



## Experimental and Modeling Studies of SO<sub>3</sub> Homogeneous Formation in the Post-flame Region

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### ABSTRACT

SO<sub>3</sub> exists in the atmosphere in the form of sulfuric acid aerosol, heavily polluting the environment and decreasing the safety of boiler equipment. This study focuses on the homogeneous formation mechanism of SO<sub>3</sub> in the post-flame region. We conducted experiments and simulations to investigate the influence of various combustion parameters on SO<sub>3</sub> generation. The formation of SO<sub>3</sub> was affected by factors such as temperature and the concentrations of O<sub>2</sub>, SO<sub>2</sub>, NO, and H<sub>2</sub>O. With a rise in temperature, the SO<sub>3</sub> concentration initially increased but then decreased, reaching its maximum at about 1000°C, which indicates that SO<sub>2</sub> can promote the formation of SO<sub>3</sub> over a certain temperature range. An increase in the O<sub>2</sub> concentration promoted the formation of O and OH radicals, which enhanced the generation of SO<sub>3</sub> from SO<sub>2</sub>. The presence of NO resulted in direct and indirect interactions between NO<sub>x</sub> and SO<sub>x</sub> species for different reaction sets, potentially enhancing SO<sub>3</sub> generation. With an increase in the H<sub>2</sub>O concentration, SO<sub>3</sub> formation initially increased rapidly before plateauing. ROP (rate of production) and sensitivity analyses suggest that adding H<sub>2</sub>O will produce O and OH, which strongly influence SO<sub>3</sub> formation. Furthermore, the sensitivity analysis indicated that radicals and the direct reaction between SO<sub>2</sub> and NO<sub>2</sub> play significant roles in SO<sub>3</sub> formation.

**Keywords:** Sulfuric acid aerosol; Chemical kinetics; Mechanism analysis; ROP analysis; Sensitivity analysis.

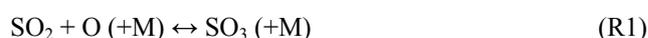
### INTRODUCTION

SO<sub>2</sub> is the atmospheric pollutant emitted from the combustion of fossil fuel. The main source of SO<sub>2</sub> is the combustion of coal (Kato *et al.*, 2016). A small amount of SO<sub>2</sub> will subsequently be oxidized to SO<sub>3</sub>. SO<sub>3</sub> causes serious damage to the equipment and environment of the boiler tail. Kagawa (2014) deemed that the growth of coal combustion has led to greater amounts of S emitted to the atmosphere. At temperatures above 200°C, as long as there is about 8% moisture in the flue gas, 99% of SO<sub>3</sub> will be converted into sulfuric acid vapor. SO<sub>3</sub> has always been in the atmosphere in the form of sulfuric acid aerosol (the diameter is generally 0.4–1.2 μm) (Hardman *et al.*, 1988). When the flue gas temperature is lower than the acid dew point, low temperature corrosion may occur on the air preheater and low temperature economizer. SO<sub>3</sub> can react with NH<sub>3</sub>, generating NH<sub>4</sub>HSO<sub>4</sub> which will obstruct the air preheater. Furthermore, SO<sub>3</sub> also reduces the rate of

mercury removal from flue gas (Moser, 2007).

Mist particles are emitted into the atmosphere, which gives smoke its blue color, and the minimum concentration of SO<sub>3</sub> causing this phenomenon is related to atmospheric conditions. In general, if the content of SO<sub>3</sub> in flue gas is above 10 ppm, smoke opacity will be significant. When the SO<sub>3</sub> concentration is 5 ppm, plume opacity can be as high as 20%. When the SO<sub>3</sub> concentration is more than 10 ppm, smoke will be visibly blue, increasing the H<sub>2</sub>SO<sub>4</sub> aerosol concentration near the power plant (Srivastava *et al.*, 2004). A U.S. EPA report showed that SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> aerosols may be associated with a series of adverse health effects, including respiratory tract irritation and difficulty breathing (Walsh *et al.*, 2006).

The concentration of SO<sub>3</sub> in flue gas is related to SO<sub>2</sub> concentration, the excess air coefficient, flue gas temperature, fly ash composition, and other factors (Lou, 2008). The conversion rate of SO<sub>2</sub> to SO<sub>3</sub> is about 0–2%. Kio (2001) determined that oxygen atoms in the high temperature combustion zone of a furnace react with SO<sub>2</sub> to form SO<sub>3</sub>:



The formation of SO<sub>3</sub> was shown by Fleig *et al.* (2009) to be the primary SO<sub>3</sub> formation pathway at 1000–1400°C:

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At 700–1000°C, SO<sub>3</sub> formation occurs via HOSO<sub>2</sub>:



It has been confirmed that (R2) and (R3) are insignificant above 1000°C, because of the low stability of HOSO<sub>2</sub> (Alzueta *et al.*, 2001). According to Han (2015), SO<sub>3</sub> formation is mainly controlled by thermodynamic equilibrium at high temperatures, and by reaction kinetics (Monckert *et al.*, 2008) at low temperatures.

During combustion, the S element in the fuel is partially converted to SO<sub>2</sub>, and if oxygen is excessive, some SO<sub>2</sub> will be further oxidized to SO<sub>3</sub> (Lee *et al.*, 1967). Previous studies have shown that the primary condition for SO<sub>3</sub> production is excess O<sub>2</sub>. If O<sub>2</sub> concentrations are below 3%, SO<sub>3</sub> production is sensitive to the O<sub>2</sub> concentration. But above this concentration, an increase in O<sub>2</sub> concentration has little effect on the formation of SO<sub>3</sub>. Combustion and flue gas cooling cover a large range of temperatures. At high temperatures (above 1300°C), formation of SO<sub>3</sub> can reach equilibrium within 2 s, while at low temperatures (i.e., 300–700°C), equilibration may take days to years. Temperature directly affects homogeneous SO<sub>3</sub> formation by changing the reaction rate and the equilibrium point of the reaction. The oxidation rate declines with the increase of temperature. It can be concluded SO<sub>3</sub> is mainly formed at intermediate temperatures of about 1000°C, given the residence time of flue gas in each temperature section. Glarborg *et al.* (1996) studied the reaction characteristics of SO<sub>2</sub> and found that peak SO<sub>3</sub> formation occurred around 950°C. On the other hand, Bayless *et al.* (2000) found that at low temperatures if free radicals (O, H, etc.) are abundant, a certain amount of SO<sub>3</sub> can also be obtained to maintain the

performance of ESP. In addition, Merryman (1979) studied staged combustion, assuming that temperature and O atom concentration were the main factors affecting formation of SO<sub>3</sub>, and suggested that temperature affects oxidation of SO<sub>2</sub> by changing the concentration of O atoms. Therefore, temperature not only affects SO<sub>3</sub> formation by changing the reaction equilibrium (the rate of SO<sub>3</sub> decomposition and formation), but also via important indirect effects.

Currently, most research is focused on the generation mechanism of SO<sub>2</sub> and NO<sub>x</sub>, ignoring SO<sub>3</sub> generation. In this paper, homogeneous formation of SO<sub>3</sub> and its influencing factors were studied by experiments and simulations, and the homogeneous formation mechanism of SO<sub>3</sub> in post-flame region was clarified.

## EXPERIMENTAL AND MODELING

### Introduction of Experimental Equipment

The experimental device is shown in Fig. 1. The setup consists of three major sections: burner, reactor, and sample collector. The inlet gas composition is SO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, NO and H<sub>2</sub>O. Gas is mixed into flue gas analyzer (testo 350). After the gas content is measured, the first three-way valve is adjusted to make N<sub>2</sub> and CO<sub>2</sub> enter the ultrasonic atomizer to carry H<sub>2</sub>O. Then adjust the second three-way valve to make all gases enter the reactor, which is heated by a tubular resistance furnace (SK-2.5-13TS). Exhaust gas then passes through a serpentine condenser tube. Using a digital display thermostatic water bath (HH-1), the condenser temperature is maintained at 80°C. The SO<sub>3</sub> concentration is measured by the U.S. EPA method 8A. The ideal one-dimensional flow reactor model is adopted, with a residence time of 4 s and a pressure of 1 atm.

The quartz tube reactor is 1065 mm long, with an outer diameter of 28 mm and an inner diameter of 24.4 mm. The total flow of the reaction gas is 3 L min<sup>-1</sup>, and the reaction gas composition is shown in Table 1.

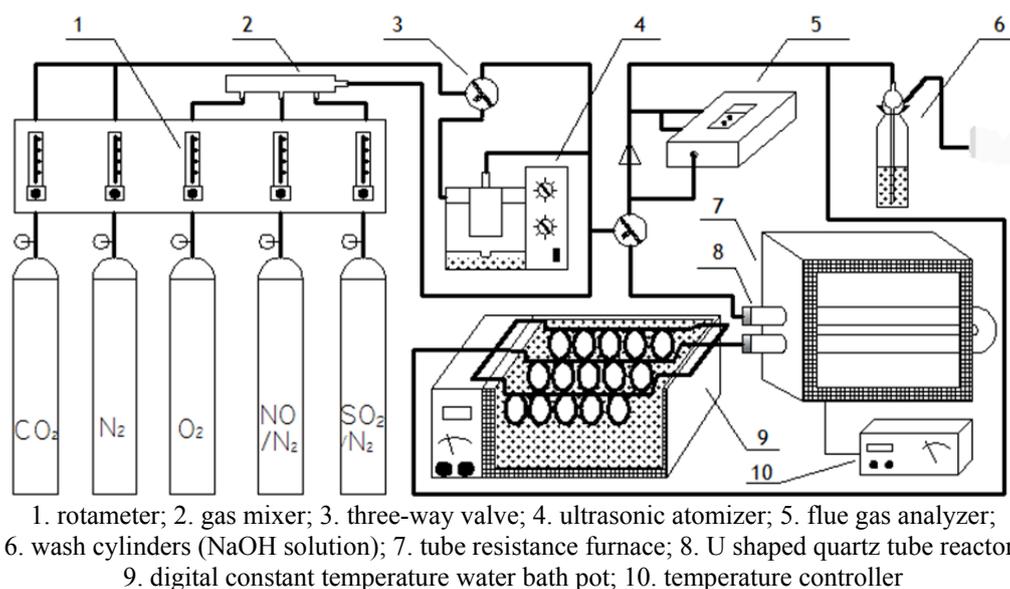


Fig. 1. Schematic diagram of experimental apparatus.

### Simulation Methods and Models

A detailed gas-phase kinetic model was utilized to discuss the measured SO<sub>3</sub> concentrations. The calculations were carried out by CHEMKIN-IV software. This combined model considers C, H, O, N, and S, include 694 reactions. But heterogeneous chemistry is not included in the mechanism. And the interactions between sulfur and chlorine are not included. The mechanism includes the oxidation of hydrocarbons based on the work of Glarborg *et al.* (1998, 2003) and Alzueta *et al.* (2008). The nitrogen chemistry and the interactions between hydrocarbons and nitrogen species are based on the work of Glarborg *et al.* (1998) and Dagaut *et al.* (2008). The sulfur chemistry in the mechanism is described in the work by Alzueta *et al.* (2001) and Giménez-López *et al.* (2011). Moreover, the reactions of sulfur-containing elements are more comprehensive in this model than previously. And the direct interactions between SO<sub>x</sub> and NO<sub>x</sub> species were considered in this model.

### RESULTS AND DISCUSSION

Gas-phase coal combustion experiments were performed to obtain speciation data of SO<sub>x</sub> under a variety of operating conditions. Sampling temperature ranged from 400°C to 1300°C within the reactor. Other factors included O<sub>2</sub>, SO<sub>2</sub>, NO, and H<sub>2</sub>O concentrations.

#### Effect of Temperature on SO<sub>3</sub> Formation

The experimental conditions were 550 ppm NO, 2000 ppm SO<sub>2</sub>, 2.22% H<sub>2</sub>O, and 5% O<sub>2</sub> (Fig. 2).

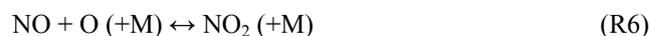
As shown in Fig. 2, the experimental results and simulated data indicated that the concentration of SO<sub>3</sub> first increased, but then decreased with increasing temperature. The maximum SO<sub>3</sub> concentration was around 1000°C. At 400–1000°C, the concentration of SO<sub>3</sub> increases with an increase in temperature, and the concentration of SO<sub>3</sub> decreased with an increase in temperature when the

temperature is higher than 1100°C. When the temperature was below 700°C, the SO<sub>3</sub> concentration was very near or below the limit of detection. Wang (2015) also observed a similar trend in SO<sub>3</sub> concentration with temperature. This model is modified to ensure that the modeling results in the middle temperature region (800–1200°C) are consistent with the experimental results, but the discrepancy in the low temperature region (400–700°C) cannot be completely eliminated.

Through ROP analysis, the main reactions of SO<sub>3</sub> were (R1)–(R4).



When the resistance furnace wall temperature is between 600°C and 800°C, the base reaction for SO<sub>3</sub> formation is (R4). The wall temperature of the resistance furnace increases the concentration of activated molecules in the reaction gas, and decomposition of H and OH with H<sub>2</sub>O increases. According to the literature (Mantashyana, 2014), O radicals are mainly produced by (R5) and decomposition of O<sub>2</sub>. The concentration of H radical increased in this temperature range, which promoted the formation of O radical. The concentration of NO<sub>2</sub> also was increased by (R6), and the rate of formation of (R4) increased as well. Higher concentrations of NO<sub>2</sub> result in (R4) playing a decisive role in the generation of SO<sub>3</sub>.



As temperature increases, the total formation rate of SO<sub>3</sub> increases rapidly. Fleig (2013) measured the formation of SO<sub>3</sub> by introducing different gas components into a one dimensional furnace. Results showed that NO promoted SO<sub>3</sub> formation at low temperatures.

**Table 1.** Gas composition in experiments.

Test	Inlet gas composition					
	N <sub>2</sub> (%)	CO <sub>2</sub> (%)	SO <sub>2</sub> (ppmv)	NO (ppmv)	O <sub>2</sub> (%)	H <sub>2</sub> O (%)
1	77.525	15	2000	550	5	2.22
2	81.525	15	2000	550	1	2.22
3	79.525	15	2000	550	3	2.22
4	75.525	15	2000	550	7	2.22
5	73.525	15	2000	550	9	2.22
6	77.675	15	500	550	5	2.22
7	77.625	15	1000	550	5	2.22
8	77.575	15	1500	550	5	2.22
9	77.475	15	2500	550	5	2.22
10	77.425	15	3000	550	5	2.22
11	77.48	15	2000	0	5	2.22
12	77.4546	15	2000	254	5	2.22
13	77.3814	15	2000	986	5	2.22
14	79.645	15	2000	550	5	0
15	67.445	15	2000	550	5	12.2
16	61.545	15	2000	550	5	18.1
17	46.445	15	2000	550	5	33.2

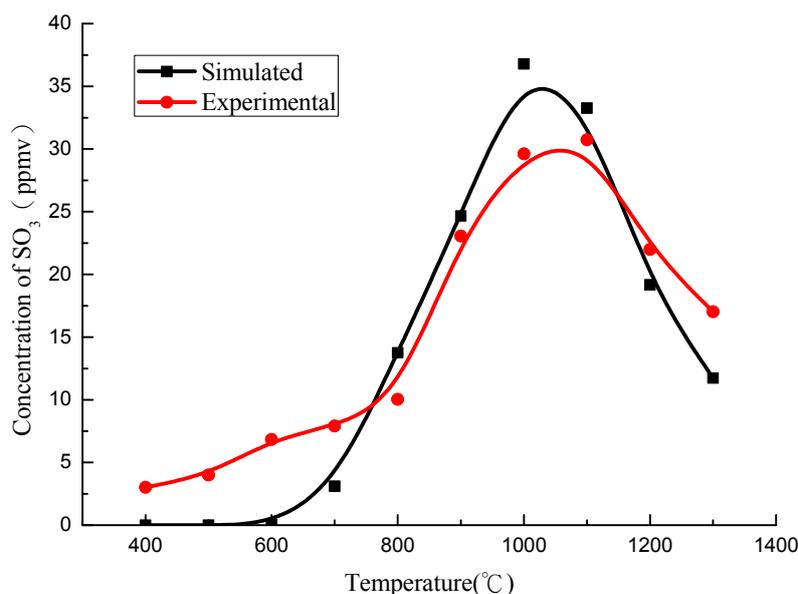


Fig. 2. Relationship between SO<sub>3</sub> concentration and temperature.

When the resistance furnace wall temperature is between 800°C and 1600°C, the basic reactions for SO<sub>3</sub> formation are (R3) and (R4). With an increase in temperature, H and OH production is enhanced by H<sub>2</sub>O decomposition. An increase in the concentration of H radicals promotes formation of O radicals, enhancing (R7) and leading to an increase in OH concentration. A combination of H and OH will promote (R2), which will facilitate (R3).



The concentration of OH radical is higher than NO<sub>2</sub>, so the effect of reaction (R3) is greater than that of (R4).

When the resistance furnace wall temperature is 1100°C, as the temperature continues to rise, the reaction rate of (R6) is accelerated and the concentration of NO<sub>2</sub> begins to decline. N<sub>2</sub> reacts with O<sub>2</sub> to generate large amounts of NO, and higher concentrations of NO inhibit (R4). Above 1100°C, the free radical HOSO<sub>2</sub> begins to decompose in the reaction gas.

Fleig *et al.* (2009) pointed out that formation of SO<sub>3</sub> in a power plant boiler mainly occurs between 900 and 1300°C, which is approximately consistent with the average temperature range of SO<sub>3</sub> generation.

#### Effect of O<sub>2</sub> on SO<sub>3</sub> Formation

The O<sub>2</sub> concentration of the combustible mixture was varied from 1% and 9% in simulations and experiments. Other inlet gas content remained unchanged.

Fig. 3 shows the outlet concentration of SO<sub>3</sub> derived for different concentrations of O<sub>2</sub> in the inlet gas. The SO<sub>2</sub> concentration was 2000 ppm in all experiments. SO<sub>2</sub> formation was favored by high O<sub>2</sub> concentrations, as well as by temperature. The concentration of SO<sub>3</sub> increased with increasing O<sub>2</sub>, but the degree of influence gradually decreased. Duan (2015) also demonstrated that oxygen enrichment enhances SO<sub>3</sub> formation. When the concentration

of O<sub>2</sub> is less than 7%, the increase in O<sub>2</sub> concentration promotes the formation of SO<sub>3</sub>. On the contrary, the influence on the formation of SO<sub>3</sub> is reduced. As shown in (R5), with increasing O<sub>2</sub> concentration, a higher concentration of O and OH radicals is expected, which contributes to higher SO<sub>3</sub> formation. Due to the fixed content of SO<sub>2</sub>, when O<sub>2</sub> concentration is low, increasing the oxygen content can rapidly increase SO<sub>3</sub> formation. However, the O<sub>2</sub> that can participate in the reaction is affected by SO<sub>2</sub> concentration and temperature, so the effect of oxygen content on the SO<sub>3</sub> production rate gradually decreases.

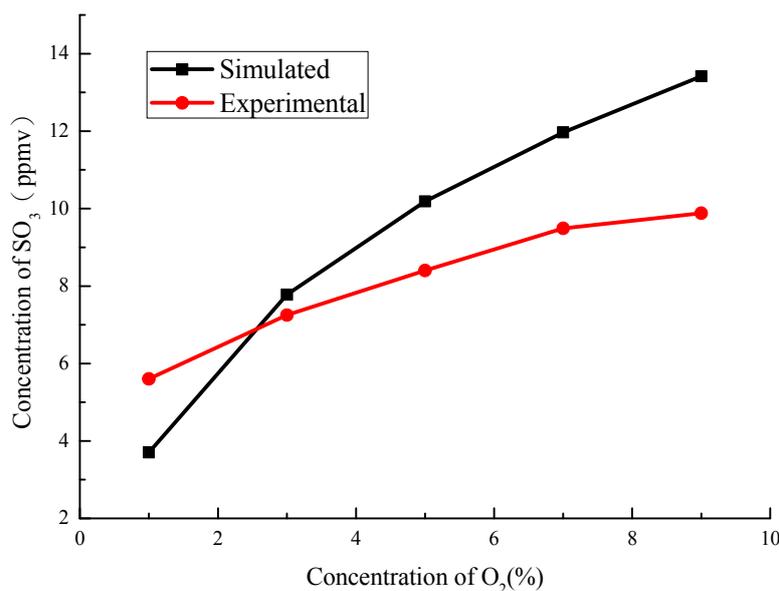
ROP analysis was performed on reactions (R1)–(R4). When the concentration of O<sub>2</sub> increases, both (R3) and (R4) play a major role in the formation of SO<sub>3</sub>. An increase in O<sub>2</sub> concentration promoted (R5) to produce more free radical O and OH, and then promoted (R6), such that (R3) plays a decisive role in the formation of SO<sub>3</sub>.

#### Effect of SO<sub>2</sub> on SO<sub>3</sub> Formation

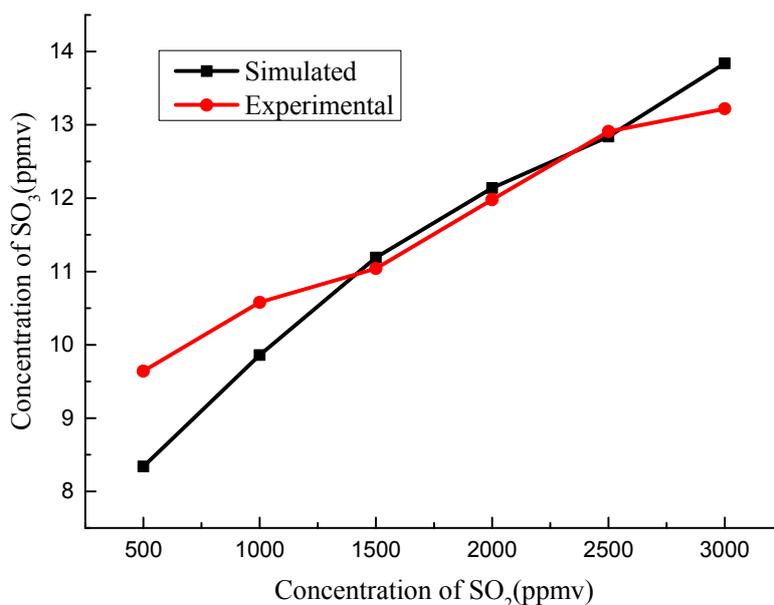
The experimental and modeling conditions were 550 ppm NO, 2.22% H<sub>2</sub>O, 5% O<sub>2</sub>, and a residence time of 4 s, SO<sub>2</sub> concentration ranged 500–3000 ppm. Fig. 4 shows the experimental and simulated SO<sub>3</sub> concentrations for different inlet SO<sub>2</sub> concentrations.

As shown in Fig. 4, both the experimental and modeling results show that the concentration of SO<sub>3</sub> increased with an increase in SO<sub>2</sub>. A similar trend was observed in a study (Belo *et al.*, 2014) investigating gas-phase conversion of SO<sub>2</sub> to SO<sub>3</sub> in a simulated oxy-combustion environment, which was explained by the dependency of the reaction order on SO<sub>2</sub> concentration.

The simulation process analyzed by ROP shows that the most important reactions for SO<sub>3</sub> formation are (R3) and (R4) with increasing SO<sub>2</sub> concentrations. Increasing the concentration of SO<sub>2</sub> promotes reaction (R2), thus promoting (R3).



**Fig. 3.** The relationship between SO<sub>3</sub> concentration and O<sub>2</sub> concentration.



**Fig. 4.** SO<sub>3</sub> formation versus SO<sub>2</sub> concentration.

#### Effect of NO Concentration

NO concentrations between 0 and 1000 ppm were analyzed in simulations and experiments to investigate the effect of NO on the final SO<sub>3</sub> concentration (Fig. 5).

NO is known to affect the amount of SO<sub>3</sub> produced in this system. Increasing NO concentration, an increase in SO<sub>3</sub> concentration was observed for both experiments and simulations. When the NO concentration is below 600 ppmv, there are some differences between experimental data and simulated data. However, for NO concentration above 600 ppmv, the experimental results are basically consistent with simulated results. In a previous investigation, Fleig *et al.* (2011) showed that small amounts of NO can result in increased SO<sub>3</sub> generation during combustion.

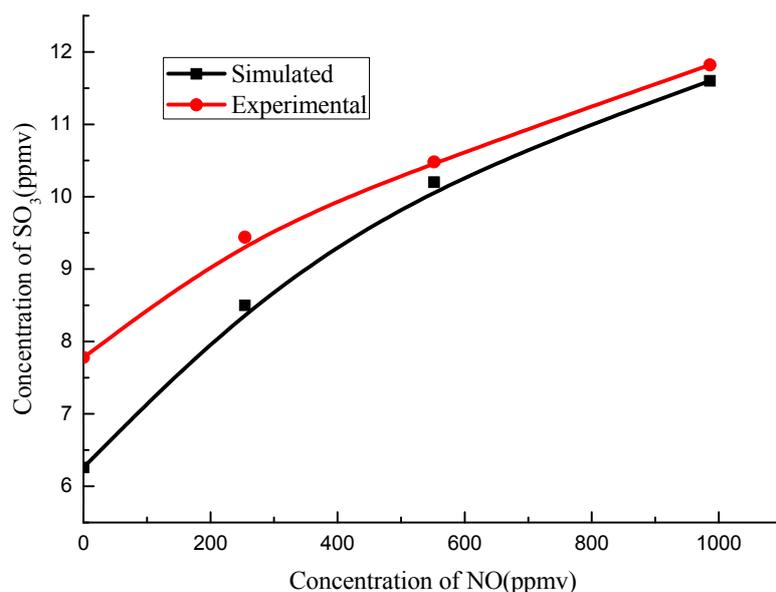
ROP analyses showed that the following reactions were important to SO<sub>3</sub> formation: (R1), (R3), (R4), and (R8). (R3) and (R4) were determined to be most important for SO<sub>3</sub> generation.



The NO inlet concentration influenced the SO<sub>3</sub> outlet concentration, because NO acts on the radical pool through (R6) and (R9).



(R9) increases OH production, which can promote (R2)



**Fig. 5.** Relationship between the concentrations of SO<sub>3</sub> and NO.

and (R3), and results in higher production rates of SO<sub>3</sub> from SO<sub>2</sub> via HOSO<sub>2</sub>. However, as (R6) indicates, when NO is converted into NO<sub>2</sub>, O is consumed. This reaction is in competition with (R1). But the most important direct interaction between NO<sub>x</sub> and SO<sub>x</sub> species is (R4), although (R6) consumes O and affects SO<sub>3</sub> generation, the SO<sub>2</sub> generated by (R6) will eventually generate SO<sub>3</sub> through (R4). Thus, the production of SO<sub>3</sub> increases with an increased NO concentration. A computational parametric study conducted by Choudhury *et al.* (2016) also concluded that the direct interaction between SO<sub>x</sub> and NO<sub>x</sub> mostly occurred via (R4), while indirect interactions changed the radical pool.

#### **Effect of H<sub>2</sub>O Concentration**

In addition to obtaining the SO<sub>3</sub> content in coal combustion flue gas under different combustion parameters, the influence of H<sub>2</sub>O was investigated through kinetic simulations and experiments (Fig. 6). There is a discrepancy between the experimental and modeling results. As far as the experimental results are concerned, the generation of SO<sub>3</sub> is very low when there is no H<sub>2</sub>O. When the inlet gas contains 2.22% H<sub>2</sub>O, the amount of SO<sub>3</sub> generation initially increases rapidly. Then with the increase of H<sub>2</sub>O content, the generation of SO<sub>3</sub> remains constant. However, the simulation results demonstrate that the concentration of SO<sub>3</sub> increases gradually with the increase of H<sub>2</sub>O content to 18.1%, and then remains unchanged. The reason for the discrepancy may be that the H<sub>2</sub>O added in the experiment may not be vaporized in time. Anyway, the trend of the experimental and modeling results is consistent. H<sub>2</sub>O has a positive effect on the formation of SO<sub>3</sub>.

When the inlet gas contains H<sub>2</sub>O, H and OH free radical concentrations will be increased via H<sub>2</sub>O decomposition through (R10) (Wine *et al.*, 1984). The free radical H thereby participates in the reaction with O<sub>2</sub>. In addition, the free radical O will react with H<sub>2</sub>O, which can promote formation

of OH. Therefore, O and OH free radical concentrations increase through these reactions. The increase in O and OH results in an increase in the SO<sub>3</sub> formation by shifting (R1) to the right. In addition, because of the increase in OH, (R2) is promoted and SO<sub>3</sub> is mainly formed via HOSO<sub>2</sub>.



Most previous studies are on the effect of H<sub>2</sub>O on SO<sub>3</sub> formation, but their conclusions are different. There is still no consistent conclusion about the effect of H<sub>2</sub>O on SO<sub>3</sub> formation. Belo (2014) suggested that the conversion of SO<sub>2</sub> to SO<sub>3</sub> is independent of water content. He found that increasing the moisture concentration from 3% to 9% did not have a significant effect on the conversion of SO<sub>2</sub> to SO<sub>3</sub>. Wang (2015) found that the outlet SO<sub>3</sub> concentration decreased drastically with the injection of steam, which indicated steam could inhibit SO<sub>3</sub> formation. Fleig *et al.* (2013) concluded that an increase in H<sub>2</sub>O concentration clearly increased SO<sub>3</sub> formation, as evidenced by experimental measurements and model predictions.

#### **SENSITIVITY ANALYSIS**

In the current research, experimental results and simulation data of others are similar, with the exception of the effect of H<sub>2</sub>O concentration. To study the effect of inlet H<sub>2</sub>O concentration on SO<sub>3</sub> generation, a sensitivity analysis was carried out.

Sensitivity analyses were performed on the model to determine the rate dominating reactions for SO<sub>3</sub> formation. The sensitivity function in the CHEMKIN-IV software was used for this purpose and the data was analyzed based on normalized coefficients. Different sets of reactions were observed to play a role in SO<sub>3</sub> formation for this mechanism. The reactions (R2), (R11), (R12), (R3), (R4), (R1) and (R-6) were found to influence SO<sub>3</sub> formation.

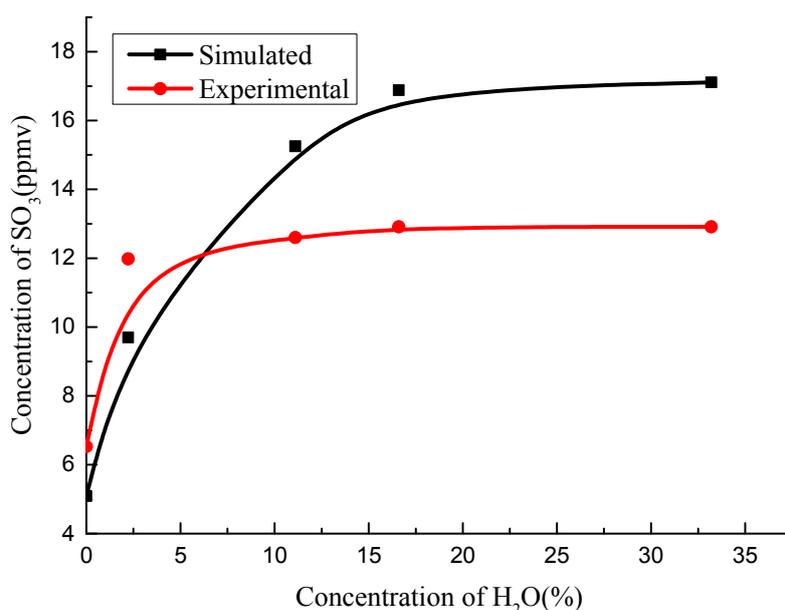


Fig. 6. Relationship between SO<sub>3</sub> and H<sub>2</sub>O concentrations.

The sensitivity coefficients of the most sensitive reactions of input gas containing H<sub>2</sub>O are shown in Fig. 7. The X-scale is the logarithmic sensitivity coefficient, which can be calculated as “ $\partial \ln m / \partial \ln k$ ”. Where  $m$  is SO<sub>3</sub> concentration in flue gas and  $k$  is the pre-exponential factor of the Arrhenius formula.



Positive sensitivities towards SO<sub>3</sub> generation were found for (R2), (R11), (R12), (R3), (R4), and (R1). Evolution of OH radicals and O<sub>2</sub> through these reactions facilitates SO<sub>3</sub> generation via (R1)–(R3). (R4) had a strong positive effect on SO<sub>3</sub> generation by the direct interaction between SO<sub>2</sub> and NO<sub>2</sub>. (R2) was found to affect SO<sub>3</sub> formation to the greatest extent. Since the inlet gas contained water, a large amount of OH and O free radicals were generated by (R10), (R5), and (R7). So that, (R2), (R11), (R12), and (R1) were encouraged, enhancing the formation of SO<sub>3</sub>.

A negative influence was observed for (R-6) due to an increase in O free radical concentration. The sensitivity analysis showed that S formation is highly sensitive to reactions involving H, OH, and O radicals.

On the other hand, when the input gas did not contain H<sub>2</sub>O, the main reactions that affect SO<sub>3</sub> generation were (R11), (R1), (R-6), (R4), and (R13). The sensitivity coefficients of the most sensitive reactions of input gas without H<sub>2</sub>O are shown in Fig. 8.



Obviously, (R11) was found to affect the SO<sub>3</sub> formation to the greatest extent, instead of (R2). In this case, (R11), (R1), (R4), and (R13) had a positive effect on SO<sub>3</sub> formation.

On the contrary, (R6) still had a negative effect on SO<sub>3</sub> formation. Compared with adding water, fewer reactions affect SO<sub>3</sub> generation. Moreover, the negative effect of (R6) is greater than when water is added. The reason for this is that without water, relatively small amounts of OH and O form.

The simulation results therefore show that the direct reaction between SO<sub>2</sub> and NO<sub>2</sub> plays an important role in the formation of SO<sub>3</sub>, whether or not H<sub>2</sub>O is in the input gas.

SO<sub>3</sub> gas generation experiments and chemical kinetic simulation results for the transformation of SO<sub>2</sub> to SO<sub>3</sub> are summarized in Fig. 9. Changing different factors influence processes (a), (b), and (c), affecting transformation of SO<sub>2</sub> to SO<sub>3</sub>.

## CONCLUSIONS

In this comprehensive study, sulfur chemistry, particularly SO<sub>3</sub> generation in the post-flame region, was investigated by both modeling and experimental methods. In particular, the influence of flue gas conditions (temperature, O<sub>2</sub>, SO<sub>2</sub>, NO, and H<sub>2</sub>O) on the formation of SO<sub>3</sub> was studied.

Modeling temperature ranged from 400°C to 1300°C. With an increase in temperature, the concentration of SO<sub>3</sub> increased initially and then decreased, achieving its maximum value at around 1000°C. Additionally, the SO<sub>3</sub> concentration increased with the SO<sub>2</sub> concentration, and the outlet SO<sub>3</sub> concentration increased with the NO and O<sub>2</sub> concentrations. H<sub>2</sub>O also contributed to the formation of SO<sub>3</sub>.

To further study the effect of the influential factors on SO<sub>3</sub> in flue gas, an improved kinetic mechanism was built based on previous research. The direct interactions between SO<sub>x</sub> and NO<sub>x</sub> species were addressed in this model, and it was found that significant SO<sub>3</sub> formation occurs due to the direct interaction of SO<sub>2</sub>, NO, and NO<sub>2</sub>. ROP analyses revealed that reactions involving O, OH, and H dominated SO<sub>3</sub> generation.

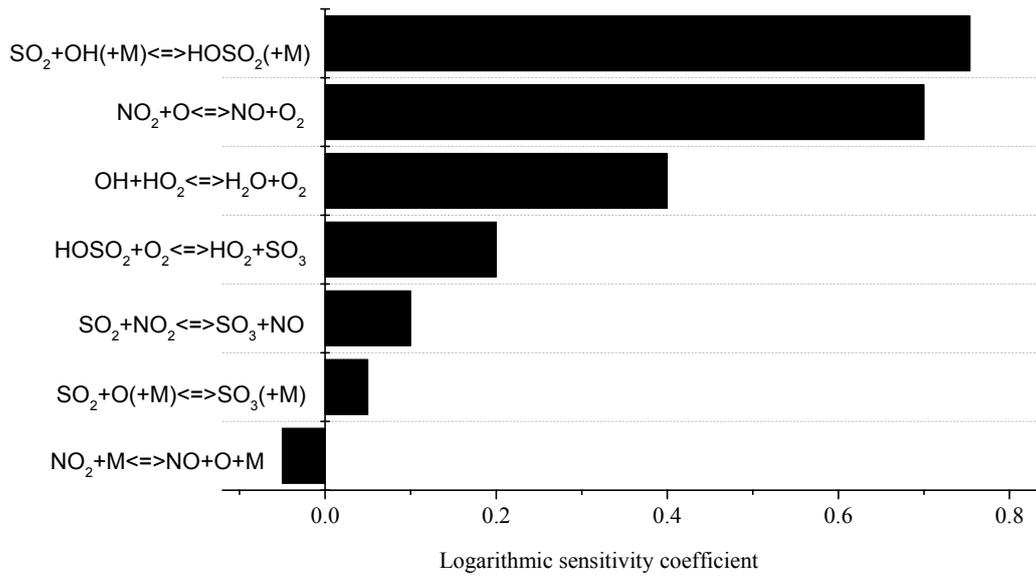


Fig. 7. Sensitivity coefficients of the most sensitive reactions of inlet gas containing H<sub>2</sub>O.

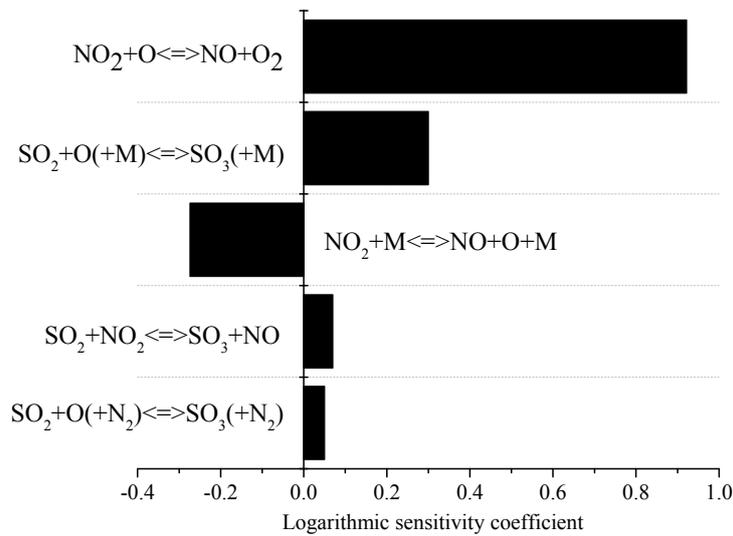


Fig. 8. Sensitivity coefficients of the most sensitive reactions of inlet gas without H<sub>2</sub>O.

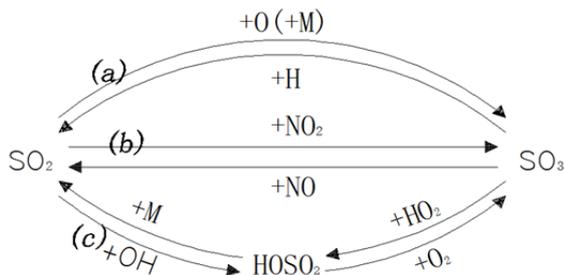


Fig. 9. Schematic of SO<sub>3</sub> generation.

Sensitivity analysis was carried out for two cases: inlet gas with and without H<sub>2</sub>O. The direct reaction between SO<sub>2</sub> and NO<sub>2</sub> played an important role in the formation of SO<sub>3</sub>. Moreover, when the inlet gas contained H<sub>2</sub>O, the subsequently generated OH and O significantly affected

the formation of SO<sub>3</sub>.

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