Simplified model of SO_2 oxidation and KCl sulphation for CFD applications

Peter Glarborg and Hao Wu

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Challenges in combustion of solid fuels

- Process efficiency
- Pollutant emission control
  - NO_x
  - SO_x, HCl
  - Unburned, PAH
  - Soot, other aerosols
  - Heavy metals
- CO_2 emission control
  - Fuel substitution
  - Carbon capture

Biomass fuels in Europe

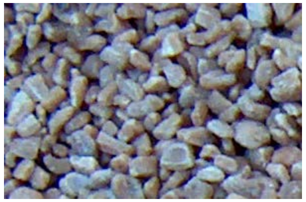
- Woody biomass fuels:
  - Bark
  - Industrial wood chips
  - Sawdust
  - Forest wood chips
  - Waste wood
  - Pellets, briquettes
- Herbaceous biomass fuels:
  - Straw, cereals
  - Grasses (miscanthus, giant reed)
- Alternative biomass fuels:
  - Kernels, shells, olive stones, shea nuts











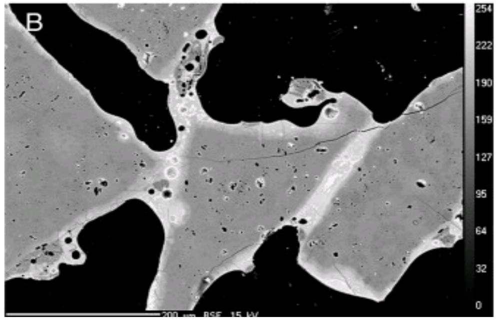

Frandsen, 2012

KCl related issues in biomass combustion

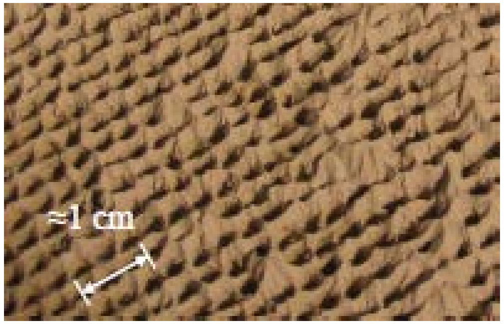
Ash deposition

KCl

Corrosion



Bed agglomeration

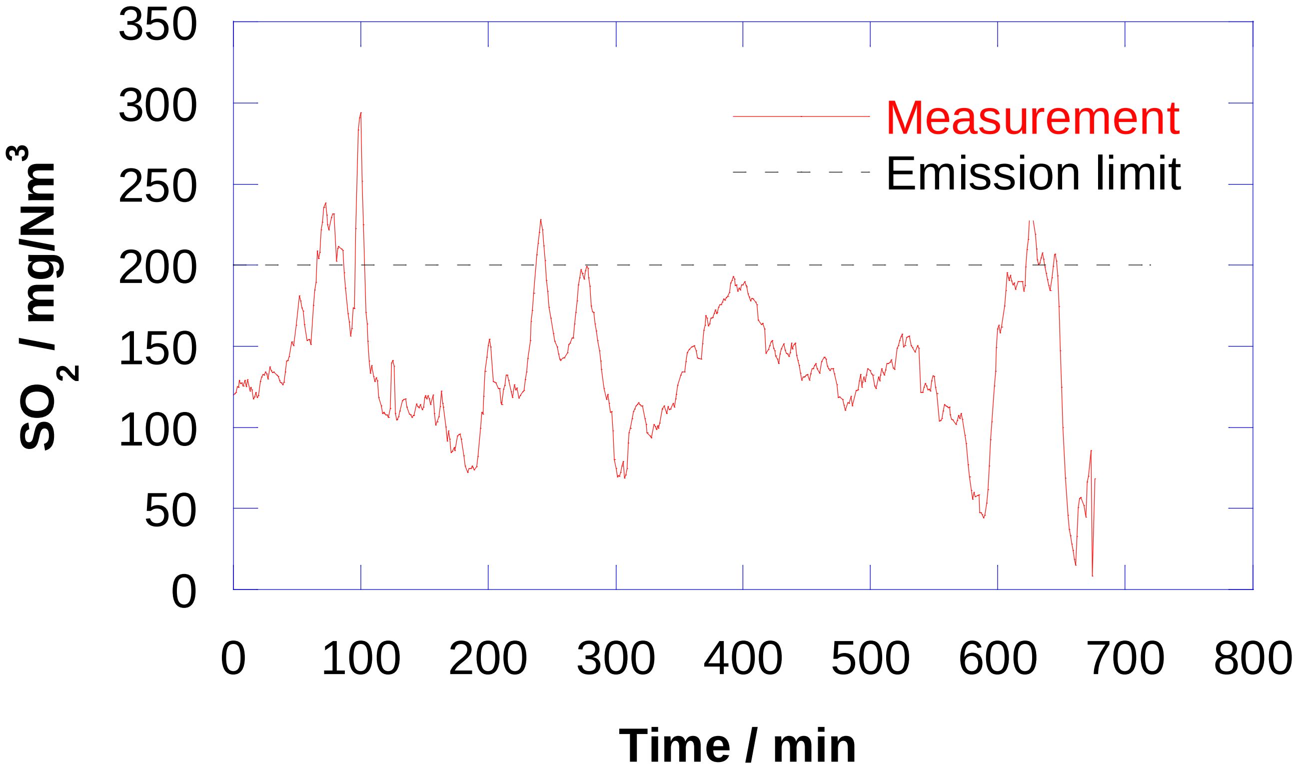


SCR deactivation

Potassium speciation in ash: concerns

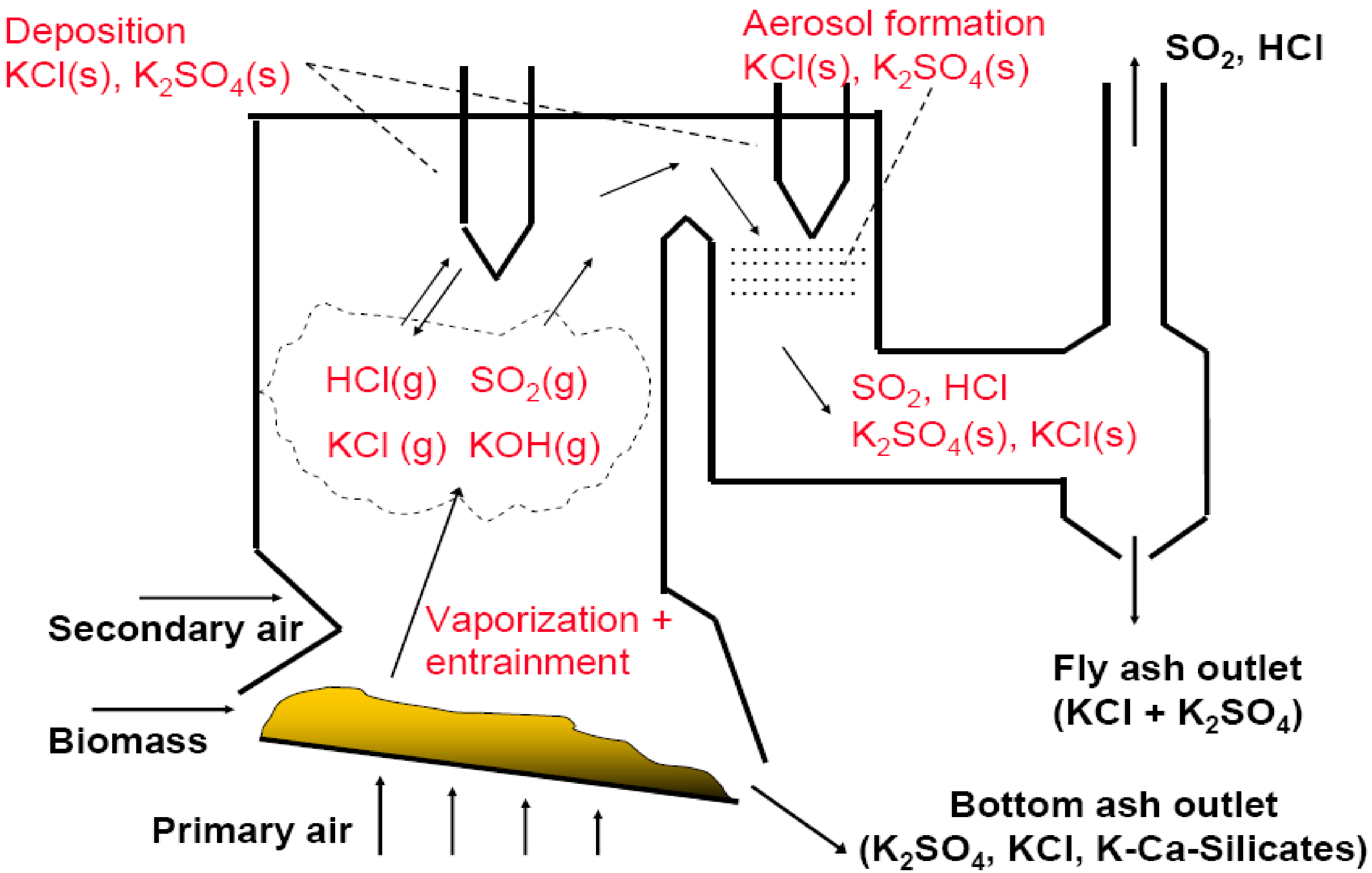
	Deposition	Corrosion	SCR deactivation	Fly ash quality
KCl	XXX	XXX	XXX	XXX
K_2SO_4	XX	X	XXX	
K-silicates	XX			
K-alumina-silicates	X			

Combustion of straw on a grate



Data from the Ensted Power Plant (Knudsen and Sander, 2004)

Grate-firing of biomass: fate of K, S, Cl



Sulfation of KCl

Proposed gas-phase sulfation mechanism:

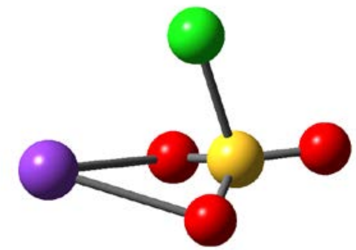
$SO_2 + ½O_2 \rightarrow SO_3$ (global, rate limiting)

$KCl + SO_3 (+M) \rightarrow KSO_3Cl (+M)$ (fast)

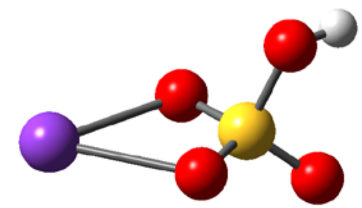
$KSO_3Cl + H_2O \rightarrow KHSO_4 + HCl$ (fast)

$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$ (fast)

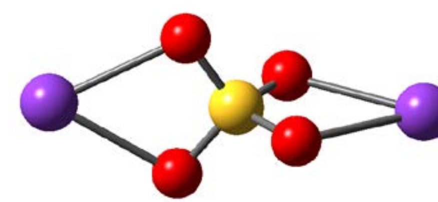
$2KCl + SO_2 + ½O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$ (net)



KSO_3Cl



$KHSO_4$



K_2SO_4

Reference reaction:

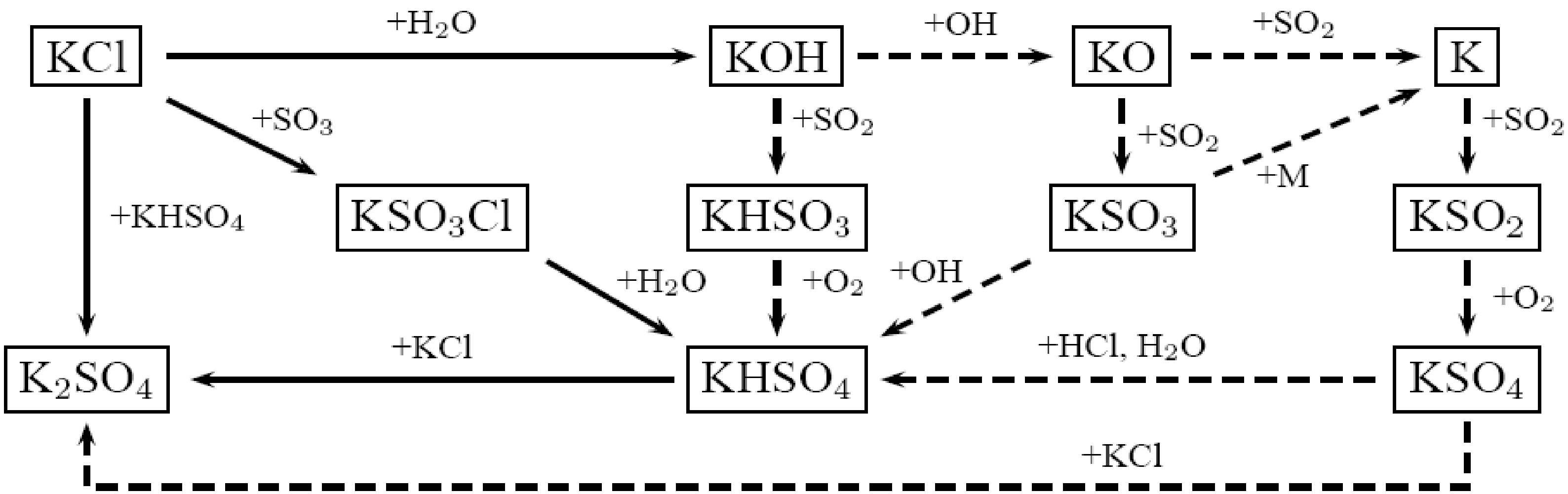
$NaOH + HCl \rightarrow NaCl + H_2O$

$k_{298} \sim 10^{14}\ cm^3\ mol^{-1}\ s^{-1}$

Silver et al. (1984)

Glarborg and Marshall (2005)

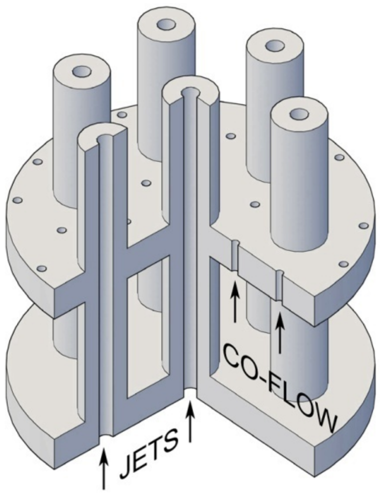
A mechanism for sulfation of KCl



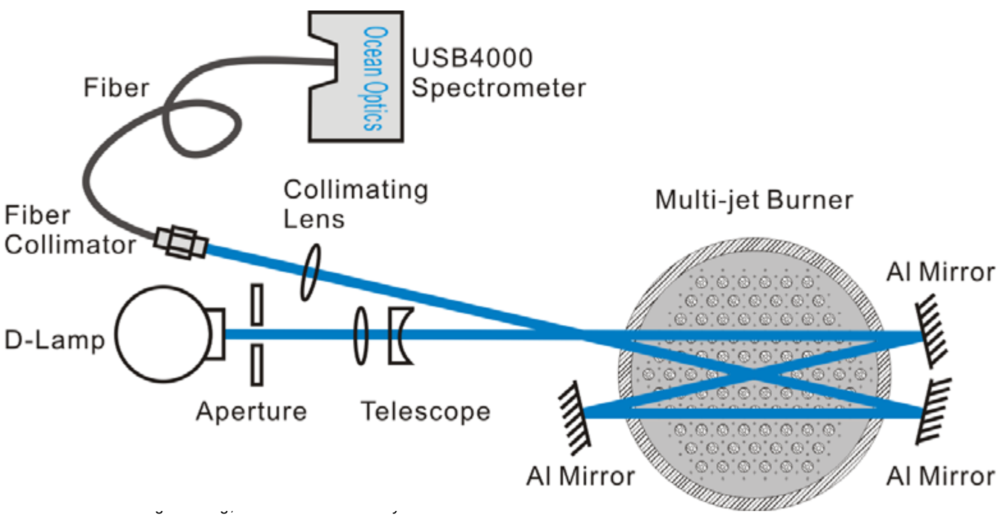
Detailed reaction mechanism: 50 species, 200+ reactions

Hindiyarti et al., 2007

Flame experiments at Lund University

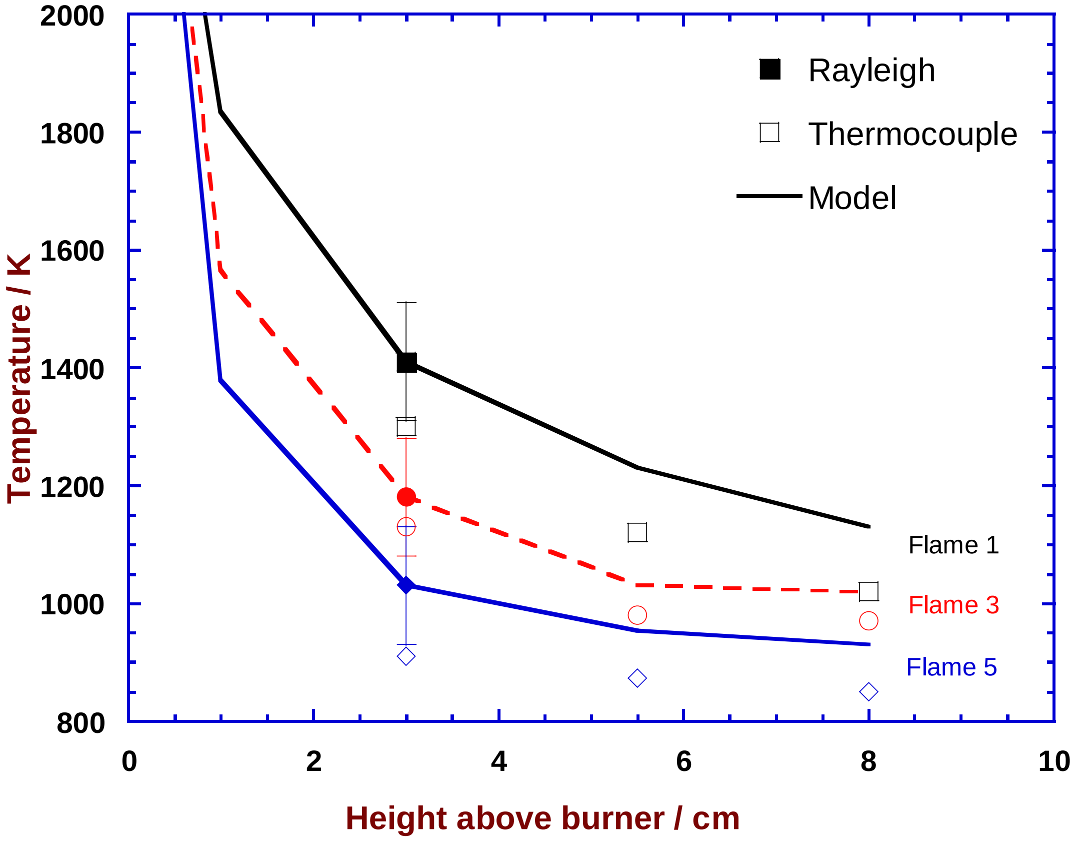


- Multi-jet (91) burner
- Atm pressure flame
- Hydrocarbon/oxygen/nitrogen
- Add KCl w/wo SO_2
- Measure temperature, KCl, HCl, SO_2



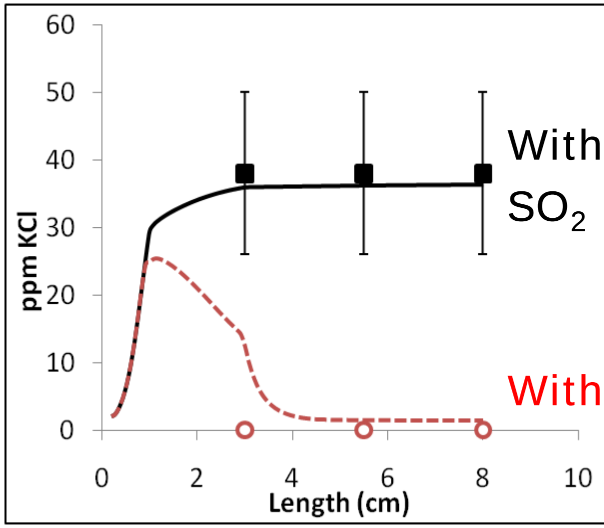
Li et al. 2013

Temperature profiles

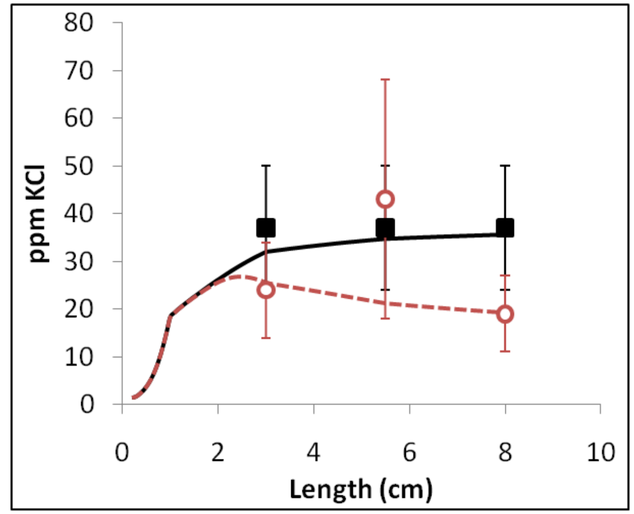


Li et al. 2013

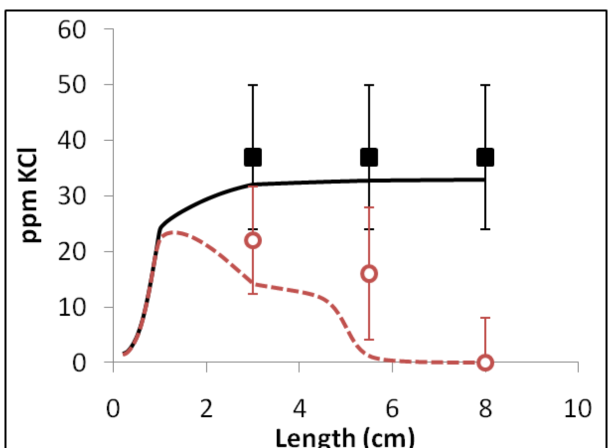
Effect of SO_2 addition on post-flame KCl



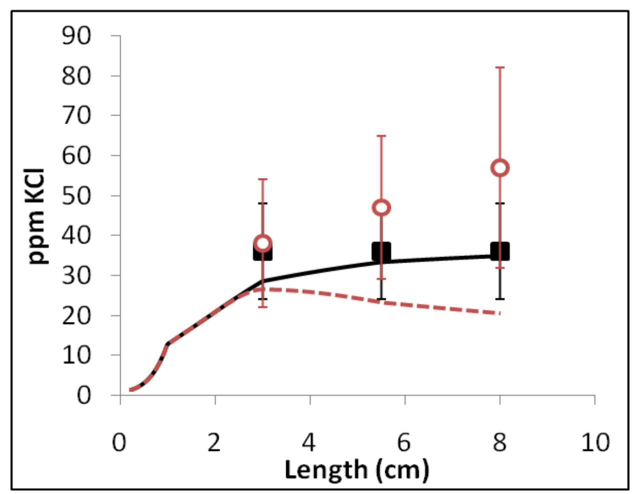
1030 K



1300 K



1100 K



1410 K

Li et al. 2013

In-furnace KCl sulfation

Gas-phase mechanism:

$SO_2 + O_x \rightarrow SO_3$

$KCl + SO_3\ (+M) \rightarrow KSO_3Cl\ (+M)$

$KSO_3Cl + H_2O \rightarrow KHSO_4 + HCl$

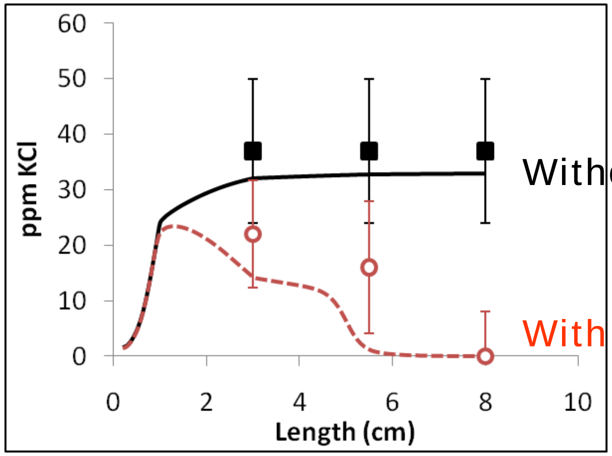
$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$

$K_2SO_4 \rightarrow$ aerosol

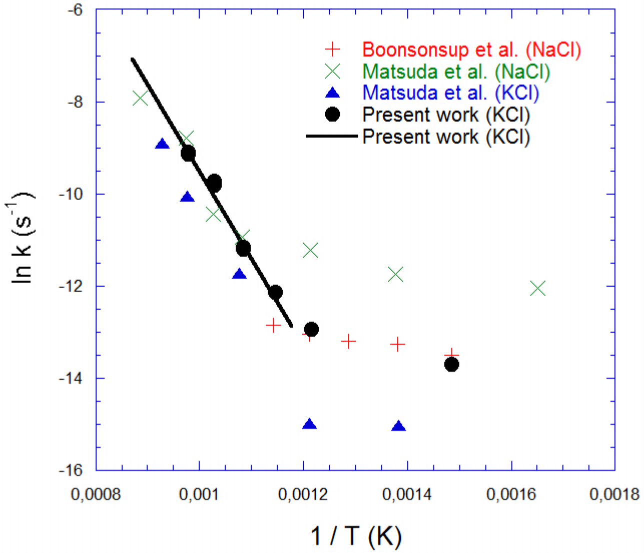
Gas-solid reaction:

$2KCl + SO_2 + ½O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$ (net)

Post-flame sulphation of KCl



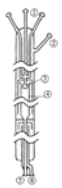
Li et al. (2012)



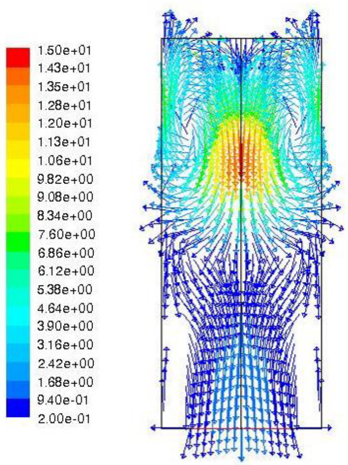
Sengeløv et al. (2013)

From basic science to technology

Semi-industrial scale experiments



Model (CFD)



Objectives

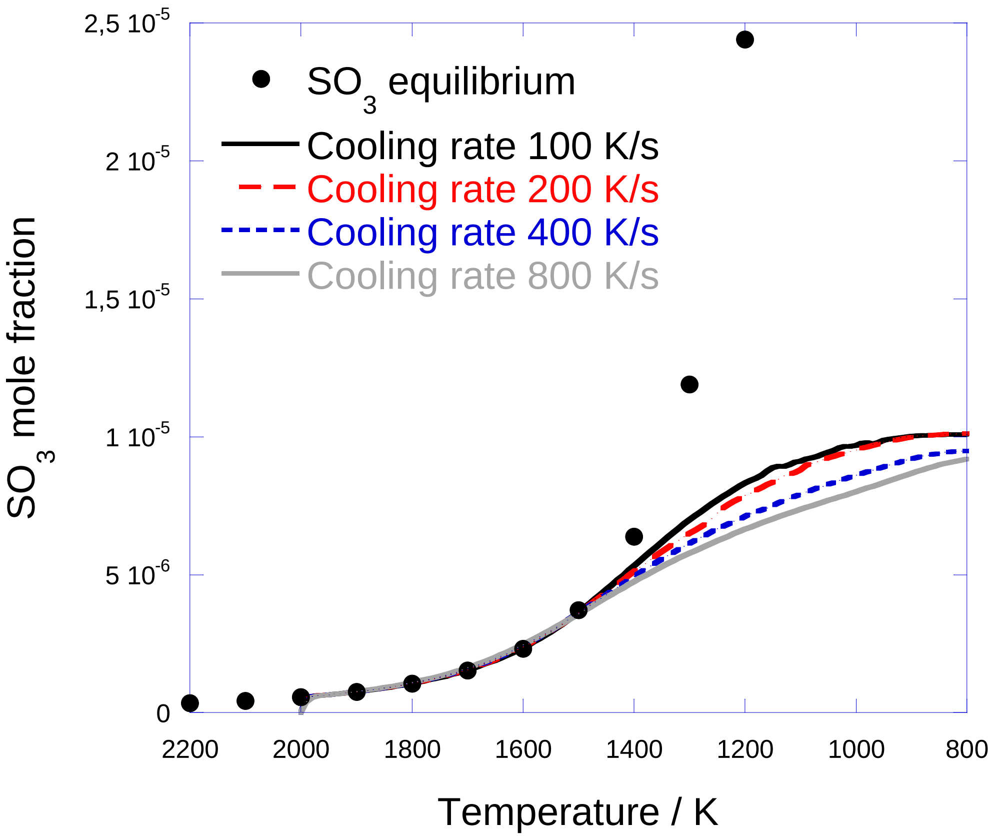
- Develop a simplified model for gas-phase sulphation of KCl
  - Describe oxidation of SO_2 to SO_3
  - Describe sulphation of KCl by SO_3
  - Describe homogeneous nucleation of K_2SO_4
- Questions:
  - Is it possible to reduce the detailed model (50 species, 200+ reactions – without fuel oxidation) to an operational size model?
  - Where does the important chemistry occur?
  - Is superequilibrium of radicals important?

Representing chemistry in CFD

- Full reaction mechanism
- Skeletal mechanism
- Analytically reduced mechanism
- Global mechanism

↑ Accuracy
Complexity

Effect of cooling rate on SO_3 formation - predictions with full mechanism



Inlet composition:

500 ppm SO_2,

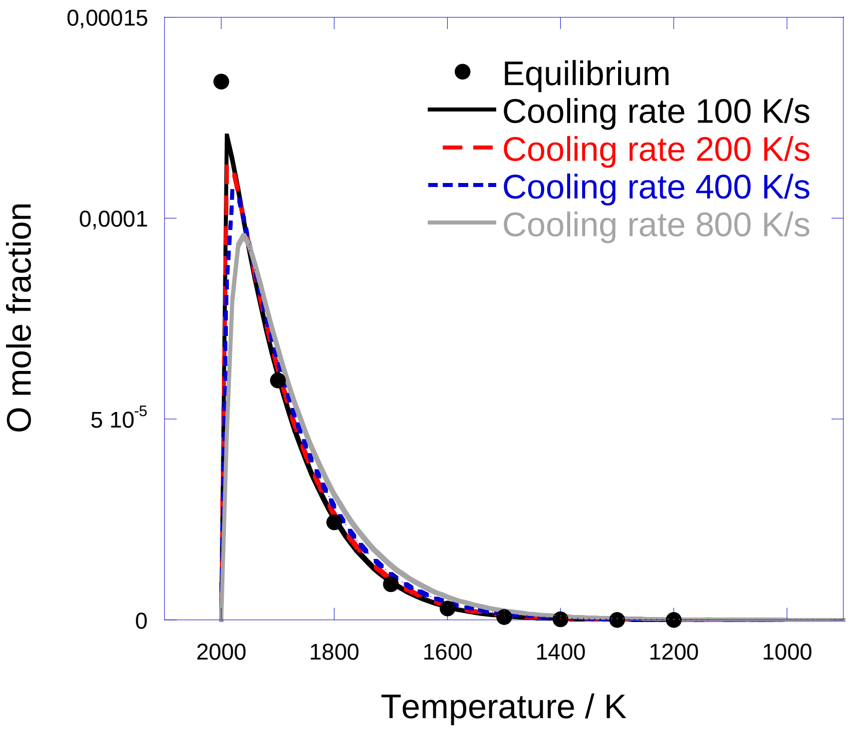
4% O_2, 10% H_2O, 5% CO_2; balance N_2

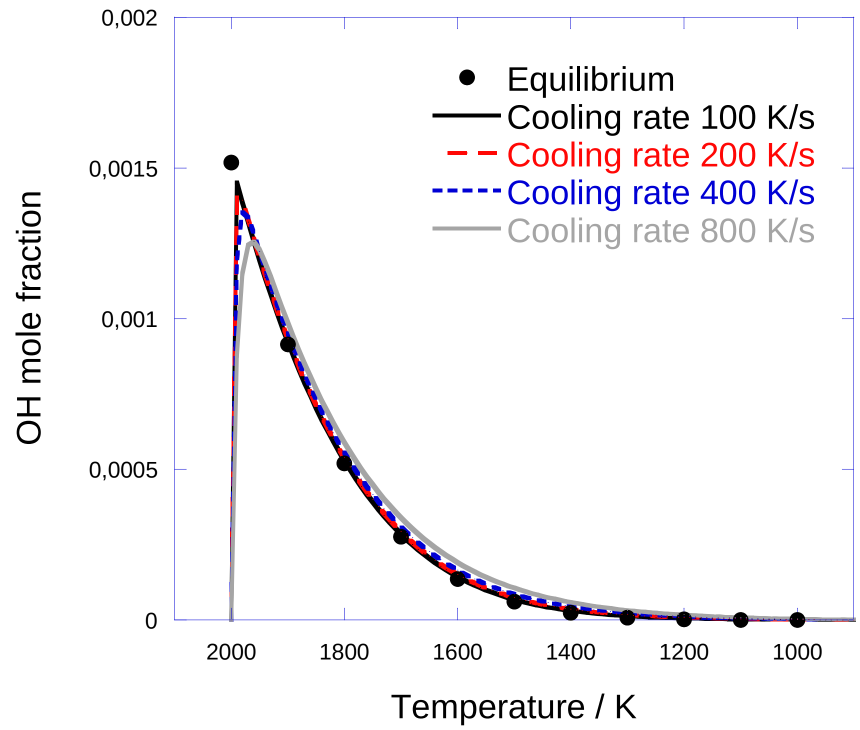
Skeletal mechanism for SO_3 formation

		A [cm,mole,s]	β	E_a [cal/mole]
1.	$SO_2 + O + M \rightleftharpoons SO_3 + M$	2.9E27	-3.58	0
2.	$SO_2 + OH + M \rightleftharpoons HOSO_2 + M$	1.7E27	-4.09	0
3.	$SO_2 + OH \longrightarrow SO_3 + H$	7.8E11	0.00	28800
4.	$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$	7.8E11	0.00	656

Minimum reaction subset that provides a satisfactory description of the relevant chemistry

Radical concentrations during cooling





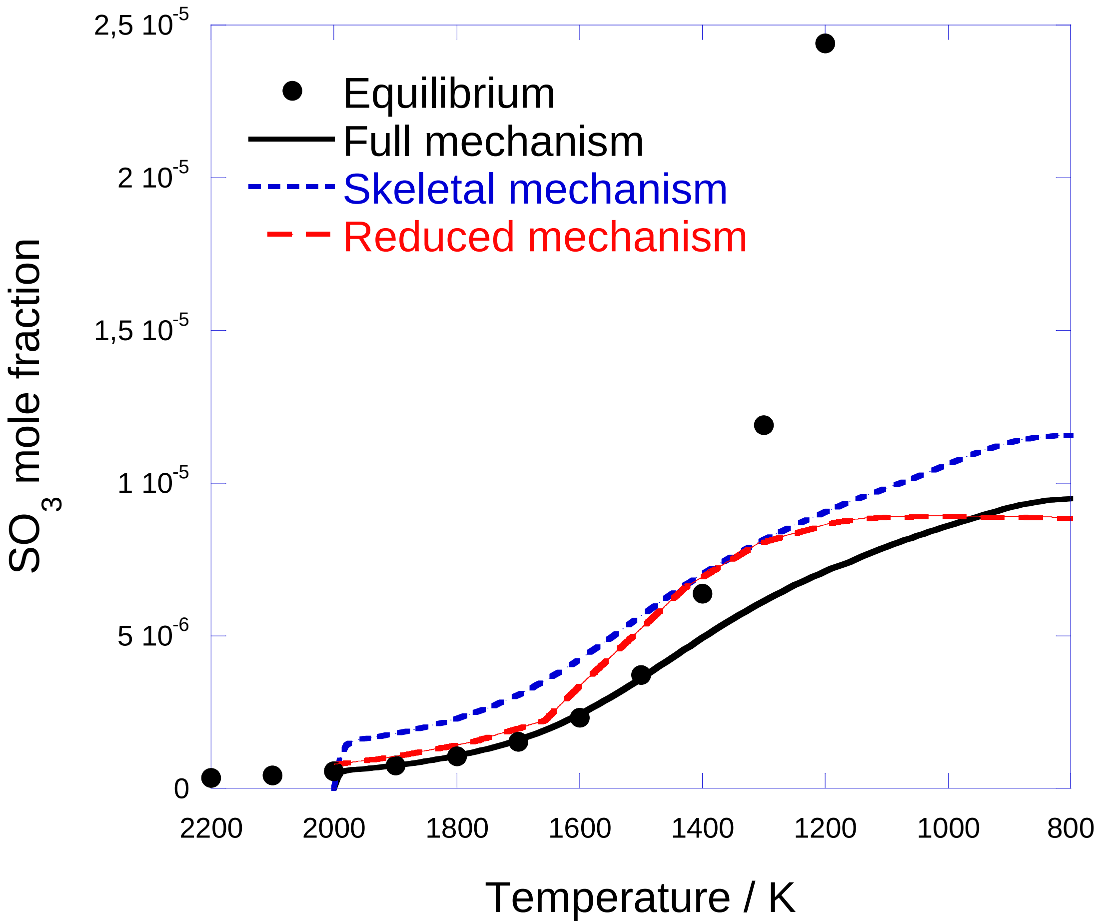
Inlet composition:

500 ppm SO_2,

4% O_2, 10% H_2O, 5% CO_2; balance N_2

Radical partial equilibrium largely maintained during cooling ☺

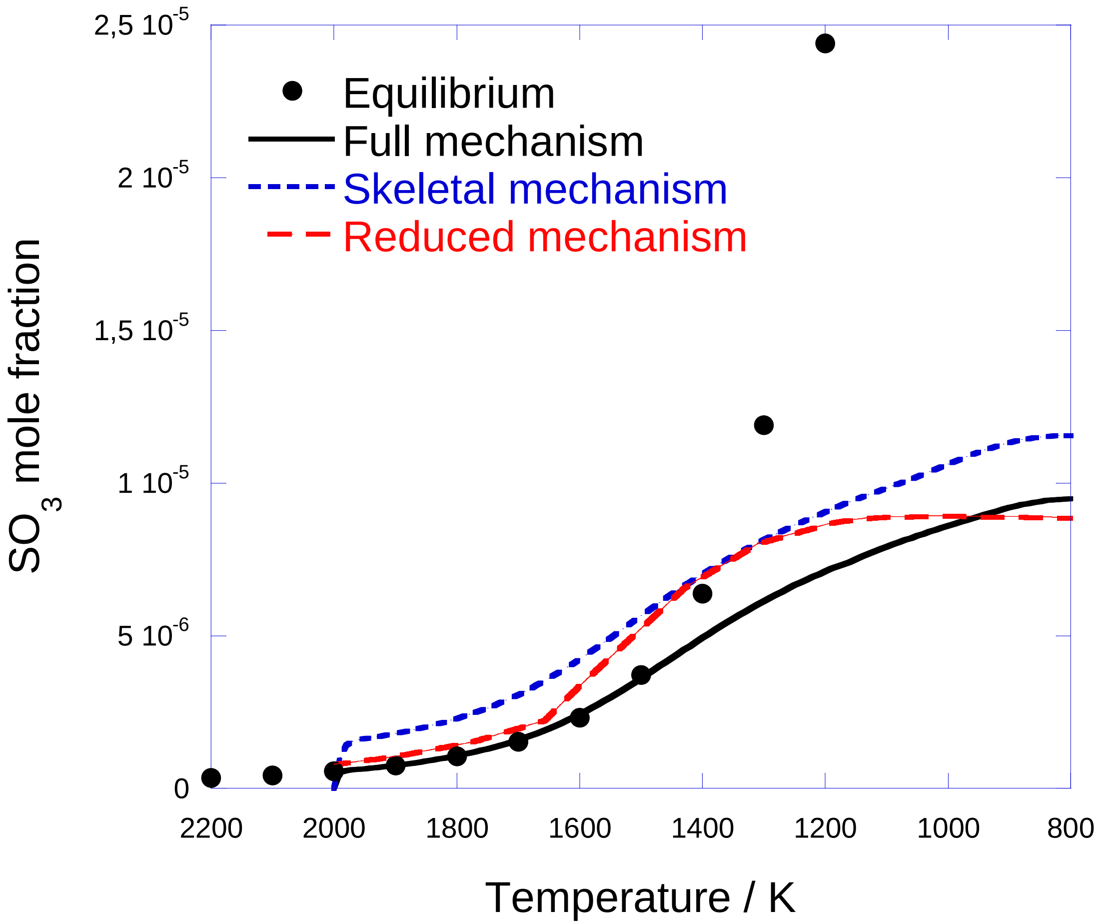
Prediction of SO_3 formation



Skeletal mechanism:

- Detailed H_2/O_2 subset
- Skeletal SO_x subset

Prediction of SO_3 formation



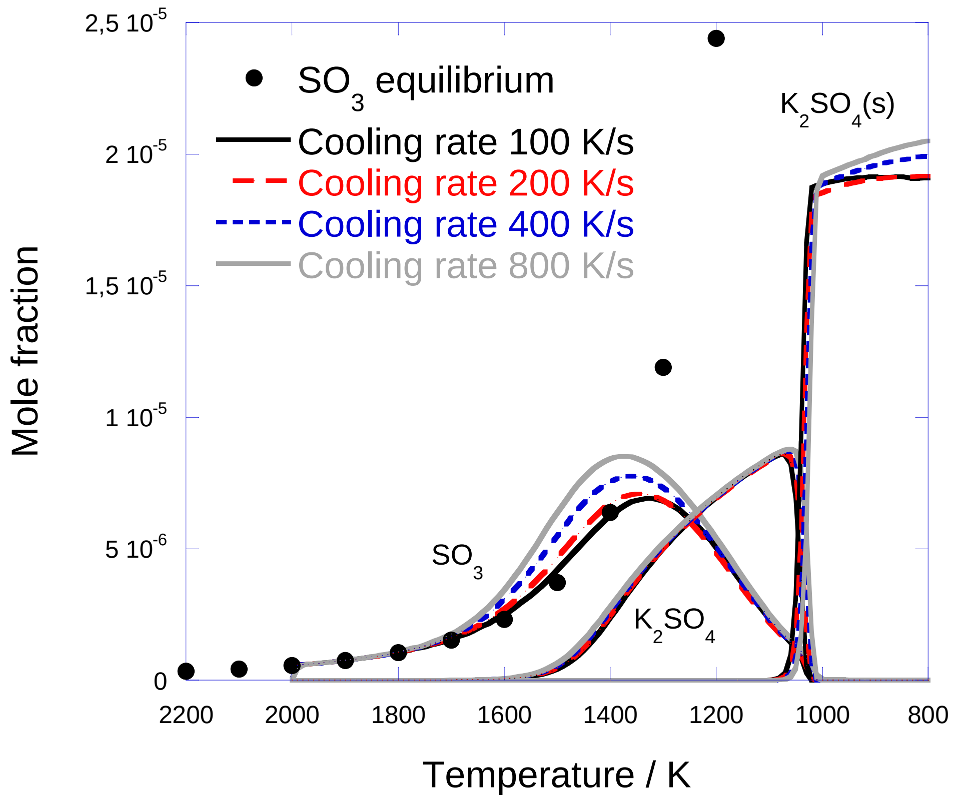
Reduced mechanism:

- Assume $HOSO_2$ in steady state
- Assume O in partial equil.
  $O_2+M = O+O+M$
- Assume OH in partial equil.
  $H_2O+½O_2 = OH+OH$
- Rates of formation:

$$\omega_{SO2} = -\omega_1 - \omega_3 - \omega_4$$

$$\omega_{SO3} = \omega_1 + \omega_3 + \omega_4$$

Effect of cooling rate on sulphation rate - predictions with full mechanism



Inlet composition:

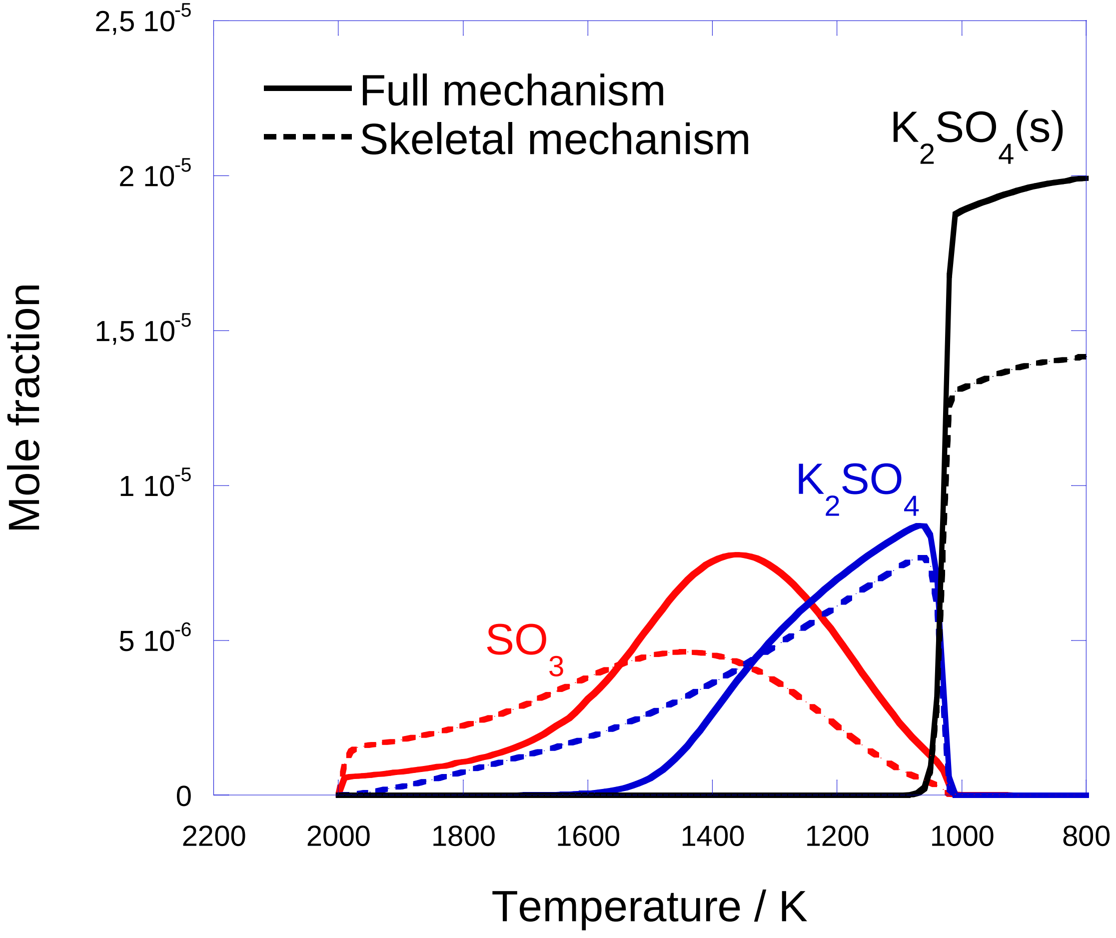
500 ppm SO_2, 50 ppm KCl

4% O_2, 10% H_2O, 5% CO_2; balance N_2

Skeletal mechanism

		A [cm,mole,s]	β	E_a [cal/mole]
1.	$SO_2 + O + M \rightleftharpoons SO_3 + M$	2.9E27	-3.58	0
2.	$SO_2 + OH + M \rightleftharpoons HOSO_2 + M$	1.7E27	-4.09	0
3.	$SO_2 + OH \longrightarrow SO_3 + H$	7.8E11	0.00	28800
4.	$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$	7.8E11	0.00	656
5.	$KCl + SO_3 + M \rightleftharpoons KClSO_3 + M$	1.9E41	-7.80	0
6.	$KClSO_3 + H_2O \rightleftharpoons KHSO_4 + HCl$	1.0E14	0.00	0
7.	$KHSO_4 + KCl \rightleftharpoons K_2SO_4 + HCl$	1.0E14	0.00	0
8.	$K_2SO_4 \longrightarrow K_2SO_4(\text{aerosol})$	1.0E-61	0.00	-300000

Predictions of sulphation
- performance of skeletal mechanism



Analytically reduced model

Simplifying assumptions:

- Assume H_2SO_4 in steady state
- Assume O in partial equilibrium (O_2+M = O+O+M)
- Assume OH in partial equilibrium (H_2O+½O_2 = OH+OH)
- Replace the fast gas-phase alkali sulphation steps by one global reaction (G):

  $SO_3 + 2KCl + H_2O \rightarrow K_2SO_4 + 2HCl$

Model:

- Components:

  SO_2, SO_3, KCl, K_2SO_4, K_2SO_4(c)

- Rates of formation:

  $\omega_{SO2} = -\omega_1 - \omega_3 - \omega_4$

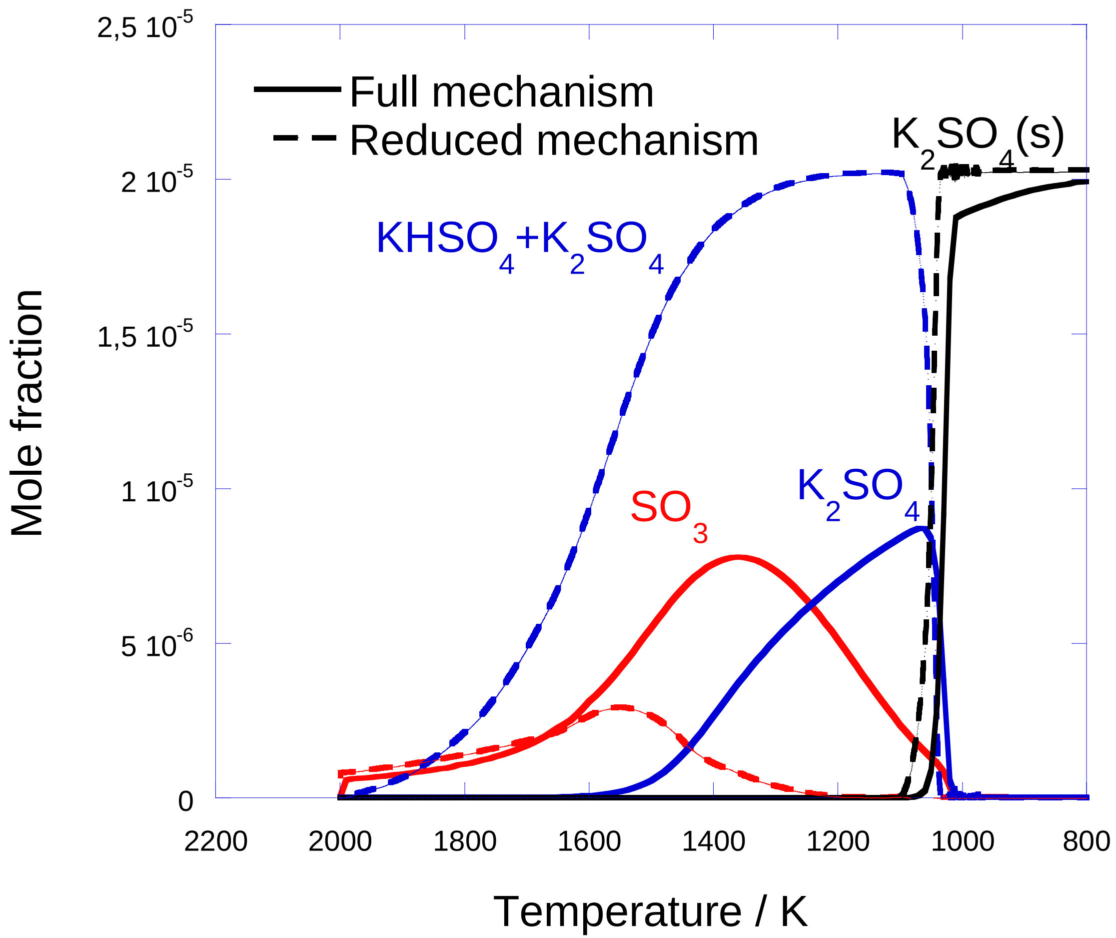
  $\omega_{SO3} = \omega_1 + \omega_3 + \omega_4 - \omega_G$

  $\omega_{KCl} = -\omega_G$

  $\omega_{K2SO4} = \omega_G - \omega_{NUCLEATION}$

  $\omega_{K2SO4(c)} = \omega_{NUCLEATION}$

Predictions of sulphation
- performance of reduced mechanism



Conclusions

- A simplified model for gas-phase sulphation of KCl in the post-flame region has been developed
  - Oxidation of SO_2 to SO_3
    - O/H radicals in partial equilibrium
    - $HOSO_2$ in steady-state
  - Sulphation of KCl by SO_3
    - One-step global reaction for sulphation
    - One-step global reaction for homogeneous nucleation of K_2SO_4
    - Provides a good estimate of the Cl/S ratio in the condensed alkali salts
    - Needs refinement to predict concentration profiles (time / temperature)