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Numerical study of HCl and SO₂ impact on sodium emissions in pulverized-coal flames

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Abstract

Sodium emissions during pulverized-coal combustion (PCC) are known to result in severe ash-related operating issues of coal furnaces, e.g., fouling, slagging and corrosion. To relieve these issues and advance the clean utilization technologies of coal, a better understanding of the fundamental mechanisms driving the formation and transformation of the sodium species is required. In the present study, sodium emissions have been simulated in both one-dimensional (1D) premixed/diffusion flames of the coal volatile and an early-stage two-dimensional (2D) pulverized-coal flame. The properties of Loy Yang brown coal are used. The DRM22 skeletal mechanism is employed for volatile-gas combustion, and the reaction of sodium species is modeled by a detailed mechanism encompassing the elements Na, C, H, O, S and Cl. The compositions of the volatile fuels are obtained from the chemical percolation devolatilization (CPD) model, including CH₄, C₂H₂, CO, H₂, CO₂ and H₂O. The initial species of Na, Cl and S in the volatile gas is set to be NaOH, HCl and SO₂, respectively. The transformation characteristics of 12 sodium species are investigated in both the 1D volatile flames and the 2D pulverized-coal flame. The response of the sodium chemistry to volatile-gas combustion is analyzed under fuel-lean, stoichiometric and

29 fuel-rich conditions. Na, NaOH and NaCl are found to be the major sodium species during the
30 combustion. Parametric studies with HCl, SO₂ or both species removed from the volatile are then
31 performed to investigate their effects on the sodium transformation characteristics in both the 1D and
32 2D flames. The results show that HCl has a much stronger ability to react with sodium species than
33 SO₂.

34 *Keywords:* Pulverized-coal combustion; Emission; Sodium chemistry; Alkali metal; HCl; SO₂

35 **1. Introduction**

36 Coal has been widely utilized to support the worldwide electric power consumption due to the
37 overall flexibility of coal combustion systems [1]. In the near future, coal will continually play a
38 major role in the energy structure of the world, considering its broad availability [2]. In practical
39 utilization of coal, alkali metals such as sodium (Na) presented in coals lead to severe ash-related
40 operating issues, e.g., fouling, slagging and corrosion [3]. This issue is also found in the combustion
41 of biomass, which is a promising renewable energy source [4]. Potassium (K), an important element
42 for plants, is usually rich in biomass. The alkali metal, i.e., Na and K, released from the combustion
43 of coal and biomass can condense on heat transfer surfaces and form an initial sticky layer, which
44 captures fly ash and leads to rapid ash deposition [5, 6]. Besides, alkali metal can also react with
45 sulfur and chlorine species to form complex compounds, which causes fouling and corrosion of the
46 furnaces [7]. These alkali metal emissions significantly limit the utilization of potassium-rich
47 biomass such as straw and sodium-rich coals such as North Dakota coal in the US, Loy Yang coal in
48 Australia and Zhundong coal in China [8]. Thus, to develop appropriate control technologies of
49 reducing or capturing these harmful alkali metal emissions, it is essential to better understand the
50 fundamental mechanisms driving the formation and transformation of alkali species and their
51 interactions with the complex multi-phase turbulent reacting flows during the combustion of

52 pulverized coal and biomass.

53 In the past decades, experimental research on sodium release and reacting dynamics evolves
54 from offline measuring techniques to online measurements using advanced laser diagnostics. Offline
55 sampling measurements can obtain the final amount and composition of sodium species by analyzing
56 the fly ash and ash deposits in the post-combustion stage [9]; while online techniques, e.g., planar
57 laser-induced fluorescence (PLIF) [10, 11] and laser-induced breakdown spectroscopy (LIBS)
58 [11-13], can directly capture the time-resolved sodium release process during the combustion. In our
59 recent study, the dynamic release of atomic and elemental sodium during the combustion of a
60 Zhundong coal pellet has been quantitatively measured by using PLIF [14] and multi-point LIBS
61 methods [15], respectively.

62 On the numerical side, van Eyk et al. [16] firstly proposed a one-step Arrhenius sodium release
63 model during the combustion of a single char pellet. A two-step kinetics model has been developed
64 in our recent study [14, 15] to quantify the sodium release during all stages of coal combustion,
65 based on simultaneous online measurements of the sodium release, pellet diameter and surface
66 temperature of a burning coal pellet. Since the burnout time and coal pellet diameter in these studies
67 are on the same order of magnitude as in a typical circulating fluidized bed (CFB) boiler, these
68 sodium release models are appropriate for CFB combustion [15]. Sodium release models for
69 pulverized-coal combustion (PCC) must still be developed.

70 Considering the homogeneous chemical reactions of alkali species, the final forms of alkali
71 species in post-combustion gases can be modeled via thermodynamic equilibrium calculation, e.g.
72 [15, 17, 18]. It has been found that the main alkali species are atomic Na/K, NaOH/KOH and
73 NaCl/KCl in equilibrium [18]. Alkali chlorides can lead to severe ash deposition and corrosion issues,
74 and a feasible method to mitigate these issues is to convert the alkali chlorides to sulfates, whose

75 melting temperatures are higher and which are therefore less problematic [19]. Hence, the
76 homogeneous chemical reaction, especially the sulfation of alkali has received more and more
77 attentions recently, e.g. [20-22]. Glarborg and Marshall [20] proposed a detailed chemical reaction
78 mechanism for homogeneous alkali reactions, which was validated against experimental results on
79 sulfation of gaseous alkali chlorides. Takuwa and Naruse [23] investigated the transformation
80 characteristics of gaseous sodium compounds in a hydrogen-air combustion system via
81 zero-dimensional (0D) isothermal simulations. However, the homogeneous reaction dynamics of
82 alkali species in a pulverized-coal flame has not been reported yet.

83 As the sharp increase of computing capacity continues, computational fluid dynamics (CFD)
84 methods for the carrier-gas flow of PCC have evolved from Reynolds-averaged Navier-Stokes
85 (RANS) simulation (e.g. [24-26]) towards high-fidelity approaches, i.e., large-eddy simulation (LES,
86 e.g. [27-34]) and direct numerical simulation (DNS, e.g., [35-37]). The high-fidelity approaches of
87 LES and DNS have demonstrated advantages over RANS in predicting local distributions of gas
88 temperature and species concentrations. Particularly in DNS, the turbulence-chemistry interaction is
89 directly resolved instead of being modeled, the simulation results can therefore provide more
90 physical insights into complex PCC dynamics and also serve as important data references for the
91 development of subgrid scale modeling.

92 In summary, the transformation dynamics of sodium species in a pulverized-coal flame have not
93 been fully revealed by previous studies. Within this context, the objective of the present study is
94 twofold. First, the responses of sodium species to one-dimensional (1D) premixed/diffusion flames
95 of coal volatile are investigated. Second, the transformation characteristics of sodium species in a
96 two-dimensional (2D) early-stage pulverized-coal flame are simulated and analyzed, excluding char
97 combustion. In our previous studies [34, 37], the reaction dynamics of sodium species in PCC were

98 investigated using a subset sodium mechanism without considering the effects of S and Cl. Here, the
99 full detailed sodium mechanism proposed by Glarborg and Marshall [20] including the elements Na,
100 C, H, O, S and Cl is employed to model the sodium reactions, and the effects of HCl and SO₂ on the
101 sodium transformation characteristics are then investigated. It should be noted that the detailed
102 sodium mechanism has been carefully validated by Glarborg and Marshall [20] against the
103 experimental results of the gas-phase sulfation of alkali chloride at combustion conditions [38].

104 It was found in [34, 37] that the multidimensional two-phase pulverized-coal flame showed a
105 partially premixing combustion mode, with first the premixed combustion mode dominating when
106 pulverized-coal particles are heated and ignited in the shear layer region where the high-temperature
107 co-flow mixes with the low-temperature air flow carrying pulverized-coal particles. After ignition
108 stabilizes, volatile fuels are rapidly released from pulverized-coal particles, leading to a dominantly
109 diffusion burning mode. In view of this fact, in order to better understand how minor sulfur and
110 chlorine species affect sodium emissions in pulverized-coal flames, it will be instructive to first
111 investigate prototype one-dimensional premixed and diffusion gaseous flames of the coal volatile
112 using detailed chemistry, leaving behind the complexity of interactions between dispersing
113 pulverized-coal particles and the gas phase, turbulent flow effects, etc. This inspection will provide a
114 first guiding light on S/Cl-affected sodium emissions in both the prototype premixed and diffusion
115 volatile flames. By comparing the one-dimensional prototype gaseous volatile flames and a more
116 realistic multidimensional two-phase pulverized-coal flame, a comprehensive understanding of
117 sodium emissions impacted by minor sulfur and chlorine species can be obtained.

118 **2. One-dimensional premixed/diffusion flames of coal volatile**

119 The reaction dynamics of sodium species in 1D premixed/diffusion flames of coal volatile is
120 studied. The volatile is released from the Loy Yang brown coal [17], for which the coal analysis data

121 are shown in Table 1. The volatile combustion is modeled by the previously validated DRM22
122 skeletal mechanism proposed by Kazakov and Frenklach [39], involving 22 chemical species and
123 104 elementary reactions. The compositions of the volatile fuels are obtained from the chemical
124 percolation devolatilization (CPD) model [40] and the Tar species is replaced by C₂H₂ [32], as shown
125 in Table 2. The compositions predicted by the CPD model have been slightly adjusted to fulfill the
126 elemental mass conservation.

127 According to [23], the initial species of Na in the volatile is set to be NaOH, while those of Cl
128 and S are set to be HCl and SO₂, respectively. The percentage of sodium that is releasable during the
129 coal pyrolysis stage is set to 19.1%, according to the experimental data [17]. However, the release of
130 sulfur and chlorine has not been measured. Considering sulfur and chlorine can be fully released
131 during the pyrolysis and char burning stages of coal combustion, their releasable proportions during
132 the pyrolysis stage are both set to 55.1%, which is the percentage of volatile yields predicted by the
133 CPD model. The mass fractions of NaOH, HCl and SO₂ in the volatile gas can then be calculated
134 (see Table 2). The detailed reaction mechanism of alkali metal species developed by Glarborg and
135 Marshall [20] includes elementary reactions over the elements Na, K, C, H, O, S and Cl. In the
136 present study, since the concentration of potassium in the coal is an order of magnitude lower than
137 that of sodium (see Table 1), the element K is not considered, which results in a detailed reaction
138 mechanism of sodium involving 36 species and 153 elementary reactions.

139 Table 1. Analysis of Loy Yang brown coal [17].

<i>Dry basis, wt%</i>	
C	67.8
H	5.20
N	0.57
S	0.24
Cl	0.06
Ash	0.80

O	25.3
<i>In ash, wt%</i>	
SiO ₂	12.9
Al ₂ O ₃	31.4
Fe ₂ O ₃	6.70
TiO ₂	0.70
K ₂ O	0.77
MgO	12.2
Na ₂ O	11.3
CaO	5.60
SO ₃	16.9

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Table 2. Modeled volatile-gas compositions of Loy Yang brown coal.

Hydrocarbon volatile compositions predicted by the CPD model (mass fractions)

CH ₄	C ₂ H ₂	CO	H ₂	CO ₂	H ₂ O
0.03707	0.30698	0.20664	0.02976	0.15394	0.25979

Non-hydrocarbon volatile compositions (mass fractions)

NaOH	HCl	SO ₂
4.0E-4	6.2E-4	48.0E-4

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For the premixed condition, a 1D freely propagating premixed flame of the volatile is simulated using CANTERA [41]. Three equivalence ratios ($\phi = 0.5, 1.0$ and 2.0) of the volatile-air mixture are considered and the inlet mixture temperature is 300 K. The equivalence ratio is computed based on the molar fractions of atomic carbon, hydrogen and oxygen [34, 37], which is therefore conserved during homogeneous combustion but not conserved during mixing. For the diffusion condition, a 1D counterflow diffusion flame of the volatile is simulated using CANTERA [41]. The mass flow rates of the volatile fuel and air inlets are 0.024 ($\text{kg/m}^2 \text{ s}$) and 0.072 ($\text{kg/m}^2 \text{ s}$), respectively, while the temperatures of both inlets are 300 K. To investigate the effects of HCl and SO₂ on sodium transformation characteristics, four different configurations with HCl and/or SO₂ removed are set up. The removed HCl/SO₂ is replaced by N₂. In total 16 cases are simulated with the three equivalence ratios in the premixed condition and different configurations of HCl and SO₂ in both the premixed

154 and diffusion conditions. The grid is limited to 250 points and the 1D domain length for premixed
155 and diffusion flame is 1.0 m and 3.0 cm, respectively.

156 **3. Pulverized-coal flame configuration and numerics**

157 A two-dimensional temporally evolving pulverized-coal jet flame is studied (Fig. 1). The
158 physical dimensions of the computational domain are 51.2 mm and 51.2 mm in the streamwise (x)
159 and spanwise (y) directions, respectively. A uniform mesh of $h = 100 \mu\text{m}$ is employed, which has
160 been shown to be able to resolve the flame structure [37]. High-speed air (bulk velocity: 10 m/s,
161 300 K) laden with pulverized-coal particles is initially set up for $|y| < 2.5 \text{ mm}$. The initial number of
162 particles is 171 and their locations follow a random uniform distribution. The initial density of
163 particles is 1400 kg/m^3 with a mono-disperse distribution of diameter of $25 \mu\text{m}$. Properties of Loy
164 Yang brown coal [17] are employed (Table 1). A low-speed hot burnt product of the hydrocarbon
165 volatile at an equivalence ratio of 0.45 (3 m/s, 1559 K) is introduced as the coflow surrounding the
166 air. The coflow stream promotes the ignition of coal particles, as the mixing of the solid-fuel/air
167 mixture with burnt products would do in a real pulverized-coal furnace. Periodic boundary
168 conditions are introduced in all directions. To facilitate the jet flow development, turbulent
169 fluctuations of 0.2 m/s (2% of the primary air velocity) are initially set within the shear layers
170 between the primary air and the coflow. The parameters of the present case are chosen according to
171 [37]. Pulverized-coal particles are treated as point sources and two-way coupling between the gas
172 phase and particles are considered.

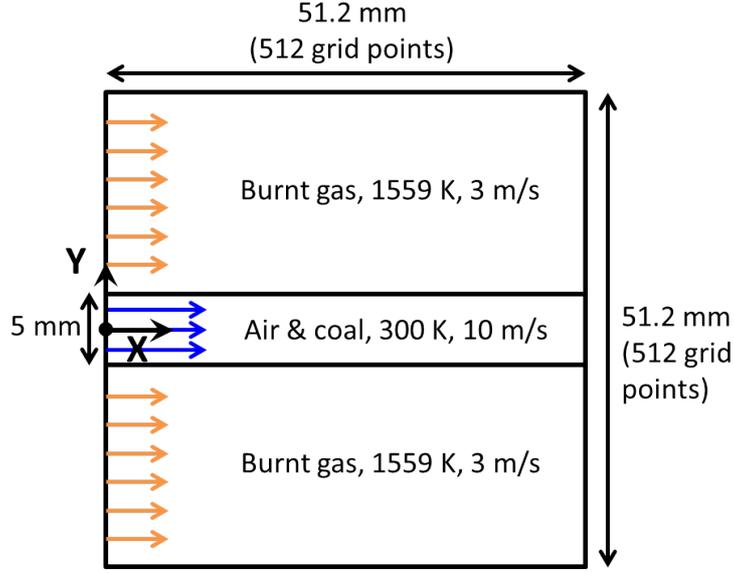


Figure 1. Schematic diagram of computational configuration.

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Coal pyrolysis, including Na/Cl/S release, volatile-gas combustion and Na/Cl/S reactions are simulated. Heterogeneous reaction of char is not considered, because its contribution is weak in a small-scale pulverized-coal flame, as already demonstrated in [32, 34, 42].

3.1. Gas phase modeling

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The governing equations for the gas and coal-particle phases are solved in the Eulerian and Lagrangian frameworks, respectively, using a low-Mach-number in-house code [30, 33, 34, 37]. The conservation equations for mass, momentum, species and temperature are solved for the gas phase:

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

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

184

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

185

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

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where $D_t(\Phi) = \partial_t(\Phi) + \partial_j(\Phi u_j)$, $\partial_j \equiv \partial/\partial x_j$, ρ is gas density (kg/m^3), u_i is gas velocity (m/s), Y_n is the mass fraction of the n th chemical species, T is gas temperature (K). The pressure is denoted by p , and $\tau_{ij} = \mu(\partial_j u_i + \partial_i u_j - 2/3 \partial_k u_k \delta_{ij})$ is the viscous stress tensor. D_n is the molecular mass diffusivity coefficient (m^2/s), λ and $C_{P,g}$ are the thermal conductivity (W/m K) and specific heat capacity (J/kg K)

190 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
 191 due to the effects of particles on the gas phase. $\dot{\omega}_{Y,n}$ is the chemical reaction source term due to
 192 homogeneous reaction. In the temperature equation, the radiative heat transfer ($\dot{S}_{T,R}$), heat exchange
 193 between the gas phase and coal particles ($\dot{S}_{T,p}$), and heat effects of homogeneous reaction ($\dot{\omega}_T$) are
 194 considered. In the present study, the Lewis number ($Le = 1.0$) and Prandtl number ($Pr = 0.7$) are
 195 assumed to be constant.

196 3.2. Particle phase modeling

197 The momentum equation of a Lagrangian coal particle can be written as:

$$198 \quad d_t u_{p,j} = f(u_j - u_{p,j}) / \tau_p \quad (5)$$

199 where $u_{p,j}$ is the velocity of the particle (m/s). The dynamic response time (s) of a particle is
 200 $\tau_p = \rho_p d_p^2 / 18\mu$, where ρ_p is the particle density (kg/m³), and d_p is the particle diameter (m). f is the
 201 drag coefficient, accounting for the high particle Reynolds number effects and the blowing effects of
 202 volatiles at the particle surface [43].

203 The particle temperature equation is:

$$204 \quad d_t T_p = (Q_{conv} + Q_{rad} + Q_{dev}) / (m_p C_{P,p}) \quad (6)$$

205 where T_p is the temperature of the particle (K), m_p mass of the particle (kg), $C_{P,p}$ specific heat
 206 capacity of the particle (J/kg K). The heat transfer due to convection, radiation, and pyrolysis
 207 (devolatilization) is $Q_{conv} = Nu C_{P,g} m_p (T - T_p) / 3 Pr \tau_p$, $Q_{rad} = \varepsilon_p \pi d_p^2 \sigma (T_R^4 - T_p^4)$, and
 208 $Q_{dev} = -\Delta h_{dev} dm_{vol} / dt$, respectively. Nu is the Nusselt number and calculated by the Ranz-Marshall
 209 correlations [44]. The radiation temperature (K) is estimated by $T_R = (G/4\sigma)^{1/4}$, where G is the
 210 incident radiation (W/m²) determined by the Discrete Ordinates Method (DOM) [45]. σ is the
 211 Stefan-Boltzmann constant (5.67×10^{-8} W/m² K⁴). ε_p is the particle emissivity and set to 0.9 [46].
 212 The weighted-sum-of-the-gray-gases model (WSGGM) [47] is employed to determine the gas

213 absorption coefficient. Finally, the mass loss rate of each coal particle (dm_p/dt), due to the pyrolysis,
214 is directly predicted by the CPD model, as in [30, 33, 34].

215 *3.3. Gas phase chemistry*

216 The gas phase chemistry employed here is the same as that in Section 2. The homogeneous
217 combustion of the hydrocarbon volatile and the sodium species reaction are modeled by the DRM22
218 skeletal mechanism [39] and the detailed alkali reaction mechanism [20], respectively. The
219 compositions of the volatile gas including the non-hydrocarbon compounds of Na, S and Cl can be
220 found in Table 2.

221 The release rate of sodium of pulverized-coal is assumed to be proportional to the volatile
222 release rate [34, 37], because the sodium vapor generated inside the porous structure of a coal
223 particle will be transported outward by the volatile yielded during the pyrolysis stage and the sodium
224 release was found proportional to the burnout of a coal particle during the early combustion stage
225 [15]. Similarly, the release rates of sulfur and chlorine are also assumed to be proportional to the
226 volatile release rate.

227 *3.4. Numerical schemes*

228 The numeric of our in-house code is based on an approach previously employed for both DNS
229 and LES [48, 49]. A second-order Crank-Nicolson scheme is used for the time advancement. A
230 second-order central difference scheme is applied to all terms in the momentum equation and the
231 scalar diffusion terms in the species and temperature equations. To secure the scalar boundedness, a
232 Quadratic Upstream Interpolation for Convective Kinematics (QUICK) scheme is employed for the
233 scalar advection terms in the species and temperature equations. An Alternating Direction Implicit
234 (ADI) method has been used, and therefore semi-implicit tridiagonal/pentadiagonal equations are
235 solved separately for each direction. A second-order Runge-Kutta (RK2) scheme is used to explicitly

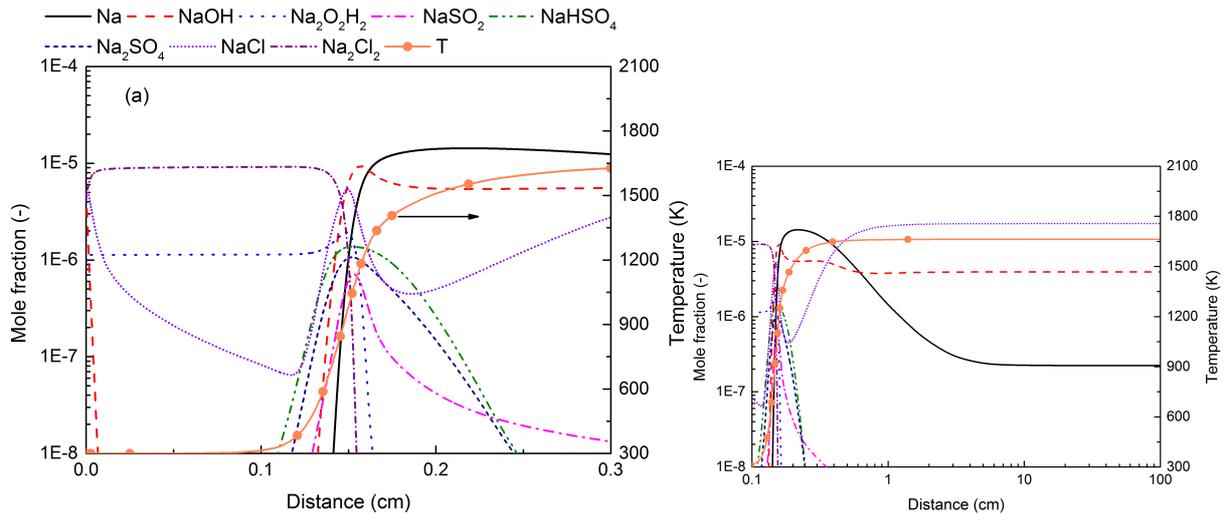
236 advance the particle equations.

237 **4. Results and discussion**

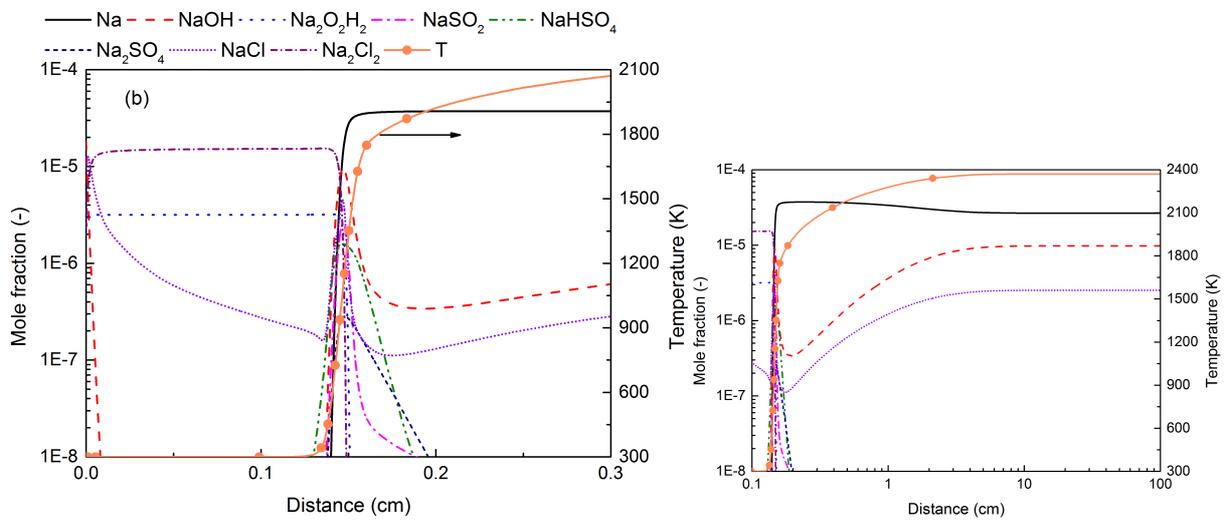
238 *4.1. Transformation characteristics of sodium species in 1D premixed flame*

239 To investigate the transformation characteristics of sodium species under different burning
240 conditions, the reactions of sodium species in 1D freely propagating volatile flames have been
241 simulated for three equivalence ratios ($\phi = 0.5, 1.0$ and 2.0), which are selected to illustrate fuel-lean,
242 stoichiometric and fuel-rich conditions. As shown in Fig. 2, the concentration of NaOH rapidly
243 decreases after the volatile mixture is injected through the inlet, which is due to the following two
244 reaction paths. First, $\text{Na}_2\text{O}_2\text{H}_2$ is produced by $2\text{NaOH} \rightarrow \text{Na}_2\text{O}_2\text{H}_2$. Second, NaOH reacts with HCl
245 in the volatile gas by $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, and NaCl subsequently forms Na_2Cl_2 via 2NaCl
246 $\rightarrow \text{Na}_2\text{Cl}_2$. It can be found that $\text{Na}_2\text{O}_2\text{H}_2$ and Na_2Cl_2 are the two major sodium species in the initial
247 unburned region with $T = 300$ K. In the combustion region where the gas temperature rapidly
248 increases, $\text{Na}_2\text{O}_2\text{H}_2$ and Na_2Cl_2 are decomposed to NaOH and NaCl, respectively, and then
249 transformed to other sodium species, i.e., Na, NaSO_2 , NaHSO_4 and Na_2SO_4 . In the post-flame,
250 high-temperature flue-gas region, the sodium species are then gradually evolving towards the
251 equilibrium. All the sulfurous sodium species are consumed, and the atomic sodium Na is the most
252 significant sodium product (> 10 ppm) under stoichiometric and fuel-rich conditions while NaCl is
253 the main sodium product (> 10 ppm) under fuel-lean condition. H radical generated from the
254 hydrocarbon combustion helps to produce Na via the following two reaction paths: $\text{NaOH} + \text{H} \rightarrow \text{Na}$
255 $+ \text{H}_2\text{O}$ and $\text{NaCl} + \text{H} \rightarrow \text{Na} + \text{HCl}$. NaOH is another major sodium product which shows a
256 concentration of 1-10 ppm under different conditions. The other four minor sodium species, i.e.,
257 NaO, NaO_2 , NaSO_3 and NaSO_3Cl , have a maximum concentration less than 0.5 ppm during the
258 whole reaction process for all the three equivalence ratios (not shown here).

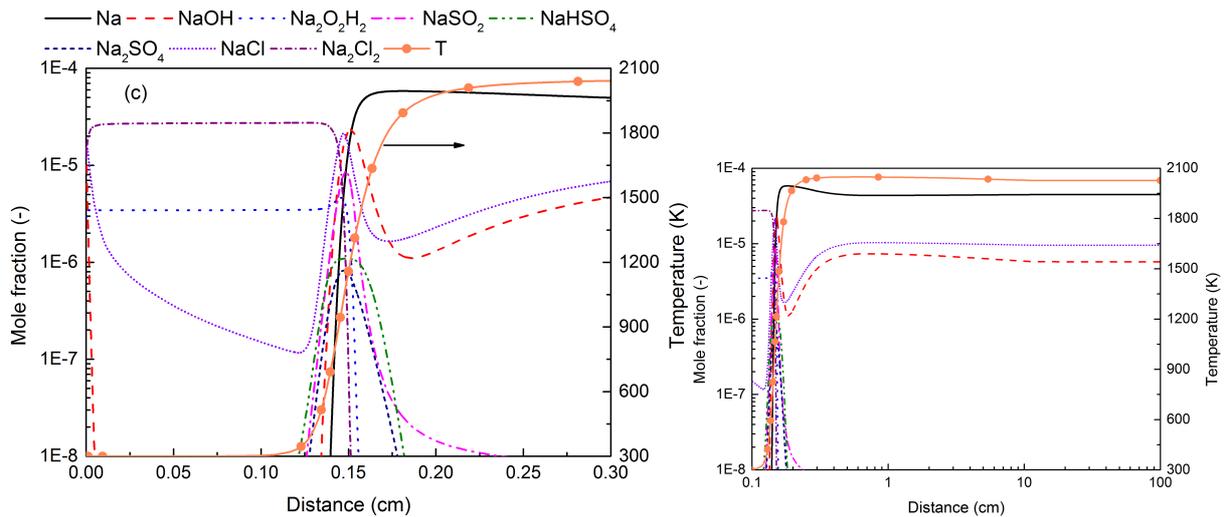
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Figure 2. Sodium species distribution versus distance along the 1D premixed volatile flame at equivalence ratio $\phi = 0.5$ (a), $\phi = 1.0$ (b) and $\phi = 2.0$ (c). The heat release zone is zoomed in and shown on the left side while the overall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

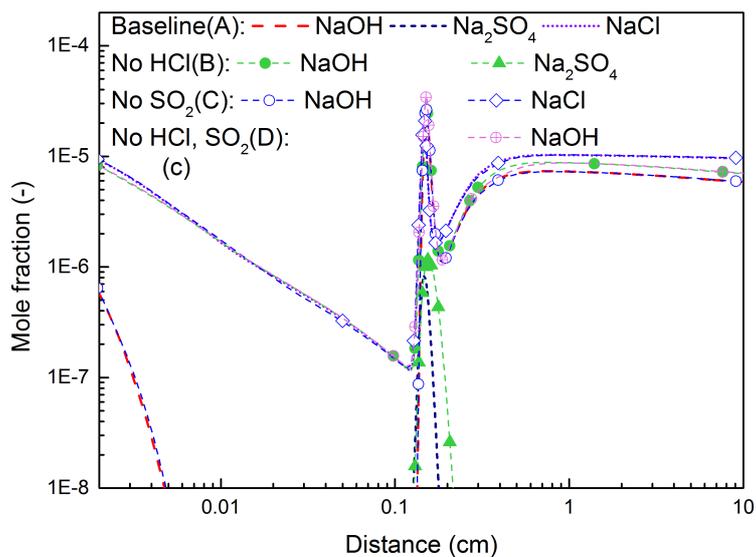
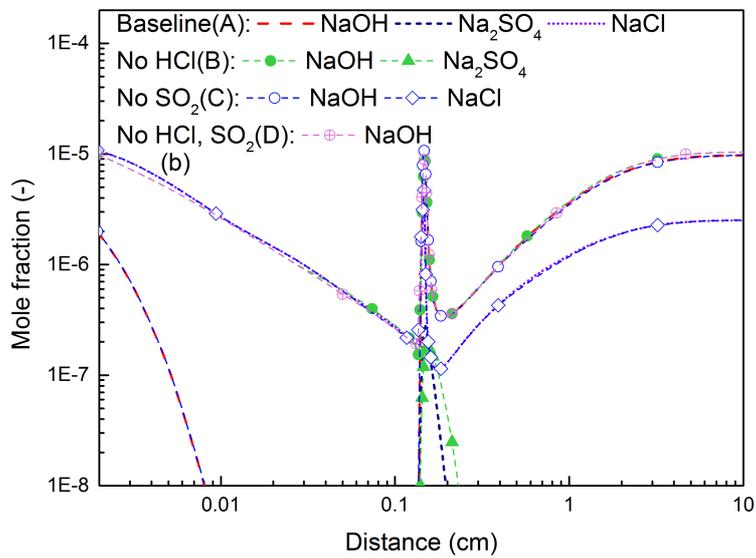
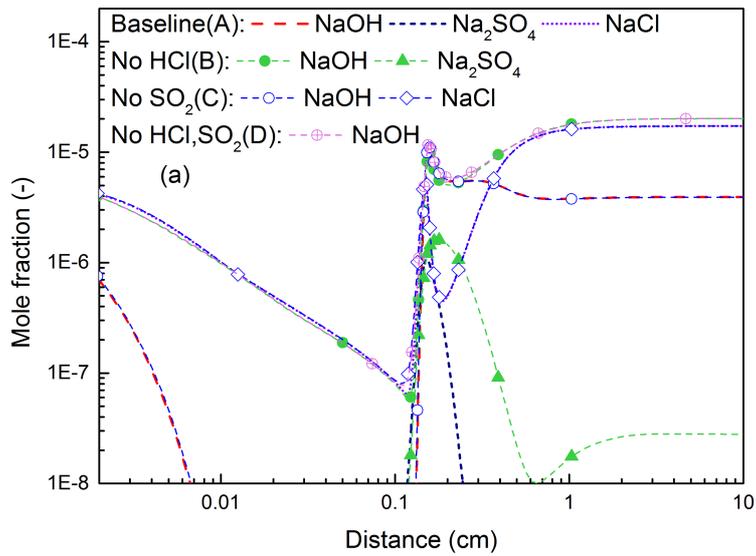
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To investigate the effects of HCl and SO₂ on sodium transformation characteristics, three

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additional configurations have been set up, which are Case B (HCl is removed from the volatile and

270 replaced by N₂), Case C (SO₂ is removed from the volatile and replaced by N₂) and Case D (both
271 HCl and SO₂ are removed from the volatile and replaced by N₂). The original baseline case is
272 referred to as Case A. For each case of A/B/C/D, three simulations are performed with $\phi = 0.5, 1.0$
273 and 2.0. Figure 3 illustrates the comparison among the cases on the representative sodium species
274 NaOH, NaCl and Na₂SO₄. The profiles are shown until Distance of 10 cm, since it can be found in
275 Fig. 2 the sodium reactions almost reach equilibrium at this position. At the initial unburned region
276 where Distance < 0.1 cm, HCl has a significant influence on the profile of NaOH, which is evident
277 by comparing the cases with HCl involved (Cases A/C) and the cases without HCl (Cases B/D). With
278 HCl presented, NaOH is consumed rapidly by HCl via $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, and the
279 produced NaCl shows a similar profile to NaOH in the cases without HCl in the initial region,
280 because the reaction kinetics of $2\text{NaOH} \rightarrow \text{Na}_2\text{O}_2\text{H}_2$ and $2\text{NaCl} \rightarrow \text{Na}_2\text{Cl}_2$ are similar. In the
281 combustion and post-flame regions, the profiles of NaCl are similar for different cases while Na₂SO₄
282 is found to have a wider distribution when HCl is not presented (comparing Case A with B),
283 especially under the fuel-lean condition. The characteristics of NaOH are more subtle. Under
284 fuel-lean and fuel-rich conditions, NaOH is found to have a lower concentration in the sodium
285 products when HCl is presented (Cases A/C), which should be attributed to $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} +$
286 H_2O . However, under stoichiometric condition, the profiles of NaOH become similar for the four
287 cases since the mole fraction of NaCl is quite low, which means the transformation from NaOH to
288 NaCl is not favored. Comparing the cases with SO₂ involved (Cases A/B) and the cases without SO₂
289 (Cases C/D), it can be found that the impact of SO₂ on representative sodium profiles such as NaCl
290 and NaOH is minor.
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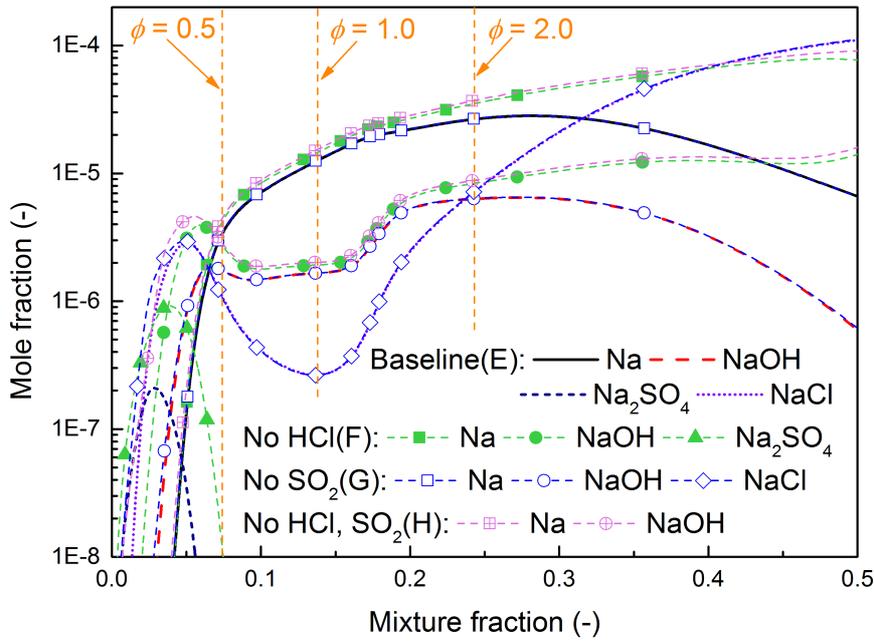
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Figure 3. Comparison of sodium species distribution versus distance along the 1D premixed volatile flame between Case A (the baseline case), Case B (HCl removed), Case C (SO₂ removed) and Case D (both HCl and SO₂ removed) at equivalence ratio $\phi = 0.5$ (a), $\phi = 1.0$ (b) and $\phi = 2.0$ (c).

300 *4.2. Transformation characteristics of sodium species in 1D diffusion flame*

301 To investigate the transformation characteristics of sodium species in diffusion flame, four cases
302 have been set up, which are Case E (the baseline case), Case F (HCl is removed from the volatile and
303 replaced by N₂), Case G (SO₂ is removed from the volatile and replaced by N₂) and Case H (both
304 HCl and SO₂ are removed from the volatile and replaced by N₂). Figure 4 shows the comparison
305 among the cases on the representative sodium species Na, NaOH, NaCl and Na₂SO₄. Here, only the
306 results of the mixture fraction $Z < 0.5$ are shown, because a higher mixture fraction is rarely observed
307 in the following 2D DNS study (see Fig. 8 below). The mixture fraction is defined as $Z = 1.0 -$
308 $Y_{N_2}/0.767$. For the two-stream mixing, 1D diffusion flame, $Z = 1$ and $Z = 0$ indicate the coal-volatile
309 and oxidizer streams, respectively. The positions of $\phi = 0.5$, 1.0 and 2.0 in the mixture fraction
310 coordinate are also indicated. It can be found that in all the four cases the mole fraction of Na
311 increases rapidly with Z in the fuel-lean region. In the fuel-rich region with $\phi > 2.0$, the profiles of
312 Na show a decreasing trend in the cases with HCl (Cases E/G), which is not observed in the cases
313 without HCl (Cases F/H). Both NaCl and NaOH have higher concentrations in fuel-lean and
314 fuel-rich regions while relatively low concentrations under the stoichiometric condition. HCl is also
315 found to decrease the concentrations of NaOH and Na in the fuel-rich region with $\phi > 2.0$. For
316 Na₂SO₄, it can reach a higher concentration when HCl is not presented but its mole fraction is still
317 below 1 ppm in the whole range of Z . Since the concentrations of sulfurous sodium species are quite
318 low, the effects of SO₂ on the profiles of Na, NaCl and NaOH are minor, as shown in the comparison
319 between the cases with SO₂ involved (Cases E/F) and the cases without SO₂ (Cases G/H).



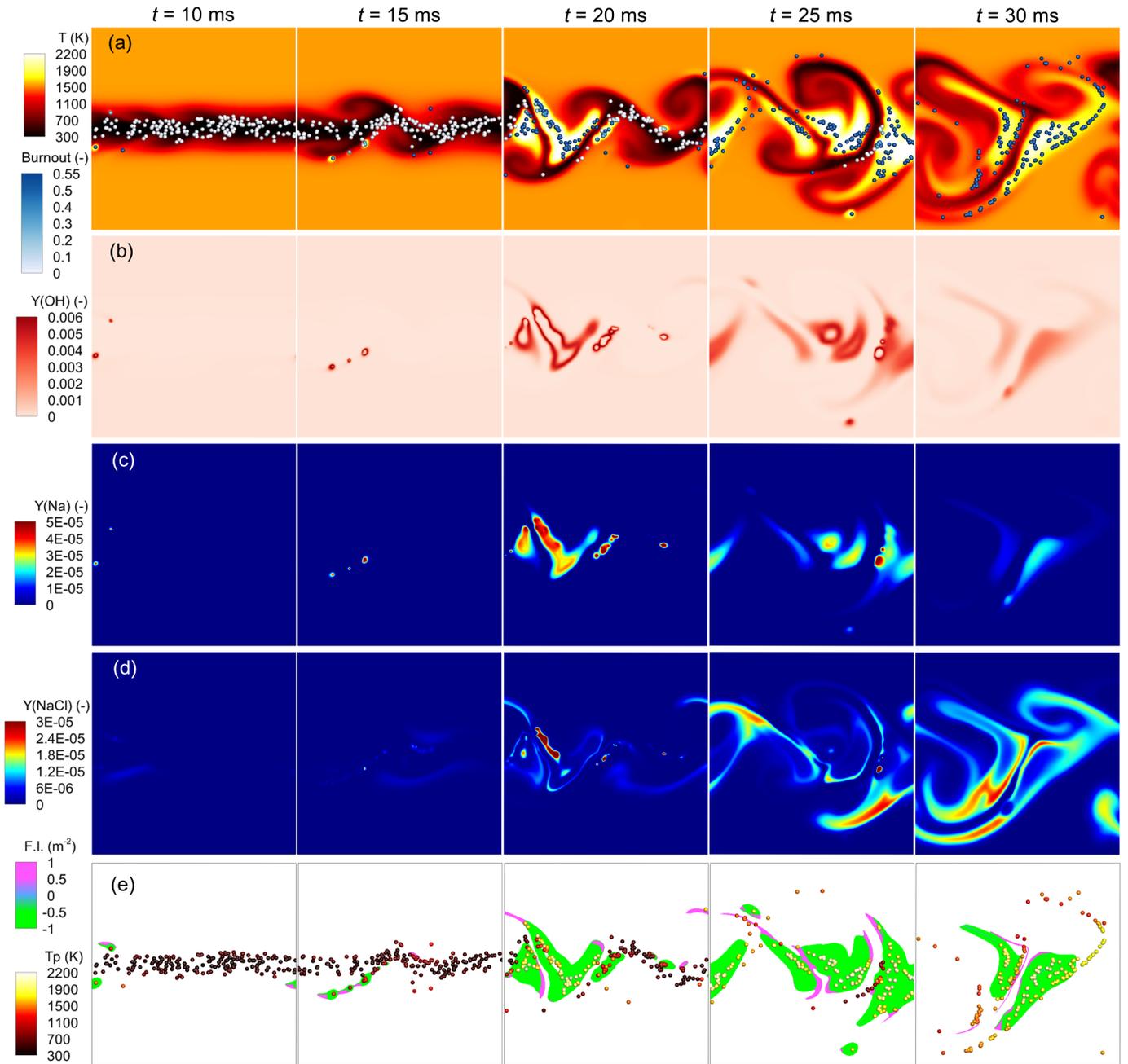
320
 321 Figure 4. Comparison of sodium species distribution in the mixture fraction space of the 1D
 322 diffusion volatile flame among Case E (the baseline case), Case F (HCl removed), Case G (SO₂
 323 removed) and Case H (both HCl and SO₂ removed).

324 *4.3. Characteristics of the 2D pulverized-coal flame*

325 The transformation characteristics of the sodium species in the 2D pulverized-coal flame are
 326 now examined. Figure 5 shows the instantaneous distributions of the (a) gas temperature and particle
 327 burnout, (b) OH mass fraction, (c) Na mass fraction, (d) NaCl mass fraction, and (e) flame index and
 328 particle temperature of the pulverized-coal flame. In the early stage, the coal particles in the jet shear
 329 layers are heated by the high-temperature coflow. Volatiles including sodium, sulfur and chlorine
 330 compounds are then released from the particles due to the pyrolysis. Isolated flame structures [27, 34]
 331 are observed at $t = 10$ and 15 ms. Some particles are ignited at first in the shear layers, but the heat
 332 release is not strong enough to ignite adjacent coal particles. At $t = 20$ ms, more and more particles
 333 are ignited and Y_{OH} propagates around them, indicating a strong heat release and rapid spreading of
 334 the flame. Atomic sodium Na reaches a high concentration in the high-temperature flame region,
 335 while NaCl accumulates around the ignited particles. With most of the coal particles in the
 336 computational domain burn out at $t = 30$ ms, the burning tends to be weaker, but a wider combustion
 337 regime can be found as the mixing continues. The mass fractions of OH radical and atomic Na are

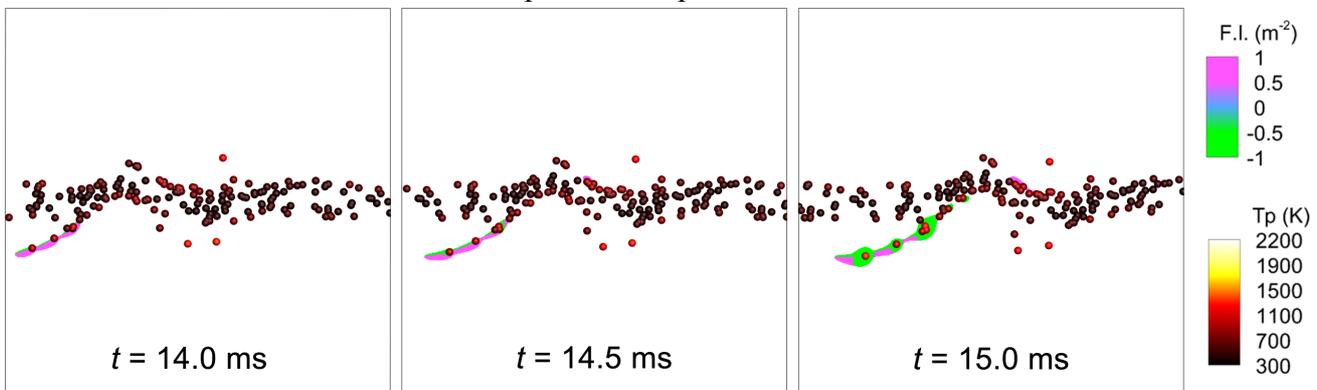
338 decreasing, but NaCl achieves a high concentration.

339 The flame index, F.I., [35, 50] is calculated from the spatial gradients of the mass fractions of
340 the volatile fuel and the oxidizer 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
341 values of F.I. probe premixed flame regimes, while negative ones indicate diffusion flame regimes.
342 In Fig. 5e, the F.I. is shown in the regions where the heat release rate exceeds 10^6 W/m³, which
343 indicates active burning regions. The maximum heat release rate in the 2D domain is 1.28×10^{10}
344 W/m³. It can be found that the diffusion combustion mode dominates in the region around coal
345 particles where high fluxes of volatile release locate, while the premixed regimes appears in the
346 surrounding area with a lower concentration of volatile. To better illustrate the characteristics of the
347 F.I. during the ignition process of coal particles, three continuous snapshots of the instantaneous
348 distribution of the F.I. at $t = 14.0, 14.5$ and 15.0 ms are shown in Fig. 6. It can be observed that the
349 first ignition of coal particles is controlled by homogeneous combustion and thus dominated by
350 premixed regimes. As the volatile around particles are ignited, the particles are heated rapidly by the
351 surrounding flame. The volatile release is then enhanced, which allows for the fuel to accumulate
352 before burning and therefore leads to a dominant diffusion combustion mode.



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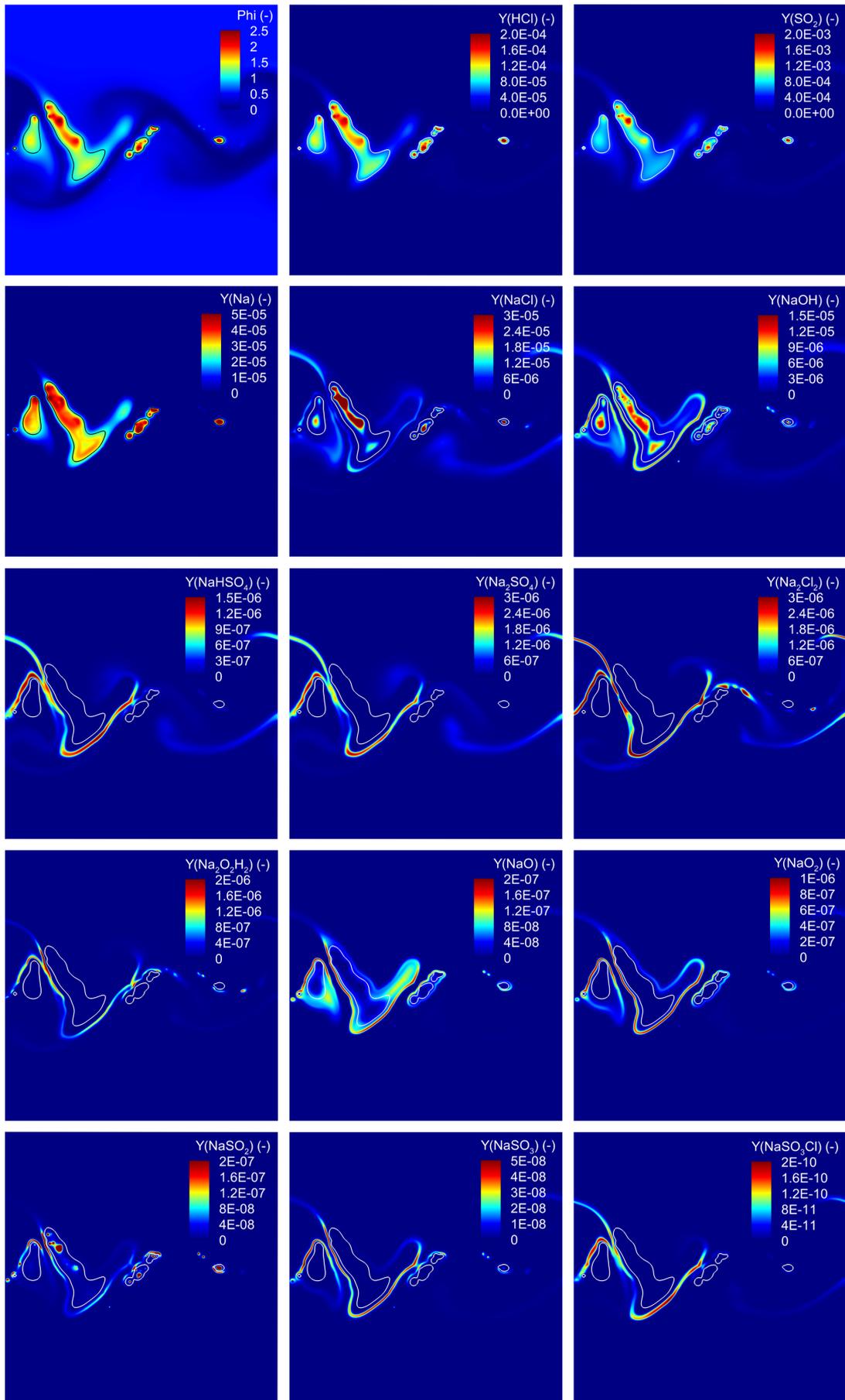
Figure 5. Time evolutions of instantaneous distributions of the (a) gas temperature and particle burnout, (b) OH mass fraction, (c) Na mass fraction, (d) NaCl mass fraction and (e) flame index and particle temperature.



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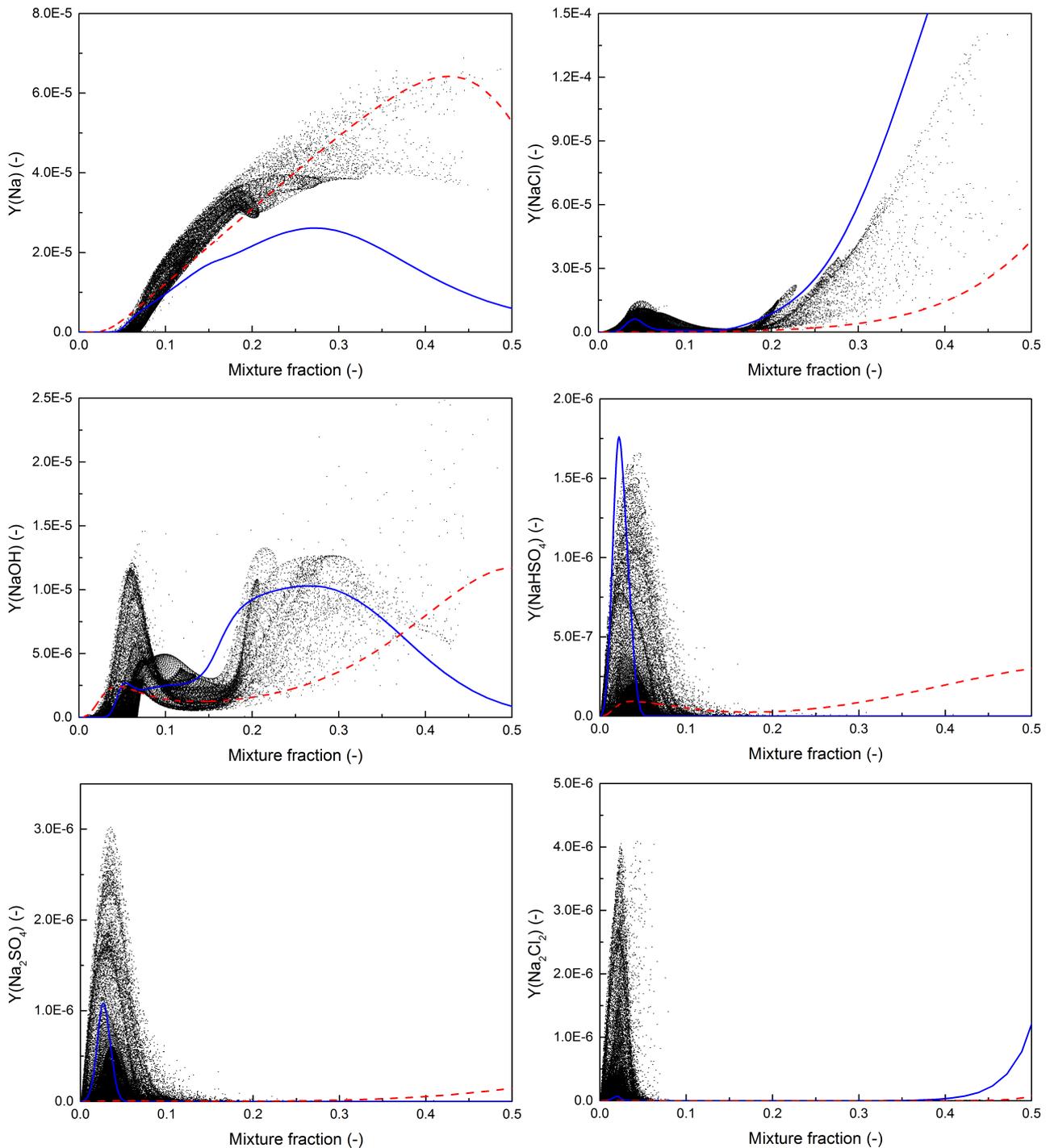
Figure 6. Time evolutions of instantaneous distribution of the flame index and particle temperature from $t = 14.0$ ms to $t = 15.0$ ms.

360 Figure 7 shows the instantaneous distributions of the mass fractions of all the twelve sodium
361 species in the DNS at $t = 20$ ms, along with the distributions of the equivalence ratio ϕ and the mass
362 fractions of HCl and SO₂. High values of ϕ are induced by the volatile stream released from coal
363 particles. The isoline of $\phi = 1$ superimposed in Fig. 7 represents the stoichiometric conditions for
364 reactions between the volatile and the oxidizer. It can be found that both HCl and SO₂ are mainly
365 located in the fuel-rich (inside the isoline) region, as they are released simultaneously with the
366 volatile stream. For the sodium species, atomic Na is also found to have a high concentration in the
367 fuel-rich region, which is in accordance with our previous study [34, 37]. Both NaOH and NaCl
368 feature a high concentration in the fuel-rich region, a moderate concentration in the fuel-lean region
369 (outside the isoline), while a low concentration in the stoichiometric region. Since NaOH is the
370 released sodium species along with the volatile, the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ explains
371 the high concentration of NaCl in the fuel-rich region. NaHSO₄ and Na₂SO₄ are the two main
372 sulfated sodium species, but their concentrations are much lower than that of NaCl. It can be
373 observed that the two sulfated sodium species mainly form in the fuel-lean region, similar to Na₂Cl₂
374 and Na₂O₂H₂, which are favored sodium species in the pre-combustion mixture. The other five minor
375 sodium species, i.e., NaO, NaO₂, NaSO₂, NaSO₃ and NaSO₃Cl, are also found to be produced under
376 the fuel-lean condition, except that NaSO₂ is also largely generated in the fuel-rich region where
377 abundant sodium and sulfur exist.



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Figure 7. Instantaneous distributions of the equivalence ratio (ϕ), the mass fractions of HCl, SO₂ and all the twelve sodium species at $t = 20$ ms. The isoline of $\phi = 1$ is superimposed.



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385 Figure 8. Scatter plots of instantaneous mass fractions of Na, NaCl, NaOH, NaHSO₄, Na₂SO₄ and
 386 Na₂Cl₂ against Z at $t = 20$ ms. Blue solid line and red dash line are the sodium profiles obtained from
 387 1D counterflow diffusion flames, corresponding to the lowest (23 s^{-1}) and highest strain rates (11318
 388 s^{-1}).

389 *4.4. Sodium species dynamics*

390 Figure 8 shows the scatter plots of instantaneous mass fractions of six sodium species against
 391 the mixture fraction, Z , at $t = 20$ ms. For the three-stream mixing, 2D pulverized-coal flame, the
 392 mixture fractions of the volatile released from pulverized-coal particles (the fuel stream), the air jet

393 which carries pulverized-coal particles (the oxidizer stream) and the high-temperature coflow are $Z =$
394 1, $Z = 0$ and $Z = 0.068$, respectively. Na, NaCl and NaOH are found to be the three major sodium
395 species in the reaction products. Y_{Na} stays almost zero in the range of $Z < 0.05$, and then increase
396 rapidly with Z . The distributions of Y_{NaCl} and Y_{NaOH} are subtler. Their mass fractions reach the first
397 peak around $Z = 0.05$, then decrease to a much lower value under the stoichiometric condition of Z_{st}
398 $= 0.138$, then increase again for higher Z and reach a much higher value under the fuel-rich condition
399 than the first peak. Finally, Y_{NaHSO_4} , $Y_{\text{Na}_2\text{SO}_4}$ and $Y_{\text{Na}_2\text{Cl}_2}$ feature a single-peak distribution within the
400 fuel-lean regime of $Z < 0.138$, similar to the mass fractions of other sodium species, i.e., $Y_{\text{Na}_2\text{O}_2\text{H}_2}$,
401 Y_{NaO} , Y_{NaO_2} , Y_{NaSO_3} , $Y_{\text{NaSO}_3\text{Cl}}$ (not shown here). The distribution of Y_{NaSO_2} is similar to Y_{NaCl} , which
402 has higher values both in the fuel-lean and fuel-rich regimes (not shown here).

403 The blue solid line and the red dash line in Fig. 8 are the sodium profiles obtained from 1D
404 counterflow diffusion flames, corresponding to the lowest and highest strain rates, respectively. The
405 high-strain rate (red dash line) slow down the consumption of NaOH and the production of NaHSO₄
406 and Na₂SO₄ in the fuel-lean regime. The generation of NaCl is also limited under the high-strain rate,
407 but the generation of atomic Na is found to be promoted. Compared with the sodium profiles from
408 1D counterflow diffusion flames, the DNS scatters basically follow a similar trend, but many data
409 points fall outside the region between the two profiles corresponding to the lowest and highest strain
410 rates. These points are likely to be representative of unsteadiness and/or partial premixing of the
411 reactants, since the volatile, after being ejected from the particles, and the ambient air are rapidly
412 mixed in a partially premixed mode, as in [51]. In addition, the radiation heat loss also contributes to
413 the mismatch between DNS scatters and profiles from 1D diffusion flames.

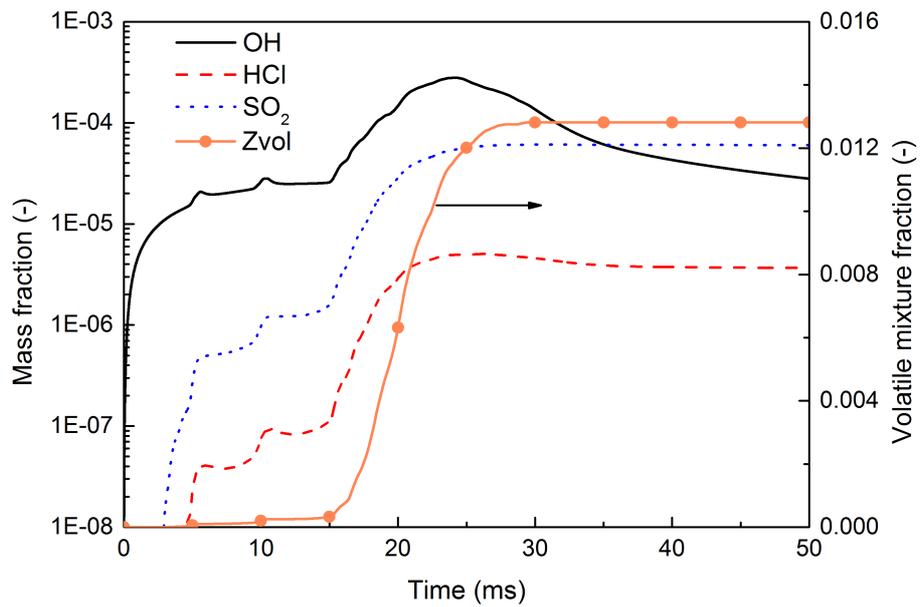
414 4.5. Statistics of the 2D pulverized-coal flame

415 Figures 9 and 10 show the time evolutions of the averaged mass fractions of OH, HCl, SO₂, Z_{vol}

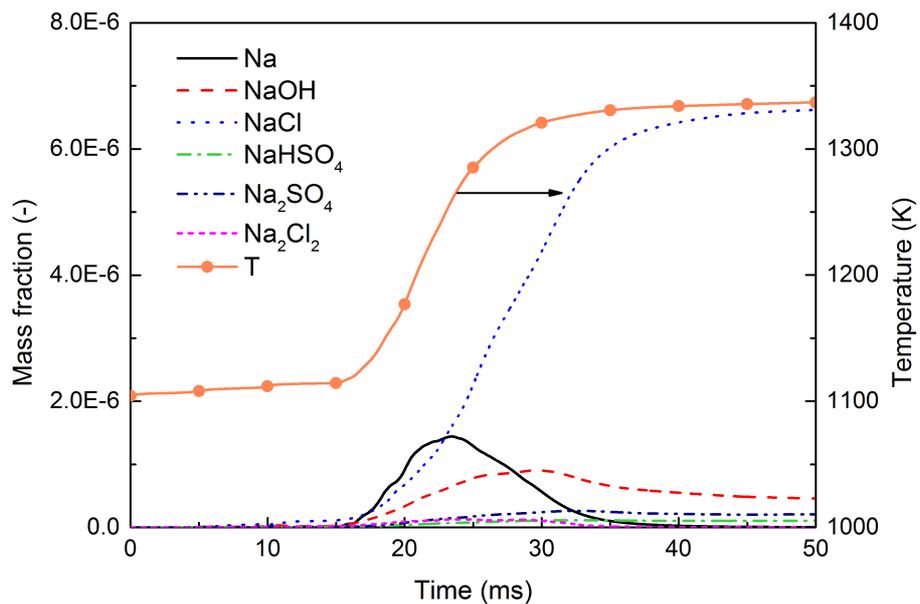
416 and six sodium species, and the averaged gas temperature of the 2D pulverized-coal flame, all of
 417 which are calculated as the mean over the 2D computational domain. Z_{vol} is the volatile mixture
 418 fraction, which is obtained from the following equation:

$$419 \quad D_t(\rho Z_{vol}) = \partial_j(\rho D_Z \partial_j Z_{vol}) + \dot{S}_{Y,p,vol} \quad (7)$$

420 where D_Z is the diffusivity coefficient of volatile (m^2/s) and is set equal to the thermal diffusivity
 421 coefficient. $\dot{S}_{Y,p,vol}$ is the source term of the mass of the volatile released from coal particles.



422
 423 Figure 9. Time evolutions of the mean mass fractions of OH, HCl, SO₂ and Z_{vol} averaged over the 2D
 424 computational domain.



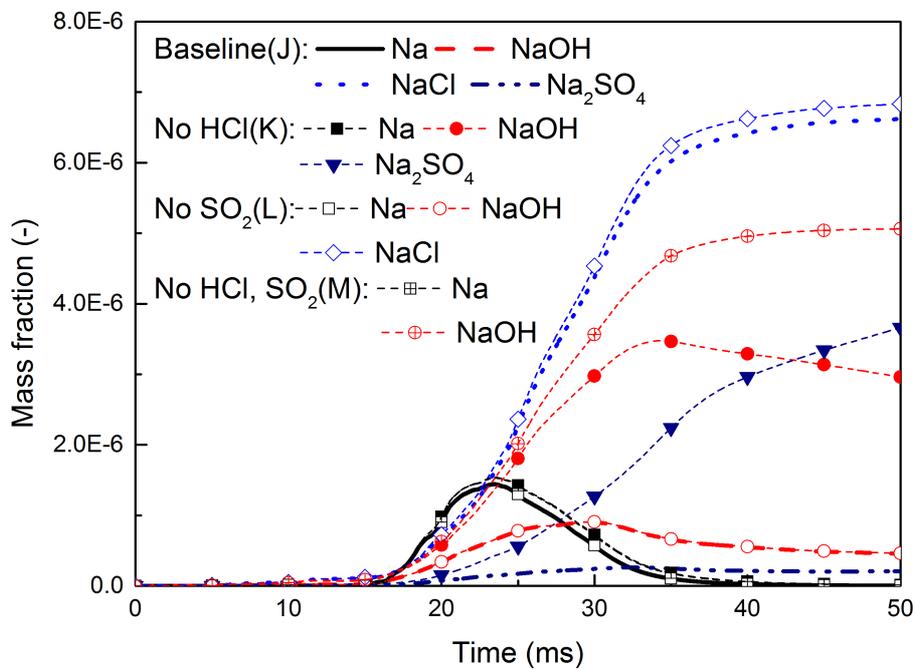
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 426 Figure 10. Time evolutions of the averaged mass fractions of Na, NaOH, NaCl, NaHSO₄, Na₂SO₄
 427 and Na₂Cl₂, and the averaged gas temperature.

428 At $t = 5$ and 10 ms, small peaks can be observed for Y_{OH} , Y_{HCl} and Y_{SO_2} , and also for the mass
429 fractions of sodium species in log-scale (not shown here). This is because the volatile around some
430 coal particles is ignited and the flame heats the particles rapidly, which therefore leads to a high flux
431 of volatile release. After $t = 15$ ms, both Z_{vol} and T increase rapidly, which indicates the
432 pulverized-coal jet is actively burning. The mass fractions of Y_{OH} , Y_{HCl} , Y_{SO_2} , Y_{Na} and Y_{NaCl} also start
433 to significantly increase after $t = 15$ ms. After $t = 30$ ms, both Z_{vol} and T remain almost constant,
434 indicating that the volatile release and homogeneous combustion have both ended. However,
435 although the averaged gas temperature remains after $t = 30$ ms, the variance of the gas temperature in
436 the domain decreases due to the turbulent mixing of the hot products and the surroundings. It
437 explains the variation of the species mass fractions after $t = 30$ ms, e.g. the decreasing Y_{HCl} , which
438 should be attributed to the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$. At the end of the simulation ($t = 50$
439 ms), NaCl is found to be the major sodium product while the other sodium species are minor.

440 *4.6. Effects of HCl and SO₂ on sodium emissions in the 2D pulverized-coal flame*

441 To investigate the effects of HCl and SO₂ on sodium transformation characteristics, three
442 additional DNS cases were set up, which are Case K (HCl is removed from the volatile), Case L
443 (SO₂ is removed from the volatile) and Case M (both HCl and SO₂ are removed from the volatile).
444 All the removed species are replaced by N₂. The original baseline DNS case is referred to as Case J.
445 Figure 11 shows the comparison between the cases on the time evolution of the representative
446 sodium species Na, NaOH, NaCl and Na₂SO₄. It can be found that without HCl and SO₂, NaOH is
447 the main sodium product at the end of the simulation (Case M). When only HCl is included in the
448 volatile, NaOH is largely consumed by HCl and NaCl forms as the main sodium product (Case L). If
449 SO₂ is presented while HCl is not, NaOH is then partly transformed to Na₂SO₄, and both NaOH and
450 Na₂SO₄ become the major sodium products (Case K). Interestingly, when both HCl and SO₂ are

451 presented (Case J), the reaction characteristics of the sodium species are very similar to Case L with
 452 HCl but no SO₂. It implies that SO₂ has only a minor contribution to the reactions with sodium
 453 species when HCl also exists in the released volatile. Hence, HCl has a much stronger ability to react
 454 with sodium species than SO₂. In view of the reaction paths, HCl reacts with sodium species in a
 455 straightforward way, e.g., $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ and $\text{HCl} + \text{Na} \rightarrow \text{NaCl} + \text{H}$. However, the
 456 reactions between SO₂ and sodium species are more complex. The SO₂ is first oxidized to SO₃, to
 457 then reacts with sodium species, e.g., NaOH, to form NaHSO₄, and finally produce Na₂SO₄ via
 458 shuffle reactions, e.g., $\text{NaHSO}_4 + \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$.



459
 460 Figure 11. Comparison of time evolutions of the averaged mass fractions of sodium species among
 461 Case J (the baseline case), Case K (HCl removed), Case L (SO₂ removed) and Case M (both HCl and
 462 SO₂ removed).

463 *4.7. Comparison of sodium emission characteristics in 1D and 2D flames*

464 The 1D premixed flame simulation results (Fig. 2) show that Na has the highest concentration
 465 in the sodium products at $\phi = 1.0$ and 2.0 , which is consistent with the 1D diffusion flame simulation
 466 results (Fig. 4). However, under the fuel-lean condition of $\phi = 0.5$, the 1D premixed flame results
 467 show the major sodium product is NaCl while in the 1D diffusion flame results it is Na. The

468 discrepancy should be attributed to the fact that the 1D premixed flame is freely propagating while
469 the 1D diffusion flame is strained. From the statistics of the 2D simulation under the baseline
470 condition, NaCl is found to be the major sodium product. The dilution effect of the coflow in the 2D
471 pulverized-coal flame leads to an overall low equivalence ratio of 0.26 (corresponding to a mixture
472 fraction $Z = 0.043$). From the 1D flame results, it can be found that indeed NaCl is the major sodium
473 product under this fuel-lean condition.

474 **5. Conclusions**

475 The transformation characteristics of sodium species in pulverized-coal combustion are
476 numerically investigated via 1D freely propagating premixed and 1D counterflow diffusion flames of
477 coal volatile, and a 2D pulverized-coal flame. Detailed chemistry has been employed for both the
478 combustion of volatile hydrocarbon fuels and the reactions of sodium species. From the 1D premixed
479 flame simulations, it is found that the most significant sodium product is Na under stoichiometric (ϕ
480 = 1.0) and fuel-rich conditions ($\phi = 2.0$) while it is NaCl under fuel-lean condition ($\phi = 0.5$). NaOH
481 is another major sodium product. HCl is found to have a significant influence on the profile of NaOH
482 in the initial unburned region. It also affects the distribution of Na_2SO_4 . However, the effects of SO_2
483 on the sodium profiles are minor. From the 1D diffusion flame simulations, HCl is found to decrease
484 the concentrations of Na and NaOH in the fuel-rich region with $\phi > 2.0$.

485 The transformation characteristics of the sodium species in a 2D pulverized-coal flame are then
486 examined. From the instantaneous distribution characteristics, atomic Na is found to have a high
487 concentration in the fuel-rich region. Both Y_{NaOH} and Y_{NaCl} feature a complex distribution over the
488 mixture fraction space, as they reach higher concentrations under both fuel-rich and fuel-lean
489 conditions and decrease to a much lower concentration under the stoichiometric condition. NaHSO_4
490 and Na_2SO_4 are the two main sulfated sodium species which form mainly in the fuel-lean region, but

491 their concentrations are much lower than that of NaCl. From the statistics of the 2D simulation, NaCl
492 is found to be the major sodium product, which is consistent with the 1D simulations. Finally, the
493 parametric study shows that HCl has a much stronger ability to react with sodium species than SO₂.

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Figure captions

Figure 1. Schematic diagram of computational configuration.

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

Figure 3. Comparison of sodium species distribution versus distance along the 1D premixed volatile flame between Case A (the baseline case), Case B (HCl removed), Case C (SO₂ removed) and Case D (both HCl and SO₂ removed) at equivalence ratio $\phi = 0.5$ (a), $\phi = 1.0$ (b) and $\phi = 2.0$ (c).

Figure 4. Comparison of sodium species distribution in the mixture fraction space of the 1D diffusion volatile flame among Case E (the baseline case), Case F (HCl removed), Case G (SO₂ removed) and Case H (both HCl and SO₂ removed).

Figure 5. Time evolutions of instantaneous distributions of the (a) gas temperature and particle burnout, (b) OH mass fraction, (c) Na mass fraction, (d) NaCl mass fraction and (e) flame index and particle temperature.

Figure 6. Time evolutions of instantaneous distribution of the flame index and particle temperature from $t = 14.0$ ms to $t = 15.0$ ms.

Figure 7. Instantaneous distributions of the equivalence ratio (ϕ), the mass fractions of HCl, SO₂ and all the twelve sodium species at $t = 20$ ms. The isoline of $\phi = 1$ is superimposed.

Figure 8. Scatter plots of instantaneous mass fractions of Na, NaCl, NaOH, NaHSO₄, Na₂SO₄ and Na₂Cl₂ against Z at $t = 20$ ms. Blue solid line and red dash line are the sodium profiles obtained from 1D counterflow diffusion flames, corresponding to the lowest (23 s^{-1}) and highest strain rates (11318 s^{-1}).

Figure 9. Time evolutions of the mean mass fractions of OH, HCl, SO₂ and Z_{vol} averaged over the 2D computational domain.

Figure 10. Time evolutions of the averaged mass fractions of Na, NaOH, NaCl, NaHSO₄, Na₂SO₄ and Na₂Cl₂, and the averaged gas temperature.

Figure 11. Comparison of time evolutions of the averaged mass fractions of sodium species among Case J (the baseline case), Case K (HCl removed), Case L (SO₂ removed) and Case M (both HCl and SO₂ removed).

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