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# Optical investigation of gas-phase KCl/KOH sulfation in post flame conditions

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ABSTRACT

A counter-flow reactor setup was designed to investigate the gas-phase sulfation and homogeneous nucleation of potassium salts. Gaseous KOH and KCl were introduced into the post-flame zone of a laminar flat flame. The hot flame products mixed in the counter-flow with cold $N_2$, with or without addition of $SO_2$. The aerosols formed in the flow were detected through Mie scattering of a 355 nm laser beam. The temperature distribution of the flow was measured by molecular Rayleigh scattering thermometry. From the temperature where nucleation occurred, it was possible to identify the aerosols formed. Depending on the potassium speciation in the inlet and the presence of $SO_2$, they consisted of $K_2SO_4$, KCl, or $K_2CO_3$, respectively. The experiments showed that KOH was sulphated more readily than KCl, resulting in larger quantities of aerosols. The sulfation process in the counter-flow setup was simulated using a chemical kinetic model including a detailed subset for the Cl/S/K chemistry. Similar to the experimental results, much more potassium sulfate was predicted when seeding KOH compared to seeding KCl. For both KOH and KCl, sulfation was predicted to occur primarily through the reactions among atomic K, $O_2$ and $SO_2$, forming $KHSO_4$ and $K_2SO_4$. The higher propensity for sulfation of KOH compared to KCl was mostly attributed to the lower thermal stability of KOH, facilitating formation of atomic K. According to the model, sulfation also happened through $SO_3$, especially for KCl ($KCl \rightarrow KSO_3Cl \rightarrow K_2SO_4$).

## 1. Introduction

Biomass, including energy crops [1], agricultural products [2] and industrial biomass waste [3], is considered as a sustainable and carbon neutral energy source. It is commonly combusted in boilers to provide heat and/or power. However, biomass such as agricultural residues may contain relatively high concentrations of potassium, chlorine and sulfur. During combustion, these elements lead to the formation of potassium chloride (KCl), potassium hydroxide (KOH), hydrogen chloride (HCl) and sulfur dioxide ($SO_2$), causing problems of slagging and fouling, corrosion, and emissions of harmful gases and aerosols [2]. The presence of KCl in the flue gas may cause severe ash deposition and corrosion on the super-heater tubes [4]. Sulfation of KCl to $K_2SO_4$ by reaction with sulfur-containing additives [5–7] has been suggested as a method to mitigate deposition and corrosion processes, since $K_2SO_4$ is less corrosive and has a higher melting point than KCl.

Sulfation can occur via homogenous reactions between gas-phase KCl/KOH and sulfur oxides, i.e. $SO_2$ and $SO_3$. There are several studies on the sulfation of gaseous KCl [5,7–16]. A detailed chemical mechanism was proposed by Glarborg and Marshall [10], involving the following reactions:

$$KCl + SO_3(+M) = KSO_3Cl(+M) \quad \text{(R1)}$$

$$KOH + SO_3(+M) = KHSO_4(+M) \quad \text{(R2)}$$

$$KSO_3Cl + H_2\ O = KHSO_4 + HCl \quad \text{(R3)}$$

$$KHSO_4 + KCl = K_2SO_4 + HCl \quad \text{(R4)}$$

$$KHSO_4 + KOH = K_2SO_4 + H_2O \quad \text{(R5)}$$

This mechanism was proven to be consistent with the experimental results of Iisa et al. [8]. The oxidation of $SO_2$ to $SO_3$ was considered to be the rate-limiting step. The importance of $SO_3$ has been supported by several experimental studies, e.g. [7,13].

More recently, Hindiyarti et al. [11] proposed a number of alternative sulfation routes to explain the observed sulfation rates at lower temperatures. One pathway involved the direct reaction between KOH and $SO_2$ to form $KHSO_3$, with oxidation of sulfite to sulfate as the rate-limiting step, instead of the oxidation of $SO_2$ to $SO_3$:

$$KOH + SO_2(+M) = KHSO_3(+M) \quad \text{(R6)}$$

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$$KHSO_3 + O_2 = KHSO_4 + O \quad (R7)$$

Another route of $K_2SO_4$ formation can be initiated by the reaction of atomic K with $SO_2$, forming KOSO, which is then oxidized to $KOSO_3$ and further to $KHSO_4$. These suggested pathways have not been confirmed experimentally, even though they are consistent with results reported by Kassman et al. [13] and Ekvall et al. [15,16].

To evaluate the detailed reaction mechanism, Li et al. [14] studied the formation of $K_2SO_4$ from gas-phase KCl and $SO_2$ in a homogeneous high temperature environment produced by a laminar burner where neither wall-based reactions nor other heterogeneous reactions could contribute to the sulfation processes. The study supported the importance of the reaction sequence R1, R3 and R4 for the sulfation of KCl.

Previous efforts have mostly focused on the sulfation of KCl. However, in combustion of low-chlorine woody biomass KOH is typically formed in larger concentrations than KCl. Despite the importance, knowledge on sulfation of KOH is still limited. In the present work, sulfation of both KOH and KCl was studied in a specially designed counter-flow reactor. Gas-phase KOH and KCl were provided by feeding micro droplets of KCl/KOH water solutions to the hot flue gas from a premixed $CH_4$/air flame, having an equivalence ratio of 0.9 or 1.1. The combustion products including the gaseous potassium compounds then mixed with an opposed $N_2$ flow containing $SO_2$ to form a gas-phase counter-flow configuration. The temperature distribution was measured and the aerosols formed in the flow were detected. The results were interpreted in terms of an updated chemical kinetic model for Cl/S/K interactions to provide a better understanding of the sulfation process.

## 2. Experiment and simulation

### 2.1. Burners

A schematic of the counter-flow burner setup is shown in Fig. 1. A uniform laminar $N_2$ flow seeded with a known amount of $SO_2$ was supplied through a 60 mm diameter sintered-metal porous plug of a McKenna burner. The outlet flow speed was 10 cm s$^{-1}$ and the temperature was 298 K. The concentration of $SO_2$ in the flow was set to 0 ppm, 245 ppm or 980 ppm, respectively.

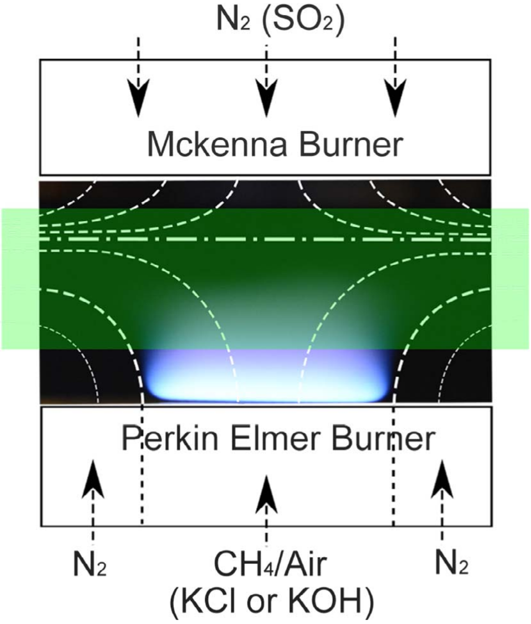

**Fig. 1.** Schematic of the counter-flow setup together with a photo of a typical flame adopted in the experiment. The white dash lines depict the flow field. The light green square indicates the region illuminated by the laser sheet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

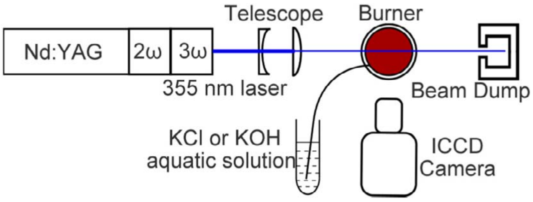

**Fig. 2.** Schematic of the laser measurement system.

A uniform laminar hot flue gas was generated on a Perkin Elmer burner, modified to allow for seeding of water solutions [17]. A chamber connected to an upper honeycomb matrix with a diameter of 23 mm was used to mix methane and air for the burner. In the present study, a premixed $CH_4$/air flow with an unburned gas speed of 15 cm s$^{-1}$ was used to generate a flat laminar flame at an equivalence ratio of either 0.9 or 1.1 above the burner. An aqueous solution containing potassium chloride or potassium hydroxide was seeded homogeneously into the flame by a nebulizer as shown in Fig. 2. The salt concentration of the aqueous solution was 0.5 mol l$^{-1}$, and the concentration of the gas-phase potassium chloride or potassium hydroxide in the hot flue gas was calculated to be around 215 ppm based on the consumption rate. A $N_2$ co-flow at room temperature was used to shield the flame from the ambient air with an exit flow speed of 15 cm s$^{-1}$. The distance between the Perkin Elmer burner and the McKenna burner was 20 mm. A stable counter-flow was formed between the $N_2$ flow from the McKenna burner and the hot flue gas from the Perkin Elmer burner. The reactions between $SO_2$ and KCl/KOH occurred in the mixing zone.

### 2.2. Laser measurement system

When the flue gas containing KCl or KOH mixed with the cold $N_2$ ($SO_2$) flow, the temperature decreased to ~1000 K and aerosols were formed. The aerosols were detected from the Mie scattering when illuminated by a 355 nm laser beam from the third harmonic of a Nd:YAG laser (Brilliant B, Quantel) operated at 10 Hz with a pulse energy of 50 mJ, formed into a laser sheet using a telescope lens system. The laser sheet passed through the counter-flow region vertically as depicted in Fig. 1. The signal of the Mie scattering from the aerosols was detected by an intensified CCD camera (ICCD, PI-MAX II, Princeton Instruments). No laser breakdown was observed from illumination of the aerosols.

Using the same system, the temperature distribution of the counter-flow was measured through Rayleigh scattering thermometry based on the following equation [18]:

$$T_{flow\ gas} = T_{air}(I_{air}/I_{flow\ gas})(\sigma_{flow\ gas}/\sigma_{air}) \quad (1)$$

where $T_{flow\ gas}$ is the temperature of the counter-flow, $T_{air}$ is the temperature of the reference gas, i.e., the ambient air, which had a temperature of 298 K, $I_{flow\ gas}$ and $I_{air}$ are the Rayleigh scattering signals of the counter-flow gas and the room temperature air, which can be obtained by the laser setup shown in Fig. 2, and $\sigma_{flow\ gas}$ and $\sigma_{air}$ are the molecular Rayleigh scattering cross sections of counter-flow gas and air. For the Rayleigh scattering cross sections, the same value was used during the temperature calculation. The uncertainty of the obtained temperature caused by the cross section difference between air and the counter flow gas was estimated to be less than 25 K for the temperature at 700 K.

### 2.3. Numerical approach

The sulfation reaction in the present setup was simulated using the counter-flow application code in CHEMKIN [19]. The composition of the hot flue gas was obtained based on the one-dimensional modeling of