A Comprehensive Experimental and Modeling Study of Sulfur trioxide Formation in Oxy-fuel Combustion

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Abstract:

This study focuses on the sulfur chemistry occurring within an oxy-combustion system by adopting a combined approach of detailed kinetic modeling and experiments. Influences of variable combustion parameters on SO₃ generation have been investigated computationally by implementing different combustion mechanisms. Results indicated significant influences of the equivalence ratio, inlet SO₂ concentration and presence of NO on SO₃ formation while the inlet O₂ concentration exhibited minimal effect. Presence of NO demonstrated different degrees of direct and indirect interactions between NO_x and SO_x species for different reaction sets. Sensitivity analysis indicated radicals to be playing a dominant role in SO₃ formation. Collected temporal profiles of SO₃ from the lab-scale combustion setup showed evidence of significant SO₃ formation at temperatures as low as 650K under realistic boiler temperature conditions. The equivalence ratio and the concentrations of SO₂, O₂ and NO were found to influence the SO₃ formation. Predictions of final SO₃ concentration from different mechanisms were comparable

22 with the experimental data; however, the trend of the temporal profiles could not be anticipated
23 by the models. Experiments conducted in the presence of NO indicated the existence of
24 interactions between NO_x and SO_x species and also the requirement of modifications to the
25 existing oxy-combustion models.

26 **Keywords:**

27 Oxy-combustion, kinetic modeling, sulfur trioxide (SO_3), nitric oxide (NO), emissions

1. Introduction:

38% of the carbon dioxide (CO₂) emissions in the United States are caused by power plants (US, 2011), which are still dominated by the usage of coal as fuel, and they are expected to remain as the main source of electricity generation for many years to come. Advancements in carbon capture and storage (CCS) technology are necessary in order to keep the CO₂ level acceptable while continuing to use fossil fuels. Post-combustion, pre-combustion and oxy-combustion are the three currently available options for CCS (Gibbins and Chalmers, 2008; Toftegaard et al., 2010; Wall et al., 2009; Wall, 2007). Oxy-coal combustion is a promising option as it inherits the flexibility of being retrofitted to existing power plants (Toftegaard et al., 2010), which will work as an advantage for the power generation sector. As the name suggests, oxy-coal combustion is the process of burning coal in oxygen (O₂) instead of air while also introducing a recycle stream into the boiler to stabilize the flame and lower the temperature. The flue gas evolved from this process is rich in CO₂ and 80% lower in volume (Buhre et al., 2005), which can be easily compressed for storage or sequestration. But as the combustion medium is changed from nitrogen (N₂) to CO₂-rich environment, significant changes in the combustion chemistry is expected while the lowered volume of flue gas along with the introduction of the recycle stream in the boiler can result in higher concentrations of different corrosive species. One of the concerns of adopting this technology involves the corrosion problem caused by increased sulfur oxide (SO_x) species concentrations (Stanger and Wall, 2011). During the devolatilization and char oxidation process, most of the sulfur content of the coal gets released in the form of sulfur dioxide (SO₂) while a certain percentage (0.1~1% in air combustion) converts to form sulfur trioxide (SO₃) (Brady and Holum, 1988) through reactions R(1)-R(3).

53 R(1) occurs at high temperature (>1150K) while R(2) and R(3) are active at lower temperature
 54 ranges (<1150K) and are termed as the secondary formation pathway (Brady and Holum, 1988;
 55 Fleig et al., 2012a; Hindiyarti et al., 2007). The generated SO₃ can later easily convert to sulfuric
 56 acid (H₂SO₄) below 700K by going through reaction R(4), while around 450K all the SO₃ is
 57 likely to be in the form of H₂SO₄ (Hardman et al., 1998).

59 There is no restriction on SO₃ or H₂SO₄ emissions placed by the Environmental Protection
 60 Agency (EPA). But emission of H₂SO₄ through the stack will produce a visible blue plume with
 61 an opacity greater than 20%, which is in violation of the EPA emission standards (Srivastava et
 62 al., 2004). Under the acid dew point, condensation of the generated H₂SO₄ can cause severe
 63 corrosion damage in the subsequent units after the boiler. The situation will get aggravated as
 64 higher concentrations of SO₃ have been observed in oxy-combustion experiments (Duan et al.,
 65 2015; Monckert et al., 2008; Tan et al., 2006). SO₂ emissions in terms of unit energy produced in
 66 oxy-coal combustion has been shown to decrease, which was attributed to the increased
 67 conversion to SO₃ and higher sulfur retention by ash (Croiset and Thambimuthu, 2001; Maier
 68 and Dhungel, 2008; Tan et al., 2006). An experimental study (Ahn et al., 2011) conducted using
 69 two different kinds of coal in a pulverized coal boiler revealed higher SO₂ concentration (in
 70 terms of volume) in oxy-fuel cases comparing to air-test cases and almost 4 times higher SO₃
 71 concentration (in terms of volume) with the maximum being at 800 K. However, on a
 72 normalized mass basis (mass SO₃ per unit energy input), air-fired pulverized coal tests showed
 73 higher SO₃ emissions while air-fired circulating fluidized bed tests exhibited similar emissions

74 compared to oxy-firing. Another study (Chamberlain et al., 2013) examining emissions of sulfur
75 species from eight different types of coal revealed the SO_2 concentration (in terms of volume) to
76 be 3 times higher in oxy-combustion environment. The collected experimental data also showed
77 the SO_3 generation to be closer to air-combustion, which was attributed to the fact that SO_3 could
78 be frozen near the equilibrium concentration in the high temperature range. Comprehensive
79 studies (Fleig et al., 2013; Fleig et al., 2012a; Fleig et al., 2011a; Fleig et al., 2011b; Fleig et al.,
80 2012b) conducted by Fleig et al., involving experiments and simulations, revealed that
81 combustion parameters such as, equivalence ratio (ϕ), SO_2 content and O_2 percentage in the
82 oxidizer to influence the formation of SO_3 under oxy-combustion environment. Sensitivity
83 analysis, performed in the post combustion zone (Fleig et al., 2013) by Fleig et al., showed the
84 dependency of SO_3 formation on oxygen (O) and hydroxyl (OH) radicals and that higher
85 concentrations of SO_3 was found to form in the burnout regions of carbon monoxide (CO). As
86 the concentration of SO_3 has been found to be higher in oxy-combustion cases, the acid dew
87 point is anticipated to be higher resulting in condensation of H_2SO_4 at higher temperatures than
88 that in air combustion units. To anticipate the evolution of SO_3 under different plant conditions a
89 complete temporal profile of SO_3 under realistic boiler condition is required. But such profiles of
90 SO_3 , especially extending to the lower temperature region, under variable operating conditions
91 are yet to be reported.

92 Alongside the sulfur chemistry, nitrogen chemistry in oxy-combustion has also been a focus of
93 several studies (Croiset and Thambimuthu, 2001; Gimenez-Lopez et al., 2010; Glarborg et al.,
94 2003; Kimura et al., 1995; Kuhnemuth et al., 2010; Liu et al., 2005; Mackrory and Tree, 2009,
95 2012; Mendiara and Glarborg, 2009; Normann et al., 2009, 2010, 2011; Obras-Loscertales et al.,
96 2015; Okazaki and Ando, 1997; Watanabe and Okazaki, 2011). Experiments revealed the

emission of nitrogen oxides (NO_x) to be significantly lowered in oxy-combustion comparing to that of air-combustion (Croiset and Thambimuthu, 2001; Kimura et al., 1995; Liu et al., 2005). Reburn mechanism (Mendiara and Glarborg, 2009) is a dominant reaction pathway for NO destruction, which mostly contributes to the NO_x reduction in the oxy-coal environment, as recycling a part of the flue gas to the boiler increases the exposure of nitric oxide (NO) to the hydrocarbon radicals. Also, removal of N_2 eliminates the possibility of the occurrence of the Zeldovich mechanism (Zeldovich, 1946), provided air ingress is negligible, thus contributing to lower NO emissions. Even though experimental and kinetic studies have been performed to study NO emissions in oxy-combustion, there is still a gap remaining regarding the interaction between SO_x and NO_x species. There has not been kinetic simulations performed to observe the effect of recycled NO on SO_3 generation in oxy-combustion cases with detailed chemistry and no experimental data on such matter is available.

The objective of this study is to elucidate the evolution trends of SO_3 in oxy-coal combustion flue gas and compare the experimental data with simulated cases using kinetic mechanisms available in the literature. For this purpose, experiments in a unique lab-scale combustion system, which represents the actual plant temperature conditions, have been conducted. The setup has the advantage of sampling from different points and obtaining the temporal profile of SO_3 under varied operating conditions. Kinetic simulations have been performed using different combustion mechanisms and these have been compared to the experimental results. Also, the interaction between sulfur and nitrogen species has been studied computationally by integrating the available reaction sets to the existing combustion mechanisms and a comparison has been made to the experimentally collected data.

2. Kinetic Simulations:

Previously, simulation studies (Alzueta et al., 2001; Giménez-López et al., 2011; Hindiyarti et al., 2007) focused on sulfur and nitrogen chemistry of oxy-combustion environment have been conducted by applying a combustion mechanism that has been developed and modified for CO₂-rich environment. The sulfur chemistry subset of this mechanism was developed by Alzueta et al. (Alzueta et al., 2001) based on the studies of Glarborg et al. (Glarborg et al., 1996) and it consists of 91 reactions. Modifications were later implemented into the mechanism to acquire better agreement with available experimental results. Hindiyarti et al. (Hindiyarti et al., 2007) conducted ab-initio calculations to investigate the SO₃ consumption and generation routes and the resultant reaction network with new rate parameters were employed to simulate different conditions. The computationally obtained results on SO₂ oxidation by applying new parameters were then compared to the experimentally available results and it was concluded that only the influence of R(5) was significant among the other reactions under investigation, (R(6)-R(7)).

To investigate the effect of high CO₂ concentration on CH₄ combustion, a reaction subset consisting of 14 reactions was applied by Glarborg et al. (Glarborg and Bentzen, 2008). It was found that CO₂ has a significant influence on the radical pool and CO burnout through reaction R(8).

Such effect of CO₂ was taken into consideration and implemented into the reaction mechanism by Gimenez-Lopez et al. (Giménez-López et al., 2011). This updated combustion mechanism,

containing 110 species and 747 reactions, was implemented by Fleig et al. (Fleig et al., 2013; Fleig et al., 2012a; Fleig et al., 2011b) in a comprehensive study to computationally elucidate the sulfur chemistry occurring during oxy-combustion. The study revealed that the equivalence ratio, O_2 , NO and SO_2 concentrations in the oxidizer affected the SO_3 formation significantly under a linear temperature profile extending from 1800-500K (Fleig et al., 2012a; Fleig et al., 2011b). The influence of various combustibles like CH_4 and CO at the post combustion zone was also investigated while a certain temperature profile consisting of an isothermal zone and a cooling section was applied (Fleig et al., 2013).

In the current study, kinetic simulations have been conducted using CHEMKIN-IV (ReactionDesign, 2013) to investigate the effect of different combustion parameters on the SO_3 evolution trend under a temperature profile representative of actual boiler conditions and the results have been compared to the experimental data. To do so, the reaction mechanism adopted by Fleig et al. (Fleig et al., 2013; Fleig et al., 2012a; Fleig et al., 2011b) and Gimenez-Lopez et al. (Giménez-López et al., 2011) has been applied. The conversion of SO_3 to H_2SO_4 at lower temperatures in a combustion system is a well-known occurrence. To take this into account, the conversion reaction R(4) from the Leeds combustion mechanism (Hughes et al., 2001) was integrated into the mechanism. This mechanism with the addition of the H_2SO_4 formation reaction will be referred to as the Alzueta mechanism in the rest of this paper.

In addition, sensitivity analysis was performed to determine the rate dominating reactions. A list of the simulated cases along with the simulation conditions is provided in Table S.1 of the supplementary materials. Oxy-combustion flame was simulated in a perfectly stirred reactor (PSR) by introducing a desired mixture of fuel and oxidizer ($CH_4/CO_2/O_2$) and the created radical pool was utilized as the inlet to a plug flow reactor (PFR). SO_2 and NO at various

concentrations were also introduced to the PFR. The PFR was subjected to a temperature profile obtained from the experiments as shown in Figure 1.

Figure 1. Temperature profile within the reactor

This profile is similar to that of an industrial boiler (Senior, 2000) with a residence time of 6s. Alongside the Alzueta mechanism, to compare the performance of different mechanisms against the collected experimental data, the Leeds mechanism (Hughes et al., 2001) was also applied in this study and sensitivity analyses were performed for both mechanisms.

Effect of NO on SO₃ formation:

In addition to obtaining SO₃ profiles in oxy-combustion under different combustion parameters, the influence of NO has also been investigated through kinetic simulations. NO has been known to have an effect on the amount of SO₃ produced in the system (Dooley and Whittingham, 1945; Fleig et al., 2011b). Earlier experiments (Dooley and Whittingham, 1945) conducted in an effort to investigate the oxidation of SO₂ in flames in the presence of NO under air combustion conditions exhibited a decline in SO₂ oxidation with increased NO introduction. The removal of O radicals by R(9) was attributed to be contributing to this decline.

The interaction between nitrogen dioxide (NO₂) and SO₂ was later investigated in the temperature range of 703-1193K (Armitage and Cullis, 1971). The kinetic parameters obtained

from the experiments at high NO concentrations (10^{-7} mol/cc) revealed that the mechanism consisted of reactions R(10) and (11) while R(10) being the rate limiting step.

However, at low NO concentrations, alike the industrial flue gases, reactions R(12)-(15) were found to take place with reaction R(13) being the rate limiting one. At low NO concentrations, reaction R(10) takes place slowly and NO is oxidized via reaction R(12) instead.

Wendt et al. (Wendt and C.V., 1973) have evaluated this reaction pathway (reactions R(10), R(11), R(12) and R(14)) for industrial furnace conditions through kinetic modeling and concluded that the contribution from these reactions to the final SO_3 concentration in the furnace was negligible and that for these reactions to be important in combustion units, the NO concentration should be at least 1000 ppmv. While these simulations represent air combustion conditions, these reactions may play an important role for oxy-combustion simulations as the NO concentration is much higher due to the flue gas recycle (Wall et al., 2009).

For oxy-combustion cases, kinetic simulations performed by Fleig et al. (Fleig et al., 2011b) revealed that small amount of NO present in the combustion medium can result in increased SO_3 generation while a higher amount will have an opposite effect. But in this model, the direct interaction between the NO_x and SO_x species were not included and the effect of NO on the radical pool was investigated. It was observed that NO present in the system affects the radical

211 pool through reactions R(16)-(18).

215 R(16) causes secondary SO_3 formation through the HOSO_2 route (reaction R(2)) by forming
216 more OH radicals and eventually resulting in higher SO_3 concentrations. But as the amount of
217 NO increases, the competition for reacting with O radicals via R(17) increases and reduces the
218 primary SO_3 formation. Moreover, R(18) at higher temperatures tends to consume the OH
219 radicals causing further reduction. While this study sheds some light on the effect of NO on
220 sulfur chemistry, it does not provide information on the direct interactions between NO_x and SO_x
221 species, i.e., the effect of NO was only investigated through the change in the radical pool. As a
222 result, further investigation is needed to better understand the effect of nitrogen oxides on sulfur
223 chemistry and direct interactions of nitrogen and sulfur species should be included in the kinetic
224 mechanisms proposed for oxy-combustion.

225 In the current kinetic study, NO was introduced into the PFR while applying the Alzueta
226 mechanism to investigate its effect on sulfur chemistry. To investigate direct SO_x - NO_x
227 interactions, the reaction subset from the Leeds mechanism containing 28 reactions for S/N/C
228 interaction was integrated to the Alzueta mechanism [referred to as Alzueta + Leeds(S/N/C)].
229 The reactions adopted from the Leeds mechanism are tabulated in Table S.2 of the
230 supplementary materials. Also, the reaction subset applied by Wendt et al. was investigated by
231 implementing the reactions to the Alzueta mechanism [referred to as Alzueta + Wendt] as well as
232 the Alzueta + Leeds(S/N/C) mechanism [referred to as Alzueta + Wendt + Leeds(S/N/C)]. For

all these cases, concentrations of NO investigated ranged from 200 to 1500 ppmv. Sensitivity analyses were also performed on all of these mechanisms.

3. Gas Phase Experiments:

For investigating the effects of different parameters on SO_3 generation, a unique lab-scale combustion setup with a firing rate of 0.5kW has been utilized. The entire combustion system has been built out of quartz for its inertness and capability of withstanding high temperature (Fry et al., 2007; Padak, 2011). As shown in Figure 2, the setup consists of three major sections, i) burner

Figure 2. Schematic of the experimental setup

collection. The burner at the top consists of 8 inlet nozzles and is connected to a reactor through a special connector. This facilitates the adjustment of the burner position to create stable flames at a variety of combustion conditions. The burner is able to simulate stable oxy-combustion flames for $\phi = 0.8-0.98$ and O_2 percentage of 28-35%. The subsequent reactor, with a diameter of 5 cm, extends to a total length of 163 cm. The first section of the reactor is heated in a Thermcraft furnace to 1100°C , required to ignite the combustible mixture and to create the

necessary radical pool. The latter part of the reactor has been equipped with 15 sampling ports, located at every 5 cm interval and is heated in four sections using heat tapes to mimic the temperature profile prevailing within a plant boiler. The resultant temperature profile is shown in Figure 1. The temperature profile data was collected by placing K-type thermocouples in each sampling port extending to the center of the reactor. Temperature data within the furnace was collected inserting a ceramic insulated thermocouple through the bottom port of the reactor. Each of the 15 sample ports, located at the lower part of the reactor, has been equipped with needle valves so that the flue gas samples from different temperature regions at the reactor can be drawn through the ports for analysis. For obtaining an accurate SO₃ profile, representative of the actual condition, samples should be cooled down rapidly in order to freeze the reactions occurring within. To serve this purpose, cooling jackets have been incorporated around the ports at high temperatures. A Thermo Flex recirculating chiller with variable flow rate option has been connected to the cooling jackets for rapid cooling of the gases.

To perform the experiments, desired CH₄/CO₂/O₂/SO₂/NO mixtures are fed through the inlet nozzles at the top of the burner to create a premixed laminar flame at the tip. After running the experiment for an hour to achieve stable condition, flue gas samples are collected from the sampling ports for analysis and the temporal profile of SO₃ is acquired. Analysis of the flue gas samples for SO₃ detection has been conducted using the salt method (Fleig et al., 2012b; Vainio et al., 2013). The salt method involves passing the flue gas samples through 1 gram of ultraclean sodium chloride (NaCl) in a packed bed reactor heated to 200⁰C. The exposed salt will undergo reaction R(19) with the SO₃ content of flue gas present in the form of H₂SO₄.

The exposed salt sample is then titrated using barium perchlorate ($\text{Ba}(\text{ClO}_4)_2$) to quantify the evolved SO_3 in the form of sodium sulfate (Na_2SO_4) (Fritz et al., 1957). While collecting the flue gas sample, in order to prevent the loss of any SO_x species due to condensation, all the sample ports and lines were maintained at 180°C . Applying the salt method, temporal profiles of SO_3 have been collected at various conditions. A detailed list of all the conditions tested is presented in Table 1.

Table 1. Test cases for experiments

Equivalence Ratio	O_2 Concentration in Oxidizer (%)	SO_2 Concentration in Oxidizer (ppmv)	NO Concentration in Oxidizer (ppmv)	Final $\text{SO}_3 + \text{H}_2\text{SO}_4$ Concentration (ppmv)
0.855	32.5	1000	-	24.5
		1800		28.5
		2500		35.5
		3200		44.5
		2500	200	85.5
			500	125
			800	32
			1000	66.5
			1500	37
				65.5
0.98	32.5	2500		22

4. Results and Discussion:

4.1. Kinetic Simulations:

SO_3 profiles along the reactor obtained by applying the Alzueta and Leeds mechanisms have been presented in Figure 3. These cases were simulated for $\phi = 0.855$, 32.5% O_2 and 2500 ppmv of SO_2 in oxidizer. For the Alzueta mechanism, the rate of production (ROP) analysis revealed the formation of SO_3 to be through reactions R(1), R(3), R(5) and R(-7). Reaction R(1) was observed to be an active route for SO_3 formation in the temperature range of 976 - 1383K while

consumption occurred through the reverse reaction in the temperature range of 1383-1394K. R(3) was found to be producing SO_3 in the range of 755-1383K while consumption through the reverse route occurred in the range of 1383-1394K. The reverse reactions, leading to SO_3 consumption, contribute to the dip in the SO_3 profile in the mentioned temperature

Figure: 3. Simulated SO_3 profile using the Alzueta and Leeds mechanisms

region. It was also observed that, R(1) acted as the dominant path for SO_3 production at the beginning of the combustion zone due to the availability of O radicals while in the cooling zone R(3) acted as the dominant one. R(5) consumed SO_3 in the temperature range of 1343-1394K where H radicals were available, but the rate of consumption was lower than the production rate through other routes. R(-7) contributed to SO_3 formation in the range of 627-1387K but at a lower rate comparing to the R(1) and R(3). This analysis revealed the overall temperature range of SO_3 formation to be 627-1383K. However, the concentration of SO_3 almost reached a constant amount at 1050K, indicating negligible production at lower temperatures. Also, around 800 K the SO_3 concentration started going downward with the H_2SO_4 concentration going upward, as the conversion to H_2SO_4 started around that temperature. For the Leeds mechanism, reactions R(1), R(3) and R(-5) were found to be the primary pathways for SO_3 production. All these reactions were found to be generating SO_3 in the temperature range of 703-1394K and no SO_3 consumption through reverse direction were observed. Even though consumption of SO_3 did not

315 occur while applying the Leeds mechanism, the SO_3 formation and consequently the final H_2SO_4
 316 concentration was found to be higher with the Alzueta mechanism.

Figure 4. Comparison between experimental and model predictions for the effect of inlet SO_2 concentration on final $\text{SO}_3 + \text{H}_2\text{SO}_4$ concentration at $\phi=0.855$ and $\text{O}_2 = 32.5\%$

Figure 5. Comparison between experimental and model predictions for the effect of inlet SO_2 concentration on conversion at $\phi=0.855$ and $\text{O}_2 = 32.5\%$

Figure 6. Model predictions for the effect of equivalence ratio (ϕ) on final $\text{SO}_3 + \text{H}_2\text{SO}_4$ concentration at $\text{O}_2 = 32.5\%$ and $\text{SO}_2 = 2500$ ppmv

Figure 7. Model predictions for the effect of O_2 percentage on final $\text{SO}_3 + \text{H}_2\text{SO}_4$ concentration at $\phi=0.855$ and $\text{SO}_2 = 2500$ ppmv

4.1.1. Effect of SO₂ Concentration:

Four different concentrations of SO₂ between 1000-3200 ppmv were introduced into the PFR in order to investigate the effect of SO₂ on the final SO₃+H₂SO₄ concentration and the results were plotted in Figure 4. As expected, with increasing the SO₂ concentration in the oxidizer, an increase in the SO₃ concentration was observed for both reaction mechanisms as seen in Figure 4. But the ratio of SO₃/SO₂ was found to be decreasing as shown in Figure 5. Previous studies (Dooley and Whittingham, 1945) attributed this decrease in conversion to the role of SO₂ working as an inhibitor. A similar trend was observed in a study (Belo et al., 2014) investigating gas-phase conversion of SO₂ to SO₃ in simulated oxy-combustion environment and it was explained by the dependency of the reaction order on SO₂ concentration. For all the simulated cases, the ratio of conversion was found to be in the range of 1.7-2.1% and 1.5-1.7% while working with the Alzueta and Leeds mechanisms, respectively.

4.1.2. Effect of Equivalence Ratio and O₂ Concentration:

The equivalence ratio of the combustible mixture was varied from 0.8 to 0.98 in the simulated cases. It was found that operating with a richer mixture, i.e., higher ϕ , resulted in a lower SO₃ concentration. The results reflecting the effect of ϕ were presented in Figure 6. When ϕ is lowered, availability of O and OH radicals are higher in the system, which eventually contributes to higher SO₃ generation. Also, higher ϕ , in other words, a richer mixture, will increase the availability of different hydrocarbon radicals, which were found to be negatively affecting SO₃ generation. In the simulated cases, O₂ concentration in the oxidizer was also varied while maintaining the ϕ at 0.855 and SO₂ concentration in the oxidizer at 2500 ppmv. The results of these simulations were presented in Figure 7. With increasing the O₂ concentration, higher

concentrations of O and OH radicals are expected, which should contribute to higher SO₃ generations. But interestingly, the effect of this parameter was found to be quite negligible for the simulated conditions.

4.1.3. Effect of Recycled SO₃:

Recycling the flue gas in an oxy-combustion system will introduce additional SO₃ into the system. To investigate the influence of such recycled SO₃ and to determine its fate while passing through the flame, cases were simulated with $\phi = 0.855$ and O₂ = 32.5% where 60% - 80% of the evolved SO₃ was recycled back to the PFR. With the introduction of such recycled stream, no change in the final SO₃ concentration was observed. The reason is that as the recycled SO₃ passes through the flame, dissociation takes place as SO₂ is favored by the equilibrium at the temperatures of the flame zone, hence no change is observed on the total SO₃ production under recycle conditions.

4.1.4. Effect of NO:

To investigate the influence of NO on SO₃ formation, different concentrations of NO were introduced in to the PFR and simulations were run using the Alzueta, Alzueta + Leeds(S/N/C), Alzueta + Wendt and Alzueta + Wendt + Leeds(S/N/C) reaction sets. All the final SO₃ and H₂SO₄ concentrations at the reactor outlet are tabulated in Table S.1

Figure 8. Model predictions for the effect of 800 ppmv NO introduction on SO₃ concentration at $\phi=0.855$, O₂ = 32.5% and SO₂ = 2500 ppmv

of the supplementary materials. Applying the Alzueta mechanism for 800 ppmv NO in the oxidizer resulted in higher $\text{SO}_3 + \text{H}_2\text{SO}_4$ amount compared to the cases that were simulated in the absence of NO. On the contrary, by increasing the NO concentration in the oxidizer to 1500 ppmv, the final $\text{SO}_3 + \text{H}_2\text{SO}_4$ concentration got slightly lowered. This effect was also observed by Fleig et al (Fleig et al., 2011b) and was attributed to the consumption of O and OH radicals by reaction R(17) and R(18). As the direct interactions between SO_x and NO_x species are not a part of the Alzueta mechanism, the changes in the generated $\text{SO}_3 + \text{H}_2\text{SO}_4$ amount can be explained by the effect of NO on the radical pool through reactions R(16)-(18). In Figure 8, this effect has been presented by comparing the SO_3 profile in the absence and presence of 800 ppmv NO. These cases have been simulated for $\phi = 0.855$, $\text{O}_2 = 32.5\%$ and inlet $\text{SO}_2 = 2500$ ppmv.

While applying the Alzueta + Leeds (S/N/C) reaction set, the highest reactor outlet concentration of $\text{SO}_3 + \text{H}_2\text{SO}_4$ was observed. The ROP analysis showed reactions R(3), R(11), R(1) and R(-7) to be generating SO_3 in the presence of NO. The Alzueta + Leeds (S/N/C) reaction set contains the same reaction R(11) as the Alzueta + Wendt reaction set but with different reaction parameters. The ROP analysis showed R(11) to be significantly important in generating SO_3 and consequently leading to a higher conversion of SO_2 .

While applying the Alzueta + Wendt reaction set, some rise in the final concentration was seen, but it was lower than that with the Alzueta + Leeds (S/N/C) reaction set. The reaction R(11) still played a significant role in SO_3 generation, but due to the difference in the reaction parameters, the contribution from this reaction was lowered. Similarly, the Alzueta + Wendt + Leeds (S/N/C) reaction set also yielded a higher concentration of $\text{SO}_3 + \text{H}_2\text{SO}_4$ in the reactor outlet and it was lower than both the Alzueta + Leeds (S/N/C) and the Alzueta + Wendt reaction sets. As both sets contain reaction R(8) with different reaction parameters, in the Alzueta + Wendt + Leeds

(S/N/C) reaction set this reaction was declared as duplicate in the chemistry set. And it was observed that, R(11) from the Leeds mechanism and R(11) from the Wendt reaction set both contributed to SO_3 generation. But lower formation through R(11) from the Wendt reaction set might have been the reason for the reduction in the overall formation of $\text{SO}_3 + \text{H}_2\text{SO}_4$. In Figure 8, comparison between the SO_3 profiles with 800 ppmv NO introduction has been presented for all the mentioned reaction sets. It should be mentioned that the cases presented in Figure 8 had been simulated excluding the H_2SO_4 formation reaction (R(4)) from the mechanism to emphasize the difference between the SO_3 profiles in the presence and absence of NO.

The computational parametric study conducted so far, under a realistic temperature profile, has showed significant influence of ϕ and inlet SO_2 concentration on the generated SO_3 amount. However, the influence of the inlet O_2 concentration was found not to be significant. It can be concluded from the simulation results that when a certain concentration of O and OH radicals has been reached in the system and a certain degree of SO_2 oxidation has been attained, the presence of higher O_2 concentration may become kinetically insignificant. Also, the presence of NO was found to be influential both through direct and indirect interactions. The direct interaction was mostly through reaction R(11) while the indirect interaction was through the change in the radical pool.

4.1.5. Sensitivity Analysis:

Without NO Introduction:

Sensitivity analyses were performed on both mechanisms (Alzueta and Leeds) to determine the rate dominating reactions for SO_3 formation. The sensitivity function in the CHEMKIN-IV software (ReactionDesign, 2013) was used for this purpose and the data was analyzed based on normalized coefficients. Different sets of reactions were observed to play role in SO_3 formation

for different mechanisms. For the Alzueta mechanism, following reactions were found to be the ones influencing (in the decreasing order) SO₃ formation mostly.

Sensitivity coefficient of the reaction R(-8) revealed that the burnout reaction of CO can have a positive effect as well as a negative effect on the SO₃ formation. The negative effect was found to be more pronounced and it was prominent in the region of temperature <1265K due to the consumption of OH radicals. Positive effect was observed at the temperature region >1265K where the produced H radicals react by the reverse reaction of R(26) and form O and OH radicals, both of which are essential for SO₃ production. Reaction R(20) was also found to have both positive and negative effects on the SO₃ formation. In the region of temperature <1265K, positive effect from this reaction can be observed as such consumption of OH radicals results in

431 forming H₂O and O₂, which can contribute to forming more O and OH radicals and this is in
 432 competition with R(-8), which also consumes OH radicals. But above 1265K, formed H radicals
 433 starts going through the reverse R(26) and the consumption of OH through R(20) starts having a
 434 negative effect on SO₃ production. Negative influence was observed from reaction R(2) due to
 435 the consumption of both SO₂ and OH radical forming relatively stable HOSO₂ radical. R(21) was
 436 found to be having a positive effect on the SO₃ production as hydrogen peroxide (H₂O₂) radicals
 437 later breakdown through R(25) and forms OH radicals. R(22) was also found to be having a
 438 negative effect below 1200K due to the consumption of OH radicals. But above 1200K, the
 439 formed H₂O starts going through the reverse R(28) forming OH radicals and a positive effect can
 440 be observed in this region. R(23) also showed a negative effect below 1265K, while a positive
 441 effect on SO₃ formation was observed above 1265K due to the effect of H radicals formed as
 442 explained. R(-7), R(24), R(25), R(26) and R(28) were found to be having a positive effect on
 443 SO₃ formation due to the production of OH radicals, necessary for SO₃ formation while R(27)
 444 had a negative effect due to the consumption of both the H radicals and O₂. Negative influence
 445 on SO₃ generation was also exhibited by R(3). Even though SO₃ can be generated through this
 446 pathway, formation of relatively stable HO₂ radical can influence the overall effect from this
 447 reaction to be negative.

448 Performing sensitivity analysis on the Leeds mechanism revealed the following reactions to be
 449 the rate determining ones (in decreasing order) regarding SO₃ formation.

458 In the Leeds mechanism, R(-26) was found to be affecting SO₃ formation to the highest extent
 459 instead of R(-8). Formations of O and OH radicals contribute to the SO₃ formation, hence a
 460 positive sensitivity coefficient. R(27), R(29) and R(-8) were observed to be negatively affecting
 461 SO₃ production due to the consumption of H and OH radicals. R(3), R(-5), R(1) and R(2) were
 462 found to be positively affecting the SO₃ evolution due to formation of SO₃ itself or the
 463 intermediate species.

464 The sensitivity analysis performed on both mechanisms showed that SO₃ formation is most
 465 sensitive to the reactions involving H, OH and O radicals. For the Alzueta mechanism, the
 466 reaction involving CO conversion was found to be of the highest significance. However, for the
 467 Leeds mechanism, the reaction forming O and OH radicals from O₂ played the greater role. Also,
 468 for the Alzueta mechanism, sensitivity of certain reactions was found to be temperature
 469 dependent, but for the Leeds mechanism no such effect was observed. This can be due to the
 470 different reaction pathways and parameters considered in each mechanism.

471 **With NO Introduction:**

472 To determine the dominant reaction pathways of NO interaction with SO_x species, sensitivity
 473 analyses were performed for the Alzueta, Alzueta + Leeds (S/N/C), Alzueta + Wendt and
 474 Alzueta + Wendt + Leeds (S/N/C) reaction sets in the presence of 200 ppmv NO in the oxidizer.
 475 Reactions influencing SO₃ generation at varied extents has been listed below and the resultant
 476 sensitivity coefficients have been presented in Figure 9.

477	$\text{NO} + \text{O} (+\text{M}) \leftrightarrow \text{NO}_2 (+\text{M})$	R(9)
478	$\text{SO}_2 + \text{NO}_2 \leftrightarrow \text{SO}_3 + \text{NO}$	R(11)
479	$\text{NO}_2 + \text{O} \leftrightarrow \text{NO} + \text{O}_2$	R(-15)
480	$\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$	R(16)
481	$\text{NO}_2 + \text{H} \leftrightarrow \text{NO} + \text{OH}$	R(30)
482	$\text{HONO} + \text{OH} \leftrightarrow \text{NO}_2 + \text{H}_2\text{O}$	R(31)
483	$\text{NO}_2 + \text{HO}_2 \leftrightarrow \text{HONO} + \text{O}_2$	R(32)
484	$\text{NO} + \text{OH} (+\text{M}) \leftrightarrow \text{HONO} (+\text{M})$	R(33)
485	$\text{H} + \text{NO} + \text{M} \leftrightarrow \text{HNO} + \text{M}$	R(34)

486 Positive sensitivities towards SO_3 generation have been exhibited by reactions R(16), R(30),
 487 R(32) and R(33) for all the reaction sets. Evolution of OH radicals and O_2 through these
 488 reactions facilitates the SO_3 generation through reactions R(1)-R(4). Reaction R(11) exhibited
 489 strong positive effect on SO_3 generation by the direct interaction between SO_2 and NO_2 for all
 490 the reaction sets except for the Alzueta mechanism. In the Alzueta mechanism, such direct
 491 interaction is not included. Also, it should be noted that reaction R(11) has different rate
 492 constants for Alzueta + Leeds (S/N/C) and Alzueta + Wendt reaction sets. The sensitivity
 493 coefficients for Alzueta + Wendt + Leeds (S/N/C) reaction set showed that SO_3 generation is
 494 more sensitive to reaction R(11) from the Leeds mechanism than the one from the Wendt
 495 reaction set. This demonstrates that reaction R(11) in the Leeds mechanism, having a different
 496 rate, is facilitating the SO_3 production more. Reactions R(9), R(-15) and R(31) negatively
 497 affected SO_3 generation for all reaction sets due to the consumption of O and OH radicals. R(34)
 498 also exhibited a slightly negative influence on SO_3 generation, but this reaction was not present
 499 in the Alzueta mechanism. From the results, it can be observed that each of the reactions listed

above had the same positive or negative effect for all four reaction sets. However, the extent of the effect was different as observed in Figure 9.

Figure 9. Sensitivity coefficients for SO_3 formation in the presence of 200 ppmv NO with different reaction sets at $\phi=0.855$, $\text{O}_2 = 32.5\%$ and $\text{SO}_2 = 2500$ ppmv

Finally, from the results of this sensitivity analysis, it can be stated that the presence of NO in the system influences the final SO_3 concentration to a great extent. Depending on the reaction set applied, it has been found to have an impact on the sulfur chemistry either through the radical pool or by a direct interaction resulting in a different SO_3 concentration in the reactor.

Comparison of these results obtained from the different reaction sets against experimentally obtained data can help to shed light on possible reaction pathways for SO_x - NO_x interaction.

4.2. Gas Phase Experimental Results:

In this study, gas phase oxy-combustion experiments were performed to obtain speciation data of SO_x under a variety of operating conditions. The sampling temperature ranged from 1100K to 600K within the reactor. For each data point, two consecutive samples were obtained from each port in the reactor without interrupting the operation. The reproducibility of the collected data has been documented by reporting the average of the two concentration values obtained from consecutive sampling. It can be seen from the presented results that there has been significant variability in the collected data, which can be attributed to the difficulty of sampling SO_3 without condensing and to the inherent uncertainty of the detection method. The collected speciation data has been compared to the simulation results, which will facilitate any further modifications to the kinetic mechanisms.

By applying the salt method, temporal profile of SO_3 was collected for the case with $\phi = 0.855$, 2500 ppmv of SO_2 and 32.5% O_2 in the oxidizer. As it is shown in Figure 10, the SO_3 concentration gradually increased from 10 ppmv at 1000 K to 42 ppmv at 600K. Comparison between the simulation results with the Alzueta mechanism and experimental data reveal that for the simulated cases, SO_3 concentration plateaus at 1050 K while for the experimental cases, significant conversion to SO_3 continues to occur till 650K.

The temporal profile collected for 1000 ppmv SO_2 in the oxidizer has been presented in Figure 11 and it reveals to have lower SO_3 generation than the 2500 ppmv SO_2 case. Other than the SO_2 inlet concentration, all other parameters in these experiments were kept constant. For the 1000

ppmv SO₂ inlet, 24.5 ppmv SO₃ was formed at the end of the reactor at 598K and for 2500 ppmv SO₂ inlet, the amount was 35.5 ppmv. The rise in the SO₃ formation was obviously due to the higher availability of SO₂ in the system. Experiments were also performed by introducing 1800 ppmv and 3200 ppmv SO₂ in the oxidizer and the samples were collected from the end of the reactor at 598K. In Figure 4, all the reactor exit concentrations of SO₃ for varied inlet SO₂ concentrations have been presented and the comparisons with the simulation results have been demonstrated. In the experimental cases, the final SO₃ concentration ranged from 24.5 ppmv to 44.5 ppmv. Comparison with the simulated results shows that for 1000 ppmv SO₂ inlet, both the Alzueta and Leeds mechanisms under predicted the final SO₃ concentration with the Leeds mechanism generating the lowest amount. But for all the other SO₂ inlet concentrations, the predictions from both mechanisms have been in good agreement comparing to experimental results. In Figure 5, the experimentally obtained conversion of SO₂ for varied inlet concentrations has been presented. The conversion gradually decreased with increasing SO₂ introduction and varied from 2.1% for 1000 ppmv of SO₂ inlet to 1.6% for 3200 ppmv of SO₂ inlet. The Alzueta mechanism also demonstrated a decreasing trend in the SO₂ conversion with increasing inlet concentrations, but the conversion for 1000 ppmv SO₂ was under predicted. For all the other cases, the predictions from the Alzueta mechanism were close to the experimental results. Similar decreasing trend for SO₂ conversion was observed with the Leeds mechanism in the range of 1800 ppmv to 3200 ppmv inlet concentrations, but an increase in conversion was observed from 1000 ppmv to 1800 ppmv SO₂ inlet. The Leeds mechanism also had under predicted the SO₂ conversion for the 1000 ppmv case, but performed well for all the other inlet concentrations.

Figure 10. Comparison between experimental and model predictions for the temporal profile of $\text{SO}_3 + \text{H}_2\text{SO}_4$ concentration at $\phi=0.855$, $\text{O}_2 = 32.5\%$ and $\text{SO}_2 = 2500$ ppmv

Figure 11. Experimental temporal profiles collected with different inlet SO_2 concentrations in the oxidizer at $\phi=0.855$ and $\text{O}_2 = 32.5\%$

Figure 12. Experimental temporal profiles collected with different equivalence ratios (ϕ) at $\text{O}_2 = 32.5\%$ and $\text{SO}_2 = 2500$ ppmv

Figure 13. Experimental temporal profiles collected with different O_2 concentrations in the oxidizer at $\phi=0.855$ and $\text{SO}_2 = 2500$ ppmv

551

552 The effect of O_2 percentage in the oxidizer stream was also investigated by collecting the SO_3

553 profiles at 34% and 32.5% O_2 . In Figure 12, it can be observed that the SO_3 generated with 34%

554 O_2 is significantly higher than the one generated with 32.5% O_2 and the amount of SO_3 generated

varied from 22 ppmv at 1100K to 74 ppmv at 598K. The increase in the O radicals due to the presence of more excess oxygen can lead to the rise in the final SO₃ amount. However, in the simulated cases, influence of the O₂ concentration on SO₃ generation was not found to be so prominent.

In Figure 13 the temporal profile of the case with $\phi = 0.98$, 2500 ppmv of SO₂ and 32.5% O₂ in the oxidizer has been presented and compared with the case with $\phi = 0.855$. It can be observed from Figure 13 that with the same SO₂ and O₂ inlet concentrations, evolved SO₃ concentration was lower for higher equivalence ratio and the temporal profile had the same gradually increasing trend with the decreasing temperature. The SO₃ concentration decreased from 35.5 ppmv for $\phi = 0.855$ to 22 ppmv for $\phi = 0.98$. Both the Alzueta and Leeds mechanisms demonstrated the decreasing trend for richer combustion environment, but generated SO₃ amounts were better predicted for the leaner combustion mixture. For $\phi = 0.98$, predicted SO₃ concentrations by the Alzueta and Leeds mechanisms were 15.56 ppmv and 16.12 ppmv, respectively, as opposed to the experimentally obtained value of 22 ppmv. For $\phi = 0.855$, predicted SO₃ concentrations by the Alzueta mechanism and Leeds mechanism were 38.4 ppmv and 35.2 ppmv, respectively, while the experimentally obtained value was 35.5 ppmv.

In Figure 14, the final SO₃ + H₂SO₄ concentrations in the presence of NO in the oxidizer at various concentrations have been presented and the comparison with different reaction sets has been demonstrated. For these experimental cases, NO has been introduced at 200, 500, 800, 1000 and 1500 ppmv and the samples have been collected from the 11th port of the reactor at 596K. The inlet SO₂ concentration in the oxidizer was kept constant at 2500 ppmv with $\phi = 0.855$ and O₂ = 32.5%. The collected data exhibited inconsistency when repeating the experiments. As it

can be observed from Figure 14, for 200 ppmv NO introduction, final $\text{SO}_3 + \text{H}_2\text{SO}_4$ concentration was 85.5 ppmv. This is significantly higher than the amount generated (35.5 ppmv) in the absence of NO. The value reached to 125 ppmv in the presence of 500 ppmv NO in the oxidizer followed by a decrease for higher NO concentrations and for 1500 ppmv NO, the generated $\text{SO}_3 + \text{H}_2\text{SO}_4$

Figure 14. Comparison between experimental and model predictions for different NO concentrations at $\phi=0.855$, $\text{O}_2 = 32.5\%$ and $\text{SO}_2 = 2500$ ppmv

concentration was 37 ppmv. If compared with the model predictions, only the Alzueta mechanism demonstrated this trend, which has been explained by the interaction of NO with the radical pool but it was not noticeable to such high degree. The amount of SO_3 generated in the presence of 500 ppmv NO has also been quite high and the results obtained from none of the reaction sets are comparable. It should be noted that the reproducibility of the experimental data obtained with the salt method is not very good when NO is present possibly due to an interference occurring between NaCl and nitrogen dioxide (NO_2) forming nitrosyl chloride (NOCl) (Finlayson-Pitts, 1983). To shed light on this, a more accurate detection method needs to be applied and the salt method may not be the appropriate method for measuring SO_3 in the presence of NO. Despite the poor reproducibility, these results still indicate that there is an interaction between NO_x and SO_x species, both direct and indirect.

5. Conclusions:

In this comprehensive study, sulfur chemistry, particularly SO_3 generation in an oxy-combustion

environment, has been investigated by both computational and experimental methods. Kinetic simulations using two different combustion mechanisms were implemented in order to observe the effects of combustion parameters on SO_3 generation. The Alzueta mechanism has been found to predict higher SO_3 concentrations compared to the Leeds mechanism in all simulated cases. Final SO_3 concentration has been observed to be increasing with increasing inlet SO_2 concentration; however, the conversion of SO_2 reduced. An increase in the equivalence ratio caused the final SO_3 concentration to decrease while increasing the inlet O_2 concentration had a slight effect on SO_3 generation. Investigation of the $\text{SO}_x\text{-NO}_x$ interaction has also been conducted by integrating different reaction sets to the Alzueta mechanism. It has been found that significant SO_3 formation occurs due to the direct interaction of SO_2 , NO and NO_2 . Along with the direct effect, NO has also demonstrated its influence on SO_3 formation through the radical pool. Sensitivity analysis revealed that the reactions involving O , OH and H radicals dominated the SO_3 generation in oxy-combustion environment. Parametric studies have been performed experimentally in a unique lab-scale setup by varying equivalence ratio, SO_2 and O_2 inlet concentrations and the temporal SO_3 profiles for these conditions have been reported. Salt method has been used as the detection method and a maximum of 20% error in reproducibility of the experimental data has been observed. The error was in the range of 3-13% for most of the data points. In all the experimental cases, significant SO_3 generation occurred till 650K, but the simulated cases indicate the SO_3 formation to reach a plateau around 1050K. Comparisons show that the two applied mechanisms are able to predict the outlet concentrations and the conversion of SO_2 for a variety of inlet SO_2 concentrations, but not the temporal profile. Also in the experimental cases, the inlet O_2 concentration has been found to influence the SO_3 generation significantly; however, the simulated cases suggested the influence to be negligible. Introduction

623 of varied concentrations of NO has been found to initially cause a rise in the final SO₃
624 generation, peaking at 500 ppmv NO followed by a decrease when the NO concentration is
625 increased. The reaction sets considered in this study for investigating the SO_x-NO_x interaction
626 computationally could not predict the high SO₃ generation in the presence of NO. But the
627 experimentally collected results in the presence of NO exhibited a larger error range than the
628 ones collected in absence of it. This indicates that the salt method may not be suitable for SO₃
629 measurement in the presence of NO. But even with the high error range, collected results have
630 demonstrated that there is still room for more improvements and modifications in the existing
631 combustion mechanisms. Also to narrow the range of variability, a more reliable detection
632 method needs to be developed, so that more accurate speciation data can be obtained
633 simultaneously under a variety of operating conditions.

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638

References:

- Ahn, J., Okerlund, R., Fry, A., Eddings, E.G., 2011. Sulfur trioxide formation during oxy-coal combustion. *International Journal of Greenhouse Gas Control* 5S, S127-S137.
- Alzueta, M.U., Bilbao, R., Glarborg, P., 2001. Inhibition and sensitization of fuel oxidation by SO₂. *Combustion and Flame* 127, 2234-2251.
- Armitage, J.W., Cullis, C.F., 1971. Studies of the Reaction Between Nitrogen Dioxide and Sulfur Dioxide. *Combustion and Flame* 16, 125-130.
- Belo, L.P., Elliott, L.K., Stanger, R.J., Spurl, R., Shah, K.V., Maier, J., Wall, T.F., 2014. High-Temperature Conversion of SO₃ to SO₂: Homogeneous Experiments and Catalytic Effect of Fly Ash from Air and Oxy-fuel Firing. *Energy Fuels* 28, 7243-7251.
- Brady, J., Holum, J., 1988. *Fundamentals of General Chemistry: With Qualitative Analysis*. J. Wiley.
- Buhre, B.J.P., Elliott, L.K., Sheng, C.D., Gupta, R.P., Wall, T.F., 2005. Oxy-fuel combustion technology for coal-fired power generation. *Progress in Energy and Combustion Science* 31, 283-307.
- Chamberlain, S., Reeder, T., Stimpson, C.K., Tree, D.R., 2013. A comparison of sulfur and chlorine gas species in pulverized-coal, air- and oxy-combustion. *Combustion and Flame* 160, 2529-2539.
- Croiset, E., Thambimuthu, K.V., 2001. NO_x and SO₂ emissions from O₂/CO₂ recycle coal combustion. *Fuel* 80, 2117-2121.
- Dooley, A., Whittingham, G., 1945. The Oxidation of Sulphur Dioxide in Gas Flames. *Transactions of Faraday Society* 42, 354-362.
- Duan, L., Duan, Y., Sarbassov, Y., Li, Y., Anthony, E.J., 2015. SO₃ formation under oxy-CFB combustion conditions. *International Journal of Greenhouse Gas Control* 43, 172-178.
- Finlayson-Pitts, B.J., 1983. Reaction of NO₂ with NaCl and atmospheric implications of NOCl formation. *Nature* 306, 676-677.
- Fleig, D., Alzueta, M.U., Normann, F., Abian, M., Andersson, K., Johnsson, F., 2013. Measurement and modeling of sulfur trioxide formation in a flow reactor under post-flame conditions. *Combustion and Flame* 160, 1142-1151.
- Fleig, D., Andersson, K., Johnsson, F., 2012a. Influence of Operating Conditions on SO₃ Formation during Air and Oxy-Fuel Combustion. *Industrial and Engineering Chemistry Research* 51, 9483-9491.
- Fleig, D., Andersson, K., Johnsson, F., Leckner, B., 2011a. Conversion of Sulfur during Pulverized Oxy-coal Combustion. *Energy and Fuels* 25, 647-655.
- Fleig, D., Andersson, K., Normann, F., Johnsson, F., 2011b. SO₃ Formation under Oxyfuel Combustion Conditions. *Industrial and Engineering Chemistry Research* 50, 8505-8514.
- Fleig, D., Vainio, E., Andersson, K., Brink, A., Johnsson, F., Hupa, M., 2012b. Evaluation of SO₃ Measurement Techniques in Air and Oxy-Fuel Combustion. *Energy and Fuels* 26, 5537-5549.
- Fritz, J.S., Yamamura, S.S., Richard, M.J., 1957. Titration of sulfate following separation with alumina. *Analytical Chemistry* 29, 157-161.
- Fry, A., Cauch, B., Silcox, G.D., Lighty, J.S., Senior, C.L., 2007. Experimental evaluation of the effects of quench rate and quartz surface area on homogeneous mercury oxidation. *Proc. Combust. Inst.* 31, 2855-2861.
- Gibbins, J., Chalmers, H., 2008. Carbon capture and storage. *Energy Policy* 36, 4317-4322.
- Gimenez-Lopez, J., Aranda, V., Millera, A., Bilbao, R., Alzueta, M.U., 2010. An experimental parametric study of gas reburning under conditions of interest for oxy-fuel combustion. *Fuel Processing Technology* 92, 582-589.
- Giménez-López, J., Martínez, M., Millera, A., Bilbao, R., Alzueta, M.U., 2011. SO₂ effects on CO oxidation in a CO₂ atmosphere, characteristic of oxy-fuel conditions. *Combustion and Flame* 158, 48-56.
- Glarborg, P., Bentzen, L.L.B., 2008. Chemical effects of a high CO₂ concentration in oxy-fuel combustion of methane. *Energy and Fuels* 22, 291-296.

686 Glarborg, P., Jensen, A.D., Johnsson, J.E., 2003. Fuel nitrogen conversion in solid fuel fired systems.
687 Progress in Energy and Combustion Science 29, 89-93.

688 Glarborg, P., Kubel, D., DamJohansen, K., Chiang, H.M., Bozelli, J.W., 1996. Impact of SO₂ and NO on CO
689 oxidation under post-flame conditions. International Journal of Chemical Kinetics 28, 773-790.

690 Hardman, R., Stacy, R., Dismukes, E., 1998. Estimating Sulfuric Acid Aerosol Emissions from Coal-Fired
691 Power Plants, DOE-FETC Conference on Formation, Distribution, Impact, and Fate of Sulfur Trioxide in
692 Utility Flue Gas Streams,, Pittsburgh, PA,.

693 Hindiyarti, L., Glarborg, P., Marshall, P., 2007. Reactions of SO₃ with the O/H radical pool under
694 combustion conditions. Journal of physical chemistry 50, 8505-8514.

695 Hughes, K.J., Turanyi, T., Clague, A.R., Pilling, M.J., 2001. Development and testing of a comprehensive
696 chemical mechanism for the oxidation of methane. International Journal of Chemical Kinetics 33, 513-
697 538.

698 Kimura, N., Omata, K., Kiga, T., Takano, S., Shikisima, S., 1995. The characteristics of pulverized coal
699 combustion in O₂/CO₂ mixtures for CO₂ recovery. Energy Conversion and management 36, 805-808.

700 Kuhnemuth, D., Normann, F., Andersson, K., Johnsson, F., Leckner, B., 2010. Reburning of Nitric Oxide in
701 Oxy-Fuel Firing;The Influence of Combustion Conditions. Energy and Fuels 25, 624-631.

702 Liu, H., Zailani, R., Gibbs, B.M., 2005. Pulverized coal combustion in air and in O₂/CO₂ mixtures with NO_x
703 recycle. Fuel 84, 2109-2115.

704 Mackrory, A.J., Tree, D.R., 2009. Predictions of NO_x in a laboratory pulverized coal combustor operating
705 under air and oxy-fuel conditions. Combustion Science and Technology 181, 1413-1430.

706 Mackrory, A.J., Tree, D.R., 2012. Measurement of nitrogen evolution in a staged oxy-combustion coal
707 flame. Fuel 93, 298-304.

708 Maier, J., Dhungel, B., 2008. Impact of recycled gas species (SO₂, NO) on emission behaviour and fly ash
709 quality during oxy-coal combustion, Proceedings of the 33rd International Technical Conference on Coal
710 Utilization & Fuel Systems, Clearwater,FL,USA, pp. 33-44.

711 Mendiara, T., Glarborg, P., 2009. Reburn Chemistry in Oxy-fuel Combustion of Methane. Energy and
712 Fuels 23, 3565-3572.

713 Monckert, P., Dhungel, B., Kull, R., Maier, J., 2008. Impact of Combustion Conditions on Emission
714 Formation (SO₂, NO_x) and fly ash, 3rd Workshop IEAGHG International Oxy-Combustion Network,
715 Yokohama, Japan.

716 Normann, F., Andersson, K., Johnsson, F., Leckner, B., 2009. Emission control of nitrogen oxides in the
717 oxy-fuel process. Progress in Energy and Combustion Science 35, 385-397.

718 Normann, F., Andersson, K., Johnsson, F., Leckner, B., 2010. Reburning in Oxy-Fuel Combustion: A
719 Parametric Study of the Combustion Chemistry. Industrial and Engineering Chemistry Research 49, 9088-
720 9094.

721 Normann, F., Andersson, K., Johnsson, F., Leckner, B., 2011. NO_x reburning in oxy-fuel combustion: A
722 comparison between solid and gaseous fuel. International Journal of Greenhouse Gas Control 5S, S120-
723 126.

724 Obras-Loscertales, M.D.L., Mendiara, T., Rufus, A., Diego, L.F.D., Garcia-Labiano, F., Gayan, P., Abad, A.,
725 Adanez, J., 2015. NO and N₂O emissions in oxy-fuel combustion of coal in a bubbling fluidized bed
726 combustor. Fuel 150, 146-153.

727 Okazaki, K., Ando, T., 1997. NO_x reduction mechanism in coal combustion with recycled CO₂. Energy 22,
728 207-215.

729 Padak, B., 2011. Mercury Reaction Chemistry in Combustion Flue Gases from Experiments and Theory,
730 Department of Energy Resources. Stanford University, p. 223.

731 ReactionDesign, 2013. CHEMKIN 10131. San Diego.

732 Senior, C.L., 2000. Gas-phase Transformations of Mercury in Coal-fired Plants. Fuel Processing
733 Technology 63, 197-213.

734 Srivastava, R.K., Miller, C.A., Erickson, C., Jambhekar, R., 2004. Emissions of Sulfur Trioxide from Coal-
 735 Fired Power Plant. *Journal of Air and Waste Management* 54, 750-762.
 736 Stanger, R., Wall, T., 2011. Sulfur impacts during pulverised coal combustion in oxy-fuel technology for
 737 carbon capture and storage. *Progress in Energy and Combustion Science* 37, 69-88.
 738 Tan, Y., Croiset, E., Douglas, M.A., Thambimuthu, K.V., 2006. Combustion characteristics of coal in a
 739 mixture of oxygen and recycled flue gas. *Fuel* 85, 507-512.
 740 Toftegaard, M.B., Brix, J., Jensen, P.A., Glarborg, P., Jensen, A.D., 2010. Oxy-fuel combustion of solid
 741 fuels. *Progress in Energy and Combustion Science* 36, 581-625.
 742 US, E.P.A., 2011. Overview of Green House Gases.
 743 Vainio, E., Fleig, D., Brink, A., Andersson, K., Johnsson, F., Hupa, M., 2013. Experimental evaluation and
 744 field application of a salt method for SO₃ measurement in Flue gases. *Energy and Fuels* 27, 2767-2775.
 745 Wall, T., Y., L., Spero, C., Elliot, L., Khare, S., Rathnam, R., Zeenathal, F., Moghtaderi, B., Buhre, B., Sheng,
 746 C., Gupta, R., Yamada, T., Makino, K., Yu, J., 2009. An Overview on oxyfuel coal combustion-State of the
 747 art research and technology development. *Chemical Engineering Research and Design* 87, 1003-1016.
 748 Wall, T.F., 2007. Combustion processes for carbon capture. *Proceedings of combustion institute* 31, 31-
 749 47.
 750 Watanabe, H.Y., J., Okazaki, K., 2011. NO_x formation and reduction mechanisms in staged O₂/CO₂
 751 combustion. *Combustion and Flame* 158, 1255-1263.
 752 Wendt, J.O.L., C.V., S., 1973. Catalysis of SO₂ oxidation by nitrogen oxides. *Combustion and Flame* 21,
 753 387-390.
 754 Zeldovich, Y.B., 1946. The oxidation of nitrogen in combustion and explosions. *Acta Physicochimica* 21,
 755 577-628.
 756
 757