Experimental and Modeling Studies of SO_3 Homogeneous Formation in Post-flame Region

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Abstract

SO_3 exists in the atmosphere in the form of sulfuric acid aerosol, seriously polluting the environment and damaging the safety of boiler equipment. This study focuses on the homogeneous formation mechanism of SO_3 in post-flame region. Experiments and simulations investigated the influences of combustion parameters on SO_3 generation. Formation of SO_3 was considered to be affected by factors such as temperature and the concentration of O_2, SO_2, NO, and H_2O. With raising the temperature, SO_3 concentration initially increased but then decreased. The concentration of SO_3 reaches the maximum at about 1000 °C. SO_2 can promote the formation of SO_3 over a certain temperature range. An increase in O_2 concentration promoted the formation of O and OH radicals, which enhanced generation of SO_3 from SO_2. The presence of NO resulted in direct and indirect interactions between NO_X and SO_X species for different reaction sets, potentially enhancing SO_3 generation. With an increase in H_2O concentration, SO_3 formation increased rapidly initially, before plateauing. ROP (rate of production) analyses and sensitivity analyses suggested that adding H_2O will produce O and OH, which have a strong influence on SO_3 formation. Furthermore, sensitivity analysis indicated that radicals play an important role in SO_3 formation, and the direct reaction between SO_2 and NO_2 is also significant to SO_3 formation.

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

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INTRODUCTION

SO_2 is the atmospheric pollutant emitted from the combustion of fossil fuel. The main source of SO_2 is the combustion of coal (Kato et al., 2016). A small amount of SO_2 will subsequently be oxidized to SO_3. SO_3 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_3 will be converted into sulfuric acid vapor. SO_3 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_3 can react with NH_3, generating NH_4HSO_4 which will obstruct the air preheater. Furthermore, SO_3 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_3 causing this phenomenon is related to atmospheric conditions. In general, if the content of SO_3 in flue gas is above 10 ppm, smoke opacity will be significant. When the SO_3 concentration is 5 ppm, plume opacity can be as high as 20%. When the SO_3 concentration is more than 10 ppm, smoke will be visibly blue, increasing the H_2SO_4 aerosol concentration near the power plant (Srivastava et al., 2004). A US EPA report showed that SO_3 and H_2SO_4 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_3 in flue gas is related to SO_2 concentration, the excess air coefficient, flue gas temperature, fly ash composition, and other factors (Lou, 2008). The conversion rate of SO_2 to SO_3 is about 0-2%. Kio (2001) determined that oxygen atoms in the high temperature combustion zone of a furnace react with SO_2 to form SO_3:

$$SO_2+O\ (+M) \leftrightarrow SO_3\ (+M) \tag{R1}$$

The formation of SO_3 was shown by Fleig et al. (2009) to be the primary SO_3 formation pathway at 1000 °C-1400 °C:

$$SO_2+O \leftrightarrow SO_3 \tag{R1'}$$

At 700-1000 °C, SO_3 formation occurs via $HOSO_2$:

$$SO_2+OH \leftrightarrow HOSO_2 \tag{R2}$$

$$HOSO_2+O_2 \leftrightarrow SO_3+HO_2 \tag{R3}$$

It has been confirmed that (R2) and (R3) are insignificant above 1000 °C, because of the low stability of $HOSO_2$ (Alzueta et al., 2001). According to Han (2015), SO_3 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_2, and if oxygen is excessive, some SO_2 will be further oxidized to SO_3 (Lee et al., 1967). Previous studies have shown that the primary condition for SO_3 production is excess O_2. If O_2 concentrations below 3%, SO_3 production is sensitive to the O_2 concentration. But above this concentration, an increase in O_2 concentration has little effect on the formation of SO_3. Combustion and flue gas cooling cover a large range of temperatures. At high temperatures (above 1300 °C), formation of SO_3 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_3 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_3 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_2 and found that peak SO_3 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_3 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_3, and suggested that temperature affects oxidation of SO_2 by changing the concentration of O atoms. Therefore, temperature not only affects SO_3 formation by changing the reaction equilibrium (the rate of SO_3 decomposition and formation), but also via important indirect effects.

Currently, most research is focused on the generation mechanism of SO_2 and NO_X, ignoring SO_3 generation. In this paper, homogeneous formation of SO_3 and its influencing factors were studied by experiments and simulations, and the homogeneous formation mechanism of SO_3 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_2, N_2, O_2, CO_2, NO and H_2O. 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_2 and CO_2 enter the ultrasonic atomizer to carry H_2O. Then adjust the second three-way valves 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_3 concentration is measured by the US 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 1065mm long, with an outer diameter of 28mm and an inner diameter of 24.4mm. The total flow of the reaction gas is 3 L/min, and the reaction gas composition is shown in Table 1.

Simulation Methods and Models

A detailed gas-phase kinetic model was utilized to discuss the measured SO_3 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_X and NO_X species were considered in this model.

RESULTS AND DISCUSSION

Gas phase coal combustion experiments were performed to obtain speciation data of SO_X under a variety of operating conditions. Sampling temperature ranged from 400 °C to 1300 °C within the reactor. Other factors included O_2, SO_2, NO, and H_2O concentrations.

Effect of Temperature on SO_3 Formation

The experimental conditions were 550 ppm NO, 2000 ppm SO_2, 2.22% H_2O, and 5% O_2 (Fig. 2).

As shown in Fig. 2, the experimental results and simulated data indicated that the concentration of SO_3 first increased, but then decreased with increasing temperature. The maximum SO_3 concentration was around 1000 °C. At 400-1000 °C, the concentration of SO_3 increases with an increase in temperature, and the concentration of SO_3 decreased with an increase in temperature when the temperature is higher than 1100 °C. When the temperature was below 700 °C, the SO_3 concentration was very near or below the limit of detection. Wang (2015) also observed a similar trend in SO_3 concentration with temperature. This model is modified to ensure that the modeling results in the middle temperature region (800-1200 °C) is 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_3 were (R1) - (R4).

$$SO_2+NO_2 \leftrightarrow NO+SO_3 \quad (R4)$$

When the resistance furnace wall temperature is between 600 °C and 800 °C, the base reaction for SO_3 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_2O increases. According to the literature (Mantashyana, 2014), O radicals are mainly produced by (R5) and decomposition of O_2. The concentration of H radical increased in this temperature range, which promoted the formation of O radical. The concentration of NO_2 also was increased by (R6), and the rate of formation of (R4) increased as well. Higher concentrations of NO_2 result in (R4) playing a decisive role in the generation of SO_3.

$$O_2+H \leftrightarrow OH+O \quad (R5)$$

$$NO+O\ (+M) \leftrightarrow NO_2\ (+M) \quad (R6)$$

As temperature increases, the total formation rate of SO_3 increases rapidly. Fleig (2013) measured the formation of SO_3 by introducing different gas components into a one dimensional furnace. Results showed that NO promoted SO_3 formation at low temperatures.

When the resistance furnace wall temperature is between 800 °C and 1600 °C, the basic reactions for SO_3 formation are (R3) and (R4). With an increase in temperature, H and OH production is enhanced by H_2O 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).

$$O+H_2O \leftrightarrow 2OH \qquad (R7)$$

The concentration of OH radical is higher than NO_2, 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 (R-6) is accelerated and the concentration of NO_2 begins to decline. N_2 reacts with O_2 to generate large amounts of NO, and higher concentrations of NO inhibit (R4). Above 1100 °C, the free radical $HOSO_2$ begins to decompose in the reaction gas.

Fleig et al. (2009) pointed out that formation of SO_3 in a power plant boiler mainly occurs between 900 and 1300 °C, which is approximately consistent with the average temperature range of SO_3 generation.

Effect of O_2 on SO_3 Formation

The O_2 concentration of the combustible mixture was varied from 1% and 9% in simulations and experiments. Other inlet gas contents remained unchanged.

Fig. 3 shows the outlet concentration of SO_3 derived for different concentrations of O_2 in the inlet gas. The SO_2 concentration was 2000 ppm in all experiments. SO_2 formation was favored by high O_2 concentrations, as well as by temperature. The concentration of SO_3 increased with increasing O_2, but the degree of influence gradually decreased. Duan (2015) also demonstrated that oxygen enrichment enhances SO_3 formation. When the concentration of O_2 is less than 7%, the increase in O_2 concentration promotes the formation of SO_3. On the contrary, the influence on the formation of SO_3 is reduced. As shown in (R5), increasing O_2 concentration, a higher concentration of O and OH radicals are expected, which contribute to higher SO_3 formation. Due to the fixed content of SO_2, when O_2 concentration is low, increasing the oxygen content can rapidly increase SO_3 formation. However, the O_2 that can participate in the reaction is affected by SO_2 concentration and temperature, so the effect of oxygen content on the SO_3 production rate gradually decreases.

ROP analysis was performed on reactions (R1)-(R4). When the concentration of O_2 increases, both (R3) and (R4) play a major role in the formation of SO_3. An increase in O_2 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_3.

Effect of SO_2 on SO_3 Formation

The experimental and modeling conditions were 550 ppm NO, 2.22% H_2O, 5% O_2, and a residence time of 4 s, SO_2 concentration ranged from 500 ppm-3000 ppm. Fig. 4 shows the experimental and simulated SO_3 concentrations for different inlet SO_2 concentrations.

As shown in Fig. 4, both the experimental and modeling results show that the concentration of SO_3 increased with an increase in SO_2. A similar trend was observed in a study (Belo et al., 2014) investigating gas-phase conversion of SO_2 to SO_3 in a simulated oxy-combustion environment, which was explained by the dependency of the reaction order on SO_2 concentration.

The simulation process analyzed by ROP shows that the most important reactions for SO_3 formation are (R3) and (R4) with increasing SO_2 concentrations. Increasing the concentration of SO_2 promotes reaction (R2), thus promoting (R3).

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_3 concentration (Fig. 5).

NO is known to affect the amount of SO_3 produced in this system. Increasing NO concentration, an increase in SO_3 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 an increased SO_3 generation during combustion.

ROP analyses showed that the following reactions were important to SO_3 formation: (R1), (R3), (R4), and (R8). (R3) and (R4) were determined to be most important for SO_3 generation.

$$SO_3+OH \leftrightarrow SO_2+HO_2 \quad \text{(R8)}$$

The NO inlet concentration influenced the SO_3 outlet concentration, because NO acts on the radical pool through (R6) and (R9).

$$NO+HO_2 \leftrightarrow NO_2+OH \quad \text{(R9)}$$

(R9) increases OH production, which can promote (R2) and (R3), and results in higher production rates of SO_3 from SO_2 via $HOSO_2$. However, as (R6) indicates, when NO is converted into NO_2, O is consumed. This reaction is in competition with (R1). But the most important direct interaction between NO_X and SO_X species is (R4), although (R6) consumes O and affects SO_3 generation, the SO_2 generated by (R6) will eventually generate SO_3 through (R4). Thus, the production of SO_3 increases with an increased NO concentration. A computational parametric study conducted by Choudhury et al. (2016) also concluded that the direct interaction between SO_X and NO_X mostly occurred via (R4), while indirect interactions changed the radical pool.

Effect of H_2O Concentration

In addition to obtaining SO_3 contents in coal combustion flue gas under different combustion parameters, the influence of H_2O was investigated through kinetic simulations and experiments (Fig. 6). There is discrepancy between experimental and modeling. As far as the experimental results are concerned, the generation of SO_3 is very low when there is no H_2O. When the inlet gas contains 2.22% H_2O, the amount of SO_3 generation initially increases rapidly. Then with the increase of H_2O content, the generation of SO_3 remains constant. However, the simulation results demonstrate that the concentration of SO_3 increases gradually with the increase of H_2O content to 18.1%, and then remains unchanged. The reason for the discrepancy may be that the H_2O added in the experiment may not be vaporized in time. Anyway, the trend of experimental and modeling is consistent. H_2O has a positive effect on the formation of SO_3.

When the inlet gas contains H_2O, H and OH free radical concentrations will be increased via H_2O decomposition through (R10) (Wine et al., 1984). The free radical H thereby participates in the reaction with O_2. In addition, the free radical O will react with H_2O, 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_3 formation by shifting (R1) to the right. In addition, because of the increase in OH, (R2) is promoted and SO_3 is mainly formed via $HOSO_2$.

$H_2O \leftrightarrow OH+H$ (R10)

Most previous studies on the effect of H_2O on SO_3 formation, but their conclusions are different. There is still no consistent conclusion about the effect of H_2O on SO_3 formation. Belo (2014) suggested that the conversion of SO_2 to SO_3 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_2 to SO_3. Wang (2015) found that the outlet SO_3 concentration decreased drastically with the injection of steam, which indicated steam could inhibit SO_3 formation. Fleig et al. (2013) concluded that an increase in H_2O concentration clearly increased SO_3 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_2O concentration. To study the effect of inlet H_2O concentration on SO_3 generation, a sensitivity analysis was carried out.

Sensitivity analyses were performed on the model to determine the rate dominating reactions for SO_3 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_3 formation for this mechanism. The reactions (R2), (R11), (R12), (R3), (R4), (R1) and (R-6) were found to influence SO_3 formation. The sensitivity coefficients of the most sensitive reactions of input gas containing H_2O are shown in Fig. 7.

$NO_2+O \leftrightarrow NO+O_2$ (R11)

$OH+HO_2 \leftrightarrow H_2O+O_2$ (R12)

Positive sensitivities towards SO_3 generation were found for (R2), (R11), (R12), (R3), (R4), and (R1). Evolution of OH radicals and O_2 through these reactions facilitates SO_3 generation via (R1)–(R3). (R4) had a strong positive effect on SO_3 generation by the direct interaction between SO_2 and NO_2. (R2) was found to affect SO_3 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_3.

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_2O, the main reactions that affect SO_3 generation were (R11), (R1), (R-6), (R4), and (R13). The sensitivity coefficients of the most sensitive reactions of input gas without H_2O are shown in Fig. 8.

$SO_2+O\ (+N_2) \leftrightarrow SO_3\ (+N_2)$ (R13)

Obviously, (R11) was found to affect the SO_3 formation to the greatest extent, instead of (R2). In this case, (R11), (R1), (R4), and (R13) had a positive effect on SO_3 formation. On the contrary, (R-6) still had a negative effect on SO_3 formation. Compared with adding water, fewer reactions affect SO_3 generation. Moreover, the negative effect of (R-6) 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_2 and NO_2 plays an important role in the formation of SO_3, whether or not H_2O in the input gas.

SO_3 gas generation experiments and chemical kinetic simulation results for the transformation of SO_2 to SO_3 are summarized in Fig. 9. Changing different factors influence processes (a), (b), and (c), affecting transformation of SO_2 to SO_3.

CONCLUSIONS

In this comprehensive study, sulfur chemistry, particularly SO_3 generation in post-flame region, has been investigated by both modeling and experimental methods. The influences of flue gas conditions (temperature, O_2, SO_2, NO and H_2O) on SO_3 formation were studied.

The experimental and modeling temperature ranged from 400 to 1300 °C. With raising the temperature, the concentration of SO_3 increased initially and then decreased, achieving a maximum value at around 1000 °C. With increasing SO_2 concentration, SO_3 concentration increased. In addition, the outlet SO_3 concentration increased with increasing NO and O_2 concentrations. H_2O also contributes to the formation of SO_3.

To further study the effect of the influencing factors on SO_3 in flue gas, an improved kinetic mechanism was built based on previous research achievements. The direct interactions between SO_X and NO_X species were considered in this model. It was found that SO_3 formation occurs significantly due to the direct interaction of SO_2, NO, and NO_2. ROP analyses revealed that reactions involving O, OH, and H dominated SO_3 generation.

Sensitivity analysis is carried out for two cases of whether the inlet gas contains H_2O. The direct reaction between SO_2 and NO_2 was found to play an important role in the formation of SO_3. When the inlet gas contains H_2O, OH and O are generated, which play an important role in the formation of SO_3.

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Tab. 1 Gas composition in experiments

Test	Inlet gas composition					
	N_2 (%)	CO_2 (%)	SO_2 (ppmv)	NO (ppmv)	O_2 (%)	H_2O (%)
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

Figure Captions

Fig. 1 Schematic diagram of experimental apparatus.

Fig. 2 Relationship between SO_3 concentration and temperature.

Fig. 3 The relationship between SO_3 concentration and O_2 concentration.

Fig. 4 SO_3 formation versus SO_2 concentration.

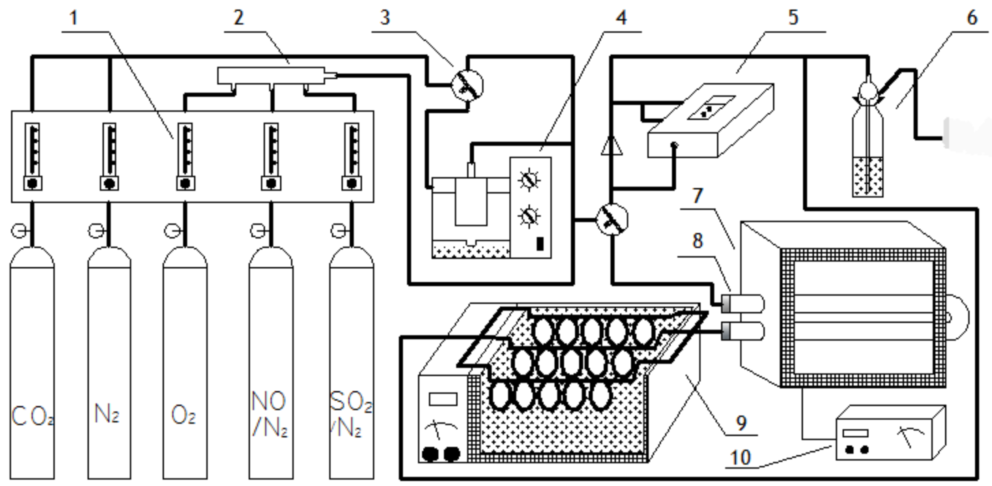
Fig. 5 Relationship between the concentrations of SO_3 and NO.

Fig. 6 Relationship between SO_3 and H_2O concentrations.

Fig. 7 Sensitivity coefficients of the most sensitive reactions of inlet gas containing H_2O.

Fig. 8 Sensitivity coefficients of the most sensitive reactions of inlet gas without H_2O.

Fig. 9 Schematic of SO_3 generation.



1. rotameter; 2. gas mixer; 3. three-way valve; 4. ultrasonic atomizer; 5. flue gas analyzer; 6. wash cylinders (NaOH solution); 7. tube resistance furnace; 8. U shaped quartz tube reactor; 9. digital constant temperature water bath pot; 10. temperature controller

Fig. 1 Schematic diagram of experimental apparatus.

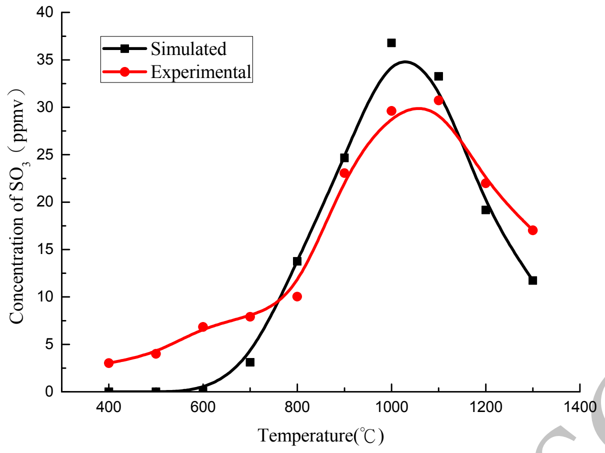


Fig. 2 Relationship between SO_3 concentration and temperature.

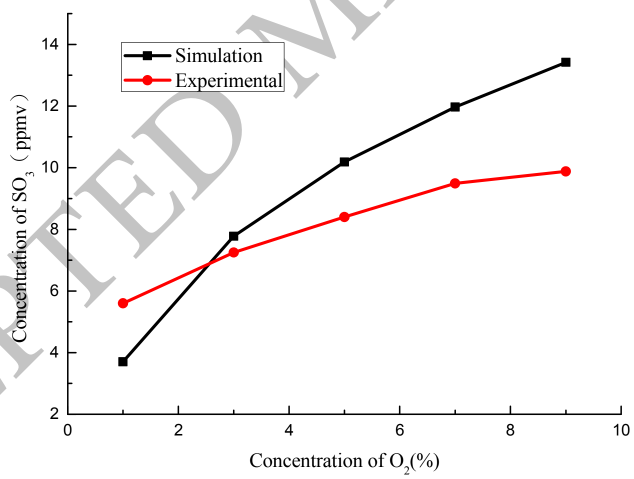


Fig. 3 The relationship between SO_3 concentration and O_2 concentration.

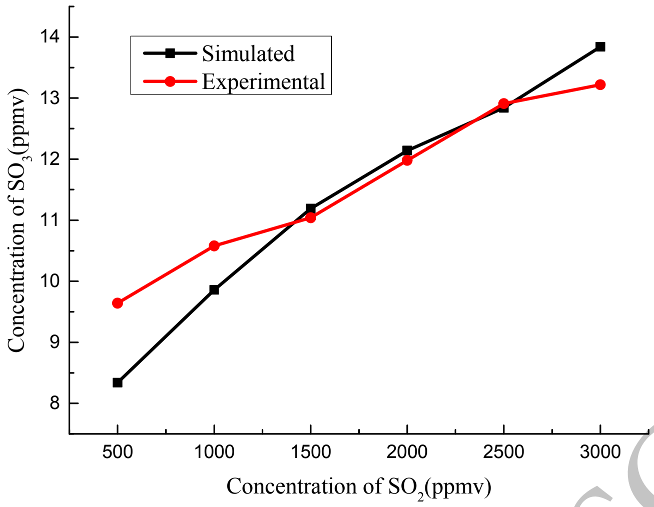


Fig. 4 SO_3 formation versus SO_2 concentration.

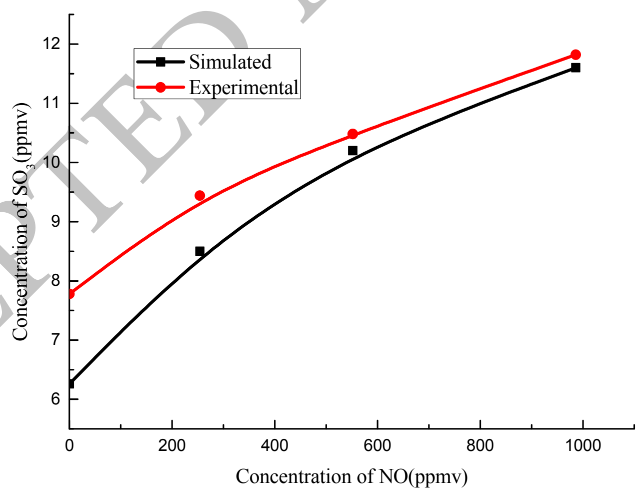


Fig. 5 Relationship between the concentrations of SO_3 and NO.

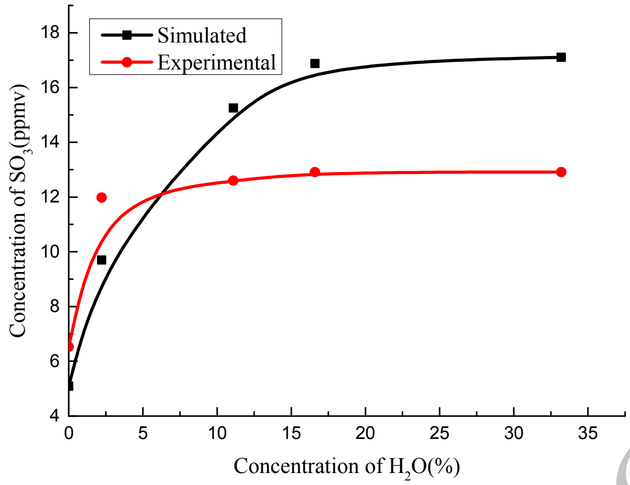


Fig. 6 Relationship between SO_3 and H_2O concentrations.

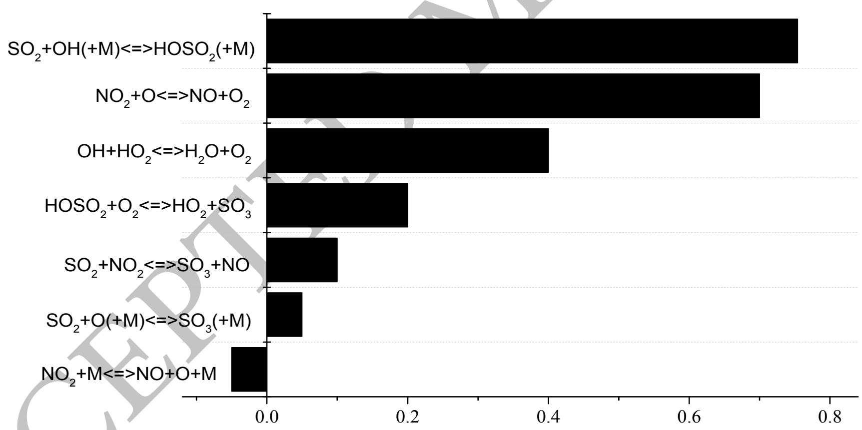


Fig. 7 Sensitivity coefficients of the most sensitive reactions of inlet gas containing H_2O.

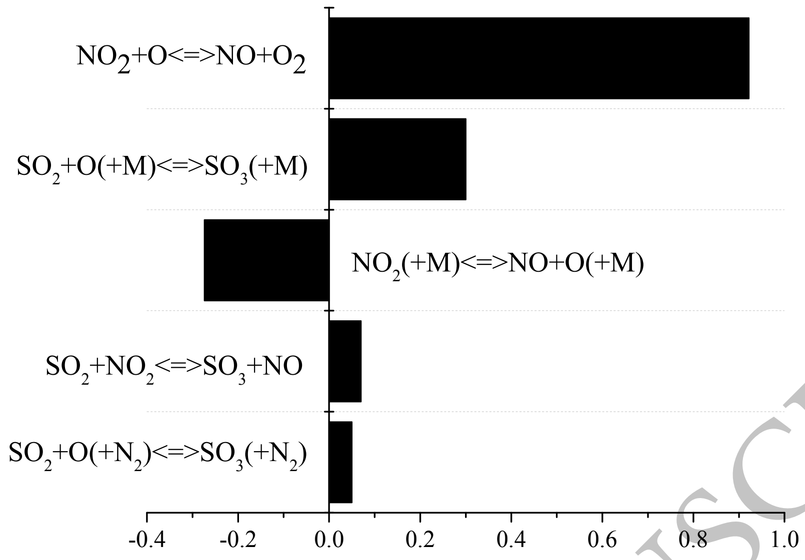


Fig. 8 Sensitivity coefficients of the most sensitive reactions of inlet gas without H_2O.

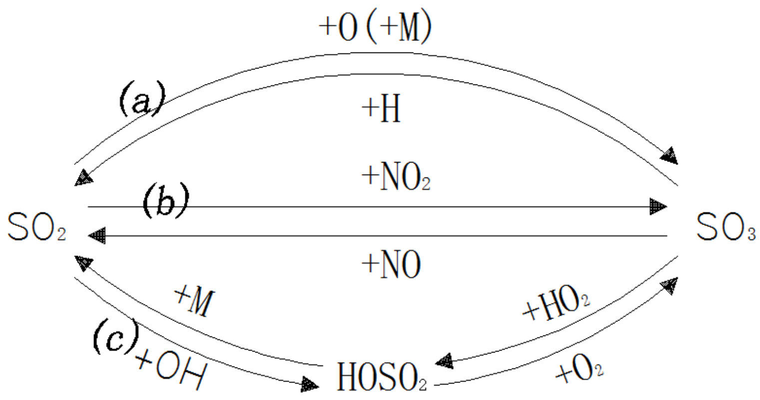


Fig. 9 Schematic of SO_3 generation.