Sulfur trioxide formation/emissions in coal-fired air- and oxy-fuel combustion processes: a review

Yerbol Sarbassov, Cranfield University, UK
Duan Lunbo, Southeast University, China
Vasilije Manovic, Cranfield University, UK
Edward J. Anthony, Cranfield University, UK

Correspondence to: Edward J. Anthony; Combustion and CCS Centre, Bedford MK43 0AL, Bedfordshire, UK. E-mail: b.j.anthony@cranfield.ac.uk

Abstract

In oxy-fuel combustion, fuel is burned using oxygen together with recycled flue gas which is needed to control the combustion temperature. This leads to higher concentrations of sulfur dioxide and sulfur trioxide in the recycled gas that can result in the formation of sulfuric acid and enhanced corrosion. Current experimental data on SO$_3$ formation, reaction mechanisms, and mathematical modelling have indicated significant differences in SO$_3$ formation between air- and oxy-fuel combustion for both the wet and dry flue gas recycle options. This paper provides an extensive review of sulfur trioxide formation in air- and oxy-fuel combustion environments, with an emphasis on coal-fired systems. The first part summarizes recent findings on oxy-fuel combustion experiments, as they affect sulfur trioxide formation. In the second part, the review focuses on sulfur trioxide formation mechanisms, and the influence of catalysis on sulfur trioxide formation. Finally, the current methods for measuring sulfur trioxide concentration are also reviewed along with the major difficulties associated with those measurements using data available from both bench- and pilot-scale units.

Keywords: Oxy-fuel combustion, sulfur dioxide, sulfur trioxide formation, catalysis
# Table of Contents

Abstract .............................................................................................................................. i  
1. Introduction .................................................................................................................. 2  
  1.1 Oxy-fuel Combustion Technology ................................................................. 2  
  1.2 Influence of Sulfur in Combustion Systems ................................................. 4  
  1.3 SO$_3$ Emissions in Combustion Systems .................................................... 6  
  1.4 Objectives and Scope of the Paper ............................................................... 8  
2. Oxy-Fuel Combustion Environment ........................................................................ 9  
  2.1 Flue Gas Recirculation .................................................................................. 9  
  2.2 SO$_2$ Emissions ........................................................................................... 10  
3. Background for SO$_3$ Formation in Combustion ............................................ 11  
  3.1 Homogeneous Conversion of SO$_2$ to SO$_3$ .............................................. 12  
  3.2 Catalytic Conversion of SO$_2$ to SO$_3$ ........................................................ 14  
  3.3 SO$_3$ Sampling Methods .............................................................................. 15  
    3.3.1 Controlled condensation method ......................................................... 15  
    3.3.2 Isopropanol absorption bottle method ................................................ 17  
    3.3.3 Salt and glass bead methods ............................................................... 18  
    3.3.4 Indirect measurements of SO$_3$ .......................................................... 18  
    3.3.5 Pentol SO$_3$ monitor ........................................................................ 19  
    3.3.6 Acid dew point measurements ............................................................ 20  
4. Influence of Oxy-fuel Parameters on SO$_3$ ......................................................... 21  
  4.1 Effect of O$_2$/CO$_2$ Environment .............................................................. 21  
    4.1.1 Effect of NO$_x$ emissions ................................................................... 22  
    4.1.2 Effect of carbon monoxide ................................................................. 23  
    4.1.3 Effect of steam ................................................................................... 24  
  4.2 Temperature and Residence Time ................................................................. 25  
  4.3 Catalytic Effect of Fly Ash ............................................................................ 28  
  4.4 SO$_3$ Emissions from Pilot-scale Studies ................................................... 30  
  4.5 Modelling Studies of SO$_3$ Formation ....................................................... 34  
5. Research Needs ....................................................................................................... 34  
6. Conclusions ............................................................................................................. 35  
Acknowledgements ........................................................................................................ 35
1. Introduction

1.1 Oxy-fuel Combustion Technology

According to the International Energy Agency (IEA), 41% of the electricity generated in 2013 was produced from coal-fired power stations, while data for 2015 indicated that about 45% of the anthropogenic CO$_2$ was produced from coal. Current energy utilization trends indicate that energy generated from fossil fuels will continue to play an important role in the world energy portfolio in the foreseeable future. In this context, carbon capture and storage (CCS) has been proposed as a strategy to mitigate greenhouse gas emissions (GHG) from fossil fuel-fired power plants and industrial processes, and the Intergovernmental Panel on Climate Change (IPCC) suggests that CCS could potentially reduce CO$_2$ emissions from those systems by 80-90%. CCS technology involves production of a highly concentrated CO$_2$ stream from a combustion process which can be transported to and stored in geological formations such as saline aquifers or depleted oil and gas reservoirs. Oxy-fuel combustion was initially proposed in 1982, to produce highly concentrated flue gas (CO$_2$) for enhanced oil recovery (EOR). The concept was later explored by Argonne National Laboratory (ANL), where oxy-fuel tests were carried out at a pilot-scale facility. In 1990, comprehensive work started on CCS concepts throughout Europe and the USA. A simplified block diagram of oxy-fuel CCS systems is presented in Fig. 1, in which the most important feature of the process is that fuel is burned in a mixture of O$_2$ and CO$_2$ and steam from flue gas recycle (FGR) in order to moderate combustion temperatures to the same level as in an air-fired unit. As combustion occurs in the

![Figure 1 Principal scheme of oxy-fuel combustion process](image-url)
effective absence of nitrogen, the flue gas consists mainly of CO$_2$ and steam, with impurities such as NO$_x$ and SO$_x$. The composition of the concentrated CO$_2$ stream from oxy-fuel combustion was studied by Liu and Shao, who found that N$_2$/Ar and O$_2$ concentrations typically varied from 1-6%, and 3-5%, respectively, depending on O$_2$ purity from the air separation unit (ASU) and the equivalence ratio. Also, the steam concentration in the flue gas was in the range of 10-40%, depending on the fuel properties and FGR. Typical emissions from coal- and gas-fired power plants are reported by the IEA (Table 1). Circulating fluidized bed combustion (CFBC) offer comparatively lower SO$_2$ and NO$_x$ emissions, and in the case of pulverized coal (PC) technologies additional flue gas clean-up is required.

Table 1 Performance of coal- and natural gas-fired power plants

| Plant (MW)                  | Capacity factor (%) | CO$_2$ (g/kWh) | NO$_x$ (mg/Nm$^3$) | SO$_2$ (mg/Nm$^3$) | PM$^1$ (mg/Nm$^3$) | Efficiency penalty (CCS) (%) |
|-----------------------------|---------------------|----------------|---------------------|-------------------|--------------------|-------------------------------|
| PC-Ultra Super Critical (1050)$^2$ | 80                  | 740            | <50 to 100 (by SCR) | <20 to 100 (by FGD) | <10                | 7 to 10 (post- and oxy-fuel combustion) |
| CFBC (460)$^3$              | 80                  | 880 to 900     | <200                | <50 (in situ)     | <50                | 7 (in situ)                   |
| PC A-Ultra Super Critical$^4$ (1000) | -                   | 669            | <50 to 100 (by SCR) | <20 to 100 (by FGD) | <10                | 7 (in situ)                   |
| IGCC (335)                  | 70                  | 669 to 740     | <30                 | <20               | <1                 | 7                             |
| NGCC (410)                  | 80                  | 400            | <20                 | Almost none       | 0                  | 8                             |

1. Particulate matter, 2. In operation (sliding pressure-type), 3. In operation (Poland), 4. Under development.

The flue gas passes through a cleaning process comprised of a series of steps, such as particle removal by an electrostatic precipitator (ESP), flue gas desulfurization (FGD) and selective catalytic reduction (SCR). The ESP system also prevents degradation of catalysts in the SCR unit. In addition, to avoid an accumulation of sulfur species in the SCR system, an FGD unit must be installed upstream of the SCR unit. Studies to date suggest that due to O$_2$ separation, flue gas treatment and CO$_2$ compression, the net efficiency of oxy-fuel systems drops 7-11% points. This increases the levelized cost of energy from such systems, which also significantly varies depending on the plant location, type of fuel and other assumptions used for evaluations.
The purified CO$_2$ stream is then compressed and transported for geological storage.$^{14-19}$ Anheden et al.$^{15}$ reported that the SO$_2$ content in the CO$_2$ stream must be <200 mg/Nm$^3$, or even as low <50 mg/Nm$^3$, depending on CO$_2$ storage site requirements. Markewitz et al.$^{18}$ recommended that SO$_x$ concentrations for CO$_2$ transportation should be kept below 100 ppm in order to reduce corrosion issues.$^{19}$ Also, SO$_2$ in the CO$_2$ stream may cause problems due to sulfation of calcium-containing minerals and formation of sulfates which decrease the permeability and may affect the storage capacity of the reservoir. In addition, nearly complete dehydration of the CO$_2$ stream is strongly desirable in order to inhibit corrosion,$^{20,21}$ and removal of various other impurities is necessary since they negatively affect all stages in the CCS chain.$^{22,23}$

Typical contents of impurities in CCS systems are shown in Table 2, specifically for three oxygen-purity scenarios for oxy-fuel technologies, resulting in 85.0%, 98.0 and 99.9% CO$_2$ in the flue gas stream, respectively.$^{24,25}$ It can be seen that SO$_2$ and SO$_3$ concentrations in the CO$_2$ streams are higher in oxy-fuel combustion than in the pre-combustion and post-combustion schemes. White et al.$^{26}$ have highlighted that the SO$_2$ and SO$_3$ compounds can be removed from the CO$_2$ stream during the compression stage in the form of H$_2$SO$_4$ and that additional purification of the raw CO$_2$ stream is not required.

As stated above, sulfur species derived from coal-fired power plants are a major issue. Sulfur removal by limestone has been found to be an effective option to control SO$_x$ emissions due to low capital and operational costs.$^{27,28}$ However, this option is not practical for PC boilers due to higher flame temperatures causing thermal decomposition of sulfation products (CaSO$_4$).$^{27,28}$ Recently, impacts of sulfur in oxy-fired PC boilers have been reviewed by Stanger et al.$^{29}$, and they noted that the formation of SO$_3$ is a major issue in coal-fired combustion boilers. However, there is less research on this issue for oxy-fuel combustion in fluidized bed combustion (FBC) boilers despite the fact that increased SO$_2$ and SO$_3$ concentrations are expected due to FGR and more pronounced corrosion issues on downstream surfaces are expected due to lower gas flow rates through the furnace.$^{30,31}$ This paper aims to provide a major overview of the subject of SO$_3$ formation and its emissions from air and oxy-fired boilers, given that at this time no such review exists.

1.2 Influence of Sulfur in Combustion Systems

The sulfur content in coal may vary from 0.2 to 11%, depending on the location and rank.$^{32,33}$ However, the values fall generally between 0.3 and 4.3%.$^{34}$ Typically, sulfur in coal is
classified as organic and inorganic. The amount of organic sulfur is typically approximately one-half to one-third of the total. Most organic and pyritic sulfur in coal is converted to \( \text{SO}_2 \) during combustion and only a small fraction of the sulfur is retained in the ash. For example, studies for North Dakota coals showed 83 to 93% sulfur conversion to \( \text{SO}_2 \), depending on sulfur content and forms of sulphur in coal. Similarly, 91% of sulfur conversion for a US eastern bituminous coal was observed by Croiset and Thambimuthu. German lignite was also investigated in a pilot-scale 100 kW oxy-PC unit at Chalmers University and showed 67% conversion. During combustion, part of the sulfur is retained in the fly ash by reacting with alkaline and alkaline earth metal compounds such as calcium carbonates, and sodium chloride. Sulfur retention by the alkaline compounds is typically roughly 10 to 15%. It has been reported that the sulfur retention in PC boilers and fluidized beds are different mainly due to different combustion temperatures. Inorganic constituents of several Australian low-rank coals and ash characteristics (after combustion in a laboratory-scale fluidized bed) were investigated and it was noted that combustion of coals with high sulfur and sodium contents resulted in formation of low-melting-point compounds such as alkali sulfates in the ash, which are deposited as a coating on bed material surfaces. This process can also cause bed material to become sticky and enhance ash build-up in the reactor. Coals with low sulfur and sodium content permit operation over a much longer time without any agglomeration and defluidization.

**Table 2 Composition of \( \text{CO}_2 \) streams for storage**

| Species       | Pre-combustion | Post-combustion | Oxy-fuel |
|---------------|----------------|-----------------|----------|
|               | Selexol | Rectisol | Purity | Purity | Purity | Purity | Purity | Purity | Purity | Purity | Purity |
| \( \text{CO}_2 \) (vol%) | 97.95   | 99.7 | 99.93 | 99.92 | 99.81 | 85.00 | 98.00 | 99.94 |
| \( \text{O}_2 \) (vol%) | 0.015 | 0.015 | 0.03 | 4.70 | 0.67 | 0.01 |
| \( \text{N}_2 \) (vol%) | 0.045 | 0.045 | 0.09 | 5.80 | 0.71 | 0.01 |
| \( \text{Ar} \) (vol%) | 0.03 | 0.15 | 4.47 | 0.59 | 0.01 |
| \( \text{H}_2\text{O} \) (ppm) | 600 | 10 | 100 | 100 | 600 | 100 | 100 | 100 |
| \( \text{NO}_x \) (ppm) | 20 | 20 | 20 | 100 | 100 | 100 |
| \( \text{SO}_2 \) (ppm) | 10 | 10 | 20 | 50 | 50 | 50 |
| \( \text{SO}_3 \) (ppm) | 20 | 20 | 20 | 50 | 50 | 50 |
| \( \text{CO} \) (ppm) | 400 | 400 | 10 | 10 | 20 | 50 | 50 | 50 |
| \( \text{H}_2\text{S}+\text{COS} \) (ppm) | 100 | 100 |

\(^1\)Total concentration of \( \text{N}_2 \) and \( \text{Ar} \); \(^2\)Total concentrations of \( \text{SO}_2 \) and \( \text{SO}_3 \)
The main challenge with burning sulfur-containing coals is corrosion, which has been extensively studied in the case of conventional\textsuperscript{32,33,40} and more recently, in oxy-fuel combustion systems.\textsuperscript{29} Most of the corrosion mechanisms associated with sulfur in air-combustion are well explored and apply equally well to oxy-combustion. Corrosion is caused by low-temperature-melting alkali salt deposits when burning coals rich in sulfur, chlorine and sodium compounds.\textsuperscript{43} Longer operation of the units can lead to damage of heat exchangers by loss of metal or formation of cracks in high-temperature zones.\textsuperscript{44} The presence of pyrite in coal is the main reason for the formation of clinkers when high-sulfur coals rich in pyrites (FeS\textsubscript{2}) were burned.\textsuperscript{43} Under such conditions, iron species occurring in high-sulfur coals act as fluxing agents, and enhance the melting of quartz and clays in the coal.\textsuperscript{43} In addition, elevated levels of SO\textsubscript{3} in the molten salt result in an increase in solubility of the oxide scale on the metal.\textsuperscript{45,46}

1.3 SO\textsubscript{3} Emissions in Combustion Systems

Formation of SO\textsubscript{3} is undesirable in combustion processes as it enhances low-temperature corrosion and formation of aerosol emissions.\textsuperscript{30} By its nature, SO\textsubscript{3} is very reactive and converts easily to sulfuric acid in the presence of water vapour.\textsuperscript{35} Formation of SO\textsubscript{3} is thermodynamically favoured at lower temperatures; however, cooling rates in practical systems retard the SO\textsubscript{3}/SO\textsubscript{2} conversion rate. Moser\textsuperscript{47} reported that the deposition of H\textsubscript{2}SO\textsubscript{4} on downstream surfaces can be avoided by increasing the outlet temperature of the flue gas. Doing so, for example, by increasing the flue gas temperature in the air heater by 1.7°C can result in an improvement of nearly 1% in the unit heat rate.\textsuperscript{47} The annual benefit derived from the removal of SO\textsubscript{3} and the consequential reduction of corrosion downstream can exceed $500,000 for a 500 MW unit.\textsuperscript{47} During combustion, most sulfur in fuel is oxidised to SO\textsubscript{2}, while a limited amount of SO\textsubscript{2} may be converted to SO\textsubscript{3}.\textsuperscript{30,34,35,38} In addition, 0.5 to 1.5 wt % of SO\textsubscript{2} present in the flue gas may further oxidize to SO\textsubscript{3}.\textsuperscript{48} The SO\textsubscript{2}-to-SO\textsubscript{3} conversion is dependent on several parameters such as: combustion temperature, O\textsubscript{2} concentration and the presence of catalytic compounds in the fly ash.\textsuperscript{49,50} Tan et al.\textsuperscript{51} have stated that the oxidation of SO\textsubscript{2} to SO\textsubscript{3} in typical PC boilers may reach 5%, depending on the sulfur content of the coal. Data from the UK power plants shown in Table 3\textsuperscript{52} indicate the effect of excess O\textsubscript{2} concentrations on the formation of SO\textsubscript{3}. It can be seen that operation under low O\textsubscript{2} concentration in the flue gas leads to significantly lower levels of SO\textsubscript{3}.

SCR technology in coal-fired power plants can cause further oxidation of SO\textsubscript{2} to SO\textsubscript{3}.\textsuperscript{30,47} According to Moser,\textsuperscript{47} this SO\textsubscript{2} oxidation to SO\textsubscript{3} in SCR can vary from 0.3% to 2%. Slightly lower values for bituminous coals (0.25-0.5%) compared to that of for sub-bituminous coals
(0.75 to 1.25%) were noted by Srivastava et al.\textsuperscript{30} A more detailed study on SO\textsubscript{2} oxidation over honeycomb SCR catalysts was presented by Svachula et al.\textsuperscript{53} According to these authors, the oxidation degree of SO\textsubscript{2} in SCR depends on several factors such as the vanadium content of the fuel and presence of other catalysts.\textsuperscript{53} In addition, the reaction rate was found to be independent of oxygen and steam concentrations, but strongly inhibited by ammonia, and slightly enhanced by NO\textsubscript{x}.\textsuperscript{53}

**Table 3 SO\textsubscript{3} formation at high and low oxygen concentrations**

| Power plant | O\textsubscript{2} % | SO\textsubscript{3} (ppm) | T\textsubscript{DP} (°C)\textsuperscript{1} |
|-------------|-----------------|-----------------|---------------------|
| Marchwood   | 3.0             | 20              | 130-160             |
|             | 0.5             | 2-7             | 116-124             |
| Poole       | 4.0             | 45              | 160                 |
|             | <0.6            | 5               | 82                  |
| S.Denes     | 1.7             | N/a\textsuperscript{2} | >130               |
|             | >1.7            | N/a             | 130                 |
| Ince        | 4.5             | 18              | N/a                 |
|             | 1.0             | 7               | N/a                 |

\textsuperscript{1}T\textsubscript{DP} - dew point; \textsuperscript{2}N/a - not available.

In wet FGD, sulfuric acid in the flue gas is rapidly cooled by liquid spray. Under these conditions, the sulfuric acid vapour undergoes a shock condensation process which leads to the formation of fine sulfuric acid aerosol particles.\textsuperscript{54} According to Peterson and Jones,\textsuperscript{54} aerosol droplets have a mean diameter of 0.1 to 1.0 \textmu m, which makes the droplets effective at scattering visible light and can lead to a visible plume.\textsuperscript{54} However, only a small percentage of the SO\textsubscript{3} will end up as sulfuric acid aerosols,\textsuperscript{47} while part of it will condense on fly ash particles and be removed in the ESP or air preheaters. The quantity of fly ash, its surface area and alkalinity have a large impact on these processes.\textsuperscript{47} The quantity of SO\textsubscript{3} removed by this mechanism is approximately 20\% to 50\% depending on the temperature and fly ash composition.\textsuperscript{47} On the other hand, some studies on capturing suspended particulate matter from coal-fired plants showed that the presence of SO\textsubscript{3} in flue gas can be somewhat beneficial for effective operation of the ESP. Among such chemicals used to improve ESP performance, SO\textsubscript{3} is often used as a conditioning agent to reduce fly ash resistivity.\textsuperscript{55,56}

In summary, FGR, FGD, the catalytic effect of fly ash and other pollutants can all increase the formation of SO\textsubscript{3} in the back end of the boiler. Relatively few studies on SO\textsubscript{3} emissions in oxy-fuel combustion are available in the literature. Thus, this paper reviews studies on SO\textsubscript{3} emissions in conventional air- and oxy-fuel combustion environments.
1.4 **Objectives and Scope of the Paper**

This paper aims to provide an extensive review on SO$_3$ emissions from coal firing in conventional air- and oxy-combustion environments. The available experimental data on SO$_3$ formation, uncatalyzed and catalyzed reactions, catalysis and the effect of combustion parameters are discussed. A brief introduction to oxy-fuel combustion, conversion of fuel sulfur to SO$_2$, and SO$_3$ emissions levels during the combustion are presented. Other issues such as effect of FGR, SO$_2$ emissions, effect of temperature and residence time, the catalytic effect of fly ash and available modelling studies are also outlined. In addition, this review includes an assessment of the existing analytical methods for measuring SO$_3$ concentrations in flue gases. Special attention is given to the experimental work conducted in laboratory-scale reactors to compare SO$_2$ to SO$_3$ conversion in air and oxy-fuel environments. Finally, the most recent investigations of SO$_3$ emissions from pilot- and industrial-scale experiments are also summarized.
2. Oxy-Fuel Combustion Environment

2.1 Flue Gas Recirculation

The amount of recycled flue gas used in the oxy-fuel systems should be sufficient to ensure flame temperatures similar to those under air-combustion conditions and comparable temperature profiles through the boiler.\textsuperscript{5} In order to reach a similar adiabatic flame temperature as that in air-combustion, \( \text{O}_2 \) concentrations in the oxidant stream should be about 30\%\textsuperscript{,13,57}. Typically, this requires two-thirds of the flue gas to be recycled, and an optimum FGR ratio lies between 0.6 and 0.8\textsuperscript{,4,20,58,59}. The recycle rate is defined as the amount of FGR per mole of fuel\textsuperscript{,57}:

\[
\text{FGR rate} = \nu \left( \frac{\lambda_{\text{FGR}}}{[\text{O}_2]_{\text{oxidant}}} - \frac{\lambda_{\text{FGR}}}{[\text{O}_2]_{\text{ASU}}} \right) \tag{1}
\]

where \( \nu \) is the stoichiometric coefficient of \( \text{O}_2 \) for fuel used and \( [\text{O}_2]_{\text{ASU}} \) and \( [\text{O}_2]_{\text{oxidant}} \) are \( \text{O}_2 \) concentrations provided to the ASU and the boiler, respectively (Fig. 2\textsuperscript{57}). Alternatively, this can be presented as the recycled flue gas ratio:

\[
\text{FGR ratio} = \frac{\text{Mol of recycled flue gas stream}}{\text{Total mol of flue gas stream of boiler outlet}} \times 100\% \tag{2}
\]

Various FGR schemes were proposed by Nakayama et al.\textsuperscript{60} In their studies, the difference between dry and wet flue gas recycle is due to the presence or absence of a dehydration (condenser) unit in the system flow (see Fig. 1). The wet FGR is extracted before the flue gas condenser\textsuperscript{,61} Dry FGR can be extracted after passing through the condenser where restrictions on the moisture and \( \text{SO}_2 \) content exist\textsuperscript{,61} An ASPEN-plus model developed by ANL indicates that \( \text{SO}_2 \) concentration builds up with increase of FGR fraction (Table 4\textsuperscript{62}).

![Figure 2 Simplified flue gas recycling scheme in oxy-fuel combustion](image-url)
Wet FGR can be employed after passing through the FGD unit if the SO$_2$ concentration in the flue gas exceeds 3000 ppm.$^{63}$ FGR can be separated into primary and secondary streams. This makes it advantageous to utilize low-reactivity bituminous coals. The primary stream should be scrubbed, dried and cooled to a temperature of around 250ºC before entering the feeding mills.$^{4,63}$ Primary recycling is also used for coal transportation and removing moisture.$^{59,64}$ Thus, the removal of water-soluble acid gases such as SO$_3$ and HCl reduce the risks of corrosion.$^{57,63}$ Around 20% of the flue gas is taken as primary recycle, whereas the majority of the gas stream is extracted as the secondary stream.$^{4,16}$ The recycled flue gas temperature is determined mainly by the technical parameters of the recirculation duct, fan dimensions and ESP.$^{59}$ Therefore, the temperature of the FGR should be maintained between 200 and 300ºC.$^{59,61,65}$ Operation of the hot recirculation fan at higher flue gas temperatures can lead to higher maintenance costs.$^{59}$

2.2 SO$_2$ Emissions

In oxy-fuel combustion, the SO$_2$ concentrations are several times higher than that in conventional air combustion. However, in terms of the specific emissions (mg/MJ), SO$_2$ emissions are lower in the case of oxy-combustion.$^{38,66}$ As discussed by Dhungel et al.$^{67}$ and Fleig et al.$^{68}$ lower specific emissions can be explained by higher SO$_2$ retention by ash, and removal of SO$_2$ by condensate in the case of dry FGR. According to Liu and Shao,$^9$ SO$_2$ concentrations in oxy-fuel combustion can be 6 times higher than in an identical air-combustion unit. Higher concentration of SO$_2$ in the flue gas occurs due to the change in volumetric flow through the combustion furnace and FGR.$^{58}$ Tan et al.$^{51}$ have concluded that SO$_2$ concentrations in the furnace were 3-4 times higher than in air combustion for east US bituminous coals. Similar SO$_2$ concentrations were noted by Fleig et al.$^{39}$ in an oxy-PC unit. Relatively lower concentrations of SO$_2$ were measured by Duan et al.$^{69}$ in a 50-kW oxy-CFB. However, the SO$_2$ concentrations presented in this study were still higher than those seen in air-combustion. Croiset and Thambimuthu$^{38}$ have also

| FGR fraction | Sulfur concentration in the flue gas (ppmv) |
|--------------|--------------------------------------------|
| 0            | 1000                                       |
| 0.1          | 1080                                       |
| 0.2          | 1230                                       |
| 0.3          | 1390                                       |
| 0.4          | 1650                                       |
| 0.5          | 1920                                       |
| 0.6          | 2370                                       |
| 0.7          | 3110                                       |
found that SO$_2$ levels with RFG tests doubled when compared to once-through tests in a 210 kW test unit. The authors observed a decreasing trend of S-to-SO$_2$ conversion from 91% in the air-fired case to 74% in O$_2$/CO$_2$ atmosphere. In FGR tests, this conversion was 64%. According to Croiset and Thambimuthu, a possible reason for lower conversion was the sulfur retention by ash. Sulfur retention was also noted in experimental tests in the Chalmers University’s 100 kW unit. Relatively low S-to-SO$_2$ conversions in this case were noted in oxy-fired tests (43%) and in air tests (67%).

At higher temperature zones, the formation of SO$_2$ can significantly affect flame behaviour, which was more evident in the presence of CO as it is reported that SO$_2$ inhibits the CO burnout rate. Investigation on a bench-scale natural gas-fired 26 kW burner showed a clear decreasing trend in terms of CO emissions when 100 ppm SO$_2$ was added under sub-stoichiometric conditions. Sulfur species can also decrease the NO levels in post-flame regions. This occurs due to the catalysis of oxygen atom recombination reactions by SO$_2$. Typical mechanisms are described by Glarborg et al.: where X and Y may be H, O or OH radicals. It is reported that under fuel-lean combustion conditions, the inhibition is mainly governed by the recombination of O radicals involving SO$_3$, while under fuel-rich or stoichiometric conditions the interaction of SO$_2$ with radicals is believed to be more complex. The most important radical removal step under stoichiometric and reducing conditions is caused by the recombination of SO$_2$ with H to form HSO$_2$:

$$\text{SO}_2 + \text{H} + \text{M} \leftrightarrow \text{HSO}_2 + \text{M}$$ (5)

The presence of SO$_2$ also has an inhibiting effect on moist CO oxidation in air-firing environments. The inhibition was more pronounced at high atomic O levels; however, the presence of NO in the system significantly reduced the SO$_2$ effect. This work has been extended recently by Giménez-Lopez et al. who explored this phenomenon experimentally under CO$_2$-rich atmosphere to simulate oxy-fuel conditions. An important inhibition effect was evident in a CO$_2$ atmosphere as compared to a N$_2$-rich environment. This was due to the competition between CO$_2$ and O$_2$ for H radicals that reduces the formation of chain carriers via the O$_2$+H chain branching reaction. Lower inhibition was seen when the stoichiometry shifted to oxidizing conditioning.

3. Background for SO$_3$ Formation in Combustion

11
3.1 Homogeneous Conversion of SO\textsubscript{2} to SO\textsubscript{3}

Past studies by Cullis and Mulcahy\textsuperscript{35} and Jorgensen et al.\textsuperscript{80} noted that photochemical tests on direct oxidation have been used to measure SO\textsubscript{3}. This direct homogeneous oxidation of SO\textsubscript{2} is written as:

\begin{equation}
\text{SO}_2 + \text{O}_2 \rightleftharpoons \text{SO}_3 + \text{O} \quad + \quad 161.9 \text{ kJ/mol} \quad (6)
\end{equation}

However, limited SO\textsubscript{3} formation via reaction (6) was observed at temperatures below 900°C. As noted by Cullis and Mulcahy,\textsuperscript{35} while direct oxidation of SO\textsubscript{2} to SO\textsubscript{3} is rather limited, it can be produced in much larger amounts catalytically. In addition to that, two dominant reaction pathways are recognized for homogeneous SO\textsubscript{2} oxidation to SO\textsubscript{3}. The primary oxidation is the direct reaction of SO\textsubscript{2} with O radicals that occurs in post-flame zones of the combustor:

\begin{equation}
\text{SO}_2 + \text{O} (+\text{M}) \rightleftharpoons \text{SO}_3 (+\text{M}) \quad (7)
\end{equation}

where, M represents a third body. Burdett et al.\textsuperscript{81} investigated the rate of the direct oxidation reaction from 630 to 1080°C. The authors have tested SO\textsubscript{3} formation in O\textsubscript{2}/N\textsubscript{2}/SO\textsubscript{2} flow and proposed the following kinetic equation to predict formation of SO\textsubscript{3}:\textsuperscript{81}

\begin{equation}
\frac{d[\text{SO}_3]}{dt} = \frac{k_1}{RT} [\text{SO}_2] [\text{O}_2] = \frac{A[\text{SO}_2][\text{O}_2]}{RT} e^{-\frac{B}{T}} \quad (8)
\end{equation}

where \(k_1=\text{A exp}(-\text{B/T})\), \(A=2.6 (\pm 1.3) \times 10^{12} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}\), \(B=23000 \pm 1200 \text{ K}\). [SO\textsubscript{2}], [O\textsubscript{2}] and [SO\textsubscript{3}] are partial pressures of respective gases. More detailed data on the kinetics of reactions (6) and (7) can be found elsewhere.\textsuperscript{82–86} The second pathway occurs under moist conditions, where oxidation of SO\textsubscript{2} is enhanced in the presence of steam that increases via O/H radical concentration:

\begin{equation}
\text{SO}_2 + \text{OH} (+\text{M}) \rightleftharpoons \text{HOSO}_2 (+\text{M}) \quad (9)
\end{equation}

\begin{equation}
\text{HOSO}_2 + \text{O}_2 \rightleftharpoons \text{SO}_3 + \text{HO}_2 \quad (10)
\end{equation}

The first route is the main source of SO\textsubscript{3} at higher temperatures,\textsuperscript{34} while the second route contributes to SO\textsubscript{3} formation during the cooling of flue gases.\textsuperscript{34,80} Formation of SO\textsubscript{3} based on reactions (9) and (10) is thermodynamically favoured when exhaust gases undergo the cooling process. Production of SO\textsubscript{3} by reaction (10) is insignificant at temperatures of 730°C and above.\textsuperscript{87}

The effect of SO\textsubscript{2} concentration on SO\textsubscript{3} formation under oxy-fuel conditions was measured by Duan et al.\textsuperscript{88} at constant reactor temperature of 600°C (Fig. 3). As can be seen, an increasing trend of SO\textsubscript{3} concentration was noted with an increase of SO\textsubscript{2} concentration in the reactor. In contrast, the conversion rate decreased with increase of SO\textsubscript{2} concentration, which can be
attributed to a pseudo-first-order reaction mechanism. These results were consistent with observations of Belo et al.89, Fleig et al.90 and Wang et al.91

![Figure 3 Effect of SO$_2$ concentration on homogeneous SO$_3$ formation under oxy-fuel condition. Test conditions: 6% O$_2$, 10% H$_2$O, CO$_2$ – balance, and 600°C (reactor temperature)](image)

The SO$_3$/SO$_2$ thermodynamic equilibrium was plotted using data from the online calculator developed by Colorado State University.92 Typical air- and oxy-fired flue gas compositions were selected with SO$_2$ levels of 1000 ppm for both air and oxy flue gases, Fig. 4. O$_2$ and H$_2$O concentrations were changed from air- to oxy-combustion conditions, while diluted N$_2$ was replaced by CO$_2$ to evaluate the SO$_3$/SO$_2$ equilibrium ratios at temperatures from 400 to 950°C. It can be seen in Fig.4 that the formation of SO$_3$ is thermodynamically favoured at lower temperatures, and for example, SO$_3$/SO$_2$ conversion was 100% at 400°C and 4.6% at 950°C. This equilibrium curve agrees with the results presented by Belo et al.89 It is also interesting to point out that air- and oxy-flue gas composition showed similar results, and only small differences are noted in the range of 500-800°C.
3.2 Catalytic Conversion of SO\textsubscript{2} to SO\textsubscript{3}

There have been a number of investigations concerning the catalytic oxidation of SO\textsubscript{2} to SO\textsubscript{3}.\textsuperscript{93} Most of these investigations indicated higher conversion of SO\textsubscript{2} to SO\textsubscript{3} via heterogeneous catalysis\textsuperscript{94–97} represented as:

\[
\text{SO}_2 + \text{O}_2 \xrightarrow{\text{Catalyst (Fe}_3\text{O}_4, \text{V}_2\text{O}_5)} \text{SO}_3 + \text{O}
\]  

(11)

Catalytic conversion of SO\textsubscript{2} to SO\textsubscript{3} by fly ash was investigated in a bench-scale reactor by Marier and Dibbs.\textsuperscript{94} They concluded that the conversion of SO\textsubscript{2} to SO\textsubscript{3} was strongly enhanced due to the iron oxide in the fly ash whereas the reverse effect was noted in the presence of unburnt carbon in the fly ash.\textsuperscript{94} Also, similar and supporting results were produced by Zhang et al.\textsuperscript{95} Extended experiments on sulfation of CaO and MgO mixed with iron oxide indicated direct relation to the catalytic conversion of SO\textsubscript{2} to SO\textsubscript{3}.\textsuperscript{94} Similar work on the kinetics of SO\textsubscript{3} adsorption by CaO and MgO was undertaken by Thibault et al.\textsuperscript{98} However, a subsequent study suggested that this might be due to the difference in grain size and porosity of the solid material.\textsuperscript{98} A modelling approach called density functional theory (DFT) was applied by Galloway et al.\textsuperscript{99} to explore binding mechanisms of SO\textsubscript{3} to other metal compounds. Compounds such as CaO, MgO, Na\textsubscript{2}O and K\textsubscript{2}O that are typically found in fly ash were included.
in the model. The authors observed that SO$_3$ binds strongly with alkali and alkaline metals, with the effect being more pronounced with alkali metals (i.e., Mg<$\text{Ca}$<$\text{Na}$<$K) through the formation of a sulfate (SO$_4^{2-}$).\textsuperscript{99} Cao et al.\textsuperscript{100} outlined two main interactions of fly ash with SO$_3$ based on temperature. First, fly ash could serve as an SO$_3$ adsorbent under low temperatures typical for the bottom section of boilers. At a temperature lower than the dew point of SO$_3$, it converts SO$_3$ to H$_2$SO$_4$ mist droplets in the presence of water. Subsequently, these droplets condense on fly ash surfaces. The pore structure of the fly ash, which is associated with the carbon residue, is responsible for condensation or adsorption of SO$_3$. Chang\textsuperscript{101} investigated infrared adsorption of SO$_2$ on $\gamma$-alumina ($\gamma$-Al$_2$O$_3$) outlining two main factors, the number of hydroxyl groups and the temperature of the catalyst. Infrared spectroscopy showed that SO$_2$ is adsorbed on $\gamma$-Al$_2$O$_3$ in the form of sulfite species. SO$_2$ could also be oxidized on $\gamma$-Al$_2$O$_3$ to form aluminum sulfate. Vanadium catalyst contains a mixture of metal compounds of vanadium and alkali metal dispersed on a silica-based support. SO$_2$ to SO$_3$ oxidation by vanadium catalysts has been widely studied for SCR technology.\textsuperscript{97}

### 3.3 SO$_3$ Sampling Methods

A number of different approaches for SO$_3$ measurement have been mentioned in the literature such as: the controlled condensation method (CCM), SO$_3$ monitor, isopropanol bottle method (IPA) and acid dew point measurements (DPM). These methods were examined by Jaworowski and Mack\textsuperscript{102} who noted the limitations of each method in terms of reproducibility and accuracy. More recently, SO$_3$ measurements have been revised by Fleig et al.\textsuperscript{103} Based on studies of Jaworowski and Mack\textsuperscript{102} and Fleig et al.\textsuperscript{103}, a summary of each SO$_3$ measurement method is given below.

#### 3.3.1 Controlled condensation method

CCM was classified as British Standard BS 1756-4:1977 and American Standard D-3226-73T, and has been the most widely used method for SO$_3$ measurements\textsuperscript{102}. However, it should be noted that both of these standards have been withdrawn.\textsuperscript{104,105} The principle of CCM is based on cooling flue gas to a temperature between the acid dew point and water dew point.
SO$_3$ is condensed in the quartz filter as well as on the glass walls of the sampling train as shown in Fig. 5. A sampling time of 30 minutes is required with a flow rate of 10 dm$^3$/min. After gas sampling, a known quantity of distilled deionized water is used to flush out the filter and condenser to collect the H$_2$SO$_4$, which is then determined by the titration method using 0.005M barium perchlorate. As shown in Fig. 5, the quartz filter is used to capture particulates before entering the condenser and impingers. The probe and quartz filter should be maintained at 260°C to avoid the formation of aerosol particles and condensation of sulfuric acid. The filtration of particulates from the sampling gas is crucial as the interaction of ash particles and SO$_3$ in the sampling train can lead to both positive and negative errors. The glass condenser should be maintained at 80 to 90°C. According to Maddalone et al. CCM in laboratory tests collected 95% of H$_2$SO$_4$ with a variation coefficient of ±6.7%, but the same authors indicated lower accuracy for the field tests. During the sampling, SO$_2$ reacts with water and dissociates into bisulfite and sulfite ions (reactions 12 and 13). The oxidation of SO$_2$ in reaction (14) depends on the concentration of sulfite ions in the solution, which makes the reaction strongly pH-dependent (Fig 6):

$$
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HSO}_3^- \\
\text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_3^{2-}
$$

(12)  

(1)

Figure 5 The modified controlled condensation method (CCM) SO$_3$ sampling scheme. 106
\[ \text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-} \]  \hspace{1cm} (14)

Figure 6 shows the calculated mole fraction of sulfur species as a function of pH at 25°C in aqueous solution. It can be seen that sulfites dominate in alkaline solution while bisulfite dominates in acid solutions with a pH range of 3-7.\textsuperscript{108} It is commonly accepted that at normal sampling conditions, the impinger solution must be slightly acidic, preventing sulfite formation and subsequent oxidation.\textsuperscript{108} Therefore, purging of impingers with air is recommended to remove SO\textsubscript{2}.

### 3.3.2 Isopropanol absorption bottle method

This method is based on EPA Method 8 with some modifications. A schematic illustration of the isopropanol absorption method is shown in Fig. 7. The extracted flue gas is first cooled down as in the CCM by a glass condenser and passed through four bottles, which are kept in an ice bath. The first bottle is filled with 10 mL of 80% isopropanol solution diluted in water, the following two bottles are filled with 3% hydrogen peroxide solution, and the fourth bottle is used to capture moisture from the gas sample with silica gel. According to Cooper,\textsuperscript{109} the most common error occurring during the
sampling of SO₃ in this method is absorption and oxidation of SO₂. Similar limitations were mentioned by Fleig et al.¹⁰³ where large amounts of SO₂ were absorbed in the isopropanol solution and resulted in a positive bias.¹⁰³

### 3.3.3 Salt and glass bead methods

The first description of the salt method was provided by Kelman in the early 1950s.¹¹⁰ This was later applied to industrial plant by Cooper et al.¹⁰⁹ The advantages of this method as highlighted by the authors are: no interference from SO₂ and simplicity of sampling. Flue gas containing SO₂ and SO₃ passes through the dry layer of NaCl and the sulfur trioxide reacts with NaCl.¹¹⁰ This method was applied to detect SO₃ concentration in a 100 kW rig at Chalmers University.¹¹¹ A schematic of the salt method is shown in Fig. 8,¹¹¹ where salt is fixed in the tube with glass wool.¹⁰⁹,¹¹² With a decrease of the gas temperature to approximately 500°C, SO₃ starts to react with water vapour to form gaseous sulfuric acid,¹⁰³,¹¹¹ which then reacts with NaCl to form Na₂SO₄ and NaHSO₄.¹¹¹ The reactions occurring during the salt method are given as:

\[
\text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{SO}_4(g) \quad (2)
\]

\[
\text{NaCl}(s) + \text{H}_2\text{SO}_4(g) \rightarrow \text{NaHSO}_4(s) + \text{HCl}(g) \quad (16)
\]

\[
2\text{NaCl} (s) + \text{H}_2\text{SO}_4(g) \rightarrow \text{Na}_2\text{SO}_4(s) + 2\text{HCl}(g) \quad (3)
\]

\[
\text{NaHSO}_4(s) + \text{NaCl} (s) \rightarrow \text{Na}_2\text{SO}_4(s) + \text{HCl}(g) \quad (4)
\]

\[
4\text{NaCl} (s) + 2\text{SO}_2(g) + 2\text{H}_2\text{O} (g) + \text{O}_2(g) \rightarrow 2\text{Na}_2\text{SO}_4(s) + 4\text{HCl}(g) \quad (19)
\]

The last reaction is undesirable as it leads to a positive bias.¹⁰³ Sulfation of NaCl is a slow reaction and mainly depends on temperature and SO₂ concentration. Vainio et al.¹¹¹ have extended this method by testing other salts (KCl, K₂CO₃, and CaCl₂) along with NaCl. Tests with NaCl and KCl showed comparable results to the CCM. Less convincing results were observed with K₂CO₃ and CaCl₂.¹¹¹

### 3.3.4 Indirect measurements of SO₃

Figure 8 Salt tube preparation

Figure 9 Arrangement for SO₃ measurements by CaC₂O₄¹¹³
Ibanez et al.\textsuperscript{113} described an indirect measurement method employing calcium oxalate, which is based on the next reaction:

\[
\text{SO}_3 + \text{CaC}_2\text{O}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{CO}
\]  

(20)

This method is sensitive to temperature control and the reaction vessel should be maintained at 325°C. A mixture of gas passes through a plug of prepared CaC\textsubscript{2}O\textsubscript{4} then through two optical cells in series (see Fig 9). The SO\textsubscript{2} content in the sample gas is monitored by means of UV spectrometry, while the SO\textsubscript{3} concentration is quantified indirectly measuring CO\textsubscript{2} in the second cell by IR spectrometry. The authors underlined that the preparation of reagent and calibration should be done very carefully to produce reliable results. A similar approach has been developed by Fateev and Clauson\textsuperscript{114}, but they presented only preliminary results.

Continuous SO\textsubscript{3} measurement by Fourier transform infrared (FTIR) and differential optical absorption spectroscopy (DOAS) was described by EPRI.\textsuperscript{115} Subsequently a modified cross-duct probe design was developed to improve SO\textsubscript{3} measurements by FTIR. The result of continuous measurements for 3 days with FTIR was in good agreement with that determined by the CCM method. However, variation of SO\textsubscript{3} across probes was 10\%.\textsuperscript{31} An indirect test of SO\textsubscript{3} with FTIR has also been attempted by measuring HCl from reaction of NaCl with H\textsubscript{2}SO\textsubscript{4}. In this case, the exit gas temperature should be kept between 200-400ºC. However, at 200ºC, only about one-half the SO\textsubscript{3} was converted to HCl.\textsuperscript{111} Chamberlain et al.\textsuperscript{116} have also attempted to measure SO\textsubscript{3} concentrations with FTIR and the uncertainty of measurement was ±20 ppm. Given this range of uncertainty, the authors could not see a difference in SO\textsubscript{3} concentrations between air and oxy-fuel combustion. Therefore, both of these indirect methods still need to be improved before they can be reliably used in practice. Roy et al.\textsuperscript{117} carried out such measurements for laboratory-scale oxy-fuel experiments, but they did not comment on the consistency of measurements and the effect of reaction conditions.

### 3.3.5 Pentol SO\textsubscript{3} monitor

This device was previously called the Severn Science reactive gas analyzer,\textsuperscript{118} and Jackson et al.\textsuperscript{118} were the first to describe this method and device. The principle of this instrument is that SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} in the gas sample are absorbed as SO\textsubscript{4}\textsuperscript{2−} in an aqueous solution of isopropanol. During the sampling, the solution is continuously passed through a bed of barium chloranilate where the following reaction occurs:
\[ \text{SO}_4^{2-} + \text{BaC}_6\text{O}_4\text{Cl}_2 + \text{H}^+ \rightarrow \text{BaSO}_4 + \text{HC}_6\text{O}_4\text{Cl}^- \] (21)

The released acid chloranilate ions absorb light at 535 nm, producing a purple-coloured solution, and the concentration of this chemical is continuously measured by a flow photometer. The amount of sulfate in the solution is proportional to the SO3 concentration entering the analyzer\textsuperscript{119}. According to Dennis and Hayhurst\textsuperscript{120}, this instrument was slow to achieve steady-state performance and required moisture in the fluidization gases to ensure reliable readings. Cooper\textsuperscript{109} applied the Severn Science gas analyzer at the Orimulsion power plant, where the average results were 25% higher than those determined by the CCM approach. One reason for higher concentrations could be absorption of SO\textsubscript{2} in the isopropanol and partial oxidation of SO\textsubscript{3}\textsuperscript{2-} to SO\textsubscript{4}\textsuperscript{2-}. This was confirmed by peaks for both SO\textsubscript{3}\textsuperscript{2-} and SO\textsubscript{4}\textsuperscript{2-} in the ion chromatograph analysis.\textsuperscript{109} The study by Fleig et al.\textsuperscript{103} supports the reliability of this method, especially over longer continuous sampling periods. However, the average readings were still 20% lower compared to those from CCM.\textsuperscript{103} Therefore, it is clear from the discussion above that there are still many issues related to accuracy of SO\textsubscript{3} measurements that need to be addressed.

3.3.6 Acid dew point measurements

The measurement of sulfuric acid dew point (ADP) temperature is one of the conventional ways to estimate the amount of SO\textsubscript{3} when H\textsubscript{2}O concentration in the flue gas is known. Taylor\textsuperscript{123} concluded that the condensation of sulfuric acid is a function of the surface temperature of the sampling tube and the water vapour content in the flue gases. Measurements of ADP were conducted using a cooled electrical conductivity probe to determine the temperature where

| Authors              | Correlations                                                                                         |
|----------------------|-------------------------------------------------------------------------------------------------------|
| Verhoff and Banchero | \( \frac{1}{T_{\text{Dew}} + 273.15} = 0.002276 - 0.00002943 \ln p_{H_2O} - 0.0000858 \ln p_{H_2SO_4} \\ + 0.00000620(\ln p_{H_2SO_4})(\ln p_{H_2O}) \) |
| Okkes                | \( T_{\text{Dew}} = 203.25 + 27.6 \log p_{H_2O} + 10.86 \log p_{SO_3} + 1.06(\log p_{SO_3} + 8)^{2.19} \) |
| ZareNezhad           | \( T_{\text{Dew}} = 150 + 11.664 \ln(p_{SO_3}) + 8.1328 \ln(p_{H_2O}) - 0.383226 \ln(p_{SO_3}) \ln(p_{H_2O}) \) |
condensation occurs.\textsuperscript{124} The probe has two electrodes and a thermocouple. The ADP is identified by a sudden increase in the conductivity between electrodes on the surfaces due to the condensed liquid sulfuric acid solution. Currently, advanced portable devices (Lancom 200) are available to measure ADP of the flue gases.\textsuperscript{124} The ADP changes with the moisture content of the flue gases, which is particularly important for an oxy-fuel combustion environment. Available correlations to estimate the ADP temperature are illustrated in Table 5. According to Verhoff and Banchero,\textsuperscript{121} two methods have been developed to define the vapour and liquid equilibrium for aqueous sulfuric acid solutions. The first method was determined by measuring the vapour-liquid compositions and temperature at equilibrium. The second method takes into account liquid and pure components to estimate the equilibrium vapour and liquid compositions via thermodynamics. Based on these two methods, Verhoff and Banchero\textsuperscript{121} have proposed a correlation to predict the dew point of sulfuric acid. More recently, ZareNezhad\textsuperscript{122} has proposed a new correlation to predict flue gas sulfuric acid. Based on these correlations, Stanger et al.\textsuperscript{29} compared both correlations for composition of flue gas derived from oxy-fuel combustion. The authors concluded that the Verhoff and Banchero method over-estimate experimental dew points at low SO\textsubscript{3} concentrations and high moisture content. The Okkes correlation has been found to be better suited for flue gases with moisture content higher than 25%.\textsuperscript{29}

4. Influence of Oxy-fuel Parameters on SO\textsubscript{3}

4.1 Effect of O\textsubscript{2}/CO\textsubscript{2} Environment

SO\textsubscript{3} concentrations in an oxy-fuel environment are several times higher than in a typical air-combustion environment.\textsuperscript{38,125} Higher SO\textsubscript{3} and SO\textsubscript{2} concentrations along with wet FGR will result in a higher ADP temperature, which leads to corrosion issues. At the bench-scale level, the formation of SO\textsubscript{3} in an O\textsubscript{2}/CO\textsubscript{2} environment was investigated by several researchers, for example by Fleig et al.\textsuperscript{90,126} Sporl et al.\textsuperscript{127} Belo et al.\textsuperscript{128} and more recently by Duan et al.\textsuperscript{88} According to these authors, elevated O\textsubscript{2} concentration in oxy-fuel combustion enhances SO\textsubscript{3} formation. Belo et al.\textsuperscript{89} have observed that O\textsubscript{2} concentrations of 3%, 5% and 10% resulted in SO\textsubscript{2} oxidation of 3-10%. These results agree well with the equilibrium calculation of Zheng and Furimsky.\textsuperscript{129} Fleig et al.\textsuperscript{90,126} concluded that replacing N\textsubscript{2} with CO\textsubscript{2} had a strong effect at higher temperatures. This might be due to higher effectiveness of third-body collisions, the effect of which is smaller at lower temperatures.\textsuperscript{88} Fleig et al.\textsuperscript{90} also noted 30% higher SO\textsubscript{3} concentrations when the CO\textsubscript{2} environment was compared to that of N\textsubscript{2}. A sensitivity analysis
at 1027°C indicated that SO₃ formation was enhanced due to the increase of concentrations of radicals due to the third-body (M) reactions:

\[
\text{HO}_2 (\text{+ M} ) \rightleftharpoons \text{H} + \text{O}_2 (\text{+ M}) \quad (22)
\]
\[
\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH} \quad (23)
\]

The formation of H radicals is enhanced via reaction (22), and they then react with O₂ to form OH radicals according reaction (23). In addition, FGR increases the level of impurities such as NOₓ, SO₂ and CO that are believed to enhance the SO₃ formation to some extent as discussed below.

### 4.1.1 Effect of NOₓ emissions

It has been noted that NOₓ may have a catalytic effect on SO₂/SO₃ conversion even at low temperatures. This effect can occur through either a direct or an indirect route by interaction with the radical pool composition. At low temperatures SO₂ may react directly with NO₂ to produce SO₃:

\[
2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \quad (24)
\]
\[
\text{NO}_2 + \text{SO}_2 \rightleftharpoons \text{NO} + \text{SO}_3 \quad (5)
\]

According to Wendth and Sternling the SO₂ oxidation was second order in respect to NO and had low activation energy at high concentrations of NO, and the reaction is of the first order in respect to NO with high activation energy at low concentrations of NO. At low concentrations of NO, reaction (24) is slow, and SO₂ oxidation can occur via the following route:

\[
\text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3 \quad (6)
\]
\[
\text{NO}_3 + \text{SO}_2 \rightleftharpoons \text{SO}_3 + \text{NO}_2 \quad (27)
\]

In addition, at low temperatures NO may indirectly increase SO₃ formation by converting HO₂ in reactions (9) and (10) back to OH radicals:

\[
\text{NO} + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH} \quad (28)
\]

This was noted by Fleig et al. when a small amount of NO (100 ppm) favoured the formation of SO₃. The authors also noted an increase in SO₃ concentrations when more OH radicals were available through reaction (28) at temperatures higher than 1027°C and SO₃ was formed through reactions (9) and (10). They also reported a notable increase in SO₃ formation in the presence of 50 ppm NO in an oxy-fuel environment.

\[
\text{H} + \text{O}_2 (\text{+ M}) \rightleftharpoons \text{HO}_2 (\text{+ M}) \quad (7)
\]

According to Glarborg et al., the rate of reaction (29) is higher in a CO₂ environment than in N₂ which favours HO₂ formation. Excess formation of OH via reaction (28) promotes
secondary formation of SO$_3$ via reactions. This effect was more pronounced in a CO$_2$ environment.$^{126}$ In the extended numerical work by Fleig et al.$^{126}$ a higher value for the third-body coefficient of 2.5 for CO$_2$ (instead of 1.0) resulted in negligible (2%) reduction of SO$_3$, which is still higher than that in the air-firing case. Thus, the impact of SO$_2$ oxidation by nitrogen oxide during cooling is likely to be small and the effect of NO can be assumed to be negligible in oxy-fuel combustion.$^{131}$

4.1.2 Effect of carbon monoxide

Previous studies showed that the CO concentration in oxy-fuel is higher than that in air combustion processes due to relatively higher flame temperatures,$^{129,132,133}$ and most CO is formed in or near the burner region.$^{133,134}$ In high-temperature zones in a CO$_2$-rich environment, the thermal dissociation of CO$_2$ can also contribute to higher CO concentrations:$^{134}$

$$\text{CO}_2 (+\text{M}) \rightleftharpoons \text{CO} + \text{O} (+\text{M}) \quad (30)$$

However, this reaction occurs only at temperatures significantly higher than 930°C.$^{134}$ CO$_2$ can compete with O$_2$ for atomic hydrogen, and will lead to the formation of CO:$^{132,134}$

$$\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH} \quad (31)$$

Simultaneously, during the formation of CO in the flame zone, the recombination of CO with OH can take place$^{85}$ and this will increase the formation of H radicals due to reverse reaction (31). This will compete with reaction (9) for OH radicals and that reduces the formation of SO$_3$ as noted in the experiments of Wang et al.$^{91}$ and Fleig et al.$^{90}$ It is worth mentioning that an early experiment from the staged combustion of a CH$_4$/H$_2$S/air mixture showed enhanced SO$_3$ formation in the presence of 1100 ppm of CO.$^{85}$ The maximum SO$_2$ oxidation took place at flame temperatures between 1300 and 1650°C for single and staged combustion. A narrow temperature range of 1100 to 1300°C was observed for the test where the secondary air supply was delayed for 30 ms. These authors postulated that the maximum SO$_3$ formation was only a transient phenomenon. The SO$_3$ concentration changed as the reactions continued in the downstream gas. In addition, there was no enhancement of SO$_3$ for residence time beyond 90 ms. The authors believe that enhancement of SO$_3$ formation was dependent on the air/fuel ratio of each combustion stage and the delay interval between the first and second stage$^{85}$. These results were also supported by Bayless et al.$^{135}$ In the experimental work of Fleig et al.$^{90}$ addition of 1000 ppm CO into the system increased the SO$_3$ formation significantly compared to the test without CO addition. The measured SO$_3$ concentrations were three times higher at a temperature of 927°C with 3% O$_2$. However, a further increase of CO to 3000 ppm showed
only a small difference compared to the 1000 ppm CO addition. In summary, it appears that the maximum SO$_3$ formation in the presence of CO takes place at temperatures between 827 and 1027°C. Lower formation of SO$_3$ at temperatures higher than 1127°C was noted by Fleig et al.$^{90}$ This indicates that SO$_3$ formation is significantly affected by the temperature where burnout of the fuel takes place. In general, these results agree well with the studies of Merryman and Levy.$^{85}$

4.1.3 Effect of steam

The wet FGR in oxy-fuel combustion can increase the steam level to 25-35% in the combustion system.$^{136}$ This increase may enhance secondary formation of SO$_3$ via HOSO$_2$ reactions (9) and (10). In the tests by Fleig et al.$^{90}$ a more pronounced effect of steam on SO$_3$ formation was noticed between 1130 and 1200°C. In the presence of steam OH radicals can be formed by the reaction of H$_2$O with O radicals:$^{84}$

\[ \text{H}_2\text{O} + \text{O} \rightleftharpoons \text{OH} + \text{OH} \]  

(32)

and also by the decomposition of steam as noted by Wine et al.$^{137}$

\[ \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \]  

(8)

Decomposition of HO$_2$ and OH release through reactions (22) and (23) shifts reaction (34) to the left and enhances SO$_3$ formation. In addition, the third-body efficiency of H$_2$O is higher than that of CO$_2$ and N$_2$.$^{90}$ Fleig et al.$^{90}$ have pointed out that an increase of H$_2$O from 0.1% to 1.1% and 8.7% result in higher SO$_3$ concentrations at temperatures between 927 and 1127°C. At 1174°C and 8.7% H$_2$O, SO$_3$ concentration reached 23 ppm. However, in the presence of combustibles, the inhibiting effect of steam in SO$_3$ formation was noted.$^{90}$ This observation agrees well with the previous conclusion of Glarborg et al.$^{77}$ A less pronounced effect of H$_2$O on SO$_3$ was noted by Belo et al.$^{128}$ The effect of steam was also studied by Duan et al.$^{88}$ at 600°C, who identified an increase of SO$_3$ concentration from 3.7 ppm to 7.1 ppm when steam increased from 5% to 15%.

In contrast to these studies, a decreasing SO$_3$ formation was observed in homogeneous tests of Wang et al.$^{91}$ In this work, higher concentrations of steam (15 to 35%) were employed to simulate wet FGR. The authors claimed that less pronounced formation of SO$_3$ was due to the inhibiting effect of steam. In oxy-fuel combustion tests, a further increase of H$_2$O to 35% showed a stronger inhibiting effect on SO$_3$, which is consistent with the result from Fleig et al.$^{90}$

According to Hindyarti et al.$^{138}$ and Glarborg et al.$^{77}$, major consumption of SO$_3$ in combustion could be due to reactions (34) to (36).
\[
\begin{align*}
\text{SO}_3 + H & \rightleftharpoons \text{SO}_2 + \text{OH} \quad (34) \\
\text{SO}_3 + \text{O} & \rightleftharpoons \text{SO}_2 + \text{O}_2 \quad (35) \\
\text{SO}_3 + \text{OH} & \rightleftharpoons \text{SO}_2 + \text{OH}_2 \quad (36)
\end{align*}
\]

In addition, in their experiments $\text{H}_2\text{O}$ concentrations were higher than $\text{SO}_2$ concentrations, and under such conditions, steam was more likely to compete for $\text{O}$ radicals. As a result, $\text{O}$ radicals formed $\text{OH}$ radicals resulting in lower $\text{SO}_3$ formation through reaction (7).

### 4.2 Temperature and Residence Time

Flint and Lindsay\textsuperscript{139} and Burdett et al.\textsuperscript{81} carried out pioneering investigations on oxidation of $\text{SO}_2$ in quartz tube reactors in air environment. In both tests an increasing trend in homogeneous $\text{SO}_3$ formation with temperature and residence time was noted. Increase of $\text{SO}_3$ formation with increase of furnace and flame temperatures was also investigated earlier by Crumley and Fletcher\textsuperscript{140} (Table 6). Later, a similar approach in an $\text{O}_2$/N\textsubscript{2} environment was explored by Belo et al.\textsuperscript{89} As shown in Table 6, the homogeneous conversion ratio from 0.04% to 0.77% was achieved by increasing temperature from 400 to 1000°C. In their test, a conversion increase was noted when the reaction temperature went above 700°C, but temperatures above 900°C were required for significant conversion for the tests with a residence time of 1 s.\textsuperscript{89} For that residence time, the maximum conversion was 0.36%, which agrees well with the previous results of Flint and Lindsay\textsuperscript{139} and Burdett et al.\textsuperscript{81} The $\text{SO}_2$ to $\text{SO}_3$ conversion vs temperature is illustrated in Fig 10. More results on homogeneous $\text{SO}_3$ formation in quartz tube reactors can be found in Table 6.
The effect of temperature on homogeneous SO₃ formation under different environments was also studied by Duan et al. In their studies SO₃ concentration increased with temperature even at the lower temperature range (400 to 700°C). The reason for SO₃ formation in this experiment could be the high SO₂ concentration (3000 ppm) employed. It is known that at lower temperatures SO₃ is formed by oxidation of molecular oxygen via reactions (9) and (10) and that SO₃ formation is thermodynamically favoured with decreasing temperature. Overall, the observations of Duan et al. agree with the findings of Belo et al. Fleig et al. have carried out experiments on homogeneous SO₃ formation over a much wider temperature range (Table 6), and they concluded that less than 1 ppm SO₃ was formed at temperatures below 727°C. The lower level of SO₃ seen in their work was due to the short residence time, as noted by Flint and Lindsay and the low level of H₂O (1.11%).

**Figure 10** Effect of reactor temperature on homogeneous formation of SO₃
### Table 6 Homogeneous SO$_3$ formation in quartz tube flow reactors

| Reference            | Reactor Size (d x l) mm | Temperature (°C) | Inlet gas composition | Flow rate (L/min) | Residence time (s) | Maximum temperature (°C) | SO$_3$/(SO$_2$+SO$_3$) (%) |
|----------------------|-------------------------|-----------------|-----------------------|-------------------|---------------------|--------------------------|--------------------------|
| Barret et al.\textsuperscript{141} | 25.4 x 610              | 1030-1530       | Air + 0.7% SO$_2$     | 3.4               | 5.5-5.7             | 1530                     | 0.2                      |
| Flint and Lindsay\textsuperscript{139} | 14 x 1829               | 500-900         | Air (+ H$_2$O-8%), SO$_2$(1400 ppm) | 1.7-8.5          | 0.9-9.6             | 900                      | 0.36 - 4.8               |
| Burdett et al.\textsuperscript{81}  | 10 x 450                | 850-1066        | SO$_2$(0-5500 ppm); O$_2$ (0-21%); bal-N$_2$ | 0.5-5            | Up to 6             | 960                      | 0.36                     |
| Belo et al.\textsuperscript{89}    | 12 x 250                | 400-1000        | Gas mixture (SO$_2$-1000 ppm, H$_2$O-3%, O$_2$-5%, bal-N$_2$) | 0.5-1.5          | 0.3-0.9             | 1000                     | 0.14 – 0.77              |
| Fleig et al.\textsuperscript{90}   | 50 x 900                | 527-1400        | SO$_2$-1000 ppm, O$_2$-3%, H$_2$O-1.11%, bal-N$_2$/CO$_2$, | 1.0              | Up to 5             | 1400                     | 0.1-1.7                  |
| Duan et al.\textsuperscript{88}    | 15.5 x 1115 (420)$^1$  | 400-700         | O$_2$-6%, SO$_2$-3000 ppm, H$_2$O, bal-N$_2$/CO$_2$, | 3.7              | 1.5                 | 700                      | 0.1–1.5                  |
| Wang et al.\textsuperscript{91}    | 50 x 1500               | 350-1050        | O$_2$-5%, SO$_2$-500, 1500, 2500 ppm, H$_2$O-0.03%, bal-CO$_2$, | 2.0              | N/S$^2$             | 950                      | 0.11                     |

$^1$ Only (420mm) of total length is heated; $^2$ N/S-Not specified. Based on size of tube and flow rate, calculation shows long residence time for this work.
4.3 Catalytic Effect of Fly Ash

Metal oxides such as Fe$_2$O$_3$, Al$_2$O$_3$ or CuO can act as a catalyst in SO$_2$ oxidation, while alkali and earth metal oxides such as MgO and CaO can adsorb SO$_3$. The catalytic effect of fly ash on SO$_3$ formation in oxy conditions was investigated by Belo et al. who found that: (i) the total conversion of SO$_2$ to SO$_3$ was only about 1.8%; (ii) the effect of Fe$_2$O$_3$ was the most pronounced; and (iii) fly ash samples produced under air- and oxy-fuel conditions showed no significant difference. Also, the SO$_3$ concentration increased to 17.8 ppm at 700°C in the presence of ash, while only 1 ppm was observed without ash. A stronger catalytic effect at 400 and 500°C was noted by Duan et al. compared to the tests of Belo et al. who noted more pronounced catalytic effect at 700°C. High CaO content in ash can significantly reduce SO$_2$ concentrations, as noted by Ahn et al. in the pilot-scale tests with PRB coal (22.2% CaO in ash). By contrast, enhanced SO$_3$ formation was observed for an Illinois coal, which contains 1.9% CaO in the ash, and a high sulfur content, as shown in Tables 7 and 8.

Hence, it may be concluded that pronounced catalytic effects were observed in bench-scale tests rather than in the pilot-scale tests. However, large units could perform differently due to the heat transfer rates, inconsistency in fuel composition and loading requirements. Interestingly, the effect of Fe was not observed in the presence of combustibles in pilot-scale tests of IFK. For this reason, detailed experiments with a wide range of coals are still required under oxy-fuel combustion conditions to evaluate both catalytic oxidation and absorption by fly ash.
Table 7 XRF analysis of ashes used for SO$_3$ tests in oxy-fuel tests

| Ash analysis | Solid Fuel | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Na$_2$O | K$_2$O | TiO$_2$ | P$_2$O$_5$ | SO$_3$ |
|--------------|------------|---------|-------------|-------------|-----|-----|--------|-------|--------|----------|------|
| Belo et al.$^{89}$ | A          | 52.9    | 34          | 7.13        | 1.41| 0.98| 0.158  | 0.518  | 2.16   | 0.275    | 0.24 |
|               | B          | 69      | 24.2        | 2.16        | 0.87| 0.737| 0.275  | 0.604  | 1.65   | 0.176    | 0.28 |
|               | C          | 53      | 26.5        | 8.34        | 4.66| 1.667| 0.979  | 1.058  | 1.13   | 1.508    | 0.97 |
| Sporl et al.$^{127}$ | A          | 58.9    | 26.2        | 6.8         | 1.2 | 0.7  | 0.1    | 0.4    | 2.4    | 0.2      | 0.3  |
|               | B          | 64.4    | 21.5        | 1.2         | 0.4 | 0.7  | 0.2    | 0.4    | 3.9    | 0.0      | 7.2  |
|               | C          | 33.2    | 23.0        | 11.4        | 7.0 | 1.8  | 1.3    | 0.9    | 1.2    | 1.8      | 22.7 |
| Couling et al.$^{142}$ | Williamson coal | 50      | 20.5        | 15.9        | 5.18| 1.14| 0.68   | 2.41   | 1.05   | 0.1      | 4.78 |
| Ahn et al.$^{125}$ | PRB coal   | 30.46   | 14.78       | 5.20        | 22.19| 5.17| 1.94   | 0.35   | 1.30   | 1.07     | 8.83 |
|               | Utah coal  | 60.89   | 14.52       | 5.09        | 6.11 | 1.39| 1.41   | 0.57   | 0.88   | 0.59     | 2.33 |
|               | Illinois coal | 49.28   | 17.66       | 14.57       | 1.87| 0.98| 1.51   | 2.26   | 0.85   | 0.11     | 2.22 |
| Kenney et al.$^{143}$ | Sub-Bit coal | 34.56   | 16.05       | 6.16        | 19.79| 4.23| 1.24   | 0.50   | 1.29   | 0.81     | 11.67 |
|               | Low-S Bit coal | 56.30   | 30.78       | 5.58        | 0.84 | 0.82| 0.23   | 2.67   | 1.78   | 0.15     | 0.71 |
|               | High-S Bit coal | 50.85   | 20.53       | 15.56       | 3.52| 0.96| 1.02   | 2.11   | 0.94   | 0.52     | 2.81 |
|               | Lignite    | 41.99   | 13.96       | 6.47        | 14.84| 4.50| 1.56   | 1.93   | 0.54   | 0.18     | 11.99 |
| Duan et al.$^{88}$ | Bituminous coal | 45.12   | 34.14       | 4.16        | 8.66| 1.36| 0.462  | 0.99   | 1.53   | 0.09     | 3.06 |
|               | Bituminous coal | 37.84   | 18.52       | 10.37       | 19.99| 4.51| 2.55   | 0.37   | 1.09   | 1.09     | 3.07 |
| Wang et al.$^{91}$ | Lignite    | 64.39   | 18.04       | 3.42        | 4.68 | 1.27| 0.90   | 0.93   | 0.48   | 0.95     | 4.69 |
|               | Bituminous coal | 48.82   | 29.81       | 3.99        | 4.57 | 1.12| 1.12   | 1.17   | 0.64   | 0.26     | 8.23 |
| Jurado et al.$^{144}$ | Cerrejon coal | 60.69   | 22.01       | 7.43        | 2.27| 2.90| 1.06   | 2.32   | 0.92   | 0.21     | 0.21 |
|               | CCP-biomass | 44.36   | 2.49        | 2.47        | 7.78 | 3.96| 0.36   | 24.72  | 0.12   | 12.04    |      |
4.4 SO$_3$ Emissions from Pilot-scale Studies

Ahn et al.$^{125}$ extensively studied SO$_3$ formation in 1.5 MW oxy-PC and 330 kW oxy-CFB combustor units. Three types of US coals were tested (PRB, Utah and Illinois), and the sulfur content is provided in Table 8. During the oxy-fuel test with Illinois coal (3.98% S) the SO$_3$ concentrations were 4 to 6 times higher at 530°C. However, similar SO$_3$ concentrations were observed for oxy- and air-combustion at higher temperatures (~930°C) in PC tests, and they were lower than those measured at 527°C, which suggests the secondary formation of SO$_3$ and the catalytic effect of metal oxides in pilot-scale tests. In oxy-CFB only Utah coal was tested, and the trend of SO$_3$ emissions was consistent with that of oxy-PC combustion. However, on a normalised base (mass per energy unit), no difference was found between oxy- and air-firing. SO$_3$ measurements were also undertaken at IFK in a 500 kW oxy-PC combustor.$^{145}$ In these tests, ESP was included along with SCR$^{145}$ and the SO$_3$ sampling was made from the inlets and outlets of ESP and SCR. Roughly 62% SO$_3$ capture was noted in the SCR unit. Higher SO$_3$ levels were noted in oxy-fuel runs and there was less influence of the SCR on the ADP.$^{146,147}$ Babcock-Hitachi tested SO$_3$ emissions in a 1.5 MWth oxy-fuel combustion facility which included SCR, clean energy recuperator (CER), FGR dry precipitator (DESP) and wet electrostatic precipitator (WESP).$^{148}$ Two different coals, with low sulfur, but high ash content, were used in this experimental campaign. SO$_3$ concentration at the DESP outlet was reduced to <1 ppm by decreasing the flue gas temperature to 90°C at the DESP inlet. Similar results were obtained for air- and oxy-fuel combustion. Most SO$_3$ was trapped in the CER unit.$^{148}$

Little data exist in the literature on SO$_3$ formation from oxy-biomass or co-firing combustion. Some SO$_3$ measurements were performed by Jurado et al.$^{144}$ in a 100 kW oxy-PC unit during co-firing combustion tests. Cerrejon coal/cereal co-products were blended at levels of 50%/50% and 75%/25%. Wet FGR was employed in these tests with varied steam content. Overall SO$_3$ concentrations appear to show slight increases with an increase of biomass percentage in the mixture, which might be due to the higher content of alkali oxides (primarily K$_2$O) in biomass fly ash. Other SO$_3$ measurements at pilot- and industrial-scale combustors are summarized Table 8. With regard to SO$_3$ measurement techniques, the CCM method is most commonly used for pilot-scale tests.
| Authors | Type of fuel and sulfur content | Type of reactor | Measurement equipment | SO₃ measurement method | SO₃ (ppm) |
|---------|--------------------------------|----------------|----------------------|-----------------------|-----------|
| Abele et al.⁶ | Sub-bituminous (S-0.57%); East-bituminous (S-0.95%); Sub-bituminous (S-0.22%); Lignite (S-0.6%); | 0.3 MWth Vertical combustor | Data acquisition: Honeywell Series S9000e controller; Gas analyzer | Controlled condensation method | Air-0.03; Oxy-0.76; |
| Tan et al.⁵¹ | | | | Not specified | Air-27 ng/J; Oxy-75 ng/J; Oxy-0.14 ng/J; |
| Ahn et al.¹²⁵ | PRB (S wt.%-0.23), Utah (S wt.%-0.53), Illinois (Swt.%-3.98) | 1.5 MW PC combustor; 0.3 MWth CFB | SO₂ Gas analyzer (CAI Model 601 NDIR) and FTIR (Nicolet Magna-IR 550) spectrometer | Controlled condensation method | PRB Air: below 5¹³ Utah Air: 5¹³ Utah Oxy: 5¹³ Illinois Air: 31¹³ Illinois Oxy: 117¹³ Air: 12¹³ Oxy: 10¹³ |
| Eddings et al.¹⁴⁹ | Illinois coal pellets (S-4.0%) | BFB reactor | FTIR | Controlled condensation method | |
| Kiga et al.⁶⁶,²⁹ | Australian low sulfur coals with: A (S-0.45%); B (S-0.96%); C (S-0.38%); | 1.2 MW IHI Aioi facility | Non-dispersive infra-red gas analyzer (HORIBA ENDA-1610), Gas chromatography (Shimadzu 14APFP); | | Coal A: Air-2; Coal A: Oxy-7; Coal B: Air-9; Coal B: Oxy-9; Coal C: Air-3; Coal C: Oxy-11; |
| Fleig et al.¹⁰³ | Propane and SO₃ injected to unit; | 100 kW Oxy-fired test unit combustor | Nondispersive infrared (NDIR) analyzers (NGA 2000 Fisher Rosemount); IC (ICS -90 DIONEX) | Controlled condensation method used as reference case to other methods: 1. Isopropanol absorption bottle method; 2. Salt method; 3. Pentol SO₃ monitor | CCM results: Air case: 34; Oxy-case 25¹⁴,⁹; Oxy-case 30¹⁴: 56; Oxy-case 35: 25 |
| Authors            | Type of fuel and sulfur content | Type of reactor | Measurement equipment | SO$_3$ measurement method | SO$_3$ (ppm)             |
|--------------------|---------------------------------|-----------------|-----------------------|---------------------------|--------------------------|
| Vainio et al.      | Mixture of gases: (SO$_2$, H$_2$O, O$_2$, N$_2$ and H$_2$SO$_4$) | Bench-scale horizontal tube reactor | ICS-90 Ion chromatography (DIONEX) | Salt method: four types of salts tested (NaCl, KCl, K$_2$CO$_3$, CaCl$_2$) | Salt method results: NaCl: Air – 30$^\dagger$; NaCl: Oxy – 46$^1$; Coals A: Air – 2; Oxy: 6 – 35$^5$; Coals B: Air – 8; Oxy: 18 – 50; Coals C: Air – 1; Oxy: 2–30; |
| Spörl et al.       | Australian coals with sulfur: (A-0.3%; B-0.7%; C-0.7%) | 20 kW combustion rig; L x D (2.5 x 0.2 m); Flow rate: 11.5 m$^3$/h | IC (DIN EN ISO 10304) | Controlled condensation method |                           |
| Monckert et al.    | Klein Kopje, Lausitz, Rhenish, Ensdorf coals (S-1%) | 0.5 MW down-fired Oxy-PC | SEM-BSE, SEM-MAP | Controlled condensation method | Air: 8; Oxy: 85; |
| Roy et al.         | Victorian coals Loy Yang, Morvell and Yallourn (S-0.5%) | 10 kW oxy-fired BFB | Gas analyzer (MX6 iBrid) GC (Agilent GC 7890A); | Calcium oxalate with glass beads | Dry Oxy: 11 mg/MJ; Air: 15 mg/MJ; Dry Oxy-fuel 14 mg/MJ; |
| Duan et al.        | Fly ash, bituminous coal (S-0.5%) | 50 kW oxy-CFB | Titration; IC DX-120 (DIONEX) | Controlled condensation method | Air-2, Oxy-8; |
| Wang et al.        | Lignite coal (S-0.6%); Bituminous coal (S-3.69%) | Oxy PC unit | ICS-90 DIONEX | Controlled condensation method | Oxy Bituminous coal: (500 to 3000 ppm SO$_2$); 13 to 105; Oxy Lignite: (500 to 3000 ppm SO$_2$); 0.5 to 80; |
| Hemis              | Illinois bituminous coal         | Hoosier Energy’ Merom Station | FTIR; IC (Desert Analytics); | FTIR and Controlled condensation method | Air tests: Day-1 FTIR-37.33 versus CCM-30.4; Day-2 FTIR-37.66 vs CCM-29.1; Air. Site1: Bituminous coal SCR inl-22; SCR out–24; Air preheater out–7; ESP in-6; |
| Cao et al.         | Bituminous and subbituminous coals (S-3.5%); | Fixed bed reactor, | IC (DX-120); | Modified controlled condensation method |                           |
| Authors       | Type of fuel and sulfur content | Type of reactor                  | Measurement equipment       | SO₃ measurement method | SO₃ (ppm) |
|--------------|--------------------------------|----------------------------------|----------------------------|------------------------|-----------|
| Kenney et al.¹⁴³ | LSB⁴ (S-0.9%),                  | Oxy-fired pilot plant            | N/A                        | SO₃ executed from four | Sub-bit Air: 0.5¹; Oxy with |
|              | HSB⁵ (S-3.2%);                 |                                  |                            | locations of boiler;   | SOₓ control: 1.6¹; LSB air: |
|              | Sub-bituminous (S-0.3%)        |                                  |                            | Controlled condensation| 28.8; oxy: 39.4; HSB air-41; |
|              | Dried lignite (S-0.7%)         |                                  |                            | method.                | Oxy-186.3; Lignite air-30;  |
|              | El Cerrejon coal (S-0.58%)     | 0.1 MW pulverized oxy-fuel combus| FTIR, ESEM/EDX, XRD       | Controlled condensation| Oxy-45.9;                      |
|              | Cereal co-product (S-0.16%)    |                                  |                            | method                 |                                      |
|              |                                |                                  |                            |                        |                                      |
| Davis¹⁵¹     | USA Williamson coal (S-1.7%);  | E.ON 1 MW Combustion Test Facility| XRF, SEM                  | SO₃ Monitor (Severn Science analyzer); | Air: EC-3.7; EC/CC (50/50%)-20.2; CC-25.4; Oxy: EC-20.6; |
|              |                                |                                  |                            | Controlled condensation| EC/CC (50/50%)-35.9; EC/CC (75/25%)-16.8; |
|              |                                |                                  |                            | method                 | Not specified;                     |
| Dhungel et al.⁶⁷ | Medium Sulfur Bituminous Coal | Emission reduction test facility 0.16 MW oxy-fired system; | Dry sorbent injection; Gas analyzer | Controlled condensation method | Not specified; roughly 3 to 5 times higher in oxy-fuel |
| Stanger et al.¹⁵² | Callide coal S-0.3 | Callide oxy-fuel plant | Controlled condensation method | Air < 0.06; Oxy: 0.6-3.7; |

¹ Average value is presented; 2. Oxy-25/30: 25% or 30% of O₂ in the oxidizer stream; ³ Range of SO₃ values is provided for this particular test as initial parameters were different. ⁴ LSB-low sulfur bituminious; ⁵ HSB- high sulfur bituminious;
4.5 Modelling Studies of SO₃ Formation

Only a few numerical studies on SO₃ formation are available in the open literature for oxy- as compared to air-combustion. Burdett et al. simulated the effect of operating bed pressure on SO₂-to-SO₃ conversion for air-combustion. The predictions for bed pressure (600 kPa) and temperature of 900°C with 10% of O₂ in the flue gas clearly indicated increasing SO₃ formation with increasing oxygen formation. This work suggests that under such conditions the potential conversion of sulfur-in-fuel to SO₃ could be as high as 20%. Fleig et al. modelled homogeneous gas-phase SO₃ formation for oxy-fuel combustion conditions with a model which is described by Giménez-Lopez et al. and which was initially developed by Glarborg et al. CHEMKIN-PRO was used to model homogeneous reactions considering plug flow reactor. More recently, Belo et al. implemented a kinetic model of Burdett et al. for residence time of 0.3 to 0.9 s (Table 6). Due to thermodynamic considerations, the maximum conversion of SO₂ to SO₃ was at low temperatures and further increases of temperature to 900 and 1000°C decreased the SO₃ by ~6.8 and ~3.2%, respectively. SO₃ formation was also modelled by Schneider and Bogdan for an oil-fired boiler.

5. Research Needs

A significant amount of effort has been made to evaluate SO₃ concentrations from laboratory-scale to commercial-scale units. However, oxy-fuel combustion requires more attention in terms of better understanding SO₃ formation mechanisms. At this point the majority of SO₃ measurements have been conducted in conventional PC and gas-fired combustion systems, while only a few studies are available for oxy-fired FB combustors and pilot-scale studies are still sparse. Major research should concentrate on the effect of FGR and catalytic conversion. SO₃ formation both depend on gases such as NO, CO and their effects may be different in oxy-fuel combustion and, hence more experiments are needed on SO₃ formation with different types of coals. Development of pressurized FBC systems would also require SO₃ formation tests as experimental data on the effect of pressure are rare.

In the case of analytical methods, all the current post-combustion SO₃ measurements still have technical challenges associated mainly with temperature control as SO₃ is a very
reactive molecule and SO$_3$ can easily be lost in the sampling line. At present, CCM is the most used and reliable technique to quantify SO$_3$ concentrations, while other methods such as the salt method or calcium oxalate with glass beads need to be improved.

6. Conclusions

The present paper reviews the formation SO$_3$ in coal combustion systems, and especially oxy-fuel technology. The following conclusions can be drawn:

- SO$_3$ concentration in oxy-fuel combustion is typically several times higher than that in air combustion. The higher level of SO$_3$ is mainly due to the increased concentrations of O$_2$, H$_2$O and SO$_2$ in the boiler.
- Wet flue gas recycling is associated with higher SO$_3$ concentration than dry flue gas recycling. An increased amount of H$_2$O promotes SO$_3$ formation apparently due to the production of OH radicals. However, H$_2$O concentrations higher than 15% in the system strongly inhibit SO$_3$ formation. Inhibition appears to be more pronounced in actual PC tests than in simulated flue gas tests.
- Higher conversion of S to SO$_3$ occurs near the burnout region where O$_2$ is found in excess amounts. In this region, gas-phase homogeneous formation is dominant for SO$_3$ formation.
- The presence of gases such as NO and CO may enhance SO$_3$ formation. However, these effects appear to be small compared to other factors such as combustion temperature, excess O$_2$ and presence of catalysts.
- SO$_3$ formation is enhanced due to catalytic effect of fly ash. Higher concentrations of Fe$_2$O$_3$ and V$_2$O$_5$ and other metal oxides increase SO$_3$ concentrations significantly. Adsorption of SO$_3$ by alkali and alkaline earth metal oxides is also an important phenomenon.
- The CCM method appears to be the most dependable technique for measuring SO$_3$ concentrations.

Acknowledgements

The authors would like to thank Dr Nelia Jurado from Cranfield University (UK) and Dr Emil Vainio from Abo Akademi (Finland) for useful advice on the controlled-
condensation method (CCM) and the salt method, and also for providing valuable information. The financial support from Nazarbayev University under “Talap” studentship is also greatly acknowledged. This work was completed as part of a PhD program at Cranfield University for one of us (YS).
References

1. IEA, Tracking Clean Energy Progress 2016, Energy Technology Perspectives 2016 Excerpt IEA Input to the Clean Energy Ministerial, (2016).
2. IEA, CO₂ Emissions from fuel combustion, Highlights, (2017).
3. IPCC, IPCC special report on carbon dioxide capture and storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change, ed by Metz B, Davidson O, de Coninck HC, Loos M and Meyer LA. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA (2005).
4. Toftegaard MB, Brix J, Jensen PA, Glarborg P and Jensen AD, Oxy-fuel combustion of solid fuels. Prog Energy Combust Sci 36(5):581-625 (2010).
5. Buhre BJP, Elliott LK, Sheng CD, Gupta RP and Wall TF, Oxy-fuel combustion technology for coal-fired power generation. Prog Energy Combust Sci 31(4):283-307 (2005).
6. Abele AR, Kindt GS, Clark WD, Payne R and Chen SL. An experimental program to test the feasibility of obtaining normal performance from combustors using oxygen and recycled gas instead of air, Report ANL/CNSV-TM-204, Argonne National Laboratory, Argonne, (1987).
7. Edge P, Gharebaghi M, Irons R, Porter R, Porter RTJ, Pourkashanian M et al., Combustion modelling opportunities and challenges for oxy-coal carbon capture technology. Chem Eng Res Des 89:1470-1493 (2011).
8. Wall T, Liu Y, Spero C, Elliot L, Khare S, Rathnam R et al., An overview on oxyfuel coal combustion—State of the art research and technology development. Chem Eng Res Des 87(8):1003-1016 (2009).
9. Liu H, Shao Y. Predictions of the impurities in the CO₂ stream of an oxy-coal combustion plant. Appl Energy 87(10):3162-3170 (2010).
10. IEA, Energy Technology Perspectives 2012; Pathways to a Clean Energy System. IEA, Paris, France (2012).
11. Davison J. Performance and costs of power plants with capture and storage of CO₂. Energy 32(7):1163-1176 (2007).
12. Müller M, Schnell U, Grathwohl S, Maier J and Scheffknecht G, Evaluation of oxy-coal combustion modelling at semi-industrial scale. Energy Procedia 23:197-206 (2012).
13. Wall TF. Combustion processes for carbon capture. Proc Combust Inst 31 (1):31-47 (2007).
14. Jordal K, Anheden M, Yan J and Strömberg L, Oxyfuel combustion for coal-fired power generation with CO₂ capture - Opportunities and challenges. In: The 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7), September. Vancouver, Canada, (2004).
15. Anheden M, Rydberg S and Yan J, Consideration for removal of non-CO₂ components from CO₂ rich flue gas of oxy-fuel combustion. In: IEA Oxyfuel Workshop. (2008).
16. Dillon DJ, White V, Allam RJ, Wall RA and Gibbins J, Oxy-combustion processes for CO$_2$ capture from power plant. Mitsui Babcock Energy Limited, Engineering investigation report No. 2005/9, IEA greenhouse gas R&D programme (2005).

17. Gibbins J, Chalmers H. Carbon capture and storage. Energy Policy 36(12):4317-4322 (2008).

18. Markewitz P, Kuckshinrichs W, Leitner W, Linssen J, Zapp P, Bongartz R et al., Worldwide innovations in the development of carbon capture technologies and the utilization of CO$_2$. Energy Environ. Sci 5:7281-7305 (2012).

19. de Visser E, Hendriks C, Barrio M, Mölnvik MJ, de Koeijer G, Liljemark S et al., Dynamis CO$_2$ quality recommendations. Int J Greenh Gas Control 2(4):474-484 (2008).

20. Andersson K, Johnsson F. Process evaluation of an 865 MWe lignite fired O$_2$/CO$_2$ power plant. Energy Convers Manag 47(18-19):3487-3498 (2006).

21. Aspelund A, Jordan K. Gas conditioning-The interface between CO$_2$ capture and transport. Int J Greenh Gas Control 1(3):343-354 (2007).

22. Burnol A, Thimon I, Ruffine L and Herri JM, Influence of impurities (nitrogen and methane) on the CO$_2$ storage capacity as sediment-hosted gas hydrates - Application in the area of the Celtic Sea and the Bay of Biscay. Int J Greenh Gas Control 35:96-109 (2015).

23. Li H, Yan J, Yan J and Anheden M, Impurity impacts on the purification process in oxy-fuel combustion based CO$_2$ capture and storage system. Appl Energy 86(2):202-213 (2009).

24. IEAGHG “Effects of Impurities on Geological Storage of CO$_2$”, 2011/04, June, 2011 Available at: http://hub.globalccsinstitute.com/sites/default/files/publications/16876/effects-impurities-geological-storage-co2.pdf [Accessed 01 December 2017].

25. Talman S. Subsurface geochemical fate and effects of impurities contained in a CO$_2$ stream injected into a deep saline aquifer: What is known. Int J Greenh Gas Control 40:267-291 (2015).

26. White V, Torrente-Murciano L, Sturgeon D and Chadwick D, Purification of oxyfuel-derived CO$_2$. Int J Greenh Gas Control 4(2):137-142 (2010).

27. Cheng J, Zhou J, Liu J, Zhou J, Huang Z, Cao X et al., Sulfur removal at high temperature during coal combustion in furnaces: a review. Prog Energy Combust Sci 29(5):381-405 (2003).

28. Anthony EJ, Granatstein DL. Sulfation phenomena in fluidized bed combustion systems. Prog Energy Combust Sci 27(2):215-236 (2001).

29. Stanger R, Wall T. Sulphur impacts during pulverised coal combustion in oxy-fuel technology for carbon capture and storage. Prog Energy Combust Sci 37(1):69-88 (2011).
30. Srivastava RK, Miller CA, Erickson C and Jambhekar R, Emissions of sulfur trioxide from coal-fired power plants. *J air waste Manag Assoc* **54**:750-762 (2004).
31. *Continuous Measurement of SO₃ in a Coal-Fired Power Plant*. EPRI, Palo Alto, CA, 2006. 1010375.
32. Attar A. Chemistry, thermodynamics and kinetics of reactions of sulphur in coal-gas reactions: A review. *Fuel* **57**(4):201-212 (1978).
33. Raask E. Sulphate capture in ash and boiler deposits in relation to SO₂ emission. *Prog Energy Combust Sci* **8**(4):261-276 (1982).
34. Glarborg P. Hidden interactions-Trace species governing combustion and emissions. *Proc Combust Inst* **31**(1):77-98 (2007).
35. Cullis CF, Mulcahy MFR. The kinetics of combustion of gaseous sulphur compounds. *Combust Flame* **18**(2):225-292 (1972).
36. Glassman I, Yetter RA, *Combustion*, Fourth Edition. Academic press Elsevier. pp. 421-420 (2008).
37. Zygarlicke CJ, Stomberg AL, Folkedahl BC and Strege JR, Alkali influences on sulfur capture for North Dakota lignite combustion. *Fuel Process Technol* **87**(10):855-861 (2006).
38. Croiset E, Thambimuthu KV. NOₓ and SO₂ emissions from O₂/CO₂ recycle coal combustion. *Fuel* **80**(14): 2117-2121 (2001).
39. Fleig D, Andersson K, Johnsson F and Leckner B, Conversion of sulfur during pulverized oxy-coal combustion. *Energy Fuels* **25**(2):647-655 (2011).
40. Cutler AJB, Raask E. External corrosion in coal-fired boilers: assessment from laboratory data. *Corros Sci* **21**(11):789-800 (1981).
41. Sheng C, Xu M, Zhang J and Xu Y, Comparison of sulphur retention by coal ash in different types of combustors. *Fuel Process Technol* **64**(1-3):1-11 (2000).
42. Vuthaluru HB, Zhang D and Linjewile TM, Behaviour of inorganic constituents and ash characteristics during fluidised-bed combustion of several Australian low-rank coals. *Fuel Process Technol* **67**(3):165-176 (2000).
43. Bryers RW. Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. *Prog Energy Combust Sci* **22**(1):29-120 (1996).
44. Harb JN, Smith EE. Fireside corrosion in pc-fired boilers. *Prog Energy Combust Sci* **16**(3):169-190 (1990).
45. Shamanna S, Schobert HH. Fireside corrosion of selected alloys by ash recovered from coal-water slurry combustion, *Fuel Process Technol* **53**(1-3):133-156 (1997).
46. James DW, Krishnamoorthy G, Benson SA and Seames WS, Modelling trace element partitioning during coal combustion. *Fuel Process Technol* **126**:284-297 (2014).
47. Moser RE. Benefits of effective SO$_3$ removal in coal-fired power plants: beyond opacity control. In: *Power Plant Air Pollutant Control, Mega Symposium*, August 28-31, Baltimore, MD (2006).

48. Nielsen MT. On the relative importance of SO$_2$ oxidation to high dust SCR DeNO$_x$ units. In: *DOE/NETL 2003 Conference on Selective Catalytic Reduction (SRC) and Selective Non-Catalytic Reduction (SNCR) for NOx Control*, pp. 1-12 (2003).

49. Fleig D, Normann F, Andersson K, Johnsson F and Leckner B, The fate of sulphur during oxy-fuel combustion of lignite. *Energy Procedia* 1(1):383-390 (2009).

50. Fleig D, Andersson K and Johnsson F, Influence of operating conditions on SO$_3$ formation during air and oxy-fuel combustion. *Ind Eng Chem Res* 51(28):9483-9491 (2012).

51. Tan Y, Croiset E, Douglas MA and Thambimuthu KV, Combustion characteristics of coal in a mixture of oxygen and recycled flue gas. *Fuel* 85(4):507-512 (2006).

52. Reid WT. External Corrosion and Deposits Boilers and Gas Turbines. (Elsevier, ed), New York (1971).

53. Svachula J, Alemany LJ, Ferlazzo N, Forzatti P and Tronconi E, Oxidation of SO$_2$ to SO$_3$ over honeycomb DeNoxing Catalysts. *Ind Eng Chem Res* 32:826-834 (1993).

54. EPRI, *SO$_3$ Mitigation Guide*, EPRI Report TR-104424, Research Project 2250-03,Prepared by Radian Corporation, Austin, Texas. Principal investigators Peterson J, Jones AF. October (1994).

55. Shanthakumar S, Singh DN and Phadke RC, Flue gas conditioning for reducing suspended particulate matter from thermal power stations. *Prog Energy Combust Sci.* 34(6):685-695 (2008).

56. Sjostrom S, Dillon M, Donnelly B, Bustard J, Filippelli G, Glesmann R et al., Influence of SO$_3$ on mercury removal with activated carbon: Full-scale results. *Fuel Process Technol* 90(11):1419-1423 (2009).

57. Hu Y, Yan J. Characterization of flue gas in oxy-coal combustion processes for CO$_2$ capture. *Appl Energy* 90(1):113-121 (2012).

58. Boot-Handford ME, Abanades JC, Anthony EJ, Blunt MJ, Brandani S, Mac Dowell N et al., Carbon capture and storage update. *Energy Environ Sci* 7(1):130-189 (2014).

59. Kather A, Scheffknecht G. The oxycoal process with cryogenic oxygen supply. *Naturwissenschaften* 96(9):993-1010 (2009).

60. Nakayama S, Noguchi Y, Kiga T, Miyamae S, Maeda U, Kawai M et al., Pulverized coal combustion in O$_2$/CO$_2$ mixtures on a power plant for CO$_2$ recovery. *Energy Convers Manag* 33(5-8):379-386 (1992).
61. Normann F, Andersson K, Leckner B and Johnsson F, Emission control of nitrogen oxides in the oxy-fuel process. Prog Energy Combust Sci 35(5):385-397 (2009).
62. Molburg JC, Doctor RD, Brockmeier NF and Plasynski S, CO₂ capture from PC boilers with O₂-firing. In: 18th Annual International Pittsburgh Coal Conference, December 4-7, Newcastle, New South Wales, Australia (2001).
63. Review of CO₂-Capture Development Activities for Coal-Fired Power Generation Plants, EPRI, Palo Alto, CA: 2007: 1012239.
64. Zanganeh KE, Shafeen A. A novel process integration, optimization and design approach for large-scale implementation of oxy-fired coal power plants with CO₂ capture. Int J Greenh Gas Control 1(1):47-54 (2007).
65. Günther C, Weng M and Kather A, Restrictions and limitations for the design of a steam generator for a coal-fired oxyfuel power plant with circulating fluidised bed combustion. Energy Procedia 37:1312-1321 (2013).
66. Kiga T, Takano S, Kimura N, Omata K, Okawa M, Mori T et al., Characteristics of pulverized-coal combustion in the system of oxygen/recycled flue gas combustion. Energy Convers Manag 38:S129-S134 (1997).
67. Dhungel B, Ellul C, Gibson JR and Fitzgerald FD, SO₃ Control in Oxyfuel Applications. In: IEAGHG Special Workshop on Oxyfuel Combustion. London: IEA Greenhouse Gas R&D Programme (2011).
68. Fleig D, Andersson K, Kühnemuth D, Normann F, Johnsson F and Leckner B, The sulphur mass balance in oxy-fuel combustion of lignite - an experimental study. In: 1st Oxyfuel Combustion Conference, Cottbus, 8-11th September (2009). Available at: http://www.ieaghg.org/docs/oxyfuel/OCC1/Session%205_A/Cottbus%20Daniel%20Fleig.pdf [accessed 5 March 2017].
69. Duan L, Sun H, Zhao C, Zhou C, Zhou W and Chen X, Coal combustion characteristics on an oxy-fuel circulating fluidized bed combustor with warm flue gas recycle. Fuel 127:47-51 (2014).
70. Durie RA, Matthews CJ and Smith MY, The catalytic formation of sulfur trioxide in fuel-rich propane-air flames. Combust Flame 15(2):157-165 (1970).
71. Zachariah MR, Smith OI. Experimental and numerical studies of sulfur chemistry in H₂/O₂/SO₂ flames. Combust Flame 69(2):125-139 (1987).
72. Miccio F, Löffler G, Wargadalam VJ and Winter F, The influence of SO₂ level and operating conditions on NOₓ and N₂O emissions during fluidised bed combustion of coals. Fuel 80(11):1555-1566 (2001).
73. Schäfer S, Born B. Hydrolysis of HCN as an important step in nitrogen oxide formation in fluidised combustion. Part II: heterogeneous reactions involving limestone. Fuel 81(13):1641-1646 (2002).
74. Wendt JOL, Ekmann JM. Effect of fuel sulfur species on nitrogen oxide emissions from premixed flames. Combust Flame 25:355-360 (1975).
75. Wendt JOL, Wootan EC and Corley TL, Postflame behavior of nitrogenous species in the presence of fuel sulfur I. Rich, moist CO/Ar/O₂ flames. *Combust Flame* **49**(1-3):261-274 (1983).
76. Corley TL, Wendt JOL. Postflame behavior of nitrogenous species in the presence of fuel sulfur II. Rich, CH₄/He/O₂ flames. *Combust Flame* **58**(2):141-152 (1984).
77. Glarborg P, Kubel D, Dam-Johansen K, Chiang HM and Bozzelli JW, Impact of SO₂ and NO on CO oxidation under post-flame conditions. *Int J Chem Kin* **28**(10):773-790 (1996).
78. Rasmussen CL, Glarborg P and Marshall P, Mechanisms of radical removal by SO₂. *Proc Combust Inst* **31**(1):339-347 (2007).
79. Giménez-López J, Martínez M, Millera A, Bilbao R and Alzueta MU, SO₂ effects on CO oxidation in a CO₂ atmosphere, characteristic of oxy-fuel conditions. *Combust Flame* **158**(1):48-56 (2011).
80. Jørgensen TL. Livbjerg H and Glarborg P, Homogeneous and heterogeneously catalyzed oxidation of SO₂. *Chem Eng Sci* **62**(16):4496-4499 (2007).
81. Burdett NA, Langdon WE and Squires RT, Rate of the coefficients for the reaction SO₂ + O₂ → SO₃ +O in the temperature range 900-1350 K. *J Inst Energy* **57**(3):373-376 (1984).
82. Mulcahy MFR, Steven JR, Ward JC and Williams DJ, Kinetics of interaction of oxygen atoms with sulfur oxides. *Symp (International) Combust* **12**(1):323-330 (1969).
83. Mulcahy MFR, Steven JR and Ward JC, The kinetics of reaction between oxygen atoms and sulfur dioxide: an investigation by electron spin resonance spectrometry. *J Phys Chem* **71**(7):2124-2131 (1967).
84. Yilmaz A, Hindiyarti L, Jensen AD, Glarborg P and Marshall P, Thermal dissociation of SO₃ at 1000-1400 K. *J Phys Chem A* **110**(21):6654-6659 (2006).
85. Merryman EL, Levy A. Enhanced SO₃ emissions from staged combustion. In: *Symp (International) Combust*. **17**(1):727-736 (1979).
86. Naïdoo J, Goumri A and Marshall P, A kinetic study of the reaction of atomic oxygen with SO₂. *Proc Combust Inst* **30**(1):1219-1225 (2005).
87. Blitz MA, Hughes KJ and Pilling M, Determination of the high-pressure limiting rate coefficient and the enthalpy of reaction for OH + SO₂. *J Phys Chem A* **107**(12):1971-1978 (2003).
88. Duan L, Duan Y, Sarbassov Y, Li Y and Anthony EJ, SO₃ formation under oxy-CFB combustion conditions. *Int J Greenh Gas Control* **43**:172-178 (2015).
89. Belo LP, Elliott LK, Stanger RJ, Spörl R, Shah KV, Maier J *et al.*, High-Temperature conversion of SO₂ to SO₃: homogeneous experiments and catalytic effect of fly ash from air and oxy-fuel firing. *Energy Fuels* **28**:7243-7251 (2014).
90. Fleig D, Alzueta MU, Normann F, Abián M, Andersson K and Johnsson F, Measurement and modeling of sulfur trioxide formation in a flow reactor under post-flame conditions. *Combust Flame* **160**(6):1142-1151 (2013).
91. Wang X, Liu X, Li D, Zhang Y and Xu M, Effect of steam and sulfur dioxide on sulfur trioxide formation during oxy-fuel combustion. *Int J Greenh Gas Control* **43**:1-9 (2015).

92. Colorado State University. Chemical equilibrium calculation. Available at: http://navier.engr.colostate.edu/~dandy/code/code-4/index.html [accessed 15 September 2017].

93. Urbanek A, Trela M. Catalytic oxidation of sulfur dioxide. *Catal Rev Sci Eng* **21**:73-133 (1980).

94. Marier P, Dibbs HP. The catalytic conversion of SO$_2$ to SO$_3$ by fly ash and the capture of SO$_2$ and SO$_3$ by CaO and MgO. *Thermochim Acta* **8**(1-2):155-165 (1974).

95. Zhang X, Zhuang G, Chen J, Wang Y, Wang X, An Z et al., Heterogeneous reactions of sulfur dioxide on typical mineral particles. *J Phys Chem* **110**(25):12588-12596 (2006).

96. Tronconi E, Cavanna A, Orsenigo C and Forzatti P, Transient kinetics of SO$_2$ oxidation over SCR-DeNOx monolith catalysts. *Ind Eng Chem Res* **38**(7):2593-2598 (1999).

97. Dunn JP, Koppula PR, Stenger HG and Wachs IE, Oxidation of sulfur dioxide to sulfur trioxide over supported vanadia catalysts. *Appl Catal B Environ* **19**(2):103-117 (1998).

98. Thibault JD. Steward FR and Ruthven DM, The kinetics of absorption of SO$_3$ in calcium and magnesium oxides. *Can J Chem Eng* **60**(6):796-801 (1982).

99. Galloway BD, Sasmaz E and Padak B, Binding of SO$_3$ to fly ash components: CaO, MgO, Na$_2$O and K$_2$O. *Fuel* **145**:79-83 (2015).

100. Cao Y, Zhou H, Jiang W, Chen CW and Pan WP, Studies of the fate of sulfur trioxide in coal-fired utility boilers based on modified selected condensation methods. *Environ Sci Technol* **44**(9):3429-3434 (2010).

101. Chang CC. Infrared studies of SO$_2$ on γ-alumina. *J Catal* **53**(3):374-385 (1978).

102. Jaworowski RJ, Mack SS. Evaluation of methods for measurement of SO$_3$/H$_2$SO$_4$ in flue gas. *J Air Pollut Control Assoc* **29**(1):43-46 (1979).

103. Fleig D, Vainio E, Andersson K, Brink A, Johnsson F and Hupa M, Evaluation of SO$_3$ measurement techniques in air and oxy-fuel combustion. *Energy Fuels* **26**:5537-5549 (2012).

104. ASTM D3226. Method of test for sulfur oxides in flue gases (barium chloranilate controlled condensation method). Withdrawn from 1978. Available at: http://www.astm.org/DATABASE.CART/withdrawn/D3226.htm [accessed 27 August 2017].

105. BS 1756-4:1977, Methods for sampling and analysis of flue gases. Miscellaneous analyses. Withdrawn from 01 February 2008. Available at: http://shop.bsigroup.com/en/ProductDetail/?pid=000000000000052803 [accessed 27 August 2017].
106. NCASI Southern Regional Center, Method 8a-Determination of sulfuric acid vapor or mist and sulfur dioxide emissions from kraft recovery furnaces; pp.1-87, (1996). Available at: https://www3.epa.gov/ttnemc01/ctm/ctm-013.pdf [accessed 19 November 2017].

107. Maddalone RF, Newton SF, Rhudy RG and Statnick RM, Laboratory and field evaluation of the controlled condensation system for SO$_3$ measurements in flue gas streams. *J Air Pollut Control Assoc* 29(6):626-631 (1979).

108. Dellinger B, Grotecloss G, Fortune CR, Cheney JL and Homolya JB, Sulfur dioxide oxidation and plume formation at cement kilns. *Environ Sci Technol* 14(10):1244-1249 (1980).

109. Cooper D. Optimization of a NaCl Adsorbent Tube Method for SO$_3$ Measurements in Combustion Flue Gases. Report B-1177; Institute för Vattenoch Luftvardsforskning (IVL): Göteborg, (1995).

110. Kelman FN. Direct method on determination of the sulfuric acid in solution with sulfuric gases and air. *Zavod Lab* 11:1316-1318 (1952) (in Russian).

111. Vainio E, Fleig D, Brink A, Andersson K, Johnsson F and Hupa M, Experimental evaluation and field application of a salt method for SO$_3$ measurement in flue gases. *Energy Fuels* 27:2767-2775 (2013).

112. Cooper D, Andersson C. Determination of SO$_3$ in flue gases using the NaCl method - a comparison with other techniques (Bestämning av SO$_3$ i rökgaser med NaCl-metoden – en jämförelse av olika metoder), VärmeForsk Report 616; (1994), (In Swedish).

113. Ibanez JG, Batten CF and Wentworth WE, Simultaneous determination of SO$_3(g)$ and SO$_2(g)$ in a flowing gas. *Ind Eng Chem Res* 47(7):2449-2454 (2008).

114. Fateev A, Clausen S. Sulfur trioxide on-line measurement technique for power plants. In: IEAGHG Workshop. *Special Workshop on Oxyfuel Combustion*. London, 25-26 January (2011). Available at: http://orbit.dtu.dk/files/10145781/Fateev_SO3_workshop_London.pdf [accessed 01 October 2017].

115. Continuous Measurement Technologies for SO$_3$ and H$_2$SO$_4$ in Coal-Fired Power Plants, EPRI, Palo Alto, CA: 2004. 1009812.

116. Chamberlain S, Reeder T, Stimpson CK and Tree DR, A comparison of sulfur and chlorine gas species in pulverized-coal, air- and oxy-combustion. *Combust Flame* 160(11):2529-2539 (2013).

117. Roy B, Chen L and Bhattacharya S, Nitrogen oxides, sulfur trioxide, and mercury emissions during oxy-fuel fluidized bed combustion of Victorian brown coal. *Environ Sci Technol* 48(24):14844-14850 (2014).

118. Jackson PJ, Hilton DA and Buddery JH, Continuous measurement of sulphuric acid vapour in combustion gases using a portable automatic monitor. *J Inst Energy* 54:124-135 (1981).

119. SO$_3$ Monitor. How much SO$_3$ do you generate? Available at: http://www.pentol.net/_pdf/so3monitor-EN.pdf [Accessed 7 September 2017].
120. Dennis JS, Hayhurst AN. The formation of SO$_3$ in a fluidized bed. *Combust Flame* 72(3):241-258 (1988).
121. Verhoff FH, Banchero JT. Predicting dew points of flue gases. *Chem Eng Prog* 70(8):71-72 (1974).
122. ZareNezhad B. New correlation predicts flue gas sulfuric acid dewpoints. *Oil Gas J* 107(35):60-63 (2009).
123. Taylor HD. The condensation of sulphuric acid on cooled surfaces exposed to hot gases containing sulphur trioxide. *Trans Faraday Soc* 47:1114-1120 (1951).
124. Stuart DD. Acid dewpoint temperature measurement and its use in estimating sulfur trioxide concentration. Available at: https://www.researchgate.net/profile/Derek_Stuart2/publication/265801421_Acid_dewpoint_temperature_measurement_and_its_use_in_estimating_sulfur_trioxide_concentration/links/59a0340c0f7e9b0fb8990820/Acid-dewpoint-temperature-measurement-and-its-use-in-estimating-sulfur-trioxide-concentration.pdf [accessed 05 November 2017].
125. Ahn J, Okerlund R, Fry A and Eddings EG, Sulfur trioxide formation during oxy-coal combustion. *Int J Greenh Gas Control* 5S: S127-S135 (2011).
126. Fleig D, Andersson K, Normann F and Johnsson F, SO$_3$ formation under oxy fuel combustion conditions. *Ind Eng Chem Res* 50(14):8505-8514 (2011).
127. Spörl R, Walker J, Belo L, Shah K, Stanger R, Maier J *et al.*, SO$_3$ emissions and removal by ash in coal-fired oxy-fuel combustion. *Energy Fuels* 28(8):5296-5306 (2014).
128. Belo LP, Elliott LK, Stanger RJ, Spörl R, Shah KV, Maier J *et al.*, Laboratory investigations on the differences in the homogeneous and catalytic conversions with fly ash of SO$_2$ to SO$_3$ from air and oxy-fuel PF combustion. In: *Impacts of Fuel Quality on Power Production*. 26-31st October, Snowbird, Utah (2014).
129. Zheng L, Furimsky E. Assessment of coal combustion in O$_2$+CO$_2$ by equilibrium calculations. *Fuel Process Technol* 81(1):23-34 (2003).
130. Armitage JW, Cullis CF. Studies of the reaction between nitrogen dioxide and sulfur dioxide. *Combust Flame* 16(2):125-130 (1971).
131. Wendt JOL, Sternling CV. Catalysis of SO$_2$ oxidation by nitrogen oxides. *Combust Flame* 21(3):387-390 (1973).
132. Kühnemuth D, Normann F, Andersson K and Johnsson F, On the carbon monoxide formation in oxy-fuel combustion—Contribution by homogenous and heterogeneous reactions. *Int J Greenh Gas Control* 25:33-41 (2014).
133. Seddighi S, Pallarès D, Normann F and Johnsson F, Carbon monoxide formation during oxy-fuel-fired fluidized-fed combustion. *Energy Fuels* 27(4):2275-2282 (2013).
134. Glarborg P, Bentzen LLB. Chemical effects of a high CO$_2$ concentration in oxy-fuel combustion of methane. *Energy Fuels* 22:291-296 (2007).
135. Bayless DJ, Jewmaidang J, Tanneer S and Birru R, Kinetics of low-temperature homogeneous SO$_3$ formation for use in flue gas conditioning for improved
electrostatic precipitator performance. In: *Proceedings of the Combustion Institute* 28:2499-2505 (2000).

136. Hecht ES, Shaddix CR, Geier M, Molina A and Haynes BS, Effect of CO$_2$ and steam gasification reactions on the oxy-combustion of pulverized coal char. *Combust Flame* 159(11):3437-3447 (2012).

137. Wine PH, Thompston RJ, Ravishankara AR, Semmes DH, Gump CA, Torabi A *et al.*, Kinetics of the reaction OH + SO$_2$ + M → HOSO$_2$ + M. Temperature and pressure dependence in the falloff region. *J Phys Chem* 88(10):2095-2104 (1984).

138. Hindiyarti L, Glarborg P and Marshall P. Reactions of SO$_3$ with the O/H radical pool under combustion conditions. *J Phys Chem A* 111(19):3984-3991 (2007).

139. Flint D, Lindsay AW. Catalytic oxidation of sulphur dioxide on heated quartz surfaces. *Fuel* 30:288 (1951).

140. Crumley PH, Fletcher AW. The formation of sulphur trioxide in flue gases. *J Inst Fuel* 29:322-327 (1956).

141. Barret RE, Hummell JD and Reid WT, Formation of SO$_3$ in a noncatalytic combustor. *J Eng Power* 88:165-172 (1966).

142. Couling D. Impact of oxyfuel operation on emissions and ash properties based on E.ON’s 1MW CTF. In: *IEAGHG Special Workshop on Oxyfuel Combustion*, 25-26 January, London (2011).

143. Kenney JR, Clark MM, Levasseur AA and Kang SG, SO$_3$ emissions from a tangentially-fired pilot scale boiler operating under oxy-combustion conditions. In: *IEAGHG Special Workshop on Oxyfuel Combustion*, 25-26 January, London (2011).

144. Jurado N, Darabkhani HG, Anthony EJ and Oakey JE, Oxy-combustion studies into the co-firing of coal and biomass blends: effects on heat transfer, gas and ash compositions. *Energy Procedia* 63:440-452 (2014).

145. Spörl R, Belo L, Shah K, Stanger R, Giniyatullin R, Maier J *et al.*, Mercury emissions and removal by ash in coal-fired oxy-fuel combustion. *Energy Fuels* 28(1):123-135 (2014).

146. Spörl R, Maier J and Scheffknecht G, Experiences and Results of SO$_3$ measurements performed under oxy-coal fired conditions. In: *IEAGHG Special Workshop on Oxyfuel Combustion*, 25-26 January, London (2011).

147. Mönckert P, Dhungel B, Kull R and Maier J, Impact of combustion conditions on emission formation (SO$_2$, NO$_x$) and fly ash. In: *3rd meeting of the oxy-fuel combustion network*. Yokohama Symposia, Yokohama, Japan: IEA Greenhouse Gas R&D programme (2008).

148. Mitsui Y, Imada N, Kikkawa H and Katagawa A, Study of Hg and SO$_3$ behavior in flue gas of oxy-fuel combustion system. *Int J Greenh Gas Control* 5S:S143-S150 (2011).

149. Eddings EG, Wang L and Ahn J, Bench-scale fluid bed experiments of SO$_2$/SO$_3$ formation and sulfur capture in N$_2$/O$_2$ and SO$_2$/O$_2$ environments. In: *IEAGHG*
150. Spörl R, Maier J, Belo L, Shah K, Stanger R, Wall T et al., Mercury and SO₃ emissions in oxy-fuel combustion. In: *Energy Procedia* **63**:386-402 (2014).

151. Davis C. Impact of oxyfuel operation on corrosion in coal fired boilers based on experience with E.ON’s 1MWth Combustion test facility. In: *IEAGHG Special Workshop on Oxyfuel Combustion*, 25-26 January, London (2011).

152. Stanger R, Belo L, Ting T, Spero C and Wall T, Mercury and SO₃ measurements on the fabric filter at the Callide Oxy-fuel Project during air and oxy-fuel firing transitions. *Int J Greenh Gas Control* **47**:221-232 (2016).

153. Glarborg P, Alzueta MU, Dam-Johansen K and Miller JA. Kinetic modeling of hydrocarbon/nitric oxide interactions in a flow reactor. *Combust Flame* **115**(1-2):1-27 (1998).

154. Schneider DR, Bogdan Z. Modelling of SO₃ formation in the flame of a heavy-oil fired furnace. *Chem Biochem Eng Q* **17**(3):175-181 (2003).