as compared to the levels of Cl release at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ .

A small fraction of the K ( $\sim 10\text{--}17\%$ ) in each of the WSI, WSII, and FR was released to the gas phase when these fuels were devolatilized at  $550^{\circ}\text{C}$ . The source of the K released at this temperature was the organically bound K in the virgin fuels (for details, see Paper V). When the temperature was increased from  $550^{\circ}\text{C}$  to  $\geq 700^{\circ}\text{C}$  further release was observed from WSI, and WSII while the release of K from FR was essentially the same. Table 4 shows that the Cl/K molar ratios in WSI and WSII are significantly higher than that in the FR. Since evaporation of KCl is a proven pathway for the release of K at temperatures  $\geq 700^{\circ}\text{C}$ ,<sup>8</sup> the observed difference in the release of K from the applied virgin fuels is plausibly related to differences in the relative contents of Cl, and K in the fuels.

Based on the discussions in the preceding paragraphs, it is possible to separate the release of Cl from that of K when biomass fuels are devolatilized at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$ . In this case, a Cl-rich gas and a K-rich char are obtained. Retaining the K in the char during devolatilization could be beneficial, as the K could be catalytically active for char conversion when the char comes in contact with steam, especially if the virgin fuel has a high K/Si molar ratio. However, operating the gasification chamber at temperatures in the range of  $<600^{\circ}\text{--}700^{\circ}\text{C}$  could be counter-productive given that: (1) more tar is usually generated at

temperatures in the range of  $<600^{\circ}\text{C}$  than at temperatures  $\geq 700^{\circ}\text{C}$ ; and (2) the rate of char gasification is generally low at temperatures  $\leq 800^{\circ}\text{C}$ .

#### 4.1.2 Char gasification

Figure 9 shows that for the same temperature and retention time (3 minutes), more Cl and K were released and the yield of char was lower when the WSI was exposed to steam, as compared to the case in which the WSI was exposed to nitrogen gas (experiments A and B). Furthermore, the differences in the levels of Cl released and yields of char were greater at  $900^{\circ}\text{C}$  than at  $800^{\circ}\text{C}$ . The lower yield of char obtained from the exposure of WSI to steam, as compared to the case in which it was exposed to nitrogen gas, indicates that the char that results from the devolatilization of WSI in steam was partially gasified with the steam.

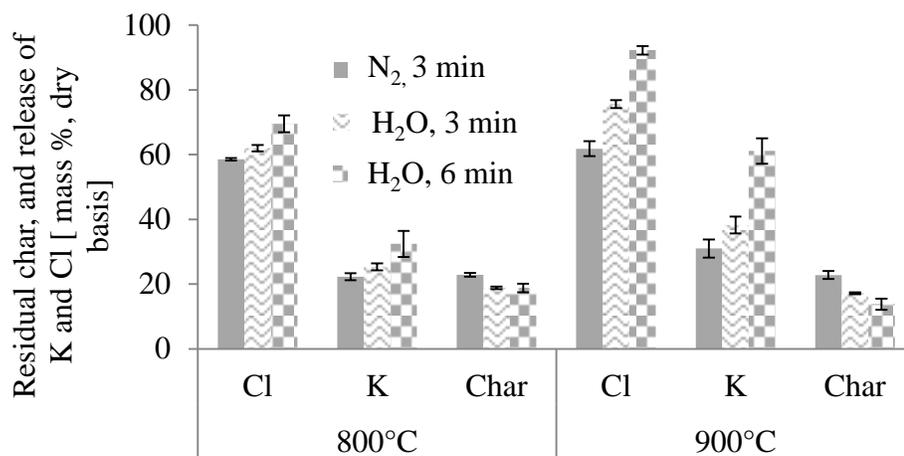


Figure 9. Residual char yield (mass% of dry fuel) and released amounts of Cl and K (mass% in dry fuel) when WSI was exposed to nitrogen for 3 minutes, steam for 3 minutes or steam for 6 minutes. The applied temperatures were  $800^{\circ}\text{C}$  and  $900^{\circ}\text{C}$ .

Since the temperature and retention time applied were the same when the WSI was exposed to  $\text{N}_2$  or steam, it is plausible that the observed difference in the release of Cl is related to partial gasification of the char with steam. Given that (1) Cl is mainly released through the evaporation of KCl at the applied temperatures, and (2) the diffusion of KCl through the fuel matrix experiences resistance depending on the degree of compactness of the fuel matrix,<sup>8, 39</sup> it can be envisaged that partial gasification of char would render the char matrix less compact, thereby decreasing the resistance to diffusion of the KCl through the fuel matrix. In the present work, the degree of compactness of the char matrix was assessed in terms of porosity. BET analysis was performed on the char obtained after exposure of the WSI to nitrogen gas and steam, as described in the *Experimental* section. This analysis showed that, for the investigated temperature interval, the char that resulted from the exposure of WSI to nitrogen gas had a significantly lower BET surface area ( $\sim 5\text{--}6\text{ m}^2/\text{g}$ ) than that of the char that resulted from exposure of WSI to steam ( $\sim 360\text{--}580\text{ m}^2/\text{g}$ ) (see Table 8). Thus, it seems likely that the higher level Cl released from the WSI observed in steam compared to nitrogen is a consequence of the char matrix being less compact in steam than in nitrogen gas.

Table 8. Pore characteristics of chars following exposure of WSI to nitrogen ( $N_2$  for 3 mins, char) or steam ( $H_2O$  for 3 mins, char). The retention time was 3 minutes.

Temperature (°C)	$N_2$ -3 mins, char		$H_2O$ -3 mins, char	
	BET SA <sup>a</sup> (m <sup>2</sup> /g)	Total PV <sup>b</sup> (cm <sup>3</sup> /g)	BET SA (m <sup>2</sup> /g)	Total PV (cm <sup>3</sup> /g)
800	5.0	0.02	361.1	0.24
900	5.6	0.02	579.6	0.35

<sup>a</sup>SA, surface area

<sup>b</sup>PV, pore volume

In similarity to the results regarding the release of Cl (discussed above), the observed difference in the release of K from WSI is related to partial gasification of the char when the WSI was exposed to steam. In addition to evaporation of KCl, gasification of char is conducive to the release of char-bound K. Furthermore, earlier studies have reported that the decomposition of  $K_2CO_3$  is enhanced in the presence of steam, as shown in R2–R4 in the *Theory* section.

Since steam gasification of char appears to facilitate the release of Cl and K, operational parameters that influence the rate of char gasification could also represent a means of controlling the release of Cl and K to the gas phase. Steam-char contacts (external and internal diffusion) and char reactivity are factors that affect the char gasification rate.<sup>67</sup> Char reactivity is affected *inter alia* by pore structure and the internal surface area in the char matrix.<sup>68</sup> These factors are in turn strongly influenced by the heating rate during devolatilization.<sup>69</sup> In Paper IV, it was observed that the char gasification rate is influenced by the axial location of the fuel particles during devolatilization and char gasification. The char gasification rate was lowest when the virgin fuel (WP11) was devolatilized on the bed surface (heating rate lower than in the dense bed), and the resulting char was gasified in the dense bed (steam-char contacts lower than on the bed surface). This suggests that the release of K and Cl would be lowest under these conditions. In addition to the axial location of the particles in the reactor, the char reactivity and consequently the char gasification rate can be affected by the temperature and retention time used. In Papers II and III, it was observed that the porosity of the char increased with temperature and retention time.

With respect to the influence of ash characteristics on the release of Cl and K during steam gasification of biomass, it was observed that the ash composition did not affect the extent to which Cl is released to the gas phase. In contrast to Cl, the ash composition (mainly acting through the Cl/K molar ratio) significantly influences the extent to which K is released to the gas phase.

From the discussion in this section regarding the release of K and Cl, it is clear that during dual fluidized bed gasification of biomass, most of the Cl in the virgin fuel follows the raw gas out of the gasification chamber, whereas most of the K follows the char to the combustion chamber.

#### 4.1.3 Char combustion

The release of Cl and K during char combustion followed patterns similar to those seen during char gasification, whereby the less compact (more porous) the char the higher the levels of Cl and K released to the gas phase. Figure 10 shows the fractions of K and Cl in  $N_2$ -3 mins char

(i.e., char resulting from exposure of the WSI to nitrogen for 3 mins) released to the gas phase when it was partially combusted for 3 minutes *in situ*. The same figure shows the fractions of K and Cl in the  $H_2O-3$  mins char (i.e., char resulting from exposure of the WSI to steam for 3 minutes) released to the gas phase when it was partially combusted for 3 minutes *in situ*. The fraction of each char sample combusted is also presented. Although the combustion time applied was the same (3 minutes), the levels of Cl and K release were generally higher from the  $H_2O-3$  mins char than from the  $N_2-3$  mins char. Furthermore, the fraction of the  $H_2O-3$  mins char that was combusted was larger than that of the  $N_2-3$  mins char. As discussed in the preceding section, the  $H_2O-3$  mins char was less compact (more porous) than the  $N_2-3$  mins char (see Table 8). Therefore, when these chars are combusted it can be expected that the evaporation of KCl and other K-salts would experience lower diffusional resistance for the  $H_2O-3$  mins char than for the  $N_2-3$  mins char.

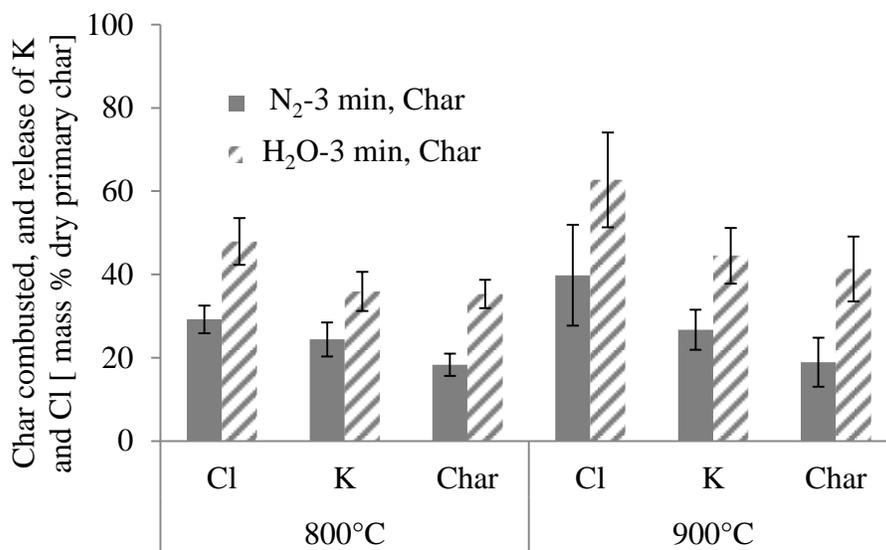


Figure 10. Release (mass% of K or Cl in the primary char) of K and Cl from primary chars during char combustion carried out at 800°C or 900°C for 3 minutes. The primary chars used resulted from the exposure of WSI (at 800°C or 900°C for 3 minutes) to either nitrogen (here denoted as:  $N_2-3$  mins, char) or steam (here denoted as:  $H_2O-3$  mins, char). The fractions (mass% of primary char) of the primary chars that were combusted are also presented.

## 4.2 Release of sulfur

The release of S from biomass fuels was found to be marginally affected by differences in ash composition when the fuel was partially converted (for details, see Paper IV). In contrast to the ash composition, the speciation of S in the fuel matrix influenced the release of S to the gas phase. In the FR, where virtually all of the S was in organic form (see Figure 5), almost complete (~93%) release of the S to the gas phase was observed when the FR was exposed to nitrogen for 1.5 minutes. However, in the WSII, where a substantial fraction of the S was water-soluble (~37%; see Figure 11), ~60% of the S was released to the gas phase when the WSII was exposed to nitrogen for 1.5 minutes. This indicates that the organic S is more likely to be completely released to the gas phase than the water-soluble S. Thus, the speciation of S in biomass fuels

provides information that can be used to assess to what extent S might be released to the gas phase from the fuel during thermal conversion.

In agreement with the results of earlier studies,<sup>8,39</sup> the release of S was observed to increase marginally for temperatures in the range of 550°–900°C during devolatilization (Figure 7). This may be attributed to fact that the release of organically bound S and the transformation and release of water-soluble S occur when the organic matrix of the fuel is decomposed by heat (devolatilization) (see Papers I, II, and V for further details). Since decomposition of the organic matrix of biomass fuels mainly takes place when the fuel particle temperature reaches 200–500°C,<sup>70-72</sup> a further increase in temperature would have a negligible effect on S release.

Figure 11 shows that the level of S released was essentially the same when the FR was exposed to steam for 5 minutes and when it was exposed to nitrogen for 1.5 minutes. This indicates that when the FR was exposed to steam, all of the S was released to the gas phase during devolatilization and the release of S during char gasification was insignificant. In the case of WSII, the higher level of S released when it was exposed to steam, as compared to the case in which it was exposed to nitrogen, indicates that some of the S was released during char gasification when the WSII was exposed to steam. Further details can be found in Papers II and V.

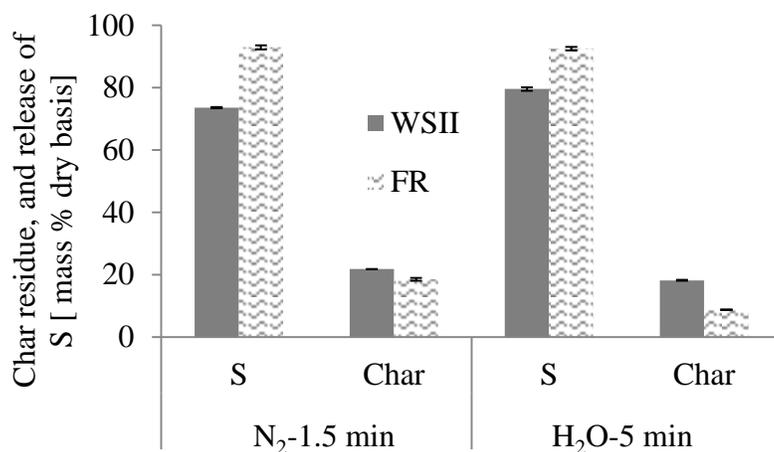


Figure 11. Levels of char residue (mass% dry fuel) and release of S (mass% in dry fuel) when WSII and FR were separately exposed to either nitrogen gas for 1.5 minutes or steam for 5 minutes.

Based on the findings described in this section, it is clear that most of the S in biomass fuels follows the raw gas out of the gasification chamber, whereas char that is almost S-free is circulated to the combustion chamber.

In stand-alone combustion systems, sulfur oxides can convert alkali chlorides into alkali sulfates,<sup>73 74</sup> which are less corrosive than alkali chlorides.<sup>74</sup> It was observed in a dual fluidized bed gasifier that the addition of sulfur to the combustion chamber decreased the concentration of alkali in the flue gas.<sup>75</sup> This was explained by the fact that the alkali sulfates that resulted from the sulfation of alkali chlorides were deposited on the bed material particles. Circulation of the bed material to the gasification chamber resulted in the release of S from the decomposition of the

alkali sulfates, and the K was available for char/tar conversion. Therefore, the findings in the present work that almost all the S in the virgin fuel follows the raw gas out of the gasification chamber and that most of the K follows the char to the combustion chamber indicate that when the char is combusted in the combustion chamber, the sulfation of alkali chlorides would be very limited. Therefore, most of the K that is released from the char during combustion follows the flue gas out of the combustion chamber, especially if silicon-lean bed materials, such as olivine, are employed. For the combustion chamber, the consequence is severe corrosion of downstream heat transfer surfaces. For the gasification chamber, the consequence is that less K becomes available to act as a catalyst for tar and char conversion.

### 4.3 Fuel-ash reactions

As mentioned in the *Introduction*, the transformation and release of K could be beneficial for the DFBG process. Several studies have shown that K (as well as Ca) is a catalyst for tar<sup>76-78</sup> and char<sup>77, 79-85</sup> conversion. Thus, one can envisage that the gasification of biomass fuels (e.g., forest residues) that contain higher levels of K and Ca than are present in wood chips/pellets (which are almost ash-free) would significantly enhance tar and char conversion. However, since these fuels may also contain higher levels of Si and P than wood chips/pellets,<sup>78</sup> ash sintering *via* reactions between K or Ca and Si or P may result in the deactivation<sup>19</sup> of Ca and K or, in the worst scenario, lead to agglomeration.<sup>31, 86, 87</sup> Therefore, having information regarding the ash-sintering characteristics of a given fuel is useful for deducing the conditions under which Ca and K could be deactivated during thermal conversion, as well as the risk for agglomeration. Chemical thermodynamic equilibrium modeling (CTEM) has been applied in several studies to assess the sintering characteristics of various biomass fuels.<sup>2, 31, 88-92</sup> In many of these studies, CTEM was carried out with various versions of the FactSage software.<sup>2, 91, 92</sup> As mentioned in the *Theory* section, ash-forming elements are present in various forms in biomass fuels, and not all of the forms of a given element are likely to participate in ash reactions at temperatures typical for fluidized bed reactor operation. Since CTEM does not discriminate between the different forms of ash-forming elements in biomass fuels,<sup>93</sup> applying only the reactive forms of each ash-forming element as input data for the fuel in CTEM may provide better results than a case in which the non-reactive forms of the ash-forming elements are also included as input data for the fuel. The various forms of ash-forming elements in biomass fuels can be ascertained by chemical fractionation (CF) (see *Theory* section). In a few previous studies, CTEM with input data from the CF of various virgin fuels was applied to assess the sintering characteristics of the fuels.<sup>31, 88</sup> One of the limitations of CTEM is that it assumes ideal mixing of all the reactants in the system (see *Theory* section). However, this is not the case for ash-forming elements in the fuel matrix, as organic materials act as barriers between ash-forming elements.<sup>46</sup> Since most of the organic materials in a virgin fuel are converted during devolatilization, the contact among ash-forming elements is probably better in the fuel-derived char (especially during the later stages of char conversion)<sup>44, 46</sup> than in the virgin fuel. Therefore, applying the elemental composition of the fuel-derived char as input data for the fuel in CTEM might yield better results than applying the elemental composition of the virgin fuel. This is particularly important for DFBG, since the char that is circulated from the gasification chamber to the combustion chamber is the fuel for the combustion chamber.

In the GoBiGas DFBG plant in Sweden, stem wood is currently used as fuel.<sup>94</sup> Replacing this fuel with forest residues, which are cheaper, would not only reduce fuel costs but might also improve the chemical efficiency of the plant, provided that ash sintering is negligible, as discussed in the preceding paragraph. In this context, assessing the sintering characteristics of the ash in forest residues can provide valuable information for selecting the optimal operational conditions at which the DFB gasifier can be operated, such that: 1) most of the Ca and K in the fuel is available to catalyze gasification reactions; and 2) the risk of agglomeration is low. To this end, CTEM was carried out with input data derived from the CF of the char obtained from the partial gasification of FR. The aims were: 1) to assess whether under typical operational conditions for DFBG (see *Theory* section), the K and Ca in the FR are in chemical forms that can act as catalysts for tar and char conversion; and 2) to assess the risk of agglomeration.

The procedure adopted is shown in Figure 12. An initial experiment (Experiment B in the *Experimental* section) was carried out in which the FR was gasified with steam at 850°C for 2.5 minutes in a fluidized bed reactor (Figure 4).

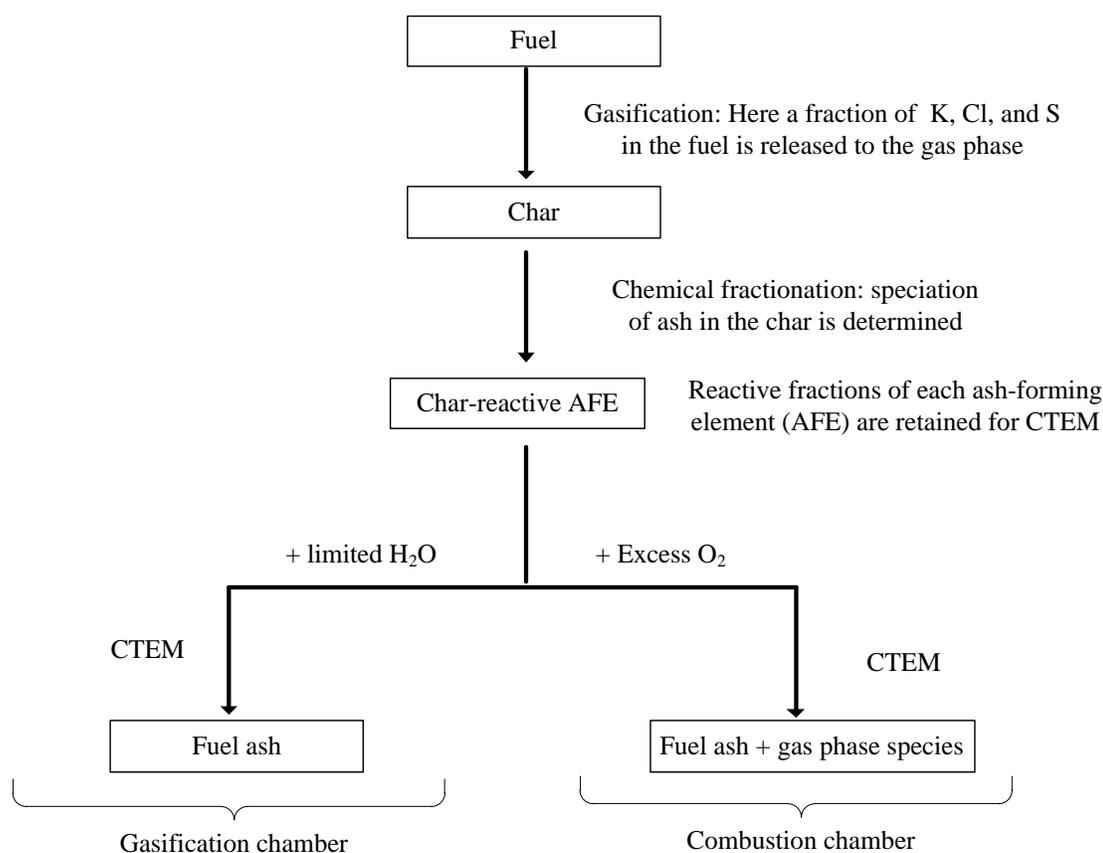


Figure 12. Procedure for studying fuel ash reactions under DFBG conditions.

The fractions of Cl, K, and S released from the FR were ~84%, ~19%, and ~94% on dry basis, respectively. The yield of the char obtained from the FR was ~16% on dry basis. Table 9 shows the elemental composition of the char. In similarity to the virgin FR (see Table 4), the ash composition was dominated by Si, Ca, and K. These were also the main elements identified on

the surface of the cross-section of a sample char particle using scanning electron microscopy (SEM) combined with energy-dispersive X-ray (EDX) analysis (see Figure 13). However, the concentrations of the aforementioned elements were much higher in the char than in the virgin fuel, which suggests that the ash-forming elements in the char are more likely to be in contact than those in the virgin fuel.

Table 9. Elemental composition of char (C) from FR gasification, as applied to studying fuel ash transformation.

Type	C	H	N	O	S	Cl	K	Na	Ca	Mg	Si	P	Fe	Al
A	83.2	0.5	0.96	4.2	0.01	0.01	0.96	0.09	2.52	0.3	1.03	0.21	0.19	0.16
B					100	100	95	50	50	44	5	9	0	0
C	83.2	0.5	0.96	4.2	0.01	0.01	0.91	0.05	1.25	0.13	0.05	0.02	0	0

- A. Elemental composition (wt%, dry char) of char obtained from the exposure of FR to steam for 2.5 minutes.  
 B. Reactive fraction (i.e., % of water-soluble and organically bound fractions) of each ash-forming element in the char.  
 C. Elemental composition (wt%, dry char) of the char based on B.

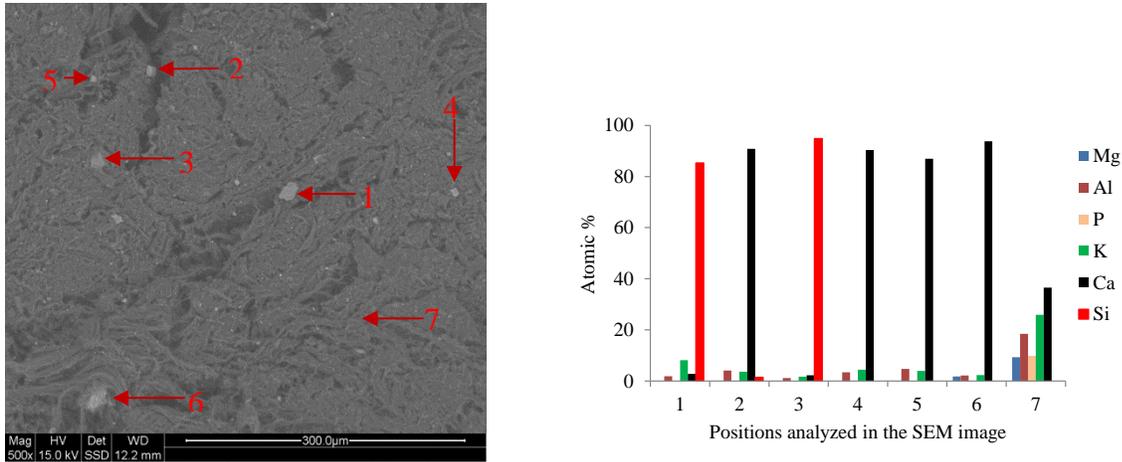


Figure 13. SEM (left) combined with EDX (right) analysis of spots on the surface of the cross-section of a sample char particle.

As mentioned in the *Theory* section, the water-soluble and the organically bound fractions of the elements in the fuel matrix are usually considered to be reactive during thermal conversion processes. For each of the elements, these fractions were determined by chemical fractionation of the char; the results are shown in Table 9 (for details, see Paper VI). The elemental composition of the char, based solely on the reactive fractions of each of the ash-forming elements, was used as the input data for the char in CTEM.

To simulate gasification conditions, H<sub>2</sub>O was added as the gasification agent to the input data for the CTEM. As mentioned in the preceding paragraphs, ~19% of the K in the FR was released to the gas phase when it was exposed to steam at 850°C for 2.5 minutes in a fluidized bed reactor. In a DFBG process, the unconverted char containing the residual K (~79% in this case) would be

circulated together with bed material to the combustion chamber. Therefore, when performing the CTEM calculations for the ash in the char prior to its circulation to the combustion chamber, an important consideration is that the gas-phase K species should be minimized or (better still) avoided. Therefore, the amount of H<sub>2</sub>O added to the input data for the CTEM was such that the gas-phase K species were minimized (<5% of the K in the char was predicted to be in the gas phase in the temperature range of 700°–900°C; see Figure 14).

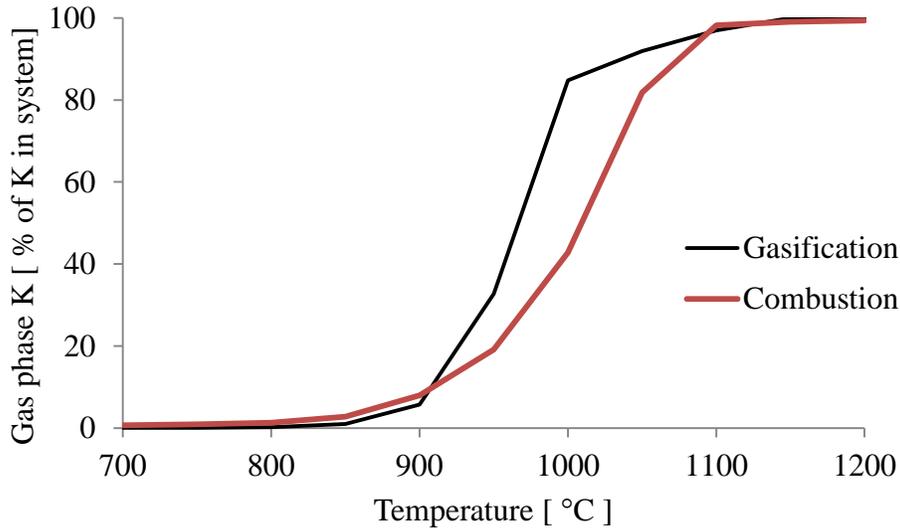


Figure 14. Fraction of K in the system that is predicted to be thermodynamically stable in the gas phase.

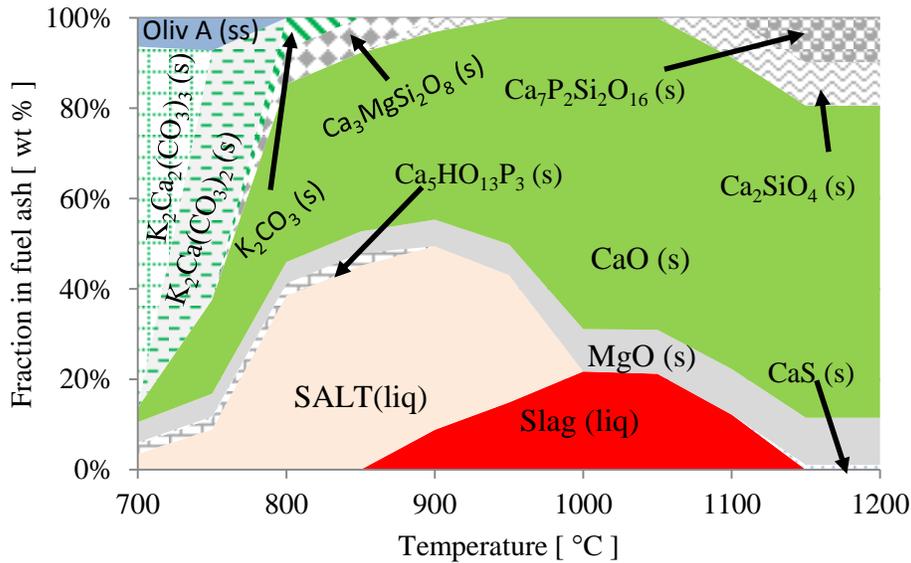


Figure 15. Predicted composition of the condensed phase of the fuel ash under gasification conditions.

Figure 15 shows the predicted ash composition of the char in the gasification chamber just before it is circulated to the combustion chamber. In the temperature interval of 800°–900°C, within which the gasification chamber is typically operated, a large fraction (~38–41 wt%) of the fuel ash and a small fraction (~0–9 wt%) of the fuel ash are predicted to be molten salts and slag, respectively. The compositions of the molten salt and slag are shown in Figure 16 and Figure 17, respectively.

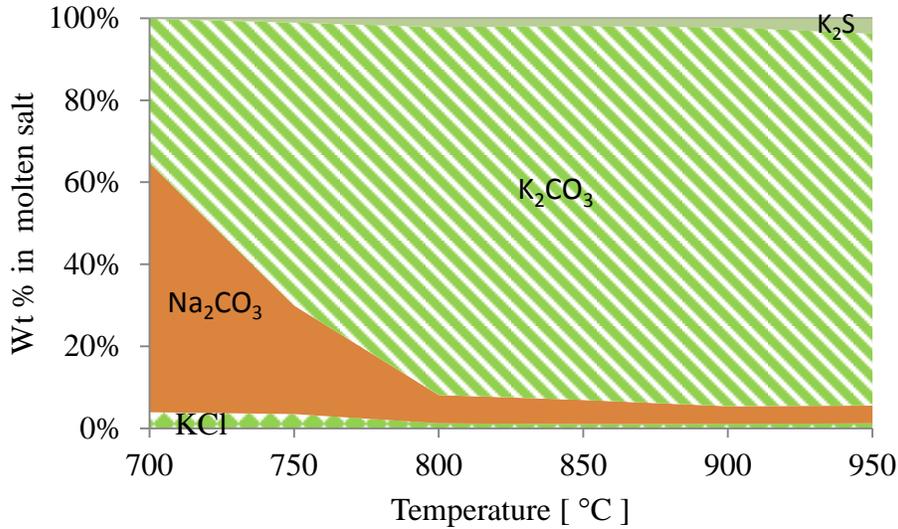


Figure 16. Compositions of molten salts in the fuel ash under gasification conditions.

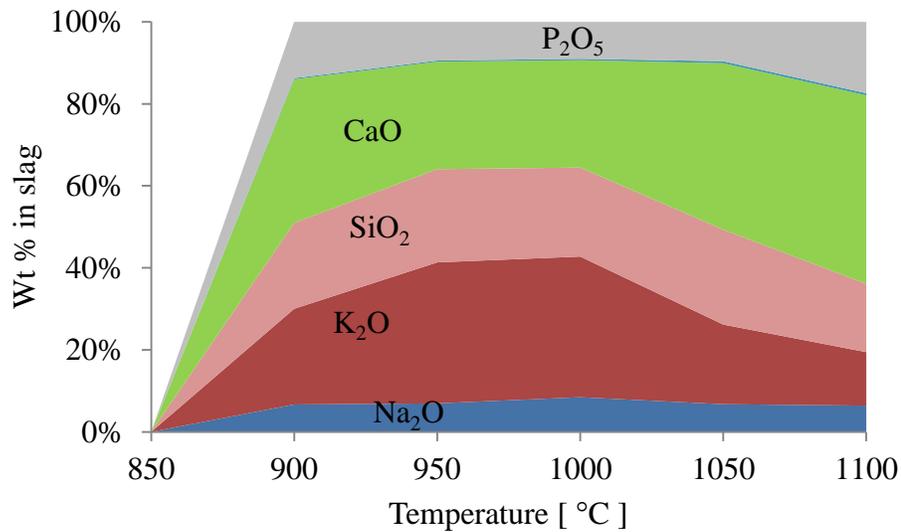


Figure 17. Compositions of molten oxides (slag) in the fuel ash under gasification conditions.

Figure 15–17 show that Ca and K are present in the ash predominantly in the forms of CaO and K<sub>2</sub>CO<sub>3</sub>, respectively, in the temperature interval of 800°–900°C. Since CaO<sup>30</sup> and K<sub>2</sub>CO<sub>3</sub><sup>80</sup> are reactive during the thermal conversion of biomass, it can be inferred from the results presented here that, even if very close association of ash-forming elements in the char matrix occurs during gasification of the FR, the K and Ca would predominantly be present in catalytically active forms in the FR-derived char. For the same temperature interval, a small fraction (0%–10%) of the ash is predicted to be present as slag. This suggests that the risk of agglomeration in the gasification chamber would be low, especially if a silica-lean bed material, such as olivine, is used.

In a DBFG process, the unconverted char and the bed material in the gasification chamber are circulated to the combustion chamber. Therefore, the composition of the reactive fraction of the unconverted char from gasification was used to study the fuel ash in the combustion chamber. The Air (N<sub>2</sub> and O<sub>2</sub>) parameter that was added to the input data contained more oxygen (6% of the flue gas) than was needed to combust completely the char (see Paper VI). Under this condition, CTEM predicted that 2%–20% of the K in the char would be in the gas phase when the char is combusted at temperatures typically applied in the combustion chamber, viz. 850°–930°C (Figure 14). Since further release of K could be expected to occur when char from the gasification chamber is combusted in the combustion chamber (Figure 10), the amount of O<sub>2</sub> that was added to the input data to perform CTEM for the char combustion case was deemed to be reasonable. The composition of the condensed phase of the fuel ash is presented in Figure 18. The compositions of the fractions of the fuel ash that are present as molten salts and slag are presented in Figure 19 and Figure 20, respectively. In the temperature interval of 850°–930°C, all the K and most of the Ca are predicted to be not associated with Si and/or P. Ca and K are predominantly present in the chemical forms of CaO and K<sub>2</sub>CO<sub>3</sub>. Therefore, even in the combustion chamber, the Ca and K in the FR-derived char could be expected to maintain their catalytically active forms. For the same temperature interval, slag was not predicted to be present, which in connection with the case for the gasification chamber suggests a low risk of agglomeration if FR is used as the fuel for DFBC.

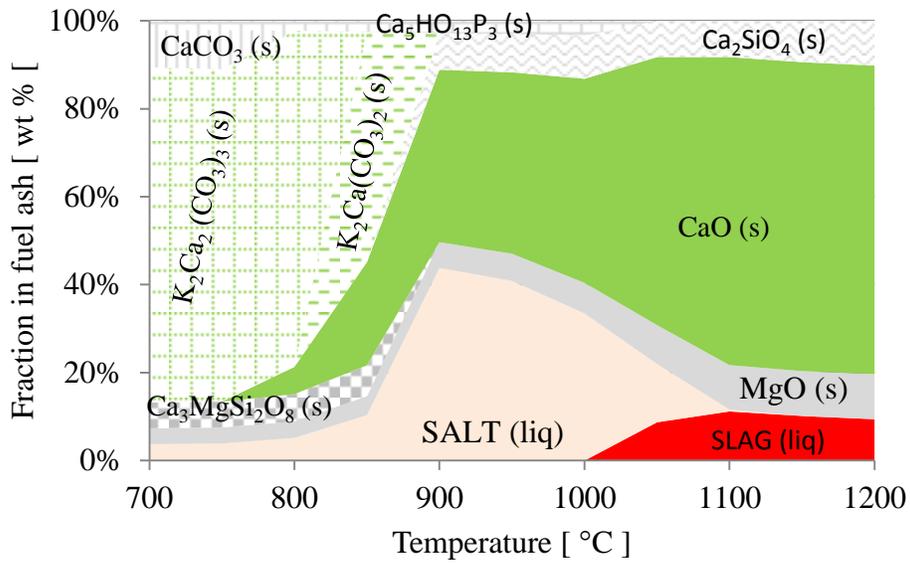


Figure 18. Predicted composition of the condensed phase of the fuel ash under combustion conditions.

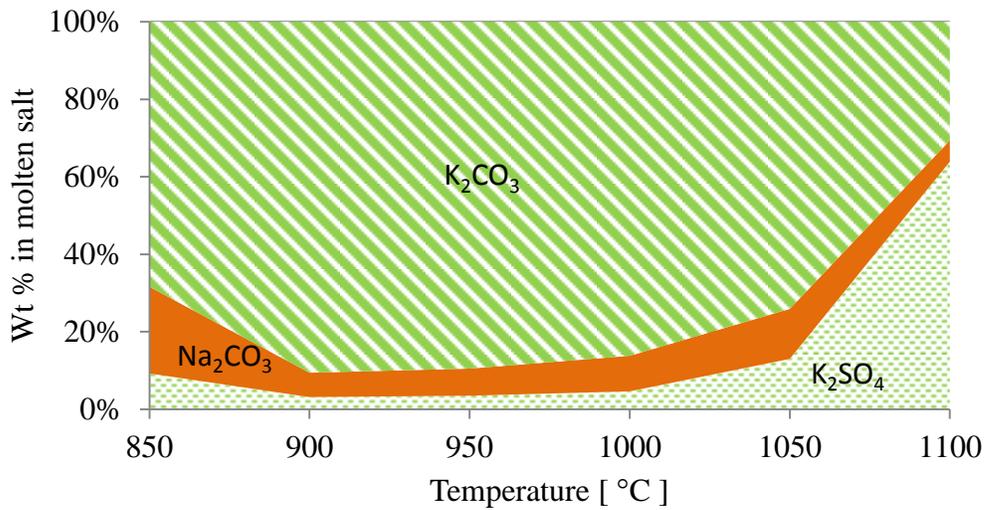


Figure 19. Composition of the molten salts in the fuel ash under gasification conditions.

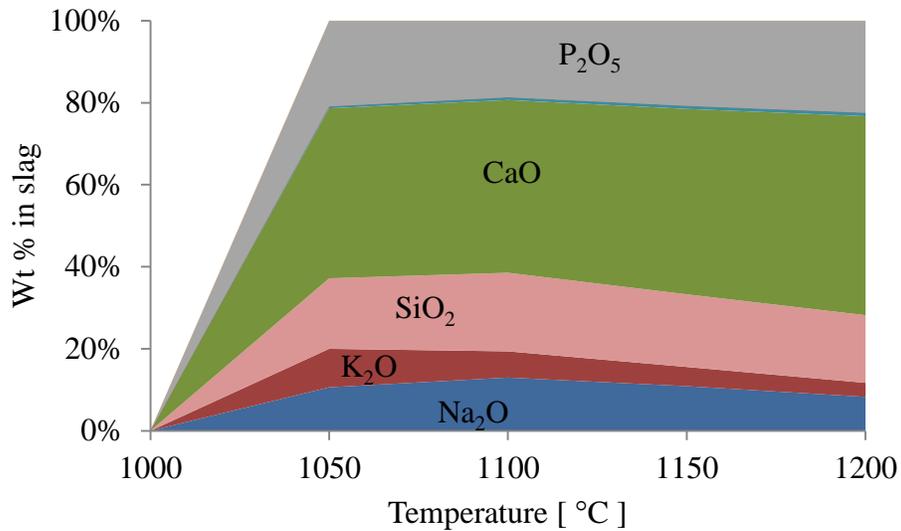


Figure 20. Composition of the molten oxides (slag) in the fuel ash under combustion conditions.

#### 4.4 Summary of the MAIN pathways for the transformation and release of K, Cl, and S

Combining the results obtained in the present work and earlier findings in the literature, the likely MAIN pathways for the transformation and release of S, Cl, and K during thermal conversion of biomass under conditions relevant to DFBG are summarized in Figure 21, Figure 22, and Figure 23 respectively.

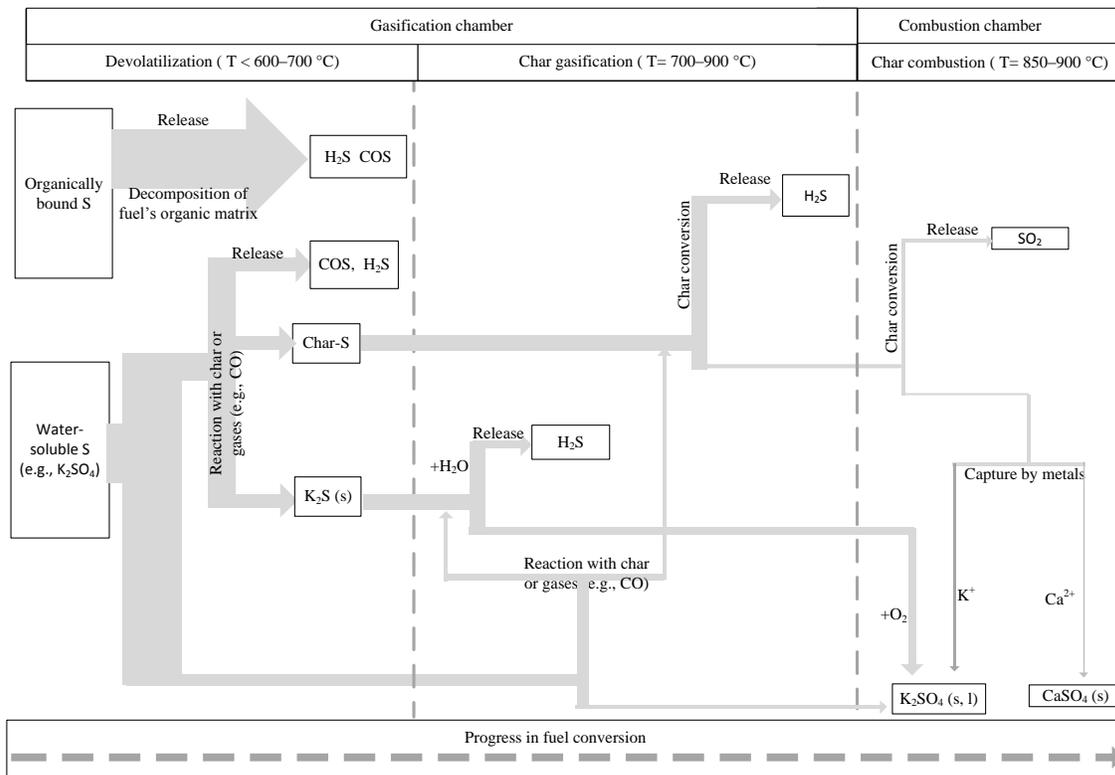


Figure 21. Likely MAIN pathways for the transformation and release of S from biomass under dual fluidized bed gasification conditions.

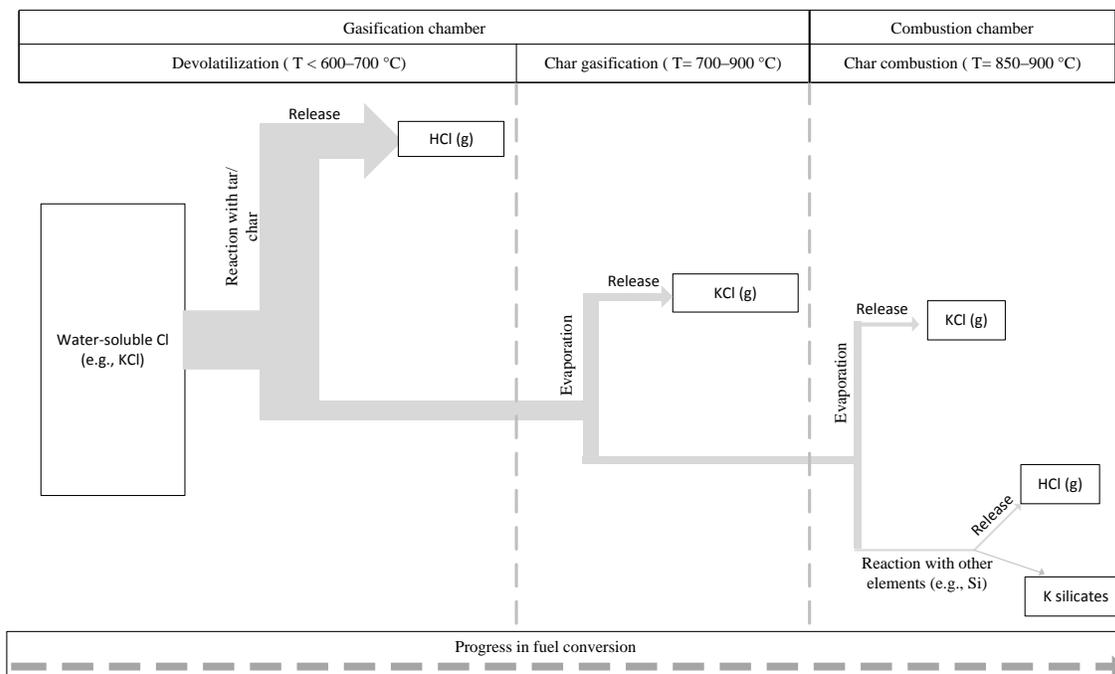


Figure 22. Likely MAIN pathways for the transformation and release of Cl from biomass under dual fluidized bed gasification conditions.

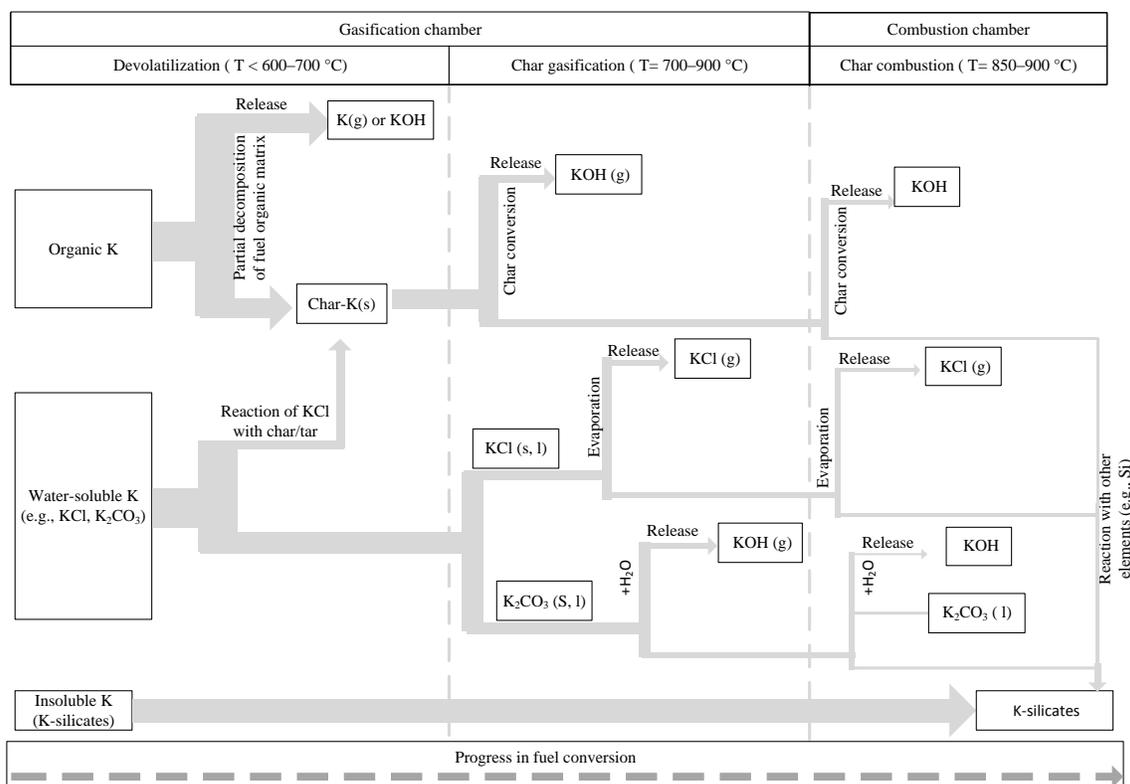


Figure 23. Likely MAIN pathways for the transformation and release of K from biomass under dual fluidized bed gasification conditions.

Based on the experimental results obtained for the fuels and operational conditions applied in the present work, the distributions of K, Cl, and S during DFBG of biomass are likely to follow the scheme presented in Figure 24, provided that: (1) the operational temperatures in the two reactors are in the range of 800°–900°C; (2) the fuel particles undergo complete devolatilization in the gasification chamber before they are circulated to the combustion chamber; (3) the fuel particles reside in the gasification chamber for 2–3 minutes (this is within the retention time for the fuel particles in gasification chambers reported in the literature; see the *Theory* section); and (4) complete combustion of the char is achieved in the combustion chamber. Most of the Cl and S follow the product gas out of the gasification chamber, while most of the K follows the char to the combustor.

In the gasification chamber, the extent of S release is mainly dependent upon the fraction of S that is organically bound in the virgin fuel, as this fraction is more likely than the other forms of S in the fuel matrix to be completely released to the gas phase (see Figure 21). The residual S in the char may not be entirely released to the gas phase in the combustion chamber, as it can be partially retained by the alkali and alkaline-earth metals (e.g., K and Ca) (see Figure 21).

The release of Cl to the gas phase in the gasification chamber mainly relies on the degree of char conversion at the applied temperature. This in turn depends on the reactivity of the char from the parent fuel, which is influenced by the heating rate of the fuel during devolatilization. The higher the level of char conversion, the less compact (more porous) the fuel matrix will be, and

the lower the resistance to the evaporation of KCl from the fuel matrix. In the combustion chamber where the char is completely combusted, complete release of the residual Cl is plausible. This occurs either through the evaporation of KCl or the reaction of KCl with other ash-forming elements, such as Si, leading to the release of Cl as HCl (see Figure 22).

Compared to the release of Cl and S, the release of K in both chambers is more influenced by the ash composition and the speciation of K in the fuel matrix. In the gasification chamber, the Cl/K molar ratio and the fraction of organically bound K in the applied fuel significantly influence the release of K to the gas phase. The higher these parameters, the more likely K will be released to the gas phase. In the combustion chamber, where the remaining organic materials in the char are combusted, the ash-forming elements are likely to have better contacts among themselves than in the gasification chamber. Therefore, reactions of K with other ash-forming elements (e.g., Si) are likely to influence the release of K to the gas phase (see Figure 23).

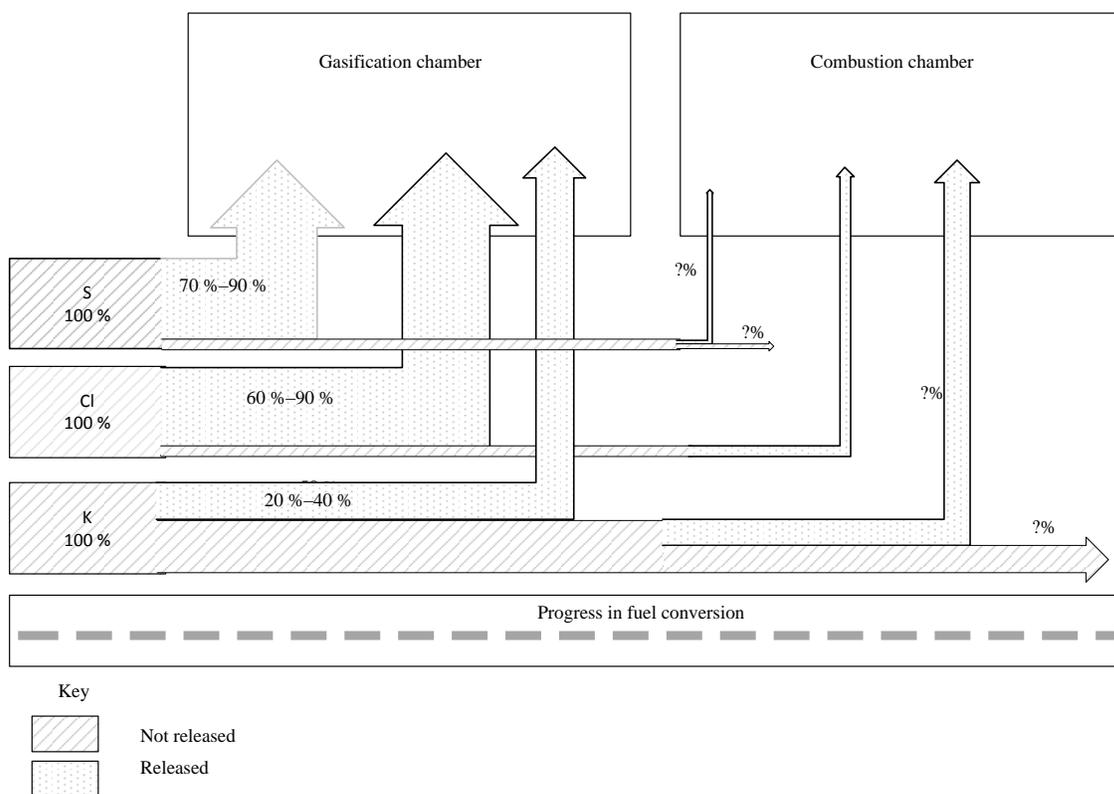


Figure 24. Likely distributions of K, Cl, and S release from biomass during dual fluidized bed gasification.

## 5 Main conclusions

The main conclusions drawn from this work are:

### 1. For Cl and K:

- Cl is released independently of K at temperatures in the range of <math>600^{\circ}\text{C}</math>–- The char generated from the devolatilization of biomass pellets is very compact (having negligible porosity). As a result, the release of Cl and K through the evaporation of their volatile salts (such as KCl) from the char matrix are significantly limited by pore diffusion at temperatures  $>700^{\circ}\text{C}</math>. Below this temperature, the compactness of the fuel has a negligible effect on the release of Cl and K, since their release is associated with the thermal decomposition of the fuel, which is heat transfer-controlled.$
- During char gasification, steam renders the char less compact by widening the existing pores and creating new pores in the char, especially at temperatures  $>800^{\circ}\text{C}</math>, at which temperatures the extent of char conversion is high. As a result, the resistance to diffusion of volatile salts out of the char matrix decreases. Consequently, the release of volatile salts is facilitated. The conversion of char with steam also leads to the release of char-bound K. Therefore, operational conditions that influence the char conversion rate would also influence the release of K and Cl.$
- While most of the Cl in virgin biomass follows the raw gas out of the gasification chamber, most of the K follows the char to the combustion chamber. Further release of K occurs during char combustion. Therefore, unless the released K is captured and recirculated to the gasification chamber, where it could be useful as a catalyst for tar and char conversion, it will follow the flue gas out of the combustion chamber.
- The release of Cl and K follows a similar pattern during char combustion and char gasification. The more porous the char prior to combustion, the higher the fraction of char combusted, and the higher the release of Cl and K.
- While the ash composition and the speciation of K in biomass fuels appear to influence the release of K, they have no impact on the release of Cl.

### 2. S

- In contrast to ash composition, the speciation of S in biomass fuels significantly influences the extent to which S is released to the gas phase during gasification. The organic form of S is more easily released to the gas phase than are the other forms of S. Therefore, the speciation of S in biomass fuels provides information that allows one to judge to what extent S could be released from the fuel to the gas phase during thermal conversion.

- Most of the S in the virgin biomass follows the raw gas out of the gasification chamber, whereas char that is almost S-free is circulated to the combustion chamber. Since sulfation of alkali-chlorides is a means to capture and recirculate the K that is released in the combustion chamber to the gasification chamber, the very low amount of S in the char circulated to the combustion chamber means that most of the K released in the combustion follows the flue gas out of the combustion chamber. As a result, less K becomes available to act as a catalyst in the process.

## 6 Future work

The present work reveals that most of the K in the virgin biomass follows the char to the combustion chamber during DFBG. For optimization of the chemical efficiency of the gasification process, it is important to recirculate some of the K in the combustion chamber to the gasification chamber in a chemical form (e.g.,  $K_2CO_3$ ,  $K_2SO_4$ ) that can catalyze gasification reactions (e.g., of tar and char). Therefore, future studies should look at ways to: (1) limit the incorporation of K into silicate structures (through, for example, the application of Si-free or S-lean bed materials); and (2) limit the ability of the gas-phase K to follow the flue gas out of the combustion chamber.

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