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# Numerical study of HCl and SO<sub>2</sub> impact on potassium emissions in pulverized-biomass combustion

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## Abstract

The potassium vapor released during the combustion of biomass are known to result in serious ash deposition, fouling and corrosion issues of biomass furnaces. To develop potassium control technologies to mitigate these issues and achieve clean utilization of biomass fuel, a better understanding of the fundamental formation and transformation mechanisms of potassium in biomass combustion is essentially required. In the present study, potassium emissions during pulverized-biomass combustion, for the first time, have been simulated in both one-dimensional (1D) premixed/diffusion flames of the biomass volatile and an early-stage two-dimensional (2D) pulverized-biomass flame. The properties of corn straw are used. The volatile-gas combustion is described by the DRM22 skeletal mechanism, while the homogeneous reaction of potassium species is modeled using a detailed mechanism encompassing the elements K, C, H, O, Cl and S. The initial species of K, Cl and S in the volatile gas is set to be KOH, HCl and SO<sub>2</sub>, respectively. The transformation characteristics of the potassium species are numerically investigated in both the 1D and 2D flames. Results show that KOH is the most significant potassium product under fuel-lean,

28 stoichiometric and fuel-rich conditions, while the productions of sulfurous and chloric potassium  
29 species are secondary. Parametric studies with HCl, SO<sub>2</sub> or both species replaced with N<sub>2</sub> in volatile  
30 gas are then performed to study their impacts on potassium emission characteristics in both the 1D  
31 and 2D flames. The results indicate that HCl has a stronger ability to react with potassium species  
32 than SO<sub>2</sub>.

33 *Keywords:* Pulverized-biomass combustion; Emission; Potassium chemistry; Alkali metal; HCl; SO<sub>2</sub>

34

## 35 **1. Introduction**

36 As a renewable fuel source, biomass resources have been utilized to supply 10–15% of the  
37 worldwide energy consumption [1], especially with an increasing application in the production of  
38 thermal power. However, advanced biomass utilization is significantly limited by severe ash  
39 formation and deposition problems resulting from alkali metal issues [2]. Potassium (K) is usually  
40 rich in biomass, since it is an important element for plants. The potassium vapor released during the  
41 combustion of biomass is easy to condense on heat transfer surfaces and form an initial sticky layer,  
42 which then captures fly ash and therefore results in rapid ash deposition [3, 4]. In addition, potassium  
43 also reacts with chlorine and sulfur species to form complex compound, which leads to serious  
44 fouling and corrosion issues [5, 6]. Thus, understanding the fundamental formation and  
45 transformation mechanisms of potassium in biomass combustion is essential for the development of  
46 potassium control technologies and a better utilization of this renewable fuel [7-9].

47 Experimental research on the release and reacting dynamics of potassium evolves from offline  
48 sampling techniques to online measurement methods using laser diagnostics [2, 10-12].  
49 Non-intrusive, time-resolved laser techniques, e.g., tunable diode laser absorption spectroscopy

50 (TDLAS) [13], collinear photo-fragmentation atomic absorption spectroscopy (CPFAAS) [14] and  
51 laser induced fragmentation fluorescence (ELIF) [15], can directly capture the dynamic release  
52 process of potassium during biomass combustion. In our recent study [16], the release of atomic and  
53 elemental potassium from a burning biomass pellet has been quantitatively measured via planar  
54 laser-induced fluorescence (PLIF) and multi-point laser-induced breakdown spectroscopy (LIBS)  
55 methods.

56 On the modeling side, Zhang et al. [17] proposed an one-step Arrhenius potassium release  
57 model during the combustion of a pinewood pellet. In our recent work [16], a two-step model was  
58 developed to describe the potassium release during both the pyrolysis and char burnout stages of two  
59 biomass samples, based on simultaneous measurements of the pellet-surface temperature, pellet  
60 diameter and potassium release of a burning biomass pellet. Since the pellet diameter and burnout  
61 time of biomass in these studies are on the same order of magnitude as in a typical circulating  
62 fluidized bed (CFB) boiler, these potassium release models are suitable for CFB combustion [18].  
63 Potassium release models for pulverized-biomass combustion are still required to be developed.

64 Considering the post-release homogeneous reactions of alkali species, it has been found that the  
65 main alkali species are atomic K/Na, KOH/NaOH and KCl/NaCl in chemical equilibrium of  
66 post-combustion gases [19], which can be well predicted by thermodynamic equilibrium calculation,  
67 e.g., [18-20]. A detailed chemical reaction mechanism for alkali species has been proposed by  
68 Glarborg and Marshall [21], and validated with experimental data on sulfation of potassium chlorides.  
69 However, the numerical investigation on reaction dynamics of alkali species in turbulent reacting  
70 flows is still quite limited. Most of the relevant research employs Reynolds-averaged Navier-Stokes  
71 (RANS) simulation (e.g. [22, 23]) with simplified alkali reaction mechanisms to study the response

72 of potassium in biomass combustion.

73 With the rapid increase of computing capacity in recent years, computational fluid dynamics  
74 (CFD) approaches for multi-phase flows are evolving towards high-fidelity methods, i.e., direct  
75 numerical simulation (DNS, e.g., [24-26]) and large-eddy simulation (LES, e.g. [27-34]). The two  
76 high-fidelity methods have shown advantages over RANS on the prediction of local gas temperature  
77 and species distributions. Our previous work [26, 34] on pulverized-coal combustion demonstrated  
78 that DNS and LES can provide detailed physical insights into complex multi-phase reacting flow  
79 dynamics and the homogeneous evolution of alkali species.

80 In sum, the reaction dynamics of potassium species in pulverized-biomass combustion have not  
81 been fully revealed by previous studies. In the present work, the responses of potassium species to  
82 one-dimensional (1D) premixed/diffusion flames of biomass volatile are firstly investigated. Then,  
83 the transformation dynamics of potassium species in a two-dimensional (2D) early-stage  
84 pulverized-biomass flame are numerically studied, excluding char combustion. **Information about the  
85 major potassium product under various conditions and the comparison between the impacts of HCl  
86 and SO<sub>2</sub> on potassium conversion are revealed, which could potentially benefit the biomass  
87 combustion community.** The full detailed potassium mechanism including the elements K, C, H, O, S  
88 and Cl proposed by Glarborg and Marshall [21] is utilized to model the potassium reactions during  
89 the simulation. It should be noted that Glarborg and Marshall [21] have carefully validated their  
90 detailed potassium mechanism against the experimental results of the homogeneous sulfation of  
91 potassium chloride at combustion conditions. **The readers might notice that there exists a newer  
92 version of potassium mechanism by Hindiyarti et al. [35], which includes additional sulfation  
93 pathways of potassium to mainly improve the prediction of the mechanism at lower temperatures**

94 [36]. However, since the present study focus on the potassium transformation under combustion  
 95 conditions, thus at rather high temperature levels, the original version of the mechanism [21] is used  
 96 to save the computational cost.

97

## 98 2. One-dimensional premixed/diffusion flames of biomass volatile

99 The reaction dynamics of potassium species in 1D premixed/diffusion flames of biomass  
 100 volatile are studied. The volatile is released from corn straw [16], for which the chemical analysis  
 101 data is shown in Table 1. The combustion of biomass volatile is modeled by the previously validated  
 102 DRM22 skeletal mechanism involving 22 chemical species and 104 elementary reactions, which is  
 103 proposed by Kazakov and Frenklach [37]. The bio-chemical percolation devolatilization (bio-CPD)  
 104 model [38-40] is used to preliminary obtain the compositions of the volatile fuels and in which the  
 105 Tar species is replaced by  $C_2H_2$  [32]. Then the obtained compositions are adjusted to fulfill the  
 106 elemental mass conservation and the lower heating value of the corn straw, as in [30, 33, 34]. The  
 107 final volatile compositions used in the present study is shown in Table 2.

108

109

Table 1. Chemical analyses of corn straw.

<i>Proximate analysis (wt%)</i>				<i>Ultimate analysis (wt%)</i>				
$M_{ad}$	$A_{ad}$	$V_{ad}$	$FC_{ad}$	$C_{daf}$	$H_{daf}$	$N_{daf}$	$S_{daf}$	$O_{daf}$
11.6	7.9	64.2	16.3	43.9	4.5	1.8	0.4	49.3
<i>Ash analysis (wt%)</i>							$Cl_{ad}$	$K_{ad}$
$SiO_2$	$Al_2O_3$	$Fe_2O_3$	$CaO$	$MgO$	$K_2O$	$Na_2O$	(mg/g)	(mg/g)
47.52	5.64	1.04	4.51	12.6	7.87	1.97	1.34	13.1

110

111 Table 2. Modeled volatile-gas compositions of corn straw.

Hydrocarbon volatile compositions (mass fractions)					
CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CO	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
0.0322	0.1805	0.2536	0.0215	0.1853	0.3024
Non-hydrocarbon volatile compositions (mass fractions)					
KOH	HCl	SO <sub>2</sub>			
0.0147	0.0018	0.0080			

112

113 Similar as previous studies on sodium emissions in coal combustion [41], KOH is set as the  
114 initial species of K, while HCl and SO<sub>2</sub> are set as the initial species of Cl and S, respectively.  
115 According to our previous experimental data [16], the percentage of potassium which is releasable  
116 during the biomass pyrolysis stage is set to 58.1%. Since the release of chlorine and sulfur has not  
117 been measured, their releasable proportions during the pyrolysis are both set to 87.3%, the volatile  
118 yields ratio predicted by the bio-CPD model [38], based on the consideration chlorine and sulfur can  
119 be fully released during the pyrolysis and char stages of biomass combustion. Mass fractions of  
120 KOH, HCl and SO<sub>2</sub> in the volatile can then be obtained, as shown in Table 2. The detailed alkali  
121 mechanism developed by Glarborg and Marshall [21] includes elementary reactions over Na, K, C,  
122 H, O, S and Cl. Here, the element Na is not considered, which leads to a detailed mechanism of  
123 potassium involving 35 species and 153 elementary reactions.

124 To study the potassium reactions under the premixed condition, a 1D freely propagating  
125 premixed flame of the biomass volatile is simulated using CANTERA [42]. The inlet volatile-air

126 mixture temperature is 300 K and three equivalence ratios, i.e.,  $\phi = 0.5, 1.0$  and  $2.0$ , of the mixture  
127 are considered. To investigate the diffusion condition, a 1D counterflow diffusion volatile flame is  
128 simulated also using CANTERA [42]. The mass flow rates of the biomass volatile and air inlets are  
129  $0.024$  ( $\text{kg}/\text{m}^2 \text{ s}$ ) and  $0.072$  ( $\text{kg}/\text{m}^2 \text{ s}$ ), respectively, while their temperatures both are 300 K. Four  
130 configurations with HCl and/or  $\text{SO}_2$  replaced by  $\text{N}_2$  are set up to study the effects of HCl and  $\text{SO}_2$  on  
131 potassium reaction characteristics. In total 16 cases are simulated. The grid is limited to 250 points  
132 while the length of the 1D computational domain for premixed and diffusion condition is 1.0 m and  
133 3.0 cm, respectively.

134

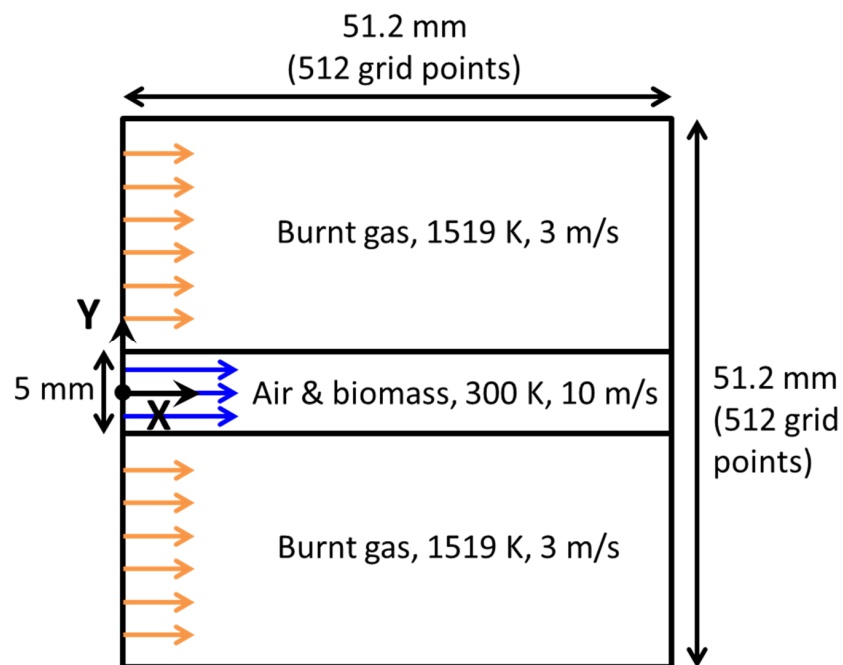
### 135 **3. Pulverized-biomass flame configuration and numerics**

136 A two-dimensional temporally evolving pulverized-biomass jet flame is studied (Fig. 1). The  
137 computational domain has physical dimensions of 51.2 mm in both the streamwise ( $x$ ) and spanwise  
138 ( $y$ ) directions. A uniform mesh of  $h = 100 \mu\text{m}$  is used, which has been demonstrated to be able to  
139 resolve the flame structure [26]. Initially, high-speed primary air (10 m/s, 300 K) laden with  
140 pulverized-biomass particles is set up for  $|y| < 2.5$  mm, and the 902 biomass particles follow a  
141 random uniform distribution. The initial density of a particle is set to  $550 \text{ kg}/\text{m}^3$  [43] and its  
142 diameter is  $25 \mu\text{m}$ , following a mono-disperse diameter distribution. The particle diameter used  
143 here might be finer than common diameters of pulverized-biomass employed in other studies, e.g.,  
144  $60\text{--}200 \mu\text{m}$  [12, 44]. However, the particle diameter cannot be larger in order to fulfill the grid  
145 resolution required by DNS and the point-particle assumption. On the other hand, this fine diameter  
146 of  $25 \mu\text{m}$  can be achieved with torrefied biomass [44]. Same as the 1D simulations, properties of  
147 corn straw [16] are employed (Table 1). Surrounding the primary air, a hot coflow (3 m/s, 1519 K)



148 is introduced with a composition and temperature of the burnout gas of the biomass volatile at an  
 149 equivalence ratio of 0.45. Periodic boundary conditions are employed in all directions. Turbulent  
 150 fluctuations of 0.05 m/s are initially put within the shear layers between the primary air and the  
 151 coflow, for the purpose of facilitating the jet development. The parameters of the present  
 152 configuration are chosen according to our previous study on pulverized-coal flames [26]. Two-way  
 153 coupling between the gas and particle phases are considered and biomass particles are treated as  
 154 point sources.

155 Biomass pyrolysis, including K/Cl/S release, volatile-gas combustion and K/Cl/S reactions are  
 156 simulated. Heterogeneous reaction of solid char is not considered, since its contribution has been  
 157 demonstrated to be weak in small-scale pulverized-coal flames [32, 34, 45]. The char content of  
 158 biomass is much lower than that of coal (see Table 1). Hence, the contribution of char combustion  
 159 in the present pulverized-biomass flame should be even weaker and therefore can be safely ignored.



160  
 161 Figure 1. Schematic diagram of computational configuration. Periodic boundary conditions in all  
 162 directions

### 163 3.1. Gas phase modeling

164 The governing equations for the gas and biomass-particle phases are solved in the Eulerian and  
 165 Lagrangian frameworks, respectively, using a low-Mach-number in-house code [26, 30, 33, 34]. The  
 166 conservation equations for mass, momentum, species and temperature solved for the gas phase are:

$$167 \quad D_t \rho = \dot{S}_{m,p} \quad (1)$$

$$168 \quad D_t (\rho u_i) = -\partial_i p + \partial_j \tau_{ij} + \dot{S}_{mom,p,i} \quad (2)$$

$$169 \quad D_t (\rho Y_n) = \partial_j (\rho D_n \partial_j Y_n) + \dot{\omega}_{Y,n} + \dot{S}_{Y,p,n} \quad (3)$$

$$170 \quad D_t (\rho T) = \partial_j \left( \frac{\lambda}{C_{P,g}} \partial_j T \right) + \frac{\lambda}{C_{P,g}^2} \partial_j C_{P,g} \partial_j T + \dot{\omega}_T + \dot{S}_{T,p} + \dot{S}_{T,R} \quad (4)$$

171 where  $D_t(\Phi) = \partial_t(\Phi) + \partial_j(\Phi u_j)$ ,  $\partial_j \equiv \partial x_j$ ,  $\rho$  is gas density (kg/m<sup>3</sup>),  $u_i$  is gas velocity (m/s),  $Y_n$  is the  
 172 mass fraction of the  $n$ th chemical species,  $T$  is gas temperature (K). The pressure is denoted by  $p$ , and  
 173  $\tau_{ij} = \mu(\partial_j u_i + \partial_i u_j - 2/3 \partial_k u_k \delta_{ij})$  is the viscous stress tensor.  $D_n$  is the molecular mass diffusivity  
 174 coefficient (m<sup>2</sup>/s),  $C_{P,g}$  and  $\lambda$  are the specific heat capacity (J/kg K) and thermal conductivity (W/m K)  
 175 of the gas mixture, respectively.  $\dot{S}_{m,p}$ ,  $\dot{S}_{mom,p,i}$ ,  $\dot{S}_{Y,p,n}$  and  $\dot{S}_{T,p}$  are the two-way coupling terms  
 176 considering the effects of particles on the gas.  $\dot{\omega}_{Y,n}$  is the source term due to homogeneous  
 177 chemical reactions. In the temperature equation, the radiative heat transfer ( $\dot{S}_{T,R}$ ), heat exchange  
 178 between the gas phase and biomass particles ( $\dot{S}_{T,p}$ ), and thermal effects of homogeneous reactions  
 179 ( $\dot{\omega}_T$ ) are taken into consideration. In the present study, the Lewis number (Le = 1.0) and Prandtl  
 180 number (Pr = 0.7) are assumed to be constant.

181

### 182 3.2. Particle phase modeling

183 The momentum equation of a Lagrangian biomass particle is:

$$184 \quad d_t u_{p,j} = f(u_j - u_{p,j}) / \tau_p \quad (5)$$

185 where  $u_{p,j}$  is the particle velocity (m/s). The dynamic response time (s) of a particle is  
 186  $\tau_p = \rho_p d_p^2 / 18\mu$ , where  $\rho_p$  is the density of the particle (kg/m<sup>3</sup>), and  $d_p$  is its diameter (m).  $f$  is the  
 187 drag coefficient, which considers both the high particle Reynolds number effects and the blowing  
 188 effects of volatiles at the particle surface [46].

189 The particle temperature equation can be written as:

$$190 \quad d_t T_p = (Q_{conv} + Q_{rad} + Q_{dev}) / (m_p C_{P,p}) \quad (6)$$

191 where  $T_p$  is the temperature of the particle (K),  $m_p$  its mass (kg),  $C_{P,p}$  its specific heat capacity (J/kg  
 192 K). The heat transfer terms by convection, radiation, and pyrolysis (devolatilization) are  
 193  $Q_{conv} = Nu C_{p,g} m_p (T - T_p) / 3 Pr \tau_p$ ,  $Q_{rad} = \varepsilon_p \pi d_p^2 \sigma (T_R^4 - T_p^4)$ , and  $Q_{dev} = -\Delta h_{dev} dm_{vol} / dt$ ,  
 194 respectively. Nu is the Nusselt number and computed by the Ranz-Marshall correlations [47]. The  
 195 radiation temperature (K) is calculated by  $T_R = (G/4\sigma)^{1/4}$ , where  $G$  is the incident radiation (W/m<sup>2</sup>)  
 196 obtained via the Discrete Ordinates Method (DOM) [48].  $\sigma$  is the Stefan-Boltzmann constant ( $5.67 \times$   
 197  $10^{-8}$  W/m<sup>2</sup> K<sup>4</sup>).  $\varepsilon_p$  is the particle emissivity and here is set to 0.9 [39]. The  
 198 weighted-sum-of-the-gray-gases model (WSGGM) [49] is employed to estimate the gas absorption  
 199 coefficient. Finally, the mass loss rate of each biomass particle ( $dm_p/dt$ ), due to the pyrolysis, is  
 200 predicted by the single first-order reaction model (SFOM) proposed by Badzioch and Hawskley [50].  
 201 The kinetic parameters of the SFOM pyrolysis model, i.e.,  $A_v$  ( $2.5 \times 10^9$  s<sup>-1</sup>),  $E_v$  ( $11 \times 10^4$  J/mol) and  
 202  $Q_v$  (1.10), have been calibrated by the bio-CPD model [38], as in [30, 33, 34].

203

### 204 3.3. Gas phase chemistry

205 Same as in Section 2, the oxidization of hydrocarbon biomass volatile and the reactions of  
 206 potassium species are modeled by the DRM22 skeletal mechanism [37] and the detailed alkali

207 reaction mechanism [21], respectively. The compositions of the volatile gas can be found in Table 2,  
208 including the non-hydrocarbon compounds of potassium, sulfur and chloride.

209 The release rate of potassium from biomass particles is assumed to be proportional to the  
210 volatile release rate [26, 34], since the potassium vapor generated inside the porous structure of a  
211 biomass particle will be transported outward by the volatile yielded during the pyrolysis stage.  
212 Besides, in our previous study the alkali release from a coal particle was found proportional to its  
213 burnout during the early combustion stage [18]. Similarly, the release rates of sulfur and chlorine are  
214 also assumed to be proportional to the volatile release rate here.

215

#### 216 3.4. Numerical schemes

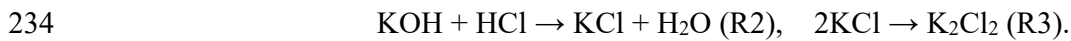
217 The numeric of our in-house code is based on an approach previously validated for both DNS  
218 and LES [51, 52]. A second-order Crank-Nicolson scheme is employed for the time advancement. A  
219 second-order central difference scheme is applied to all terms in the momentum equation and the  
220 scalar diffusion terms in the species and temperature equations. In order to secure the scalar  
221 boundedness, a Quadratic Upstream Interpolation for Convective Kinematics (QUICK) scheme is  
222 used for the scalar advection terms in the species and temperature equations. An Alternating  
223 Direction Implicit (ADI) approach has been adopted, and semi-implicit tridiagonal/pentadiagonal  
224 equations are solved separately for each direction. A second-order Runge-Kutta (RK2) scheme is  
225 employed to explicitly advance the particle equations.

226

## 227 4. Results and discussion

### 228 4.1. Transformation characteristics of potassium species in 1D premixed flame

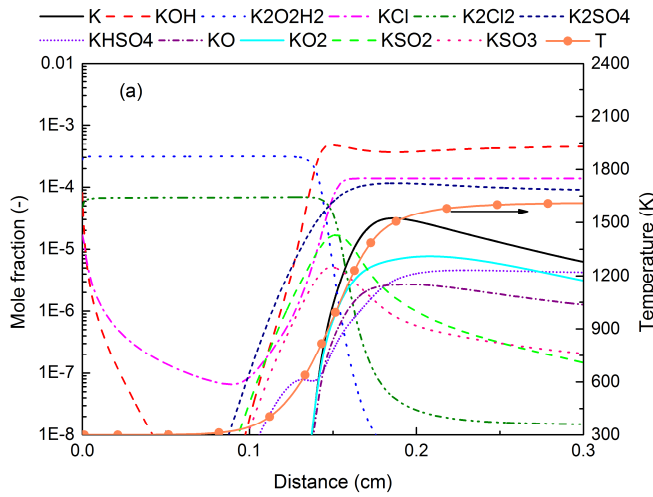
229 The reactions of potassium species in 1D premixed volatile flames have been investigated for  
230 three equivalence ratios ( $\phi = 0.5, 1.0$  and  $2.0$ ), representing fuel-lean, stoichiometric and fuel-rich  
231 conditions. From Fig. 2, it can be found that the concentration of KOH rapidly decreases in the initial  
232 unburned region with  $T = 300$  K, which should be attributed to the following two reaction paths:



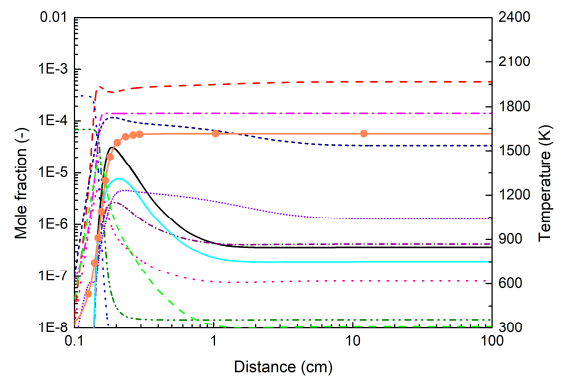
235 First, KOH is consumed to generate  $\text{K}_2\text{O}_2\text{H}_2$  via Reaction R1. In addition, KOH also reacts with HCl  
236 in the volatile as Reaction R2, and  $\text{K}_2\text{Cl}_2$  is subsequently formed through Reaction R3.  $\text{K}_2\text{O}_2\text{H}_2$  and  
237  $\text{K}_2\text{Cl}_2$  are the two major potassium species in the initial unburned region. **It should be noted that at**  
238 **low temperature, the potassium is in condensed form, possibly as aerosol. Hence, the results in the**  
239 **initial unburned region of the canonical laminar flame are questionable. However, this issue will get**  
240 **relieved in the following investigation of 2D pulverized-biomass flame (Section 4.3) because the**  
241 **potassium is released along with volatile and therefore at much higher temperature.** When the  
242 combustion happens and therefore the temperature increases around Distance of 0.15 cm,  $\text{K}_2\text{O}_2\text{H}_2$   
243 and  $\text{K}_2\text{Cl}_2$  are then decomposed to KOH and KCl, respectively, and further transform to other  
244 potassium species, e.g., K,  $\text{KO}_2$ ,  $\text{KSO}_2$ ,  $\text{KHSO}_4$  and  $\text{K}_2\text{SO}_4$ . In the post-flame region, the potassium  
245 species then gradually evolve towards equilibrium. It can be observed that KOH is the most  
246 significant potassium product ( $\sim 10^3$  ppm) for all the three equivalence ratios, while KCl has the  
247 second highest concentration ( $\sim 10^2$  ppm). The sulfurous potassium species  $\text{K}_2\text{SO}_4$  is found to be the  
248 third major potassium product (34 ppm) under the fuel-lean condition; while under the stoichiometric

249 and fuel-rich conditions, the third major potassium product changes to atomic potassium K (> 60  
 250 ppm). Another minor potassium species,  $\text{KSO}_3\text{Cl}$ , has a maximum concentration less than 0.01 ppm  
 251 during the whole reaction process for all the three equivalence ratios and therefore is not shown in  
 252 the figure.

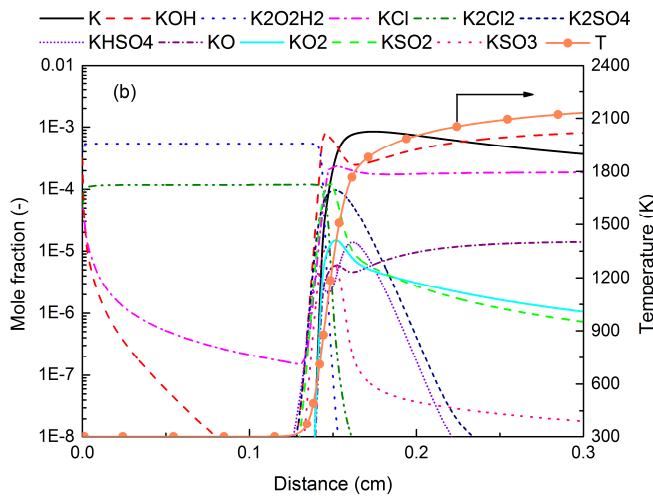
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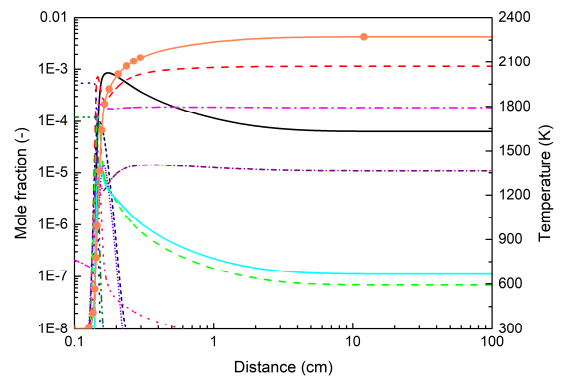
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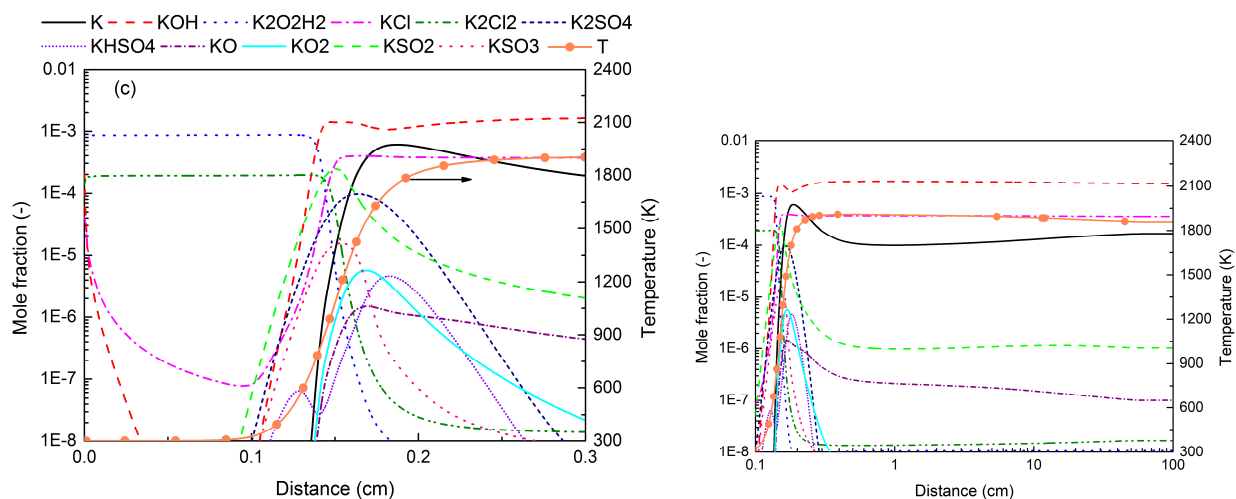
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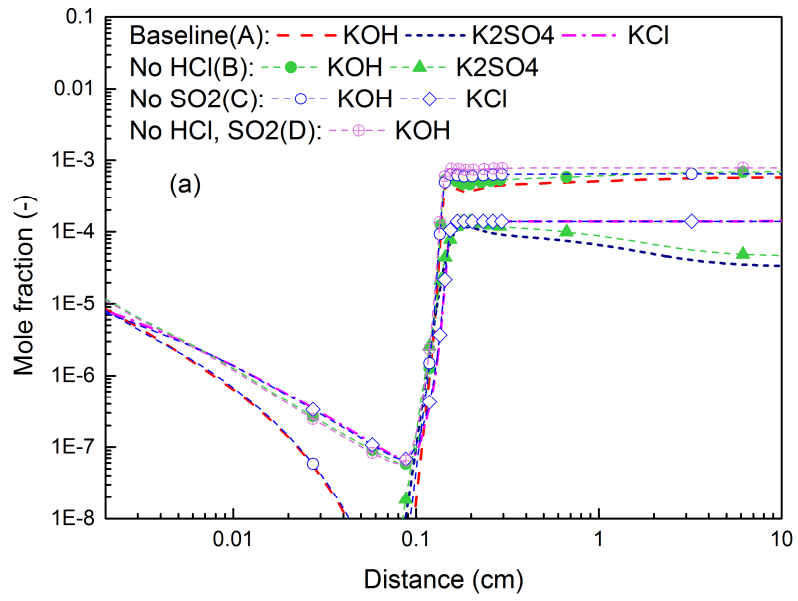
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258  
 259 Figure 2. Potassium species distribution versus distance along the 1D premixed volatile flame at  
 260 equivalence ratio  $\phi = 0.5$  (a),  $\phi = 1.0$  (b) and  $\phi = 2.0$  (c). The heat release zone is zoomed in and  
 261 shown on the left side while the overall flame is shown on the right side.

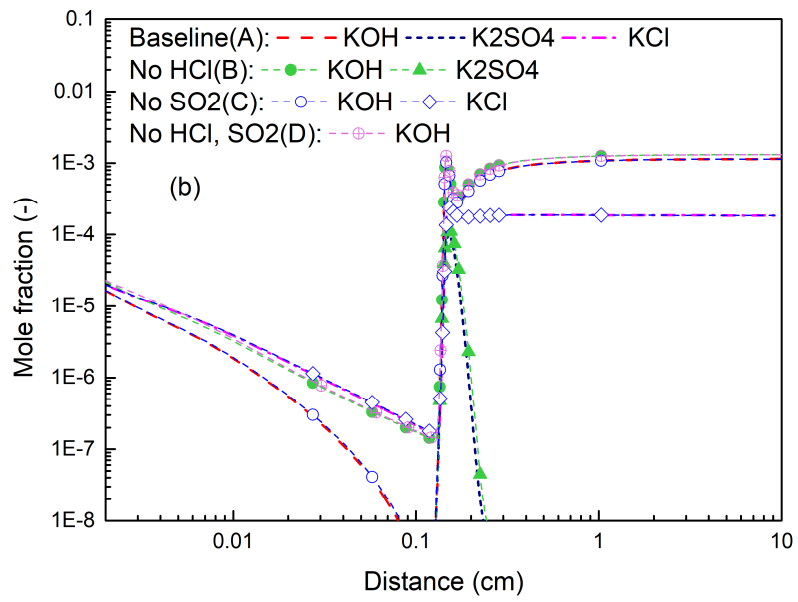
262 To study the effects of HCl and SO<sub>2</sub> on potassium transformation characteristics, three  
 263 additional configurations have been employed, which are Case B (HCl in the volatile is replaced by  
 264 N<sub>2</sub>), Case C (SO<sub>2</sub> in the volatile is replaced by N<sub>2</sub>) and Case D (both HCl and SO<sub>2</sub> in the volatile are  
 265 replaced by N<sub>2</sub>). The original case is referred to as baseline Case A. Three simulations ( $\phi = 0.5, 1.0$   
 266 and 2.0) are performed for each Case A/B/C/D. The comparison of the representative potassium  
 267 species KOH, KCl and K<sub>2</sub>SO<sub>4</sub> is shown in Fig. 3. The profiles are plotted until Distance of 10 cm, as  
 268 it can be found in Fig. 2 that the potassium reactions almost reach equilibrium at this position. KOH  
 269 is found to be the main potassium product for the four cases. When HCl and/or SO<sub>2</sub> is presented, a  
 270 minor part of potassium is transformed to KCl and/or K<sub>2</sub>SO<sub>4</sub>. However, the mole fraction of the  
 271 produced KCl and/or K<sub>2</sub>SO<sub>4</sub> is much lower than that of KOH. Hence, the profiles of KOH are close  
 272 to each other for the four cases in the combustion and post-flame regions.

273



274

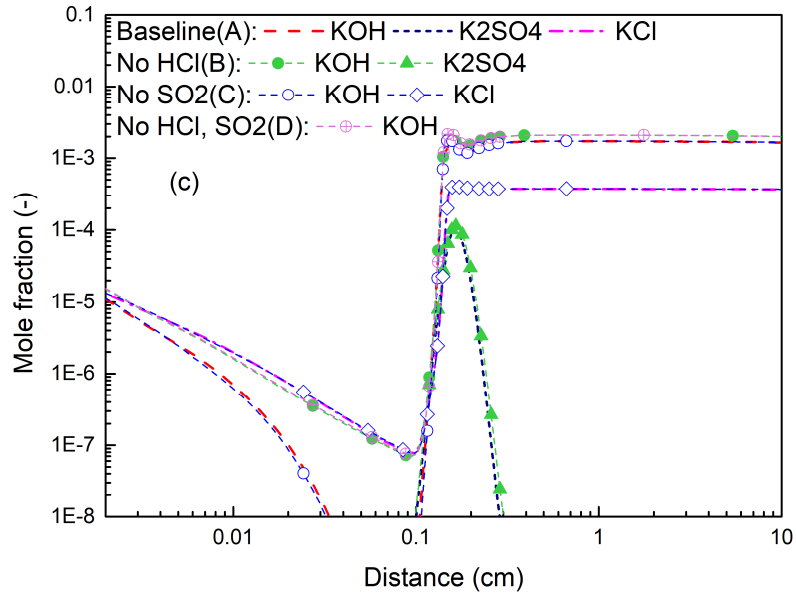
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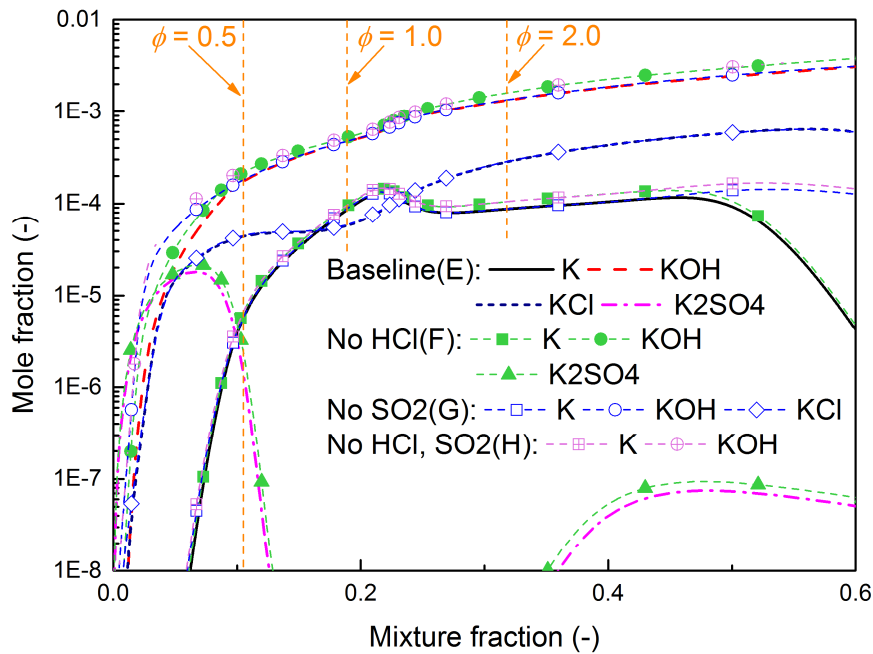


278  
 279 Figure 3. Comparison of potassium species distribution versus distance along the 1D premixed  
 280 volatile flame between Case A (the baseline case), Case B (HCl replaced by N<sub>2</sub>), Case C (SO<sub>2</sub>  
 281 replaced by N<sub>2</sub>) and Case D (both HCl and SO<sub>2</sub> replaced by N<sub>2</sub>) at equivalence ratio  $\phi = 0.5$  (a),  $\phi =$   
 282 1.0 (b) and  $\phi = 2.0$  (c).

283 *4.2. Transformation characteristics of potassium species in 1D diffusion flame*

284 To further investigate the response of potassium species in diffusion flame, other four cases  
 285 have been set up: Case E (the baseline case), Case F (HCl in the volatile is replaced by N<sub>2</sub>), Case G  
 286 (SO<sub>2</sub> in the volatile is replaced by N<sub>2</sub>) and Case H (both HCl and SO<sub>2</sub> in the volatile are replaced by  
 287 N<sub>2</sub>). Comparison among these cases on the representative potassium species K, KOH, KCl and  
 288 K<sub>2</sub>SO<sub>4</sub> is shown in Fig. 4. It may be noted that only the region of the mixture fraction  $Z < 0.6$  are  
 289 shown, because a higher mixture fraction is hardly observed in the following 2D DNS study (see Fig.  
 290 7 below). The mixture fraction could be calculated as  $Z = 1.0 - Y_{N_2}/0.767$ . For the present  
 291 two-stream mixing case of 1D diffusion flame,  $Z = 0$  and  $Z = 1$  indicate the oxidizer and  
 292 biomass-volatile streams, respectively. The positions of  $\phi = 0.5$ , 1.0 and 2.0 in the mixture fraction  
 293 space are also illustrated in Fig. 4. It can be found that in the fuel-lean region the mole fraction of K  
 294 increases rapidly with  $Z$  for all the cases. In the very rich region of  $Z > 0.5$ , the profile of K drops in

295 the cases (E/F) with  $\text{SO}_2$ , which is not observed in the cases (G/H) without  $\text{SO}_2$ . Both KOH and KCl  
 296 show a monotonically increasing trend along with  $Z$ , although the increasing rate get suppressed at  
 297 the stoichiometric condition. For  $\text{Na}_2\text{SO}_4$ , it reaches a concentration of  $\sim 20$  ppm at the fuel-lean  
 298 region around  $Z = 0.05$ , but becomes minor ( $< 0.1$  ppm) for all the other conditions. Similar as in the  
 299 previous premixed flames, the profiles of KOH in the four cases here are also close to each other,  
 300 because the productions of sulfurous and chloric potassium species are limited.  
 301

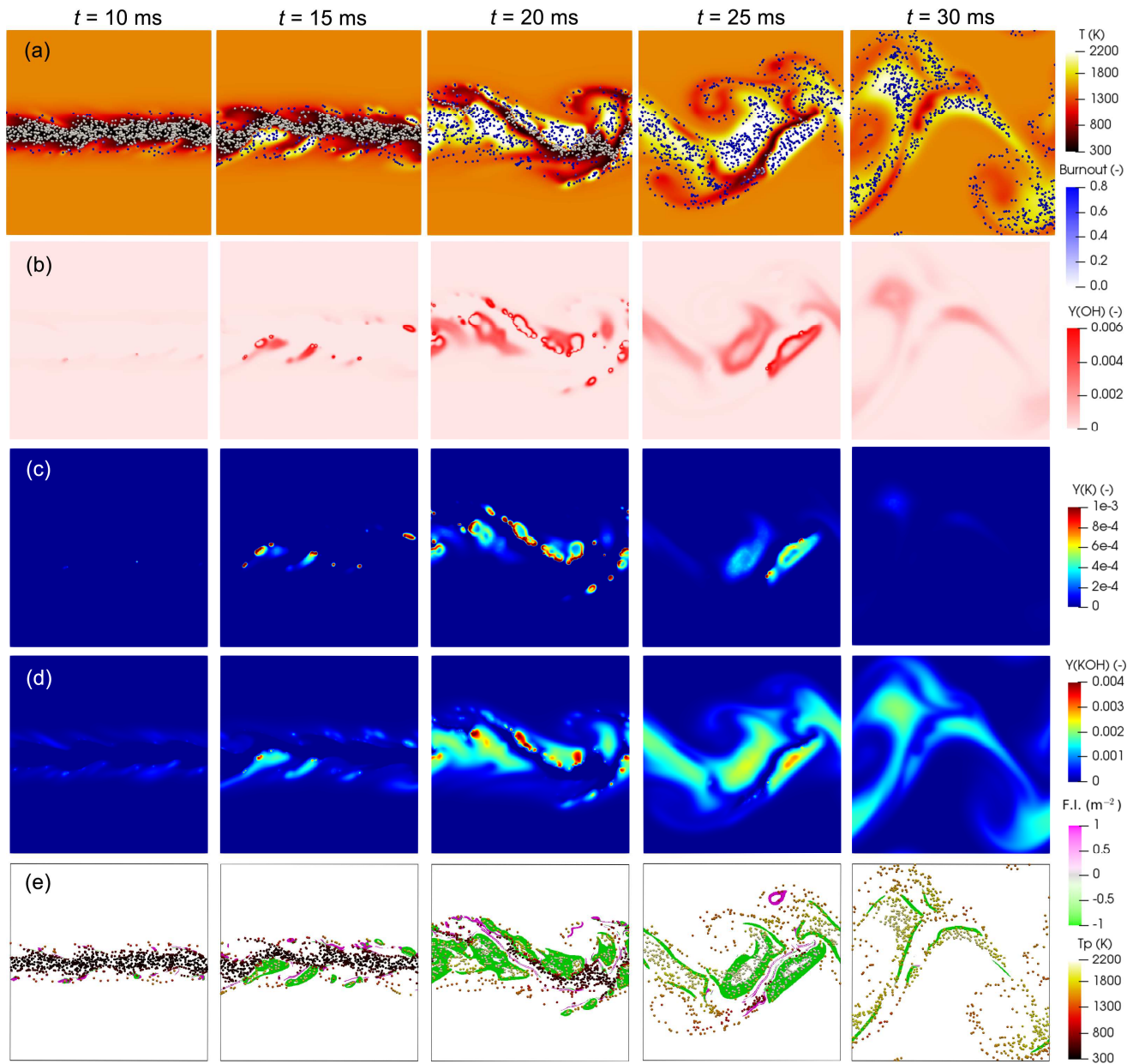


302  
 303 Figure 4. Comparison of potassium species distribution in the mixture fraction space of the 1D  
 304 diffusion volatile flame among Case E (the baseline case), Case F (HCl replaced by  $\text{N}_2$ ), Case G  
 305 ( $\text{SO}_2$  replaced by  $\text{N}_2$ ) and Case H (both HCl and  $\text{SO}_2$  replaced by  $\text{N}_2$ ).

### 306 4.3. Characteristics of the 2D pulverized-biomass flame

307 The transformation of potassium species in the 2D pulverized-biomass flame is then  
 308 sequentially examined. Figure 5 shows the evolution of some important quantities of the flame: (a)  
 309 gas temperature and particle burnout, (b) OH mass fraction, (c) K mass fraction, (d) KOH mass  
 310 fraction, and (e) flame index and particle temperature. In the early stage of  $t = 10\text{--}15$  s, biomass

311 particles in the jet shear layers are heated by the high-temperature coflow. Volatiles including  
312 potassium, chlorine and sulfur compounds are then released from these particles via the pyrolysis  
313 process. Isolated flame structures [27, 34] can be observed at  $t = 15$  ms, which are formed due to  
314 individual particles ignited in the shear layers. At  $t = 20$  ms, more and more particles get ignited and  
315  $Y_{OH}$  propagates, representing a strong heat release of the rapid spreading flame. Atomic potassium K  
316 has a high concentration in the high-temperature burning zone, while KOH accumulates around the  
317 ignited particles. Finally, at  $t = 30$  ms, the flame tends to be weak as most of the biomass particles in  
318 the computational domain burn out. However, a wider flame regime can be observed since the  
319 turbulent mixing continues. The concentrations of OH radical and atomic K drop, but that of KOH  
320 remains a significant level.

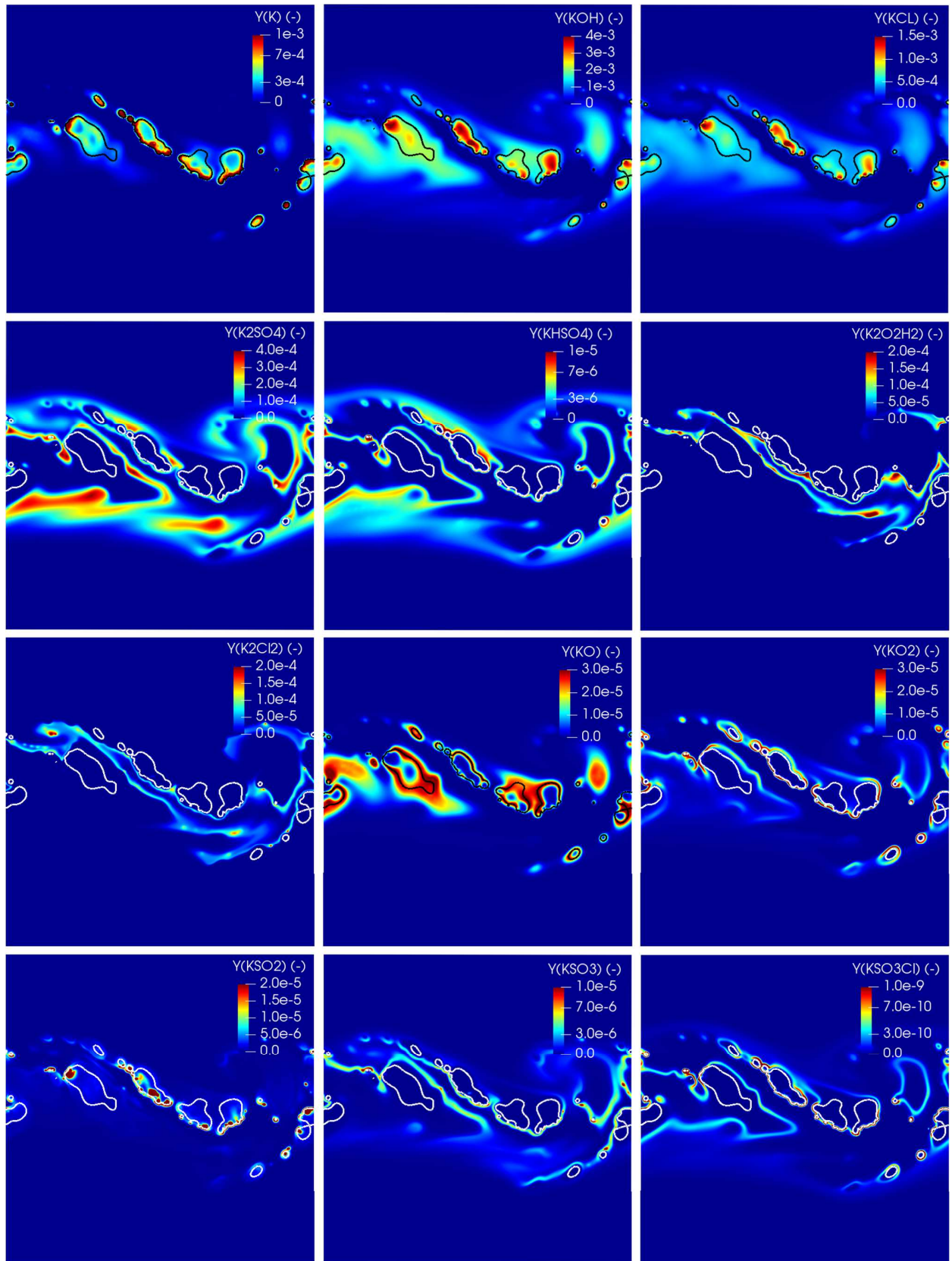


321  
 322 Figure 5. Time evolutions of instantaneous distributions of the (a) gas temperature and particle  
 323 burnout, (b) OH mass fraction, (c) K mass fraction, (d) KOH mass fraction and (e) flame index and  
 324 particle temperature.

325 Based on the spatial gradients of the mass fractions of volatile fuel and oxidizer, the flame index,  
 326 F.I. [24, 53, 54], can be computed as:  $F.I. = \nabla Y_f \nabla Y_{O_2}$ , where  $Y_f = Y_{CH_4} + Y_{CO} + Y_{C_2H_2} + Y_{H_2}$ . Positive  
 327 F.I. values indicate premixed flame regimes, while negative ones for diffusion flame. F.I. distribution  
 328 of the biomass flame is shown in Fig. 5e for the regions where the heat release rate exceeds  $10^7$   
 329  $W/m^3$  and therefore are actively reacting regions. The maximum heat release rate in the 2D domain

330 is  $3.03 \times 10^{10} \text{ W/m}^3$ . It can be found that at the beginning stage of  $t < 15 \text{ ms}$ , the first ignition of  
331 biomass particles is controlled by premixed combustion. Then after the biomass jet reaches actively  
332 reacting state, the volatile released from particles accumulates before burning and therefore leads to a  
333 dominant diffusion combustion mode [26].

334 [Figure 6](#) shows the instantaneous distributions of all the twelve potassium species considered in  
335 the DNS at  $t = 20 \text{ ms}$ . The isoline of  $\phi = 1$  is superimposed, which represents the stoichiometric  
336 condition of combustion between the biomass volatile and the oxidizer. It can be found that atomic K  
337 has a high concentration in the regime close to the isoline, where the volatile fuel is actively burning  
338 and the temperature is high. Both KOH and KCl feature a high concentration in the fuel-rich region  
339 (inside the isoline), and a moderate concentration in the fuel-lean region (outside the isoline). KOH  
340 is the released potassium species along with the volatile, while the high concentration of KCl in the  
341 fuel-rich region can be explained by the Reaction R2.  $\text{KHSO}_4$  and  $\text{K}_2\text{SO}_4$  are the two major sulfated  
342 potassium species, which mainly form in the fuel-lean region, but their concentrations are much  
343 lower than the potassium chloride KCl. The two favored potassium species in the pre-combustion  
344 mixture  $\text{K}_2\text{Cl}_2$  and  $\text{K}_2\text{O}_2\text{H}_2$  are observed only in the fuel-lean region, since they will decompose  
345 under high temperature. The other five minor potassium species, i.e., KO,  $\text{KO}_2$ ,  $\text{KSO}_2$ ,  $\text{KSO}_3$  and  
346  $\text{KSO}_3\text{Cl}$ , are produced under the fuel-lean condition, while  $\text{KSO}_2$  achieves a high concentration in  
347 the fuel-rich region where abundant potassium and sulfur exist.



348

349 Figure 6. Instantaneous distributions of all the twelve potassium species at  $t = 20$  ms. The isoline of  $\phi$

350

$= 1$  is superimposed.

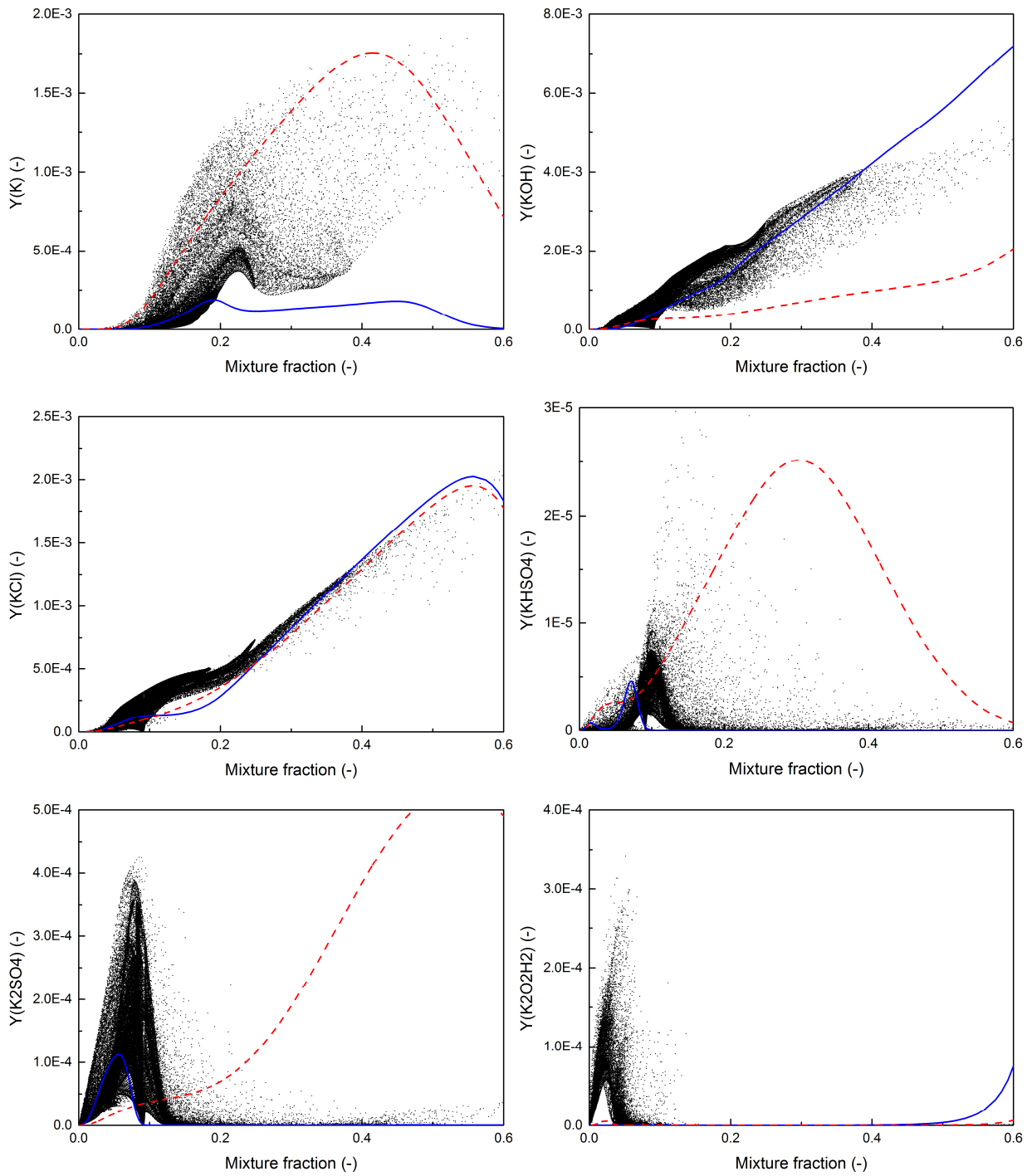
351

#### 352 4.4. Potassium species dynamics

353 Figure 7 shows the instantaneous scatter plots of six representative potassium species against  
354 the mixture fraction at  $t = 20$  ms. For the three-stream mixing in the 2D pulverized-biomass flame,  
355 the mixture fractions of the volatile released from biomass particles (the fuel stream), the air jet  
356 carrying these particles (the oxidizer stream) and the high-temperature coflow are  $Z = 1$ ,  $Z = 0$  and  $Z$   
357  $= 0.093$ , respectively. K, KCl and KOH are the three major potassium species in the reaction  
358 products. The distributions of  $Y_{\text{KCl}}$  and  $Y_{\text{KOH}}$  are almost linear with  $Z$ , while that of  $Y_{\text{K}}$  is subtler.  $Y_{\text{K}}$   
359 stays almost zero for the lower range of  $Z < 0.05$ , to then increases rapidly until  $Z = 0.22$ , and then  
360 holds a moderate increasing rate for the fuel-rich regime of  $Z > 0.22$ . Finally,  $Y_{\text{KHSO}_4}$ ,  $Y_{\text{K}_2\text{SO}_4}$  and  
361  $Y_{\text{K}_2\text{O}_2\text{H}_2}$  feature a single-peak distribution within the fuel-lean regime of  $Z < Z_{\text{st}} = 0.189$ .

362 The potassium profiles obtained from 1D diffusion flames are also shown in Fig. 7 with the blue  
363 solid line and the red dash line corresponding to the lowest and highest strain rates, respectively. It  
364 can be found that the high-strain rate (red dash line) helps to enhance the transformation of KOH to  
365 K, KHSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>, while the production of KCl is insensitive to the strain rate. This is because  
366 the KCl-formation reactions are almost instantaneous (of the order of a few micro seconds), and  
367 therefore can hardly be affected by the relatively much slowly varying strain rate. It can also be  
368 observed in Fig. 2 that the reaction zone of KCl is much thinner than the other potassium products.  
369 Compared with the line plots from 1D diffusion flames, the DNS scatters generally follow a similar  
370 trend, but lots of data points fall outside the region between the red dash and blue solid lines. These  
371 points are likely to represent the unsteadiness and/or partial premixing of the reactants, because the  
372 volatile ejected from the particles is rapidly mixed with the ambient air in a partially premixed mode,  
373 as in [55]. Besides, the radiation heat loss also contributes to the discrepancy between line plots from

374 1D diffusion flames and DNS scatters.



375

376

377

378 Figure 7. Scatter plots of instantaneous mass fractions of K, KCl, KOH, KHSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>O<sub>2</sub>H<sub>2</sub>  
379 against  $Z$  at  $t = 20$  ms. Blue solid line and red dash line are the potassium profiles obtained from 1D  
380 counterflow diffusion flames, corresponding to the lowest ( $21 \text{ s}^{-1}$ ) and highest strain rates ( $8556 \text{ s}^{-1}$ ).

381

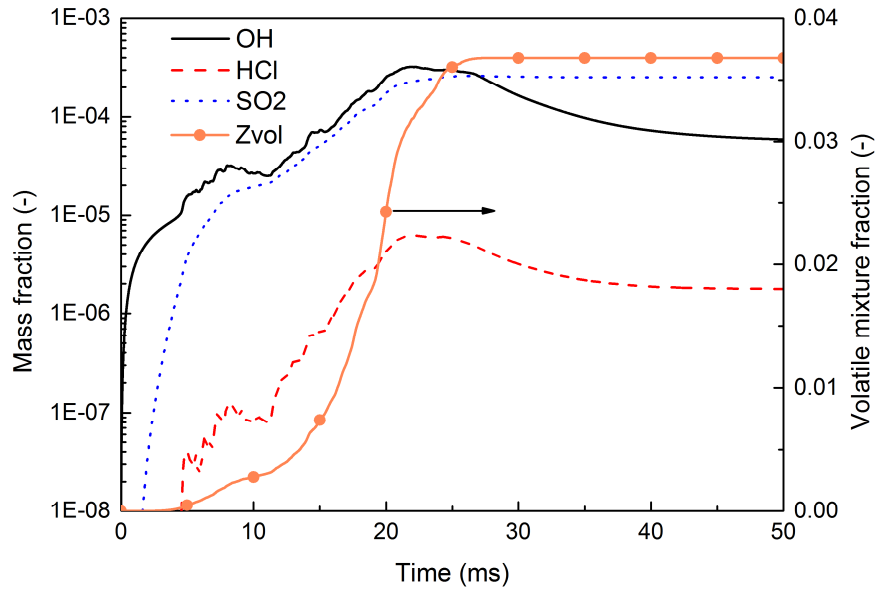


382 4.5. Statistics of the 2D pulverized-biomass flame

383 Figures 8 and 9 show the time evolutions of the mean mass fractions of OH, HCl, SO<sub>2</sub>, Z<sub>vol</sub> and  
 384 six representative potassium species, and the mean gas temperature of the biomass flame. All of  
 385 these quantities are averaged over the entire 2D computational domain. Z<sub>vol</sub> is the volatile mixture  
 386 fraction, which can be obtained from:

$$387 \quad D_t (\rho Z_{vol}) = \partial_j (\rho D_Z \partial_j Z_{vol}) + \dot{S}_{Y,p,vol} \quad (7)$$

388 where  $D_Z$  is the diffusivity coefficient of volatile gas (m<sup>2</sup>/s) and its value is set equal to the thermal  
 389 diffusivity.  $\dot{S}_{Y,p,vol}$  is the source term of the volatile mass released from biomass particles.

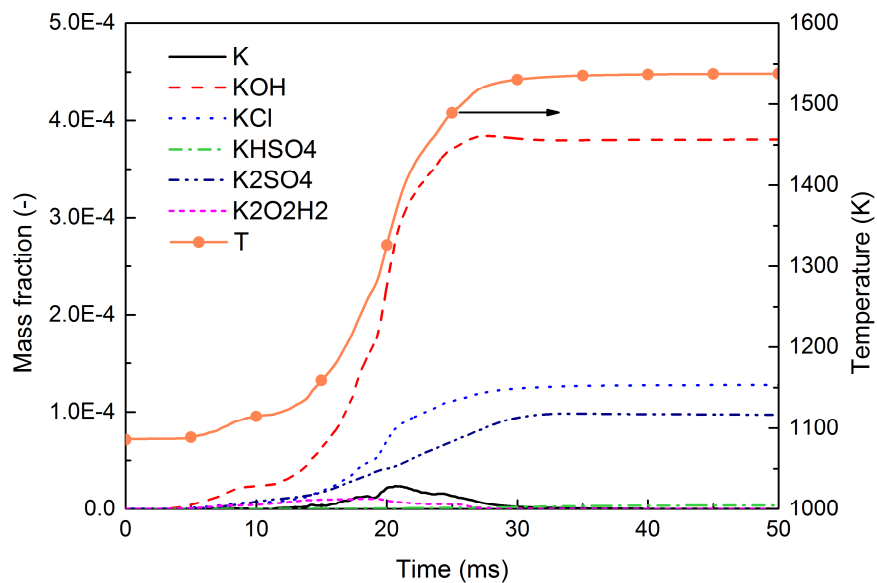


390  
 391 Figure 8. Time evolutions of the mean mass fractions of OH, HCl, SO<sub>2</sub> and Z<sub>vol</sub> averaged over the 2D  
 392 computational domain.

393 It can be observed that the first ignition of the biomass jet happens at  $t = 5$  ms. The mass  
 394 fractions of potassium species and the gas temperature start to increase and small peaks can be found  
 395 for  $Y_{OH}$  and  $Y_{HCl}$ . This is because the volatile fuel gets ignited around some particles, which in turn  
 396 heats up the particles rapidly and therefore bring a high flux of volatile release. After  $t = 15$  ms, the  
 397 biomass jet is actively burning which reflects in both  $T$  and  $Z_{vol}$  increase rapidly, same as the mass

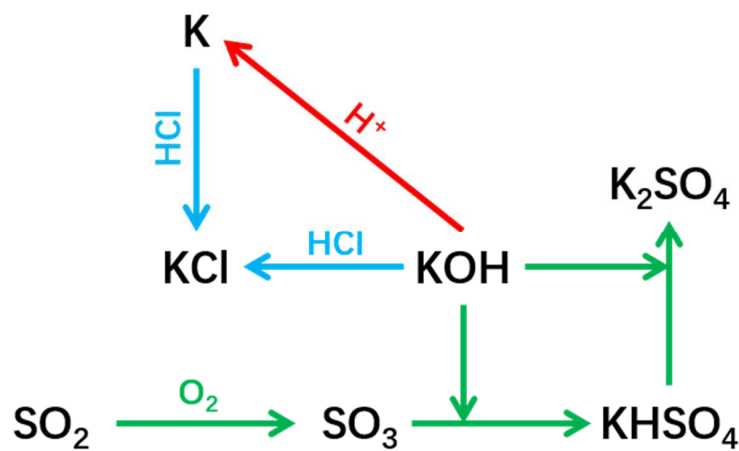
398 fractions of  $Y_{OH}$ ,  $Y_{HCl}$ ,  $Y_{SO_2}$ ,  $Y_{KOH}$  and  $Y_{KCl}$ . After  $t = 30$  ms, both  $T$  and  $Z_{vol}$  remain almost constant,  
 399 indicating the end of the combustion of the biomass jet. However, although the average of gas  
 400 temperature in the domain becomes stable, its variance is further decreasing due to turbulent mixing  
 401 of the hot burnout gases and the surroundings. This explains the variation of the species mass  
 402 fractions after  $t = 30$  ms, e.g. the decreasing of  $Y_{HCl}$  due to Reaction R2. At the end of the simulation  
 403 ( $t = 50$  ms), KOH is found to be the major potassium product. **Comparing the DNS predictions at the**  
 404 **end of the simulation to a reference equilibrium calculation by CANTERA [42] of a**  
 405 **zero-dimensional (0D) homogeneous reactor under the temperature of 1538 K, which is the final**  
 406 **averaged temperature of the 2D DNS domain, the relative errors are of 2.07% for KOH, 2.93% for**  
 407 **KCl and 21.85% for  $K_2SO_4$ . The larger error for  $K_2SO_4$  should be attributed to the slower sulfation**  
 408 **reactions, as shown in Fig. 2a, and therefore it would take a much longer time for  $K_2SO_4$  to reach**  
 409 **equilibrium. Furthermore the 2D DNS domain does not reach a homogeneous state at  $t = 50$  ms,**  
 410 **which also contributes to the discrepancy between the DNS predictions and equilibrium results.**

411



412  
 413 Figure 9. Time evolutions of the mean mass fractions of K, KOH, KCl, KHSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>Cl<sub>2</sub>,  
 414 and the mean gas temperature.

415 The major pathways of potassium transformation in the pulverized-biomass flame is  
 416 summarized in Fig. 10. It can be found that HCl reacts with potassium species in a straightforward  
 417 way, i.e.,  $\text{HCl} + \text{KOH} \rightarrow \text{KCl} + \text{H}_2\text{O}$  and  $\text{HCl} + \text{K} \rightarrow \text{KCl} + \text{H}$ . In contrast, the formation of sulfated  
 418 potassium species is more complex. The  $\text{SO}_2$  is first oxidized to  $\text{SO}_3$ , to then reacts with  $\text{KOH}$  to  
 419 form  $\text{KHSO}_4$ , and finally produce  $\text{K}_2\text{SO}_4$  through a shuffle reaction,  $\text{KHSO}_4 + \text{KOH} \rightarrow \text{K}_2\text{SO}_4 +$   
 420  $\text{H}_2\text{O}$ .



421  
 422 **Figure 10. Major pathways of potassium transformation during pulverized-biomass combustion.**

#### 423 4.6. Effects of HCl and $\text{SO}_2$ on potassium emissions in the 2D pulverized-biomass flame

424 Three additional DNS cases are set up to investigate the effects of HCl and  $\text{SO}_2$  on potassium  
 425 transformation characteristics: Case K (HCl in the volatile is replaced by  $\text{N}_2$ ), Case L ( $\text{SO}_2$  in the  
 426 volatile is replaced by  $\text{N}_2$ ) and Case M (both HCl and  $\text{SO}_2$  in the volatile are replaced by  $\text{N}_2$ ). Case J  
 427 refers to the original baseline DNS case. The comparison between the four cases is shown in [Figure](#)  
 428 [11](#). In all the cases, KOH is the main potassium product at the end of the simulation. However, with  
 429 HCl and/or  $\text{SO}_2$  present, part of KOH is transformed to KCl and/or  $\text{K}_2\text{SO}_4$ , respectively. Based on  
 430 the initial mass fractions ( $Y_0$ ) of KOH/HCl/ $\text{SO}_2$  in the volatile ([Table 2](#)) and the final mass fractions  
 431 ( $Y_{\text{final}}$ ) of KCl/ $\text{K}_2\text{SO}_4$  in the burnout gases, we can calculate the conversion rate ( $\alpha$ ) of KCl and

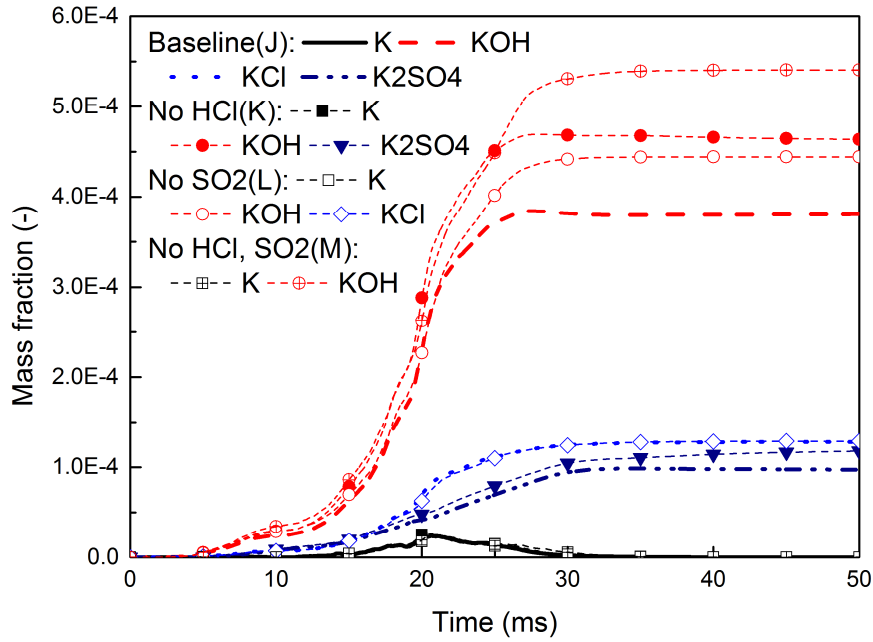
432  $K_2SO_4$  as:

$$433 \quad \alpha_{KCl} = \frac{Y_{final,KCl}/M_{KCl}}{Z_{vol,final} \cdot \min(Y_{0,KOH}/M_{KOH}, Y_{0,HCl}/M_{HCl})} \times 100\% \quad (8)$$

$$434 \quad \alpha_{K_2SO_4} = \frac{Y_{final,K_2SO_4}/M_{K_2SO_4}}{Z_{vol,final} \cdot \min(0.5Y_{0,KOH}/M_{KOH}, Y_{0,SO_2}/M_{SO_2})} \times 100\% \quad (9)$$

435 where  $M$  denotes the molar mass. The obtained conversion rate of KCl in Case L is  $\alpha_{KCL} = 95.1\%$ ,  
 436 while that of  $K_2SO_4$  in Case K is  $\alpha_{K_2SO_4} = 14.7\%$ . The conversion rate of KCl is much higher than  
 437 that of  $K_2SO_4$ , indicating HCl has a much stronger ability to react with potassium species than  $SO_2$ .

438



439  
 440 Figure 11. Comparison of time evolutions of the mean mass fractions of potassium species among  
 441 Case J (the baseline case), Case K (HCl replaced by  $N_2$ ), Case L ( $SO_2$  replaced by  $N_2$ ) and Case M  
 442 (both HCl and  $SO_2$  replaced by  $N_2$ ).

#### 443 4.7. Comparison of potassium emission characteristics in 1D and 2D flames

444 The 1D premixed flame simulations (Fig. 2) show that KOH is the most significant potassium  
 445 product under various equivalence ratios in fuel-lean, stoichiometric and fuel-rich conditions. This is  
 446 consistent with the 1D diffusion flame simulation results (Fig. 4). However, some discrepancies can

447 be observed between the premixed and diffusion flame predictions. For instance, the premixed flame  
448 results show that the second major potassium product is KCl under all the conditions, which is not  
449 the case in the diffusion flame under stoichiometric condition, where atomic K has a higher  
450 concentration than KCl. The reason of the discrepancy should be that the 1D diffusion flame is  
451 strained while the 1D premixed flame is freely propagating. In fact, Fig. 7 indeed shows that a higher  
452 strain rate could promote the production of K, while KCl is insensitive to the variation of strain rate.  
453 Finally, the statistics of the 2D biomass flame also demonstrates that KOH is the major potassium  
454 product. The overall equivalence ratio of the 2D flame is 0.55 (corresponding to a mixture fraction  $Z$   
455 = 0.094), and therefore its potassium emission statistics are close to that of the 1D flames under the  
456 fuel-lean condition.

457

## 458 **5. Conclusions**

459 The emission characteristics of potassium species in biomass combustion are numerically  
460 investigated via 1D premixed/diffusion flames of biomass volatile, and a 2D pulverized-biomass  
461 flame. Complex chemistry has been used for both the volatile hydrocarbon combustion and the  
462 potassium species reactions. From the 1D premixed flame simulations, it is found that KOH is the  
463 most significant potassium product for all the three equivalence ratios, while KCl has the second  
464 highest concentration. The 1D diffusion flame simulations also support that KOH is the major  
465 potassium products while the productions of sulfurous and chloric potassium species are secondary.

466 The emission characteristics of the potassium species in a 2D pulverized-biomass flame are then  
467 examined. The instantaneous distribution characteristics show that KOH, KCl and K are the three  
468 major potassium species in the reaction zone. The distributions of  $Y_{KCl}$  and  $Y_{KOH}$  are almost linear