Oxidation of Reduced Sulfur Species: Carbonyl Sulfide

Glarborg, Peter; Marshall, Paul

Published in:
International Journal of Chemical Kinetics

Link to article, DOI:
10.1002/kin.20778

Publication date:
2013

Citation (APA):
Sulphation of condensed potassium chloride by SO$_2$

Louise With Sengeløv$^1$, Troels Bruun Hansen$^1$, Carmen Bartolomé$^2$, Hao Wu$^1$, Kim H. Pedersen$^3$, Flemming J. Frandsen$^1$, Anker D. Jensen$^1$, Peter Glarborg$^1$

$^1$Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
$^2$CIRCE (Centre of Research for Energy Resources and Consumption), University of Zaragoza, C/Mariano Esquillor Gómez, 15, 50018 Zaragoza, Spain
$^3$FLSmidth A/S, Vigerslev Allé 77, DK-2500 Valby, Denmark

The interaction between alkali chloride and sulphur oxides has important implications for deposition and corrosion in combustion of biomass. In the present study, the sulphation of particulate KCl (90-125 μm) by SO$_2$ was studied in a fixed bed reactor in the temperature range 673-1023 K and with reactant concentrations of 500-3000 ppm SO$_2$, 1-20% O$_2$, and 4-15% H$_2$O. The degree of sulphation was monitored by measuring the formation of HCl. Analysis of the solid residue confirmed that the reaction proceeds according to a shrinking core model and showed the formation of an eutectic at higher temperatures. Based on the experimental results, a rate expression for the sulphation reaction was derived. The model compared well with literature data for sulphation of KCl and NaCl, and the results indicate that it may be applied at even higher SO$_2$ concentrations and temperatures than those of the present study. Simulations of sulphation of KCl particles with different size indicate that only for very small KCl particles, below 1 μm, a considerable
in-flight sulphation is achievable at the short gas residence times typical of combustion systems.

Keywords: KCl, sulphation, biomass combustion

Introduction

The sulphation of alkali chlorides has important implications for thermal conversion of biomass. During pyrolysis and combustion of biomass at temperatures above about 1073 K, potassium is partly released to the gas-phase,\(^1\text{--12}\) typically as potassium chloride. For agricultural residues the KCl release can be significant,\(^3,4,11,13,14\) while woody biomass contains smaller quantities of K and Cl.\(^8,9,13\text{--16}\) Once released, gaseous KCl may be sulphated by reaction with SO\(_3\)\(^17\text{--22}\) or it may, during cooling, condense on particulates or heat transfer surfaces.\(^18,23\text{--26}\) If the particle loading in the system is low, KCl may form an aerosol by homogeneous nucleation.\(^24,25,27\)

Potassium chloride has a number of adverse effects in combustion units. Once deposited on heat transfer surfaces, it may act to lower the melting temperature of the deposit, forming a sticky surface that promotes further deposition.\(^26,28\) Furthermore, its presence in the deposits may lead to severe corrosion by a mechanism where both potassium and chlorine are active in destroying the metal oxide protective layer.\(^29\) Another adverse effect of KCl is the ability to deactivate SCR catalysts;\(^30\text{--33}\) a phenomenon that limits the application of SCR for NO\(_x\) control in biomass fired systems.
The sulphation of condensed alkali chlorides proceeds as a gas-solid or gas-liquid reaction that may involve SO$_2$\textsuperscript{34} or SO$_3$\textsuperscript{35}.

\begin{equation}
2\text{KCl}(s, l) + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4(s, l) + 2\text{HCl} \tag{1}
\end{equation}

\begin{equation}
2\text{KCl}(s, l) + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4(s, l) + 2\text{HCl} \tag{2}
\end{equation}

Here s and l denote solid and liquid species, respectively, while the remaining species are gaseous. These reactions have been reported to be slower than the homogeneous sulphation occurring in the gas-phase,\textsuperscript{17,36} leading to the assumption that the in-flight sulphation of particulate KCl is insignificant in a furnace where the residence time in suspension is of the order of a few seconds. However, for KCl condensed on deposits, the available reaction time for sulphation is orders of magnitude longer. Corrosion due to HCl release close to the metal surface is in discussion,\textsuperscript{29,37-39} but recent results indicate that the sulphation reaction serves to reduce the corrosion propensity.\textsuperscript{40}

In addition to its relevance for biomass combustion, the sulphation of alkali chlorides has implications for industrial production of HCl,\textsuperscript{34} HCl emissions from municipal solid waste incinerators\textsuperscript{41,42} and kraft recovery boilers,\textsuperscript{43} as well as for corrosion of gas turbine engine components\textsuperscript{35} and cement kilns.\textsuperscript{44} Despite the importance, there are only few reported experiments on sulphation of solid alkali chlorides. Most previous studies investigated the sulphation of NaCl(s) by SO$_2$.\textsuperscript{34,36} In more recent work, Matsuda and coworkers\textsuperscript{45,46} compared the sulphation rates of NaCl(s), KCl(s), and CaCl$_2$(s). The reported experiments were typically conducted with a fixed bed of alkali chloride, varying temperature and concentrations of SO$_2$, O$_2$, and H$_2$O. While these studies offer data for reaction rates and orders in reactants, results were mostly obtained for SO$_2$ concentrations of 3000 ppm and larger; i.e., considerably above the levels typically found in combustion systems. For this
reason, rate coefficients may not extrapolate well to practical conditions.

The objective of the present work is to study the sulphation of condensed KCl by SO$_2$ in the temperature range 673-1023 K and lower SO$_2$ concentrations than in previous work. Experiments are conducted in a fixed bed reactor with reactant levels of 500-3000 ppm SO$_2$, 1-20% O$_2$, and 4-15% H$_2$O, and the degree of sulphation monitored by measuring the formation of HCl. A rate expression for the sulphation reaction is derived and results are compared to data from literature.

**Experimental**

The experiments were conducted in a fixed bed quartz reactor, with solid KCl placed on a porous quartz plate in an isothermal zone. A schematic of the reactor is shown in Figure 1. Reactant gases (SO$_2$, O$_2$, and H$_2$O in N$_2$) were introduced separately into the reactor and mixed just above the porous plate. The reactor temperatures were measured under inert conditions with a type K thermocouple (accuracy ±3 K). The temperature in the isothermal zone of the reactor was accurate within 10 K. The product gas was collected in the bottom part of the reactor, and led to the online gas analyzers. Heated lines were used to avoid cold-spots where condensation could occur. The concentrations of HCl and SO$_2$ were measured continuously. The HCl analyzer (Servomex Servotough 2510) had an accuracy of ±1% of the measurement range (0-200 or 0-1000 ppm, depending on conditions). The exit concentration of SO$_2$ was measured with an analyzer accuracy of ±3%, but the possible adsorption of SO$_2$ onto tube surfaces contributes to the uncertainty for this species. In selected experiments, the KCl conversion to K$_2$SO$_4$ was
quantified from analysis of the solid residue collected from the tests by ICP (Inductively Coupled Plasma) Spectroscopy. However, the uncertainty with the ICP analysis was considerable, partly due to difficulties in separating the sample from the quartz wool.

The experiments were conducted with commercial solid potassium chloride (purity 99.5%), and a mixture of SO₂, O₂, and N₂ from gas cylinders. Water vapor was added by saturating a nitrogen stream. The KCl was prepared by grinding and sieving to obtain a size range of 90-125 μm. 1 g of sample material was used for each experiment. The KCl sample was placed in between two layers of quartz wool to limit loss of solid or molten material.

After placing the KCl sample inside the quartz reactor, it was exposed to N₂ for 30 minutes to allow the temperature to reach the desired value. Then the N₂ was replaced with a mixture of O₂, SO₂, H₂O, and N₂ (total gas flow of 1000 ml/min STP). After one hour of sulphation, the reactant gas was replaced by inert. The mass of the water bottle was determined and the flows were checked to ensure that they did not deviate significantly from the set-point values.

During experiments, the reactor pressure was about 1.05 atm, varying slightly depending on the packing of the fixed bed. In the results discussed in the present work, the progress of reaction was based on the measurement of the exit concentration of HCl from the reactor. The measured consumption of SO₂ corresponded well to the formation of HCl. Reaction rates based on analysis of the solid residue collected from the tests were in reasonable agreement with data obtained from HCl detection, but involved a significantly larger uncertainty.
Residual particles, collected from selected experiments, were sectioned and analyzed by SEM-EDS (scanning electron microscopy and electron dispersive X-rays spectroscopy). Furthermore, the fixed experiments were supplemented with results obtained from simultaneous thermal analysis (STA) with a heating rate of 5 K min\(^{-1}\).

**Numerical Procedure**

Following Matsuda et al.,\(^4^6\) the reaction rate was defined as \(\frac{dX}{dt}\), where \(X\) is the fractional conversion of KCl. \(X\) is defined as

\[
X = \frac{m_0 - m}{m_0}
\]  

(3)

where \(m_0\) (kg) is the initial mass of the KCl particle and \(m\) (kg) is the mass of the remaining unconverted KCl particle. For each experiment, \(\frac{dX}{dt}\) was determined from the correlation:

\[
\frac{dX}{dt} = \dot{V} [\text{HCl}] \frac{\text{MW}_{\text{KCl}}}{m_{\text{KCl}}}
\]  

(4)

Here \(\dot{V}\) is the total gas flow, \([\text{HCl}]\) is the peak concentration of HCl, \(\text{MW}_{\text{KCl}}\) is the molecular weight of KCl, and \(m_{\text{KCl}}\) is the initial sample mass of KCl.

In the interpretation of the data, it is assumed that the particle is spherical and converted according to an unreacted shrinking core model under chemical reaction control. The assumption of a shrinking core model is based on the results reported by van Lith et al.\(^3^9\) Further support is provided by the SEM-EDS analysis of the residual particles in the present work, as discussed below. Mass transfer limitations in the gas-film or the product layer are neglected, since the particles are small, and, since the rate is determined at low conversions of KCl.
With the assumption of a shrinking core model, the rate of conversion is given as
\[
\frac{dX}{dt} = k'(1 - X)^{2/3} \cdot F(Y_{SO_2}, Y_{O_2}, Y_{H_2O}) \tag{5}
\]
Here, the rate constant \( k' \) [s\(^{-1}\)], in Arrhenius form, describes the temperature dependence, and \( F \) describes the functional dependence on the reactant mole fractions \( Y_i \).

Two formulations of the rate expression were used to analyze the experimental results. The first equation is similar to the one used by Matsuda et al.\(^\text{46}\)
\[
\frac{dX}{dt} = k_A(1 - X)^{2/3}(Y_{SO_2})^l(Y_{O_2})^m(Y_{H_2O})^n \tag{6}
\]
In the second formulation, we employ a Langmuir-Hinshelwood expression to describe the dependence on the \( SO_2 \) concentration:
\[
\frac{dX}{dt} = k_B(1 - X)^{2/3}\frac{Y_{SO_2}}{1 + K \cdot Y_{SO_2}}(Y_{O_2})^m(Y_{H_2O})^n \tag{7}
\]
Equations 6 and 7 are only valid for the specific particle size \( R_0 \) used in the experiments. To predict the sulphation rate for other particle sizes, we derive a surface area based rate constant \( k'_s \) [kg \( m^{-2} \) \( s^{-1} \)], which is assumed to be universal for particles of difference size. Substitution of Eq. 3 for \( X \) into Eq. 5 yields:
\[
\frac{dm}{dt} = -k' \cdot m_0 \cdot \left( \frac{m}{m_0} \right)^{2/3} \cdot F(Y_{SO_2}, Y_{O_2}, Y_{H_2O}) \tag{8}
\]
For a spherical particle, the equation above can be converted to:
\[
\frac{dm}{dt} = -k' \cdot \frac{1}{3} R \cdot \rho_{KCl} \cdot 4\pi r^2 \cdot F(Y_{SO_2}, Y_{O_2}, Y_{H_2O}) \tag{9}
\]
where \( R \) (m) is the initial radius of the particle, \( \rho_{KCl} \) (kg \( m^{-3} \)) is the density of the KCl particle, and \( r \) (m) is the radius of the remaining unconverted
particle. From Eq. 9, the surface area based rate constant $k'_s$ can be obtained:

$$k'_s = k' \cdot \frac{1}{3R} \cdot \rho_{KCl}$$  \hspace{1cm} (10)

Since Eq. 10 is assumed valid for all particle sizes, the conversion-based rate constant $k_1$ (s$^{-1}$) for a particle with an initial radius of $R_1$ can be calculated as:

$$k'_1 = k' \frac{R_0}{R_1}$$  \hspace{1cm} (11)

In the present study, the diameters of the KCl particles were in the range 90-125 $\mu$m. By assuming an equal mass distribution (with an interval of 1 $\mu$m) of the particles in this size range, we calculate a harmonic mean radius $R_0$ of 53.2 $\mu$m.

**Results and Discussion**

Experiments on sulphation of solid KCl were conducted, varying temperature (673-1023 K) and reactant concentrations (500-3000 ppm $SO_2$, 1-20% $O_2$, 4-15% $H_2O$). All reported concentrations are volume based and on a wet basis. In the following, the effect of temperature and gas composition on the sulphation rate is investigated. Based on these data, a model for the rate of sulphation is established and compared with results from the literature.

**Effect of temperature**

For the baseline gas composition (959-965 ppm $SO_2$, 4.8% $O_2$, 3.9-4.6% $H_2O$, balance $N_2$), the temperature was varied in the range 673-1023 K. Figure 2 shows the measured HCl profiles for the different temperatures.
At the lowest temperatures, the amount of HCl generated is comparatively small and the reaction rate derived is more uncertain. Above 900 K, the formation of HCl increases rapidly with temperature. At 1023 K, a second peak in HCl is observed after approximately 2500 s reaction time, indicating a sudden increase in the reaction rate. We attribute this phenomenon to a phase transition from a solid to a melt, likely due to the formation of an eutectic mixture of KCl and K$_2$SO$_4$. The melting is supported by the detection of an increased pressure in the reactor, caused by blocking of the pores in the quartz plate by the molten phase.

To confirm that a KCl-K$_2$SO$_4$ eutectic was formed during the experiments at 1023 K, the collected residual particles were sectioned and analyzed by SEM-EDS. Typical results are presented in Figure 3, where a mixture of KCl-K$_2$SO$_4$ with a lamellar structure is observed. Such a regular lamellar structure is a characteristic microstructure of an eutectic, strongly supporting the presence of a KCl-K$_2$SO$_4$ eutectic under the given experimental conditions. The formation of an eutectic has been reported earlier by Fielder et al. in sulphation of NaCl(s) by SO$_3$ above 900 K. Matsuda et al. reported eutectic formation in sulphation of CaCl$_2$ but not for KCl or NaCl. The SEM-EDS analysis also shows that the core of the KCl particles is unreacted and that the sulphation reaction takes place on the surface. These results support the assumption of a shrinking core model.

Figure 4 shows an Arrhenius plot of the sulphation reaction. It is evident that a change in reaction mechanism takes place between 823 and 873 K, in agreement with observations in the literature for KCl, NaCl, and CaCl$_2$. In the present study, the activation energy for the high-temperature mechanism is determined to be 157 kJ mol$^{-1}$, in good agreement with the values
of 137 kJ mol$^{-1}$ (KCl) and 144 kJ mol$^{-1}$ (NaCl) reported by Matsuda and coworkers,\textsuperscript{45,46} but somewhat higher than the 115 kJ mol$^{-1}$ derived for NaCl by Henriksson and Warnqvist.\textsuperscript{34} Due to the small number of data points in the 623-873 K range and the limited experimental accuracy at low HCl concentrations, we cannot reliably determine the activation energy for the low-temperature mechanism, but our results are consistent with values of 3.4-23 kJ mol$^{-1}$ reported for KCl and NaCl.\textsuperscript{36,45,46}

The reason for the observed change in mechanism is still unresolved. Results from simultaneous thermal analysis (STA) for KCl indicated a phase transition of KCl around 1058 K, but no change in the crystal form of KCl was observed in the temperature range 823-923 K. Potassium sulphate exhibited a reversible change in crystal form at around 860 K, in agreement with literature reports,\textsuperscript{47,48} but the enthalpy of transformation is only about 5.8 kJ mol$^{-1}$\textsuperscript{48} and cannot in itself explain the change in activation energy of the sulphation reaction.

A plausible explanation for the observed change of mechanism is that the sulphation at low temperatures involves a condensed-phase intermediate, perhaps a potassium sulfite, with reduced thermal stability at temperatures above 900 K. Another possibility is that the low-temperature reaction involves SO$_3$, rather than SO$_2$, as reactant. The reaction between KCl(s,l) and SO$_3$ has been shown to proceed essentially without an activation energy.\textsuperscript{35} Even though quartz is not very effective as a catalyst for SO$_2$ oxidation,\textsuperscript{49} its presence (wool bed, reactor surface) may facilitate formation of SO$_3$ in quantities sufficient to explain the observed (small) conversion. A mechanism that involves surface oxidation of SO$_2$ would also help to explain the large scatter in reported sulphation rates in the 600-900 K range (see below).
It should be noted that the sulphation products at low temperatures (e.g. 673 K) may be dominated by potassium pyrosulphate (K₂S₂O₇), which is thermodynamically favored compared to K₂SO₄ under these conditions.⁵⁰ For both SO₂ and SO₃ as reactants, the formation of K₂S₂O₇ is exothermic. When the temperature is increased to a range of 823-873K, decomposition of K₂S₂O₇ to SO₃ + K₂SO₄ (α or β phase) becomes important. This reaction is endothermic, with calculated reaction enthalpies of 65-75 kJ mol⁻¹.⁵⁰

**Effect of reactant concentrations**

A range of experiments were conducted at 923 K to determine the dependence of the sulphation rate on the concentrations of SO₂, O₂, and H₂O. Figure 5 shows results for variation of the SO₂ concentration, maintaining the concentrations of O₂ and H₂O at constant levels. A regression for the range 500-1500 ppm SO₂ is consistent with an \((Y_{SO₂})^{0.78}\) dependence (shown as the long-dashed line). As the SO₂ concentration is increased further (3000 ppm), the reaction order in SO₂ appears to decrease, possibly due to a saturation in SO₂ when adsorbing on the surface. Over the range 500-3000 ppm, the best fit is obtained with \((Y_{SO₂})^{0.59}\) (short-dashed line). These values can be compared with a reaction order of 0.5, obtained for the range 3000-13000 ppm SO₂ by Matsuda et al.⁴⁶ An alternative to a power fit is the Langmuir-Hinshelwood type expression (Eq. 7) of the type \(Y_{SO₂}/(1 + K \cdot Y_{SO₂})\) (shown as a solid line for \(K = 708\)), which may provide a more accurate extrapolation to higher concentrations of SO₂.

Figure 6 shows results for variation of O₂. These data, obtained over a wide range of O₂ concentrations (1-20%), are consistent with a reaction order of
0.37, in good agreement with the value of 0.4, obtained for the range 2.5-15% O₂ by Matsuda et al. The water vapor level was varied between 4.3 and 15% (Figure 7). The water concentration was more difficult to control and to quantify than the other reactant concentrations, but our results show only little sensitivity of the sulphation rate towards H₂O in the investigated range. A best fit to the data yields a reaction order in H₂O of 0.15, but within the uncertainty of the data, the sulphation rate can be assumed independent of [H₂O]. The results obtained by Matsuda et al. indicate that above 923 K the water vapor level (5-20%) has a larger impact on the sulphation rate, but this cannot be verified from the present work.

**Rate expression for KCl sulphation**

Based on the experimental data, we have determined the sulphation rate as a function of temperature (873-1023 K) and reactant concentrations as follows. For SO₂ concentrations of 500-1500 ppm, the Eq. 6 format works well and we get:

\[
\frac{dX}{dt} = 3.7 \cdot 10^6 \exp(-18900/T)(1 - X)^{2/3}(Y_{SO_2})^{0.78}(Y_{O_2})^{0.37} \tag{12}
\]

For a wider range of SO₂ concentrations, we recommend the Eq. 7 format with the following parameters:

\[
\frac{dX}{dt} = 2.7 \cdot 10^7 \exp(-18900/T)(1 - X)^{2/3} \frac{Y_{SO_2}}{1 + 708 \cdot Y_{SO_2}}(Y_{O_2})^{0.37} \tag{13}
\]

The Arrhenius plot in Figure 8 compares the present results with data from the literature by Boonsongsup et al. for NaCl, and Matsuda et al. for NaCl and KCl. The comparison is complicated by the fact that the measurements were conducted in different SO₂ concentration ranges. The data
shown in the figure by Boonsongsup et al. and by Matsuda et al. were obtained at 9000 ppm SO$_2$, while in the present work the SO$_2$ range was 500-3000 ppm. We extrapolate our results to the higher SO$_2$ level using the Langmuir-Hinshelwood formulation (Eq. 7) for the high temperature range (873-1023 K). The two data points obtained at the lowest temperatures were corrected using the ($P_{SO_2}$)$^{0.2}$ dependence reported by Matsuda et al.$^{46}$

The data for the sulphation rate of KCl and NaCl obtained by Matsuda et al.$^{46}$ above 873 K are in good agreement with the results of the present work. Our rate constant for KCl is slightly higher than that reported by Matsuda et al., perhaps because their value is derived for longer reaction times, where product layer diffusion may have affected the sulphation rate. For the low temperature regime, the scatter in the data is significantly larger. Our results are in good agreement with those reported by Boonsongsup et al. and in between data reported by Matsuda et al. for KCl and NaCl, respectively.

**Extrapolation to higher temperatures**

In order to evaluate how well the model extrapolates to higher temperatures, predictions were compared to data reported by Iisa et al.$^{17}$ They studied sulphation of KCl particles (65-125 μm) at temperatures of 1173-1373 K in an entrained flow reactor. At these temperatures, a significant fraction of the KCl evaporates to the gas phase, and three mechanisms of sulphation may be active:

(A) Sulphation of particulate KCl by reaction with SO$_2$

(B) Sulphation of particulate KCl by reaction with SO$_3$
(C) Sulphation of gaseous KCl by reaction with SO$_3$

Part of the inlet SO$_2$ may be oxidized homogeneously to SO$_3$, and presence of SO$_3$ increases the sulphation rate of both particulate KCl$^{35}$ (mechanism B) and gaseous KCl$^{17,19-22}$ (mechanism C) considerably. Issa et al. analyzed both the coarse particles collected in the cyclone and the fine particles captured in the filter; from these data they determined the degree of sulphation of both particulate and gaseous KCl.

The results reported by Issa et al. indicate an accelerated sulphation rate of the particulate KCl at longer residence times in the reactor. We attribute this mostly to interference from mechanisms B and C. Potassium sulphate, formed in the gas-phase (C), may condense on the coarse KCl particles, and also reaction of KCl(s) with SO$_3$ (B) may have contributed to the observed degree of sulphation. The B and C sulphation mechanisms are both controlled by the rate of SO$_3$ formation in the gas-phase. If they were important for the observed sulphation degree of solid KCl particles, the homogeneous and heterogeneous sulphation rates should be similar. Indeed, this is in agreement with the observations of Issa et al. for longer reactor residence times ($>1$ s).

Issa et al.$^{17}$ reported the sulphation degree of particulate KCl as a function of temperature and reactor residence time. Figure 9 compares $dX/dt$ values derived from these data with predictions using equation 7. Unfortunately, data for short residence times were only reported for a temperature of 1373 K (0.6 s). The data shown for 1173 K were obtained for a residence time of 1.0 s and they are more prone to be influenced by mechanisms B and C, since SO$_3$ has had more time to form. Considering the uncertainty, the level of agreement between the entrained flow reactor data and the model is satisfactory.


In-flight sulphation of particulate KCl

To assess the extent of in-flight sulphation of particulate KCl, the conversion has been calculated for different particle sizes and temperatures. The calculations were based on Eq. 13, correcting for the effect of particle radius following Eq. 11:

\[
\frac{dX}{dt} = 2.7 \cdot 10^7 \exp (-18900/T) (1 - X)^{2/3} \frac{Y_{SO_2}}{1 + 708 \cdot Y_{SO_2}} (Y_{O_2})^{0.37} \frac{R_0}{R_1}
\]

(14)

Here, \(R_0\) is 53.2 \(\mu m\); the harmonic mean diameter of the particle size range (90-125 \(\mu m\)) used in deriving the kinetic parameters.

The results are shown in Figure 10, which are obtained based on a gas mixture with 1000 ppm \(SO_2\) and 5% \(O_2\), and a residence time of 1 s. It can be seen that only for very small KCl particles (0.1-1 \(\mu m\)), a considerable in-flight conversion (in the range 1-100\%) can be achieved. However, KCl aerosols, from homogeneous nucleation (at low particle loadings) or from heterogeneous condensation on \(K_2SO_4\) nuclei, are unlikely to form at temperatures above 1100 K. At temperatures below this value, the conversion of the sub-micron particles is limited to below 20\%. For particles with diameters larger than 10 \(\mu m\), the conversion is only a few percent even at very high temperatures. These results indicate that in-flight sulphation of particulate KCl in combustion systems is limited, in agreement with earlier findings.\(^{17,36}\)

Conclusions

The sulphation of condensed KCl by \(SO_2\) was studied in the temperature range 673-1023 K and with reactant concentrations of 500-3000 ppm \(SO_2\),
1-20% O₂, and 4-15% H₂O. Experiments were conducted in a fixed bed reactor and the degree of sulphation monitored by measuring the formation of HCl and analysis of the solid residue. Based on the experimental results, the rate of the sulphation reaction can be described by the expression 

\[ \frac{dX}{dt} = 2.7 \times 10^7 \exp(-18900/T)(1 - X)^{2/3} \frac{Y_{SO_2}}{1 + 708 - Y_{SO_2}} (Y_{O_2})^{0.37}. \]

The model compares well with literature data for sulphation of KCl and NaCl, and the results indicate that it may be applied even at higher SO₂ concentrations and temperatures than those of the present study. Simulations of the condensed phase sulphation of KCl particles with different size indicate that only for KCl particles below 1 μm a considerable in-flight sulphation may be achieved in combustion systems.

Acknowledgements

Funding from EU Contract No. 23946 “Demonstration of a 16 MW High Energy Efficient Corn Stover Biomass Power Plant“, from Energinet.dk as part of the Eranet Bioenergy program, from the Danish National Advanced Technology Foundation, and from FLSmidth A/S is gratefully acknowledged.

References


[53] Elliott, R., Eutectic solidification processing: crystalline and glassy alloys, 1983
Figure 1: Schematic of the fixed bed reactor.
Figure 2: Measured HCl concentrations as a function of temperature and reaction time. Temperature: 673-1023 K; gas composition: 959-965 ppm SO$_2$, 4.8% O$_2$, 3.9-4.6% H$_2$O, balance N$_2$. 
Figure 3: SEM (back-scattered electrons, acceleration voltage 15 kW) image of the sectioned residual particles collected from the KCl sulfation experiment at 1023 K, with the selected areas comprised of: (1) KCl; (2) a mixture of KCl/K₂SO₄ with a molar ratio of about 1:2.1; (3) SiO₂ (quartz wool used in the experiment).
Figure 4: Arrhenius plot for the rate constant of sulphation of KCl and NaCl with SO$_2$. Temperature: 673-1023 K; gas composition: 959-965 ppm SO$_2$, 4.8% O$_2$, 3.9-4.6% H$_2$O, balance N$_2$. 
Figure 5: Comparison between the measured and calculated value of $\frac{dX}{dt}$ as a function of SO$_2$ concentration. Temperature: 923 K; gas composition: 500-3000 ppm SO$_2$, 4.8% O$_2$, 4.0-4.6% H$_2$O, balance N$_2$. 
Figure 6: Comparison between the measured and calculated value of $dX/dt$ as a function of $O_2$ concentration. Temperature: 923 K; gas composition: 959-968 ppm $SO_2$, 1.0-19.9% $O_2$, 3.8-4.6% $H_2O$, balance $N_2$. 
Figure 7: Comparison between the measured and calculated value of $dX/dt$ as a function of $H_2O$ concentration. Temperature: 923 K; gas composition: 947-962 ppm SO$_2$, 4.8% O$_2$, 4.3-15.3% H$_2$O, balance N$_2$. 
Figure 8: Arrhenius plot for the rate constant of sulphation of KCl and NaCl with SO₂. Nominal conditions for the comparison: SO₂: 9000 ppm; O₂: 5.0%; H₂O: 10%; N₂: balance. Literature data from Booonsongsup et al.⁶ for NaCl, and Matsuda et al.⁴ for NaCl and KCl. The present data for KCl were obtained at conditions with 959-965 ppm SO₂, 4.8% O₂, and 3.9-4.6% H₂O. To extrapolate to the conditions of the figure, SO₂ was corrected according to the Langmuir-Hinshelwood expression (high temperature) and to (P_{SO₂})⁰.² (low temperature,⁴) respectively, while no corrections were made for O₂ and H₂O.
Figure 9: Comparison between measured and calculated values of $dX/dt$ as a function of temperature. The experimental data are drawn from the entrained flow reactor work of Lisa et al.\textsuperscript{17} while the calculated values are obtained from equation 7. Temperatures: 1173 K (residence time 1.0 s) and 1373 K (residence time 0.6 s); gas composition: 2% SO\textsubscript{2}, 5% O\textsubscript{2}, 10% H\textsubscript{2}O; N\textsubscript{2}; balance.
Figure 10: Calculated conversion (%) of KCl particles under different size and temperature conditions by using equation 7. The calculations are based on 1000 ppm SO$_2$, 5% O$_2$, and a residence time of 1 s.