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Shedding light on the governing mechanisms for insufficient CO and H₂ burnout in the presence of potassium, chlorine and sulfur

Teresa Berdugo Vilches⁎, Wubin Wengb, Peter Glarborgc, Zhongshan Lib, Henrik Thunmana, Martin Seemann⁴

Division of Energy Technology, Chalmers Tekniska Högskola, Sweden
Division of Combustion Physics, Lund University, P.O. Box 118, S-221 00 Lund, Sweden
Chemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

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ABSTRACT

Based on the experiences of insufficient burnout in industrial fluidized bed furnaces despite adequate mixing and availability of oxidizer, the influence of potassium on CO and H₂ oxidation in combustion environments was investigated. The combustion environments were provided by a laminar flame burner in a range relevant to industrial furnaces, i.e. 845 °C to 1275 °C and excess air ratios ranging from 1.05 to 1.65. Potassium, in the form of KOH, was homogeneously introduced into the hot gas environments to investigate its effect on the radical pool. To quantitatively determine key species that are involved in the oxidation mechanism (CO, H₂, KOH, OH radicals, K atoms), a combination of measurement systems was applied: micro-gas chromatography, broadband UV absorption spectroscopy and tunable diode laser absorption spectroscopy. The inhibition effect of potassium on CO and H₂ oxidation in excess air was experimentally confirmed and attributed to the chain-terminating reaction between KOH, K atoms and OH radicals, which enhanced the OH radical consumption. The addition of chlorine or sulfur could reduce the concentrations of KOH and K atoms and consequently eliminated the inhibition on CO and H₂ oxidation. Existing kinetic mechanisms underestimate the inhibiting effect of potassium and they fail to predict the effect of temperature on CO and H₂ concentration when potassium and sulfur co-exist. This work advances the need to revise existing kinetic mechanisms to fully capture the interplay of K and S in the oxidation of CO and H₂ in industrial fluidized bed furnaces.

1. Introduction

Combustion technologies are important sources of heat and electricity in today’s society, and they are likely to play a role in the future energy system as a stabilizing complement to intermittent energy sources. To ensure that combustion takes place in the most efficient and clean way, combustion units are subject to strict regulations on emissions, e.g. limits on CO, NOₓ, SOₓ, dioxins. Among the regulated emissions, CO should be kept below 150–500 ppm at the stack for a given excess air concentration of usually 6% for biomass and 11% for waste. The exact values depend on the permissions for different plants and are defined in national and local legislation, e.g. Regulation (2001:253) for combustion of waste in Sweden [1].

A common reason for CO emissions is a local deficit of O₂ due to mixing limitations between fuel and air. Therefore, commercial combustors operate with excess air, resulting in a concentration of some percent O₂ at the stack. The problem of CO emissions is exacerbated in facilities that combust biomass and inhomogeneous solid fuels such as waste streams. In those cases, moderate temperatures (typically 750–900 °C) are applied to reduce the risk of uncontrolled ash melt and corrosion issues derived from the impurities in the fuel, as well as prevent overheating of the furnace material; a measure that can also challenge the complete oxidation of CO into CO₂. Besides mixing and temperature, CO oxidation can be influenced by the chemical interaction between the inorganic impurities in the fuel and the fuel oxidation reactions. In fact, even trace levels of active species like alkali compounds can drastically influence the combustion chemistry in thermal conversion processes [2].

The literature on the effect of alkali on the oxidation of CO is inconclusive and the underlying mechanisms are still under discussion. Both, promoting and inhibiting effects of alkali species on CO oxidation have been observed and are theoretically possible [2]. This reflects the strong dependence of the reactions on operating conditions, as well as the complex interrelation between inorganic and organic chemistry.

⁎ Corresponding author.
E-mail address: berdugo@chalmers.se (T. Berdugo Vilches).

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The overall step \( H + OH \rightarrow H_2O \), where two radicals are removed. Radical removing reactions are \( R1 \) and \( R2 \). The sequence corresponds to diradicals removal reactions \([2,9,10]\). According to Glarborg \([2]\), the main inhibitory effect of alkali is mostly attributed to gas-phase radical removing reactions. Contrarily, Ekvall et al. \([8]\) did not observe an influence of \( K \) on the oxidation of \( CO \) during air-combustion of propane in a 100-kW experimental rig at temperatures above 1000 °C, while a promoting effect was found under oxy-fuel conditions.

The inhibiting effect of \( K \) and \( S \) is also relevant to the oxidation of \( CO \) in co-existence with other species present in biomass such as chlorine could also interfere with the \( K \) chemistry \([12]\) and, thereby, influence the \( CO \) oxidation. Chlorine by itself has been found to inhibit \( CO \) oxidation in a number of investigations. Under moist conditions, Roesler et al. \([17]\) found that trace levels of \( HCl \) (0–200 ppm) at atmospheric pressure clearly inhibited \( CO \) oxidation in the temperature range of 500–900 °C. Wu et al. \([18]\) found that the inhibiting effect was more pronounced in oxygen-rich conditions than at stoichiometric or oxygen-lean conditions. The inhibiting effect of \( Cl \) has also been observed under fluidized bed operation in the CANMET 0.8 MW CFBC combustor using coal as fuel and operating at 850 °C \([19,20]\).

Biomass and waste fuels typically contain chlorine, sulfur and potassium. An understanding of the \( CO \) oxidation in large scale combustors calls for a better knowledge of the interplay of these species on the oxidation chemistry. The aim of this work is to shed light on the governing mechanisms for insufficient \( CO \) burnout due to the presence of \( K \), despite adequate mixing and availability of oxidizer that has been observed in large scale combustors. A laminar burner system was employed to map the influence of \( K \) on the oxidation of \( CO \) during air-combustion of propane in a 100-kW experimental rig at temperatures above 1000 °C, while a promoting effect was found under oxy-fuel conditions.

The inhibiting effect of alkali is mostly attributed to gas-phase radical removal reactions \([2,9,10]\). According to Glarborg \([2]\), the main radical removing reactions are \( R1 \) and \( R2 \). The sequence corresponds to the overall step \( H + OH \rightarrow H_2O \), where two radicals are removed.

\[
\begin{align*}
\text{KOH} + H & \rightarrow K + H_2O \quad \text{(R1)} \\
K + OH + M & \rightarrow KOH + M \quad \text{(R2)} \\
H + O_2 & \rightarrow OH + O \quad \text{(R3)} \\
CO + OH & \rightarrow CO_2 + H \quad \text{(R4)}
\end{align*}
\]

Other trace species than alkali, e.g. sulfur and chlorine, are also known to influence the \( CO \) oxidation \([2]\). The experience of the Chalmers fluidized bed boiler in Fig. 1 exemplifies the strong response of the \( CO \) emissions to the addition of elemental sulfur. With 1 kg/h of sulfur the \( CO \) emissions went rapidly from 1200 ppm to zero, in a system containing 3 tons of olivine bed and fed with 1.8 ton/h of biomass. A similar drastic response was observed in a 26-kW bench-scale diffusion flame during combustion of natural gas under slight sub-stoichiometric conditions and with the addition of 0–100 ppm of \( SO_2 \) \([11]\). In contrast, other work has reported that the addition of \( SO_2 \) or higher levels of sulfur in the fuel inhibit \( CO \) oxidation, in a laboratory flow reactor \([12]\) and in the fluidized bed reactors \([13,14]\), respectively. Alzueta et al. \([15]\) described sulfur promotes the oxidation of \( CO \) under nearly stoichiometric conditions, while it mildly inhibits it under fuel lean and rich conditions. Yet, this explanation disagrees with the observations at the Chalmers boiler, where the promoting effect of \( S \) on \( CO \) oxidation occurred with excess air (3.5% vol in the flue gases or excess air ratio 1.2).

Most previous research indicates that the sulfur chemistry has a direct influence on \( CO \) oxidation \([11,15]\), while the experience at Chalmers with \( K \)-containing biomass and addition of \( S \) \([3]\) also points at interrelations between the \( S \) and \( K \) chemistry that affect the \( CO \) oxidation. Hypothetically, this can occur via e.g. sulfation reactions \([8,16]\) that alter the speciation of \( K \) in the reaction environment. Similarly, other species present in biomass such as chlorine could also interfere with the \( K \) chemistry \([12]\) and, thereby, influence the \( CO \) oxidation. Chlorine by itself has also been found to inhibit \( CO \) oxidation in a number of investigations. Under moist conditions, Roesler et al. \([17]\) found that trace levels of \( HCl \) (0–200 ppm) at atmospheric pressure clearly inhibited \( CO \) oxidation in the temperature range of 500–900 °C. Wu et al. \([18]\) found that the inhibiting effect was more pronounced in oxygen-rich conditions than at stoichiometric or oxygen-lean conditions. The inhibiting effect of \( Cl \) has also been observed under fluidized bed operation in the CANMET 0.8 MW CFBC combustor using coal as fuel and operating at 850 °C \([19,20]\).
with potassium. The series of experiments carried out in each set are listed in Table 2. In the first set, potassium was firstly added in different concentrations at constant temperature and excess air ratio (series K1); secondly, the excess air ratio was varied at constant temperature and with a fixed seeding rate of potassium (series K2); and thirdly, the temperature was varied at constant excess air ratio and seeding rate of potassium (series K3). In the second experimental set, the influence of sulfur in co-existence with a fixed seeding flow of potassium was investigated at different temperatures while keeping the excess air ratio constant (series SK). Finally, the effect of chlorine was investigated with a single test (labelled ClK in Table 2) that involved the simultaneous addition of K and Cl, and that was compared to a similar case with addition of K and in the absence of Cl.

The concentrations of CO and H2 in the flue gas was measured with a micro gas chromatograph (µ-GC); the concentration of total potassium was measured using He and Ar as carrier gases, respectively. A sampling tube made by stainless steel was used to extract the flue gas at a height of about 5 mm above the burner outlet. A gas sample of approximately 300 mL was collected in a gas bag with the help of a syringe. During sampling, the gas was cooled down in the sampling tube, and it was filtered and dried in a LC-NH2 adsorption column before entering the gas bag. Thereafter, the gas bag was connected to the inlet of the µ-GC, so the instrument could take samples from it.

For each test, one gas bag was filled with a sample gas, and its content was analysed five times, i.e. five repeat chromatograms were created per flame conditions. Each chromatogram is the result of a point-injection (10–30 ms sampling time), which was taken in intervals of 4 min to allow the necessary analysis time required by the µ-GC. The concentrations of H2 and CO presented in this work for each test are the average of the five repeat chromatograms, and the error bars represent the corresponding standard deviation.

Table 1

<table>
<thead>
<tr>
<th>Flame Case</th>
<th>Gas flow rate (sl/min)</th>
<th>Excess air ratio λ</th>
<th>Gas product Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jet-flow</td>
<td>Co-flow</td>
<td></td>
</tr>
<tr>
<td>CH4 Air</td>
<td>O2</td>
<td>N2 Air</td>
<td></td>
</tr>
<tr>
<td>T1O1</td>
<td>2.69</td>
<td>13.29</td>
<td>2.89</td>
</tr>
<tr>
<td>T2O1</td>
<td>2.48</td>
<td>12.91</td>
<td>2.45</td>
</tr>
<tr>
<td>T3O1</td>
<td>2.27</td>
<td>11.84</td>
<td>2.25</td>
</tr>
<tr>
<td>T4O1</td>
<td>1.86</td>
<td>9.68</td>
<td>1.83</td>
</tr>
<tr>
<td>T4O2</td>
<td>1.86</td>
<td>9.68</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Experimental sets</th>
<th>Series</th>
<th>Variable</th>
<th>Range of variation</th>
<th>Flame conditions</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Effect of potassium on CO oxidation</td>
<td>K1</td>
<td>Potassium seeding</td>
<td>0–32 ppm</td>
<td>T4O1</td>
<td>K-seeding11 ppm</td>
</tr>
<tr>
<td></td>
<td>K2</td>
<td>Excess air ratio λ</td>
<td>1.04–1.67</td>
<td>T4O1, T4O2, T4O3</td>
<td>K-seeding11 ppm</td>
</tr>
<tr>
<td></td>
<td>K3</td>
<td>Temperature</td>
<td>845–1275 °C</td>
<td>T1O1, T2O1, T3O1, T4O1</td>
<td>K-seeding 11 ppm</td>
</tr>
<tr>
<td>(2) Effect of Cl and S on CO oxidation in co-existence with K</td>
<td>SK</td>
<td>Temperature</td>
<td>845–1275 °C</td>
<td>T1O1, T2O1, T3O1, T4O1</td>
<td>S-seeding150 ppm</td>
</tr>
<tr>
<td></td>
<td>ClK</td>
<td>–</td>
<td>–</td>
<td>T4O1</td>
<td>Cl-seeding 400 ppm</td>
</tr>
</tbody>
</table>

*Flame conditions described in detail in Table 1.

2.2. Seeding of K, S and Cl

To introduce potassium into the hot gases, a water solution of potassium carbonate with a concentration of 0.5 mol/l was used. As shown in Fig. 2, solution fogs were generated through an ultrasonic fogger and transported by air into the jet chamber. As the potassium carbonate passed through the flames, gas-phase potassium hydroxide can be formed in the hot gas. The potassium concentration in the hot gas could be adjusted from 0 to 31 ppm by varying the flow rate of the air for transporting solution fogs. The concentration of total potassium seeded into the hot flue gas was estimated from the measurements of KOH and K atoms. The seeding of trace amount of K2CO3 was observed to have negligible effect on the flue gas temperature.

In the experiments with sulfur, SO2 was seeded from a gas cylinder into the hot gas after the mixing with co-flow air/N2. To seed chlorine to the flame, chloroform (CHCl3) was added into the hot gas system. The CHCl3 liquid was stored in a bubbler and kept at 10 °C using a chilled bath (PolyScience). A N2 flow was used to carry CHCl3 vapor into the jet chamber. Potassium chloride was generated by the co-seeding of potassium carbonate. The seeding of sulfur was done at a concentration of 150 ppm while the seeding of chlorine was approximately 400 ppm, which could fully convert KOH in to K2SO4 or KCl at the temperature of 845 °C.

2.3. GC system

The micro-gas chromatograph (µ-GC) was a Varian CP4900 with two channels equipped with a PoraplotQ and a M S5A column, and using He and Ar as carrier gases, respectively. A sampling tube made by stainless steel was used to extract the flue gas at a height of about 5 mm above the burner outlet. A gas sample of approximately 300 mL was collected in a gas bag with the help of a syringe. During sampling, the gas was cooled down in the sampling tube, and it was filtered and dried in a LC-NH2 adsorption column before entering the gas bag. Thereafter, the gas bag was connected to the inlet of the µ-GC, so the instrument could take samples from it.

For each test, one gas bag was filled with a sample gas, and its content was analysed five times, i.e. five repeat chromatograms were created per flame conditions. Each chromatogram is the result of a point-injection (10–30 ms sampling time), which was taken in intervals of 4 min to allow the necessary analysis time required by the µ-GC. The concentrations of H2 and CO presented in this work for each test are the average of the five repeat chromatograms, and the error bars represent the corresponding standard deviation.

2.4. TDLAS system

The TDLAS system applied in the measurement of K atoms has been previously described in refs. [23,24]. In this system, a laser at wavelength of 769.89 nm was used to detect the potassium atoms with its transition of 4S1/2→4P1/2. The laser was provided by an external cavity laser (Toptica, DL100), and it had a power of about 3 mW and a beam size of about 1 mm². The cavity laser was controlled by an...
analogy control package with a temperature control module (DTC 110), a current control module (DCC 110), and a scan module (SC 110). The scan module was adopted to make the laser have scanning of the wavelength with a range over 35 GHz at a repetition rate of 100 Hz. The power of the laser was monitored by two photodiodes (PDA100A, Thorlabs), and the scanning range was measured by a high-finesse confocal Fabry-Perot etalon (Topoca, FPI 100), shown in Fig. 2(b). As the laser passed through the hot flue gas containing potassium atoms, the light was absorbed and the concentration of potassium atoms can be derived through the Beer-Lambert law \[24,25\]. In the present study, the laser beam located at about 5 mm above the burner outlet with a path length of 8.5 cm. The potassium line was determined to have a Voigt profile with a full width at half maximum (FWHM) of 5.34 GHz.

2.5. UV absorption spectroscopy system

In the experiments, the concentrations of K atoms, KOH, KCl and OH radicals were measured by UV absorption spectroscopy in the hot gas environments. As shown in Fig. 2(c), a deuterium lamp was used to generate a collimated UV light with a beam size of about 5 mm. The UV light was guided by five UV-enhanced aluminium mirrors to pass through the hot gas with a path length of 522 mm \[26\]. After the passage, the light was collected and analysed by a spectrometer.

The experimental absorbance data were obtained through the division between the intensity of UV light after the passage of the flame with potassium seeding and the one without potassium seeding. It was used to determine the concentration of KOH and KCl in the hot gas through the Beer-Lambert law. In the calculation, the UV absorption cross-sections of KOH and KCl measured by Weng et al. \[24\] was used. Typical UV absorption spectrum obtained in KOH concentration measurement are shown in Fig. 3 represented by the black dots. Two absorption peaks centred at around 250 nm and 330 nm can be observed due to the absorption of gas-phase KOH, as described in our previous studies. The absorbance of KOH was simulated using its UV absorption cross-sections, and it could be well overlapped to the measured results as the concentration was set to 11.5 ppm (see Fig. 3 with a red line). The differences between the measured one and the simulated one are the additional absorption at around 404 nm and two dips at around 283 nm and 310 nm. The former one was from the K-atom absorption, while those two dips were formed due to the reduction of OH radicals in the flame after the seeding of potassium. In the measurement of OH radicals, the absorption at around 310 nm were obtained through the division between the intensity of UV light after the passage of the flame and the one without flame. A typical experimental result was shown in the inset of Fig. 3 with black dots. This measured OH absorbance can be fitted (as shown by the solid line) to retrieve the OH concentration.

Fig. 2. Schematic of the experimental setup. (a) The structure of the burner system with GC sampling system. (b) TDLAS system for K-atom measurement. (c) UV absorption spectroscopy system for quantitative measurements of KOH, KCl and OH radical.

Fig. 3. UV absorption spectrum obtained for KOH and OH measurement. The measured absorbance values were presented with black dot and the corresponding fitting curves based on UV-absorption cross-section of KOH \[24\] and OH \[27,28\] were shown with red lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
through LIFBASE [28]. As a result of the line-of-sight nature of the absorption spectroscopy technique, the concentration obtained by this method is the average concentration along the horizontal direction from the centre to the edge of the hot flue gas.

3. Modelling

The simulations were conducted using Chemkin PRO [29] as described by Weng et al. [30]. A one-dimensional stagnation reactor in Chemkin PRO was adopted to simulate the reaction occurring in the hot flue gas along the central axial direction. The gas inlet of the reactor was assigned to be the mixture of the hot flue gas at 3 mm from the jet flame fronts and the co-flow gas. The composition of the hot flue gas produced from the premixed jet flames was obtained using a one-dimensional free propagation premixed flame model in Chemkin PRO with the GRI-3.0 mechanism [31]. The temperature along the axial direction in the reactor was set to be the one measured by a type B thermocouple in the burner. The measured temperature was corrected based on the heat transfer theory due to heat losses by thermal radiation. The axial distance in the reactor was set to 64 mm, which was the distance between the flame front and the flow stabilizer. The horizontal distribution of the species concentration was obtained using a one-dimensional opposed-flow model in Chemkin PRO as reported by Weng et al. [30]. Through this model, the reaction between the hot flue gas and the ambient air on the edge of the hot flue gas was mimicked. Average concentrations on the horizontal direction were derived from the horizontal distribution of species obtained in the simulations to obtain a result that could be compared to the measurements by absorption spectroscopy. Thus, both the theoretical and experimental concentrations shown in the results section refer to the average on the horizontal direction.

The modelling was conducted with a chemical kinetic model that accounted for both the K–Cl–S interactions, including chlorination and sulfation of potassium, and the impact of the trace species on the O/H radical pool. With a few changes, the K–Cl–S mechanism reported by Weng et al. [16] was chosen for the calculations. This mechanism draws on previous work on alkali metals [32–34] as well as sulfur [35] and chlorine [36] chemistry. In the present work, the alkali subset was revised, with a particular emphasis on the interaction of potassium species with the radical pool. The full mechanism is available as Supplementary Material.

Reactions of potassium species with the radical pool were discussed in previous work [2,7,32]. Few of these steps have been characterized experimentally, and most rate constants have been estimated by analogy with reactions of sodium and lithium. Most of the K/O/H subset is the same as that proposed by Glarborg and Marshall [32]. However, the thermochemistry for KO2 and the rate constant for 

\[ \text{K} + \text{O}_2 + \text{M} = \text{KO}_2 + \text{M} \]

were drawn from the more recent work of Sorvajärvi et al. [37]. Under oxidizing conditions, the KO2 radical may play an important role due to its relatively high thermal stability. Alkali superoxides have been reported to enhance radical removal in premixed flames [38–41] and KO2 is believed to participate in the reaction sequences leading to sulfation of KOH [42]. While the 

\[ \text{K} + \text{O}_2 + \text{M} \]

reaction is now well established, there are no measurements available for the chain terminating step 

\[ \text{KO}_2 + \text{OH} = \text{KOH} + \text{O}_2 \]

in the present work, we have chosen a rate constant for 

\[ 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

this value is possibly an upper limit. Another reaction of interest is the oxidation of CO by KO2 to form CO2 + KO. Perry and Miller [43] set this step to be very fast, with a rate constant of 

\[ 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

but their modelling predictions were not sensitive to the value. The Perry and Miller rate constant, which is sufficiently fast to eliminate inhibition of CO oxidization by potassium species under the present conditions, is not supported by any experimental or theoretical work, and we believe that a more realistic value is 

\[ 2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \].
4. Results

The concentration of CO, H2, KOH, OH and K for the experimental series listed in Table 2 are shown in Figs. 4–11. The measurements are presented and discussed in two parts corresponding to the two sets of experiments in Table 2: those related to the influence of potassium on CO oxidation at different operating conditions; and those related to the influence of sulfur and chlorine in co-existence with K.

4.1. The effect of operating conditions on inhibition by KOH

Fig. 4 shows results for K atoms and OH measured in a hot flue gas temperature of 845 °C and an excess air ratio of 1.04, i.e. series labelled as K1 in Table 2. The concentration of K atoms increased with the total potassium seeded but levelled out at high potassium loadings. The concentration of OH decreased strongly as the total potassium concentration was increased from 0 to 2 ppm. With potassium levels above 2 ppm, the OH radical concentration in the hot gas was below the detection limit. This shows that the presence of K atoms strongly enhances the consumption of OH radicals in the hot gas environment.

The corresponding concentrations of CO and H2, measured by the µ-GC, are shown in Fig. 5. The levels of CO and H2 increased from 0 ppm to 1800 ppm and 700 ppm, respectively, as the potassium seeding increased to 31 ppm. As the concentration of potassium in the flame increased, the concentrations of CO and H2 increase until they level off. This trend is in agreement with that obtained by Hindiyarti et al. [7] in

Fig. 7. The variation of the concentration of CO and H2 at different excess air ratio with a temperature of 845 °C and 11 ppm K seeding.

Fig. 8. The variation of the concentration of KOH (a) and K atoms (b) at different temperature and SO2 seeding at excess air ratio of 1.04 and about 11 ppm of K seeding.

Fig. 9. The variation of the concentration of OH radical at different temperature with an excess air ratio of 1.04. The red line indicates the case without K and SO2 seeding; black line indicates the case with K seeding but without SO2 seeding; blue line indicates the case with K and SO2 seeding. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 10. The variation of the concentration of CO at different temperature with an excess air ratio of 1.04. The red line indicates the case without K and SO2 seeding; black line indicates the case with K seeding but without SO2 seeding; blue line indicates the case with K and SO2 seeding. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 11. The variation of the concentration of OH radical at different temperature with an excess air ratio of 1.04. The red line indicates the case without K and SO2 seeding; black line indicates the case with K seeding but without SO2 seeding; blue line indicates the case with K and SO2 seeding. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The results confirm that potassium has a strong inhibiting effect on the oxidation of CO and H2. The modelling predictions are in qualitative agreement with the measurements, but there are quantitative differences. While the K atom concentration is slightly underpredicted, the impact of K on the OH level is significantly smaller than observed. The simulations correctly predict a significant inhibition of the oxidation of CO by the addition of potassium, but the effect on H2 is underpredicted.

The inhibiting effect of potassium on the oxidation of CO/H2 in the hot flue gas was also observed at higher excess air ratios, i.e., $\lambda = 1.04$–1.67, as shown in Fig. 6. In this experimental series (series K2 in Table 2), the excess air was adjusted by modifying the amount of air and N2 in the co-flow. The temperature was kept constant to 845 °C and the potassium seeding to 11 ppm. The concentration of K atoms decreased significantly with the increase of excess air ratio. However, all the cases showed a significant consumption of OH. The concentrations of CO and H2 are shown in Fig. 7, where the inhibiting effect becomes weaker with the increase of excess air ratio. Under the conditions tested, the inhibiting effect of K on the oxidation of H2 can no longer be detected at excess air ratios above 1.35.

The simulation results are in reasonable agreement with the experimental data. Similar to the observations at $\lambda = 1.04$, the OH concentration in the presence of potassium is overpredicted, while at zero KOH feeding, OH is predicted within 30%.

In the experimental series K3 (see Table 2), the temperature was varied in the range 845–1275 °C, while the excess air ratio was kept at 1.04 and the seeding of K2CO3 corresponded to 11 ppm of total potassium. The resulting concentrations of KOH and K atoms are presented in Fig. 8, and the concentration of OH in the cases with and without K is shown in Fig. 9 (see cases without sulfur seeding in the figures). Potassium can enhance the consumption of OH under different temperatures. The corresponding concentrations of CO and H2 in the hot gas with and without potassium seeding are shown in Fig. 10 and Fig. 11, respectively. The inhibition effect was weakened with the increase of temperature and there is almost no effect as the gas temperature increased to 1275 °C. This is in line with the findings of Ekvall et al. [8] that found no inhibiting effect by potassium at temperatures above 1000 °C.

The model predicts the variation in the concentration of potassium and OH radicals as a function of flue gas temperature satisfactorily. The difference between the trends of the concentration of K atoms obtained in the simulation and in experiment might be caused by the small in-homogeneity of the oxygen concentration in the hot flue gas considering the strong influence of oxygen concentration on the K atom concentration as shown in Fig. 6, but still the simulation and experimental results were at the same concentration level and much smaller than the concentration of KOH as shown in Fig. 8.

4.2. Influence of sulfur and chlorine on K-inhibition

The results derived from the tests with seeding of sulfur are shown in Figs. 8–11, where they are labelled as with SO2. In the cases with co-seeding of potassium (series SK in Table 2), the addition of sulfur show larger influence in the low temperature range compared to the cases at higher temperature. For instance, with the addition of sulfur at 845 °C the concentrations became closer to the conditions without potassium seeding (compare black and blue solid lines in Figs. 10–11). This observation is in line with the sulfation reaction [8]. At 845 °C, the presence of sulfur reduces the formation of K atoms and promotes conversion of KOH to K2SO4 particles. Consequently, more OH survived at this temperature, as shown in Fig. 9. Due to the removal of gas phase potassium by the sulfation process the inhibitory effect of potassium is mitigated.

The results prove the interplay between potassium and sulfur in the CO oxidation under the conditions tested, and confirm the hypothesized mechanism involved in the large scale tests at the Chalmers unit [3]. Therefore, the direct effect of sulfur in the oxidation process, as described by several authors for fuels that are free of impurities [11–15] is not sufficient to capture the influence of sulfur in combustion units with more complex fuels. The complexity of the reaction process is increased by the dependence of the behaviour of sulfur at different temperatures as seen in Figs. 10–11 and air excess ratio as described by Alzueta et al. [15].

In the test with seeding of chlorine (ClK in Table 2), the presence of approximately 400 ppm of Cl caused all the potassium in the hot gas to be converted into KCl, which was measured by the UV absorption system, as shown in Fig. 8. After seeding of Cl, a much smaller level of K atoms was detected; about 30 times smaller compared to the KOH case. At the same time, the OH concentration increased from 0 ppm to 10 ppm, as presented in Figs. 8 and 9, while the H2 and CO concentrations reduced to 0 ppm (cf. Figs. 10 and 11). This is in contrast to the inhibiting effect of Cl on the oxidation of CO commonly reported in literature [17–20], which emphasizes the relevance of the combined effect of active species in complex systems. The data show clearly that the presence of sulphur or chlorine effectively eliminate the inhibition effect of potassium on the CO/H2.

The model predicts correctly the removal of KOH and K atoms with SO2 or Cl seeding, especially at the temperature of 845 °C. Potassium sulfate and potassium chlorine are more stable in the gas phase than potassium hydroxide, resulting in lower predicted concentrations of K atoms in the hot flue gas and higher levels of OH radicals (cf. Fig. 9). As a result, the inhibition effect on CO oxidation is weakened (cf. Fig. 10). However, at the temperature above 985 °C, a larger deviation of the CO concentration in the cases with and without K as shown in Fig. 10–11.

5. Conclusion

This work sheds light on the true mechanism behind insufficient combustion in industrial furnaces in the presence of potassium despite adequate mixing and availability of oxidizer. It is demonstrated that trace level of potassium, i.e. tenths of ppm, inhibits the gas-phase oxidation of CO and H2 in the temperature range of 845–1275 °C and equivalence ratio of 1.04–1.65. Up to 2000 ppm CO and 700 ppm H2 was observed to survive the oxidation in oxygen rich hot environments.
due to the co-existence of trace amount of potassium. The experiments showed that higher temperature and higher oxygen concentration, respectively, weakens the inhibiting effect of potassium. The reduction of OH concentration due to the existence of K atoms is experimentally measured and identified as the main cause for the inhibition of the oxidation of CO and H2. It was further shown that salsation of the potassium species led the effect to be eliminated. These findings provide an explanation to the casualty between increasing CO concentration and the presence of potassium in flue gases, as well as to the positive impact of sulfur additions in large scale combustion units on the CO emissions. Existing kinetic models capture the qualitative interrelation between potassium, OH radicals, CO, and H2, respectively, at $845 ^\circ C$ and excess air ratio 1.04, as well as the effect of varying excess air ratio. However, the inhibiting effect of potassium is more intense in practice than what the predictions indicate. The model fails to predict the experimental trends at varying temperature when sulfur and potassium coexist in the combustion environment, and the predictions of H2 concentration are generally less accurate than those for CO. Overall, this work serves as a basis for the improvement of the theoretical description of the reaction mechanism involved in the inhibition of H2 and CO oxidation by potassium species and calls for the revision of existing mechanisms.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References