SO$_3$/SO$_x$ ratio in oxy-fuel combustion – the impact of operational conditions

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Background

- The role of gas-phase sulphur chemistry in HTC and LTC
  - Sulphation of alkali via $SO_3$
  - Formation of sulphur-containing corrosive salts
  - Prevention of chlorine-based salts being formed
  - Increased acid dew point temperature
Lab-scale experiments at Zaragoza Univ.
Kinetic modelling

- Chemkin/mechanism
  - Plug flow
  - Detailed gas-phase chemistry kinetics
  - S-chemistry during fuel oxidation in $\text{CO}_2/\text{N}_2$ atmospheres
- Hindiyarti, Glarborg and Marshall, 2007 and Gimenez-Lopez et al., 2011
Key reactions in kinetic mechanism

\begin{align*}
\text{SO}_2 + O (+M) & \rightleftharpoons \text{SO}_3 (+M) \quad (1) \\
\text{SO}_3 + H & \rightleftharpoons \text{SO}_2 + OH \quad (2) \\
\text{SO}_2 + OH (+M) & \rightleftharpoons \text{HOSO}_2 (+M) \quad (3) \\
\text{HOSO}_2 + O_2 & \rightleftharpoons \text{SO}_3 + \text{HO}_2 \quad (4)
\end{align*}
100 kW propane experiments at Chalmers Univ.

Propane
- $\text{SO}_2$-injection
- $\text{SO}_3$-measurements
- Controlled condensation
- Air-fuel and oxy-fuel
Post flame $\text{SO}_3$ formation

Influence of temperature & gas composition: $\text{O}_2$, temperature, $\text{SO}_2$, $\text{CO}_2$, $\text{CO}$ and Oxy vs. Air-fuel
Lab-scale experiments: influence of $O_2$

- $SO_2$: 1000 ppm
- $N_2$-base
- $O_2$: 0.1-20.3%
- $T_e$: 800-1500 K
\[
\begin{align*}
\text{SO}_2 &+ \text{O} (+\text{M}) \rightleftharpoons \text{SO}_3 (+\text{M}) \quad (1) \\
\text{SO}_3 &+ \text{H} \rightleftharpoons \text{SO}_2 &+ \text{OH} \quad (2) \\
\text{SO}_2 &+ \text{OH} (+\text{M}) \rightleftharpoons \text{HOSO}_2 (+\text{M}) \quad (3) \\
\text{HOSO}_2 &+ \text{O}_2 \rightleftharpoons \text{SO}_3 &+ \text{HO}_2 \quad (4)
\end{align*}
\]
Lab-scale experiments: influence of temperature

- SO₂: 1000 ppm
- O₂: 3%
- N₂-base
- H₂O: 1.1%
100 kW experiments: influence of temperature

- Temperature
- Air-fuel
- Oxy-fuel
  - OF 30
  - OF 25
Lab-scale experiments: influence of SO$_2$

- N$_2$ atmospheres
- 3 vol% O$_2$
- 250, 500, 1000 ppm SO$_2$
100 kW experiments: oxy-fuel vs air

- Air vs. OF30
- SO₂
- Oxygen/fuel ratio
- CO₂/N₂-base

![Graph showing SO₃/SOₓ ratio vs λ (λ)]

+ Air, 885 ppm SO₂
⊙ OF30, 2438 ppm SO₂
Lab-scale experiments: influence of CO$_2$ and CO

- CO$_2$ or N$_2$; CO: 0 or 1000 ppm; SO$_2$: 1000 ppm; O$_2$: 3%; N$_2$-base
\[
\text{SO}_2 + \text{O} (+\text{M}) \rightleftharpoons \text{SO}_3 (+\text{M}) \quad (1)
\]

\[
\text{SO}_3 + \text{H} \rightleftharpoons \text{SO}_2 + \text{OH} \quad (2)
\]

\[
\text{SO}_2 + \text{OH} (+\text{M}) \rightleftharpoons \text{HOSO}_2 (+\text{M}) \quad (3)
\]

\[
\text{HOSO}_2 + \text{O}_2 \rightleftharpoons \text{SO}_3 + \text{HO}_2 \quad (4)
\]
Conclusions

- Increase in O₂ concentration
- Increase in SO₂ concentration

- Increase in SO₃ concentration
- Increase in SO₃ concentration

- Presence of CO or CH₄ concentrations
- Increase in H₂O concentration

- Strong increase in SO₃ formation
- Increase in SO₃ formation in absence of CO

- Decreases SO₃ formation during CO oxidation

- Increase in CO₂ concentration

- Slight increase in SO₃ formation in absence of CO

- Decreases SO₃ formation during CO conversion

- Availability of NO

- Can increase SO₃ formation due to its influence on the radical pool
Conclusions

Absence of airborne $N_2$
Change in flue gas residence time (depending on FGR ratio)

Increase in $SO_2$ concentration
Longer residence time: increase in $SO_3$ concentration

Change from dry to wet FGR

Increase in $H_2O$ concentration favors $SO_3$ formation, but the decrease in $SO_2$ concentration will counteract

Change in temperature conditions (mainly dependent upon the $O_2$ concentration in the oxidizer)

Influences the release of sulfur from the coal and the capture of $SO_x$ by ash-forming matter

Influences the level of $SO_3$ formation$^{9,25}$
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