



Synergistic alkali diagnostics: PF-TDLAS and surface ionization detection in a high-temperature reactor

Downloaded from: <https://research.chalmers.se>, 2026-10-15 07:45 UTC

Citation for the original published paper (version of record):

Andersson, V., Thorin, E., Allguren, T. et al (2026). Synergistic alkali diagnostics: PF-TDLAS and surface ionization detection in a high-temperature reactor. Proceedings of the Combustion Institute, 42. <http://dx.doi.org/10.1016/j.proci.2026.106578>

N.B. When citing this work, cite the original published paper.



Contents lists available at ScienceDirect

Proceedings of the Combustion Institute

journal homepage: www.elsevier.com/locate/proci



Synergistic alkali diagnostics: PF-TDLAS and surface ionization detection in a high-temperature reactor

Viktor Andersson^{a,*}, Emil Thorin^b, Thomas Allguren^a, Florian M. Schmidt^b, Klas Andersson^a

^a Department of Space-, Earth- and Environment, Chalmers University of Technology, SE-416 96, Gothenburg, Sweden

^b Department of Applied Physics and Electronics, Umeå University, 90187, Umeå, Sweden

ARTICLE INFO

Keywords:

Online alkali measurement
Surface ionization
Laser absorption
High-temperature alkali chemistry

ABSTRACT

Alkali plays a critical role in most systems using biogenic fuels, yet quantification is difficult and often method-dependent, due to partitioning between particles and gas, chemical conversion, and strong interactions with surrounding surfaces. Building on the limited prior work combining online alkali diagnostics, we demonstrate a combined diagnostic approach using photofragmentation tunable diode laser absorption spectroscopy (PF-TDLAS); in situ, path-averaged, gaseous potassium chloride (KCl) and potassium hydroxide (KOH) and surface ionization detection (SID; point-sampled total potassium (K), gas and particles) in a well-controlled heated reactor with potassium aerosol seeding. Reactor temperature, atmosphere (air, N₂, CO₂), and the amount and chemical form of injected potassium (chloride, hydroxide, carbonate or sulfate) were varied, and the data were interpreted with computational fluid dynamics (CFD) and thermodynamic equilibrium calculations. Together, the diagnostics resolve potassium partitioning and speciation and quantify what reaches an extraction point: at low temperature they indicate particulate K (high SID, negligible PF-TDLAS signals); at higher temperatures, they capture the particle-to-gas transition. In this work, the transition occurred around 700 °C rather than ~550 °C predicted by equilibrium, since the injected jet remained colder locally (CFD). At 900 °C, both diagnostics respond consistently in terms of absolute K concentrations and as a function of alkali seeding, while revealing speciation differences (KCl(g) for KCl seeding; KOH(g) plus minor KCl(g) for KOH seeding). Atmosphere and seed chemistry further modulate the signals: CO₂ reduces delivered K-loading and promotes carbonate formation during KOH seeding, suppressing KOH(g) in PF-TDLAS, while maintaining elevated total-K in the SID. This combined framework shows that alkali measurement is intrinsically multi-factor and that PF-TDLAS and SID should be applied synergistically, not interchangeably.

Novelty and significance statement: Building on the only earlier combined optical/SID alkali study known to us, we present a coordinated, quantitative PF-TDLAS/SID deployment in a more well-controlled high-temperature reactor, substantially expanding the scope by varying temperature, atmosphere, and the amount of injected potassium, and by adding KOH, K₂CO₃, and K₂SO₄ seeding. PF-TDLAS provides in situ, path-averaged gas-phase KCl(g) and KOH(g), while SID measures extractive total potassium (gas and particles). The novelty lies in integrating these complementary measurements with CFD-resolved flow and temperature fields and thermodynamic equilibrium calculations to develop a mechanistic interpretation framework for alkali quantification under non-uniform reactor conditions. This framework rationalizes how phase-partitioning, transport/surface losses, spatial non-uniformity, sampling bias, and chemistry-dependent transformations jointly govern the PF-TDLAS and SID signals. The result is a transferable framework for robust alkali quantification with repeatable sub-ppm sensitivity, improving cross-comparability for combustion-relevant systems where alkali partitioning and losses govern fouling, corrosion, emissions, and catalytic effects.

* Corresponding author.

E-mail address: viktand@chalmers.se (V. Andersson).

<https://doi.org/10.1016/j.proci.2026.106578>

Received 13 March 2026; Accepted 15 June 2026

Available online 22 September 2026

1540-7489/© 2026 The Authors. Published by Elsevier Inc. on behalf of The Combustion Institute. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Alkali species (mainly K and Na) are central in high-temperature systems like biomass and waste conversion, recycling and catalytic processing. They contribute to operational challenges such as corrosion, fouling, aerosol formation, and particle agglomeration, while also catalyzing key processes such as fuel cracking, gasification reactions, and char conversion [1]. Quantification is vital both for mitigating damage and exploiting desirable chemistry, but difficult in practice as alkali repartitions between particles and gas, interconverts (depending on availability of Cl^- , OH^- , CO_3^{2-} , SO_4^{2-} etc.) and interacts strongly with reactor and sampling surfaces [2]. Hence reported concentrations depend on gas composition, temperature, mixing, and sampling strategy, not only on bulk conditions. This work focuses on potassium, the dominant and often most influential alkali species in biomass systems [3].

Two diagnostic approaches are widely used but rarely combined. In

situ optical methods, such as photofragmentation tunable diode laser absorption spectroscopy (PF-TDLAS), provide time-resolved, path-averaged measurements of gaseous K-compounds [4]. Extractive methods, such as surface ionization detection (SID), measure total alkali (gas and particles) in a sampled stream [5]. Coordinated applications are vital to separate true alkali chemistry from transport, surface interaction, or sampling bias.

In this work, potassium aerosol compounds are seeded into a heated reactor while potassium is measured with PF-TDLAS and SID simultaneously. Reactor temperature, gas atmosphere, and the amount and chemical form of the injected potassium are varied, and the results are interpreted using thermodynamic equilibrium calculations (TECs) and computational fluid dynamics (CFD). Objectives are to: (i) compare PF-TDLAS and SID under similar conditions; (ii) resolve the alkali particle-to-gas transition; (iii) estimate system losses and sampling bias; and (iv) show how the diagnostics complement each other to capture detailed alkali behavior. To our knowledge, coordinated alkali measurements

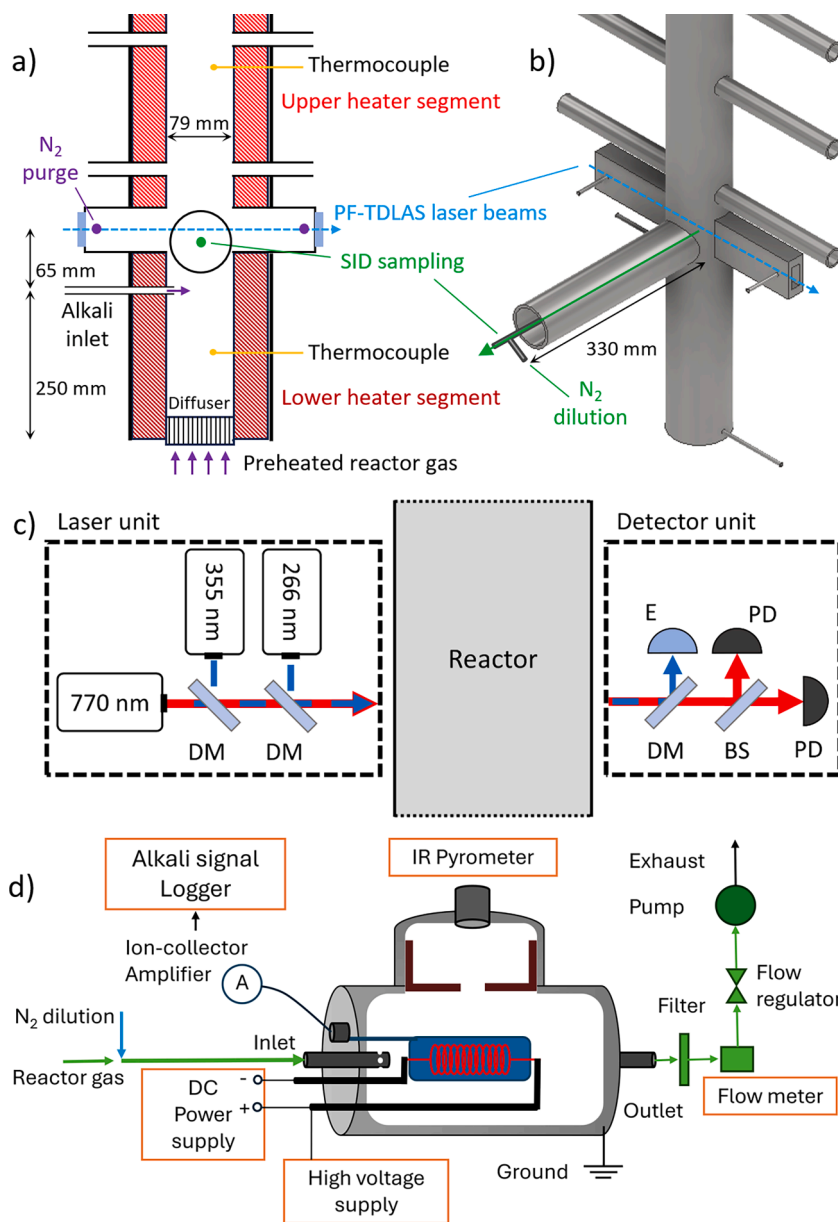


Fig. 1. Reactor schematic in (a) 2D and (b) 3D, showing alkali measurement zones and alkali seeding port. (c) Schematic of the PF-TDLAS system, DM – dichroic mirror, BS – beamsplitter, E – energy meter, PD – photodetector. (d) Schematic of a SID including a heated filament (red), ion collector (blue), and the surrounding equipment.

combining optical diagnostics and SID have only been reported once previously [6]. This study extends that work by adding KOH, K_2CO_3 , and K_2SO_4 seeding, using a more well-controlled reactor, and integrating CFD and TEC analysis to establish a unified framework for interpreting phase partitioning, chemistry-dependent speciation, transport losses, and measurement bias across conditions.

2. Experimental setup

The experiments were conducted in a vertical up-draft reactor (Fig. 1a–b.), consisting of a 95 cm tall stainless-steel tube (253MA) with an inner diameter of 79 mm. The reactor temperature was controlled by two cylindrical electric heating elements, each consisting of two half-cylinder resistive heaters (Fibrothal). Pre-heated gas entered the bottom of the reactor at a flow rate of $2.5 \text{ L}\cdot\text{min}^{-1}$. The reactor gas atmosphere varied between air, N_2 and CO_2 . The reactor featured four see-through ports at different heights, three with circular cross section and the bottom one with rectangular cross section, and one cylindrical single-ended port aligned perpendicularly to the lowest optical port. A PF-TDLAS system (Fig. 1c) was connected to the lowest optical port for in situ measurements of gas-phase KOH and KCl (blue dashed line in Fig. 1a). This port was fitted with 3° wedged CaF_2 windows and purged with $0.5 \text{ L}\cdot\text{min}^{-1} N_2$ or CO_2 to prevent window fouling and gas intrusion to the port extension. For the SID measurements, reactor gases were continuously extracted at $200 \text{ mL}\cdot\text{min}^{-1}$ through a stainless-steel tube with 4 mm inner diameter, inserted into the reactor center through the single-ended port (green arrow in Fig. 1b). This flow corresponds to $<5\%$ of the total inlet flow and is therefore not expected to significantly perturb the global reactor conditions. The extracted gases were rapidly diluted with $1.2 \text{ L}\cdot\text{min}^{-1} N_2$, leading to rapid cooling that promotes nucleation of gaseous potassium species into submicron particles. These particles are carried by the resulting $1.4 \text{ L}\cdot\text{min}^{-1}$ stream and transported to the SID with relatively low and well-characterized losses compared to gas-phase species [7,8]. Consequently, the SID measures the fraction of potassium (gas and particles) that survives transport to the detector, rather than the in situ gas-phase concentration in the reactor. Alkali aerosol losses in the sampling lines were accounted for, according to previous work [9]. Remaining measurement ports were sealed during experiments.

A stable and controllable flow of alkali aerosol particles were introduced 65 mm below the measurement zone through a tube with inner diameter of 4 mm. The aerosols consisted of either KCl, KOH, K_2CO_3 or K_2SO_4 suspended in a carrier flow of $2.0 \text{ L}\cdot\text{min}^{-1}$. The aerosols, with a mean mode particle diameter around 50 nm, were generated with a constant-output atomizer (TSI 3076) by atomizing aqueous alkali solutions with the same gas as used for the reactor gas (air, N_2 or CO_2) through a critical orifice. The particle mass concentration, which is proportional to particle size, was controlled via the solution concentration.

In the CO_2 experiments, the MFCs were operated at the same nominal readings as for air/ N_2 . Because the manufacturer-specified correction factor for CO_2 is 0.7 [10], the actual CO_2 volumetric flows were approximately 30% lower: 1.75, 0.35, and $1.4 \text{ L}\cdot\text{min}^{-1}$ reactor gases, window purge gas and aerosol gas, respectively. This affected aerosol formation, delivery and reactor flow conditions. The SID dilution gas was N_2 in all experiments and was therefore not affected.

2.1. PF-TDLAS alkali diagnostics

The PF-TDLAS technique detects KOH and KCl by exploiting dissociative transitions, where atomic K fragments are produced by photo-fragmentation of KOH and KCl by two pulsed UV lasers (266 and 355 nm) and probed with a third laser at 770 nm, from which the concentrations of KOH and KCl can be calculated according to [11]. The system comprises a laser unit, housing three overlapping beams combined by dichroic mirrors, and a detector unit, where the UV beams are separated

from the 770 nm probe and sent to an energy meter, while the probe beam is split and guided to two photodetectors: a detector measuring the momentary increase in atomic K after fragmentation of KOH and KCl by the UV pulses, and a detector monitoring background atomic K using tunable diode laser absorption spectroscopy (TDLAS). The PF-TDLAS accuracy is obtained by propagation of uncertainties in key experimental parameters, resulting in an absolute accuracy of 10% based on previous work [12–14]. The KOH and KCl concentrations are derived from the absorbance of the K fragments, experimental parameters (temperature and path length) and fundamental constants [11]. In this work, the detection limit was around 10 ppb for both KOH and KCl, as defined by the measurement noise level.

The system was operated at an acquisition rate of 50 Hz and each measurement consisted of an average of 25 acquisitions, resulting in a temporal resolution of 0.5 s. In this study, the reactor temperatures were too low to produce detectable levels of background atomic K (detection limit 0.3 ppb). In such cases, the optimal settings for K fragment detection with respect to the atomic K absorption profile must be found manually for quantification of KOH and KCl. This procedure is described in Fig. S1 in SI. Further details on PF-TDLAS design and operation are provided in [14].

The CO_2 atmosphere causes additional collisional broadening of the atomic K absorption line compared to air and N_2 environments. Separate calibration measurements showed that the line width increases by approximately 30% in CO_2 . Since the PF-TDLAS quantification relies on the absorption cross section of atomic K fragments, this broadening affects the measured absorbance signal. If not accounted for, the broadened line shape would lead to an underestimation of the KOH(g) and KCl (g) concentrations by approximately 20%. A CO_2 line-broadening correction was therefore applied to all CO_2 experiments (Sec. S1 in Supplementary Information).

2.2. SID alkali diagnostics

Surface ionization occurs when atoms desorb from a hot metal surface in ionic form [15,16]. The ionization probability depends on the surface work function (ϕ), the atom's ionization potential (IP), and the surface temperature [17,18]. For most elements, $\phi < IP$, favoring neutral desorption while ion desorption is negligible. In contrast, alkali metals generally have $IP < \phi$, which strongly favors ion desorption. At 1500 K, ionization probabilities exceed 99% for K and $\sim 90\%$ for Na [19]. Other alkali metals (Li, Rb, Cs) ionize efficiently but are seldom found in combustion gases, while alkaline earths and transition metals bind too strongly to the platinum surface to desorb below 1500 K [20]. Consequently, SI offers high sensitivity and selectivity for Na and K, with minimal interference from other species.

The SID (Fig. 1c) consists of a resistively heated platinum filament shaped into a 14×3 mm coil of 10 turns, positioned close to a 14×56 mm metal ion collector plate. The filament is operated at ~ 1500 K with a positive bias (+300 V), while the collector is grounded. As sample gas passes over the filament, alkali aerosol compounds evaporate and thermally dissociate on the surface before desorbing as ions. The ions are drawn toward the grounded collector, where the flux is measured as an electrical current, directly proportional to the alkali mass concentration in the gas flow. Half of the extracted reactor gas ($0.7 \text{ L}\cdot\text{min}^{-1}$ after dilution) is drawn through the SID by downstream suction. Filament temperature is monitored using an infrared pyrometer (spectral range $\sim 1.6 \mu\text{m}$, temperature range 385–1600 °C), providing ionizing surface temperature, which directly governs ionization efficiency. The ion current is converted to mass concentration using calibration curves obtained for KCl, KOH, K_2CO_3 and K_2SO_4 , as described in SI and [9].

2.3. Simulations

TECs were carried out to qualitatively predict the temperature dependence of the K species, using the Equilib module of FactSage 8.3

with the FactPS compound database and the FTOxid solution models [21]. Global equilibrium was calculated for each seeding chemical (KCl, KOH, K_2CO_3 and K_2SO_4) and gas atmosphere (air, N_2 and CO_2) at 1 atm in the temperature range between 20 and 1500 °C. Varying amounts of H_2O were included in the calculations to investigate the effect on moisture from the aerosol generation process on the gas-phase K. The fraction of K species in the gas phase was extracted from the calculations, by normalization to the initial amount of K.

CFD simulations were conducted in ANSYS Fluent to resolve reactor flow and temperature fields. In this work, CFD is used to interpret spatial non-uniformity, local thermal history, and sampling-location effects, rather than to predict absolute alkali concentrations. Details on CFD methodology, including model assumptions, boundary conditions, and numerical settings, are provided in the SI (Sec. S3).

3. Results & discussion

3.1. CFD simulations

Fig. 2 shows CFD modelling results of steady-state temperature and “alkali-origin” mass-fraction (tracer of the aerosol inlet) fields in the reactor during operation with air and a set temperature of 900 °C. In this work, the CFD is used solely to identify spatial features of the reactor that are critical for interpreting the alkali measurements. Cross-sections of the XZ and YZ planes are shown in the left and right column,

respectively. The PF-TDLAS line-of-sight (LOS) crosses the reactor through the lower optical port and the SID samples through the single-ended side port, as indicated in Fig. 2a.

The temperature profile between 550 – 900 °C (i.e., dark blue zones represent temperatures ≤ 550 °C), with a maximum global temperature of 920 °C is shown in Fig. 2a. The reactor core is approximately 900 °C, whereas the side ports cool rapidly to ≤ 550 °C. The aerosol stream enters cold (≤ 550 °C) and is heated only after penetrating the hot bulk flow, implying minimal thermal exposure of the inlet tube and thus limited entry losses of alkali. This is because nanometer-sized aerosol particles are effectively transported in tubes with minimal losses to the tube walls [7]. In the measurement region, temperatures are well above the evaporation thresholds of submicron KOH and KCl aerosol particles (around 500 and 550 °C, respectively [22]), slightly above that of K_2CO_3 (~ 650 °C), and below that of K_2SO_4 (~ 900 °C) [22]. Thus, KCl and KOH are expected to be fully gaseous during air operation, whereas K_2SO_4 should remain particulate. K_2CO_3 is an intermediate case, for which evaporation and conversion to gaseous K species may depend strongly on local thermal history, residence time, moisture, and gas atmosphere. At lower operating temperatures, the simulations indicate that portions of the aerosol jet would likely remain below the evaporation threshold temperature of all potassium compounds.

Fig. 2b shows the local mass fraction originating from the aerosol inlet between 0 and 0.5 (i.e., red color mark areas where the mass fraction of aerosol gas is ≥ 0.5). Thus, a value of 0.5 means 50% aerosol

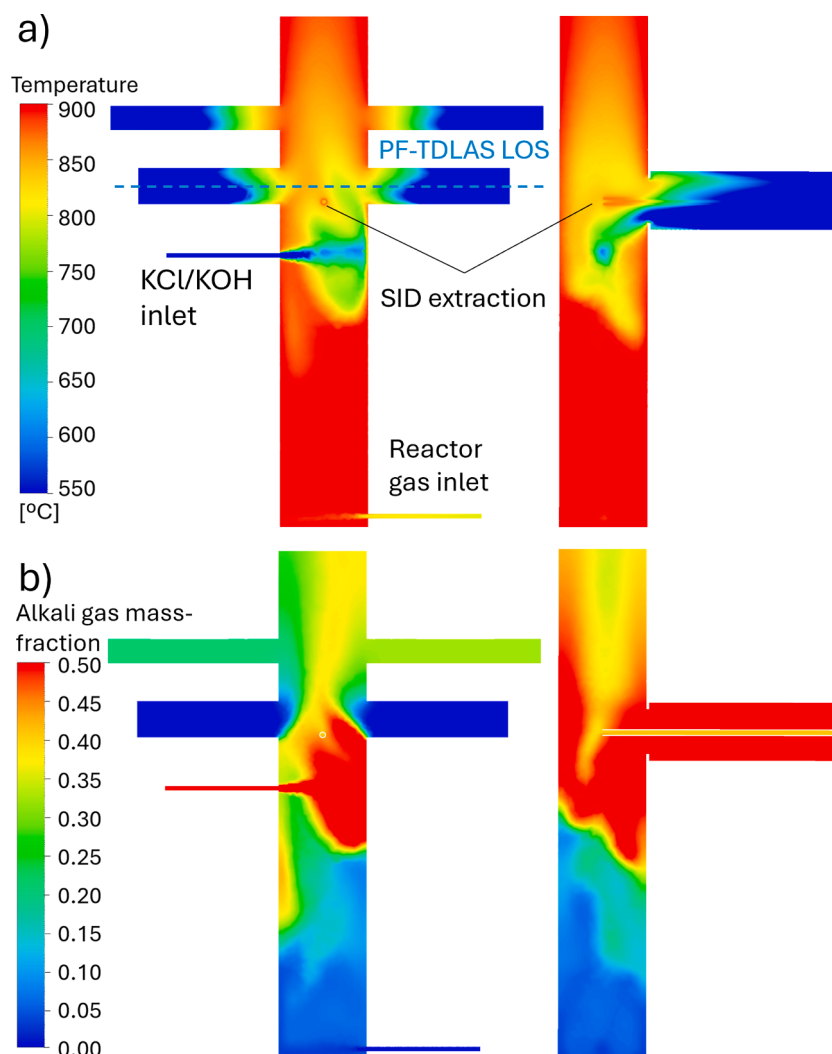


Fig. 2. CFD profiles for (a) temperature and (b) mass-fraction of alkali gas when the reactor operates at 900 °C with air. Panels orientation: XZ-left, and YZ-right.

gas and 50% gas from other inlets. The horizontal aerosol jet crosses the reactor and impinges on the opposite hot wall, promoting gas-to-wall interactions and potential loss of alkali before it reaches the measurement location. Window-purge intrusion from the optical ports pushes cold gas into the core, producing a “bottleneck” behavior in the concentration profile along the PF-TDLAS LOS, while the SID samples a more localized region with comparatively smaller spatial variation. Consequently, cross-sectional non-uniformity biases the LOS (and thus quantification) compared to the SID point extraction, even when alkali is entirely gaseous. The corresponding velocity field is provided in Fig. S4 in SI. It confirms that the tracer distribution in Fig. 2b is governed by jet impingement, purge-flow intrusion, local recirculation, and a small SID-induced disturbance confined to the probe tip. CFD results are shown for the air case; treatment of CO₂ and associated modelling limitations are discussed in Sec. S3 in SI.

3.2. Reactor temperature dependence

Fig. 3 shows the temperature dependence of potassium concentration measured by PF-TDLAS and SID in an air atmosphere during KCl and KOH seeding from 0.4 M atomizer solutions. Qualitative TEC predictions of the gas phase K fractions are included for comparison. The TEC curves were generated with 0.8% H₂O in the gas phase, estimated from atomizer specs and gas flows. The predicted KCl(g) fraction during KCl seeding is unaffected by moisture in the system, while KOH(g) is strongly affected by H₂O concentration, with increasing moisture lowering the onset temperature. The estimated H₂O concentration of 0.8% resulted in a difference in onset temperature of about 50 °C, in good agreement with the experimental observations.

For KCl seeding (Fig. 3a) at 600 °C, the SID reports a high total-K signal while PF-TDLAS detects no KCl(g) or KOH(g), showing that K resides in the condensed phase. Although TECs and literature place

evaporation near ~550 °C [22], CFD indicates that the aerosol jet is colder than the operating temperature; below ~700 °C the jet does not exceed the evaporation temperature before reaching the measurement zone, explaining the absence of signal from PF-TDLAS. As operating temperature rises toward 900 °C, the SID total-K signal decreases by roughly one order of magnitude, while PF-TDLAS KCl(g) increases, reflecting alkali particle evaporation followed by gas-phase loss. Gaseous K species have molecular diffusivities orders of magnitude larger than submicron particles [7,9], leading to rapid transport to surrounding surfaces and significant losses prior to detection. Particles, by contrast, remain coupled to the bulk flow and are more efficiently transported to the sampling location. After extraction, the sample is rapidly diluted and cooled, promoting nucleation of gaseous potassium into submicron particles that are transported with relatively low and well-characterized losses. The SID signal therefore represents a transport-filtered potassium concentration, where gas-phase species are preferentially lost prior to detection. Importantly, comparison with PF-TDLAS shows that the dominant gas-phase losses occur within the reactor itself, prior to extraction, rather than in the sampling lines. This is evidenced by the strong decrease in both PF-TDLAS and SID signals at high temperature, compared to the high recovery at low temperature where potassium remains in the particulate phase. In addition, strong radial non-uniformity develops after volatilization due to aerosol jet impingement and purge-gas intrusion. PF-TDLAS integrates across the reactor core and is therefore less sensitive to these gradients, whereas the point-sampled SID is more strongly affected by local concentration variations and probe-induced bias. Consequently, the apparent SID signal may decrease further with temperature due to the combined effects of gas-phase losses and spatial non-uniformity, compared to the path-averaged PF-TDLAS. Speciation shows that the gas-phase is dominated by KCl(g), with KOH(g) remaining negligible, as predicted by TEC.

KOH seeding (Fig. 3b) yielded comparable SID signals at 600 °C

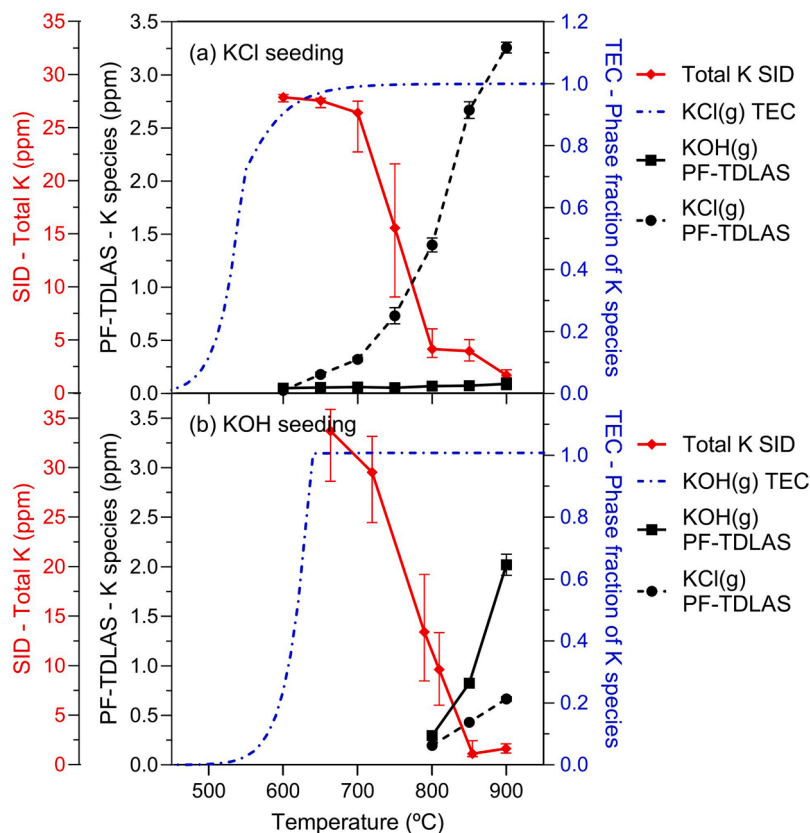


Fig. 3. Alkali concentration measured by PF-TDLAS (black) and SID (red) during (a) KCl, and (b) KOH injection at different reactor temperatures. TEC prediction (blue).

(~ 33 ppm vs. ~ 30 ppm), showing that both salts introduce a similar total K loading in particulate form. As temperature increases, the SID total-K again drops by nearly one order of magnitude, where $\sim 90\%$ of the originally injected K is lost before detection at 900°C . The losses are slightly stronger for KOH than for KCl. No KOH(g) was detected by PF-TDLAS below 800°C , which reflects the detection limit of the system (10 ppb) rather than confirmed absence. This is supported by TECs that predict ~ 5 ppb under these conditions. At higher temperature, both KOH(g) and KCl(g) are detected. At 900°C the total gas-phase K during KOH seeding (~ 2 ppm) is lower than for KCl seeding (~ 3 ppm) but still of the same order of magnitude. The observed KCl(g) during KOH seeding is attributed to chlorine ‘memory’ in the system. Chlorine can be released from residual KCl deposits and/or chloride-containing corrosion products on stainless-steel surfaces formed during prior KCl exposure (chlorine-cycle behavior), providing HCl/Cl that converts KOH(g) to KCl(g) in the hot zone. KOH is also especially reactive at high temperatures [23], which likely promotes wall uptake of KOH(g) and thus larger apparent losses than for KCl.

The error bars in Fig. 3–6 reflect the temporal variability of the measured current (SID) and concentration (PF-TDLAS) under steady operating conditions, quantified from time-resolved data. Temporal stabilities of the alkali signals were verified separately (Sec. S4, Fig. S5), showing stable mean concentrations over 10 min. The largest SID variability occurs in the particle–gas transition regime (650 – 800°C), where coexisting condensed and gaseous phases enhance signal fluctuations (seen for both KOH and KCl seeding).

3.3. Alkali seed concentration dependence

Building on the temperature-dependent phase transition and loss mechanisms described above, the concentration dependence further illustrates how these processes scale with alkali loading. Fig. 4 shows how the measured alkali scales with the atomizer concentration in air at 900°C . For KCl seeding (Fig. 4a), the PF-TDLAS KCl(g) signal increases almost linearly with solution concentration, from ~ 1 to 6 ppm, while KOH(g) remains at background level, confirming KCl as the dominant gas-phase species. The SID signal also rises nearly linearly with solution concentration but at lower absolute levels (~ 0.3 – 1.7 ppm). Importantly, both diagnostics respond with similar relative scaling and the lower SID values may be attributable to sampling losses (Section 3.2).

For KOH seeding (Fig. 4b), PF-TDLAS detects KOH(g) as the main species with a smaller KCl(g) component; both increase with solution concentration but with a smaller slope than KCl(g) in Fig. 4a. The KCl(g) may again arise from chlorine ‘memory’ (Section 3.2). The SID signal also rises with concentration and remains in the same concentration range as PF-TDLAS, but with a weaker dependence on solution

concentration. The general trend shows that absolute levels of total K from both instruments are lower than for KCl seeding, consistent with the higher reactivity/stronger wall uptake of KOH(g) (Section 3.2), which limits the amount of potassium that survives transport to the sampling location (Section 3.2). In addition, SID exceeds PF-TDLAS at low seeding concentrations, likely due to spatial non-uniformity and measurement geometry. PF-TDLAS provides a LOS average, while SID samples locally and may probe regions with higher alkali concentration (Section 3.1).

3.4. Gas atmosphere dependence

In addition to transport and phase-partitioning effects, the gas atmosphere introduces chemical pathways that modify alkali speciation and apparent concentrations. Fig. 5 shows measured alkali concentrations in air, N_2 and CO_2 gas atmospheres at 900°C reactor temperature during seeding of KOH and KCl from 0.4 M atomizer solutions.

For KCl seeding (Fig. 5a), the KCl(g) concentration measured by PF-TDLAS remains in air (~ 5.7 ppm) and N_2 (~ 5.4 ppm), indicating that gas-phase KCl is only weakly affected by replacing air with N_2 under otherwise identical operating conditions. In CO_2 , however, KCl(g) drops to 3.6 ppm ($\sim 37\%$ below air). This decrease is attributed primarily to a reduced alkali delivery from the atomizer in the CO_2 experiments, where the actual atomizer flow was $1.4 \text{ L}\cdot\text{min}^{-1}$ rather than $2.0 \text{ L}\cdot\text{min}^{-1}$ because the CO_2 MFC setpoint was not adjusted to compensate for the gas correction factor (Section 2). Independent atomizer characterization (Fig. S6 in SI) shows a strong reduction in generated KCl mass concentration at $1.4 \text{ L}\cdot\text{min}^{-1}$ relative to $2.0 \text{ L}\cdot\text{min}^{-1}$. Therefore, the CO_2 KCl case should not be interpreted as an isolated atmospheric-chemistry effect, but primarily as a combined effect of lower delivered K loading and possible changes in transport. KOH(g) remains at background during KCl seeding for all atmospheres, consistent with KCl being the dominant gas-phase carrier at 900°C under these conditions. The SID total-K is lower than the PF-TDLAS KCl(g), as expected from gas-phase losses and extraction effects. The SID total-K shows a similar trend to PF-TDLAS, with the highest concentration observed in air (~ 1.1 ppm), and about a 35% reduction (~ 0.7 ppm) in CO_2 atmosphere. However, the SID shows a clear difference between air and N_2 operation. A separate atomizer-to-SID test at identical liquid KCl concentration and $2.0 \text{ L}\cdot\text{min}^{-1}$ carrier flow yielded $1327 \mu\text{g}\cdot\text{m}^{-3}$ total-K in air versus $1059 \mu\text{g}\cdot\text{m}^{-3}$ in N_2 , suggesting that part of the air-to- N_2 offset can originate from differences in aerosol generation/transport and/or SID response, in addition to reactor/sampling losses.

For KOH seeding (Fig. 5b), the PF-TDLAS detects KOH(g) at ~ 2.0 and ~ 1.7 ppm, in air and N_2 respectively, whereas in CO_2 the KOH(g) signal collapses to ~ 0.25 ppm. Part of this decrease is attributable to the lower

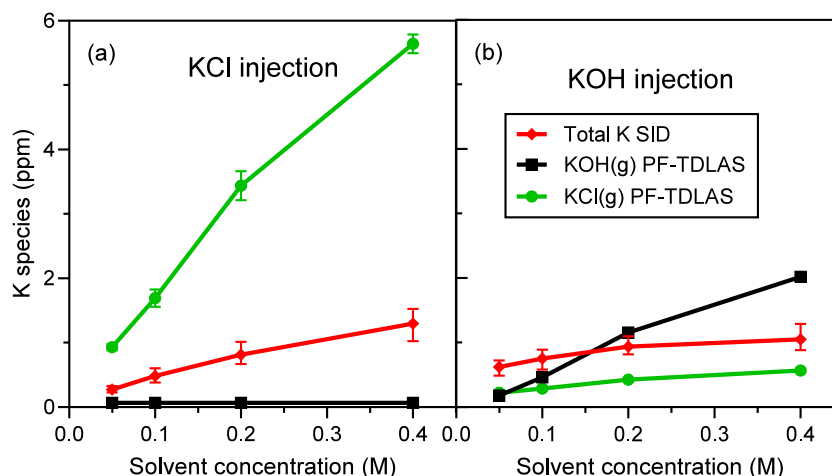


Fig. 4. K concentrations measured by PF-TDLAS and SID for different solvent concentrations of (a) KCl and (b) KOH.

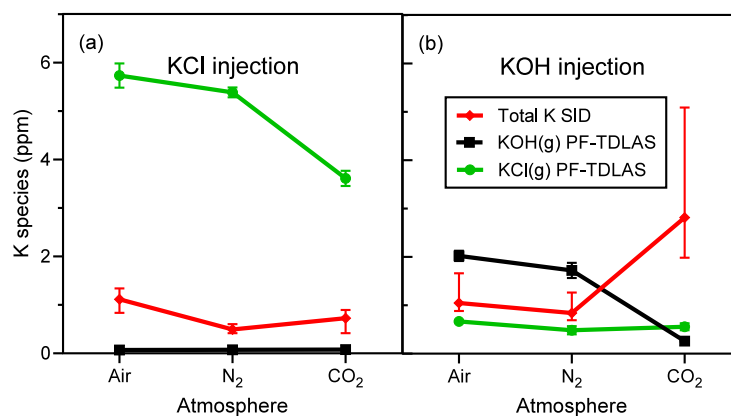


Fig. 5. K concentrations measured by PF-TDLAS and SID for different reactor atmospheres during (a) KCl injection and (b) KOH injection.

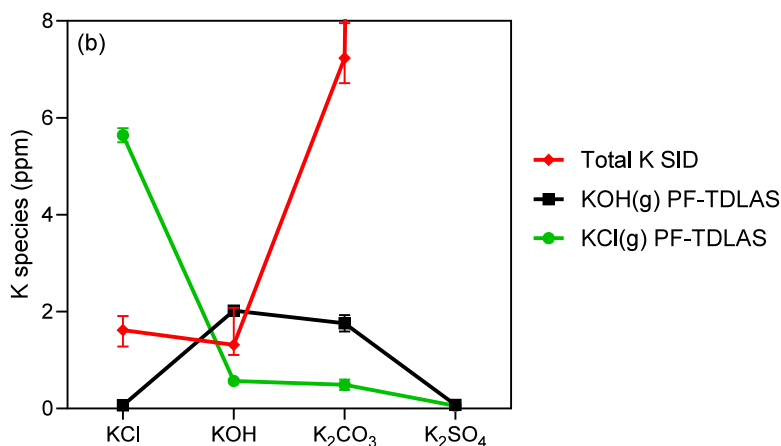


Fig. 6. K concentrations measured by PF-TDLAS and SID during seeding with KCl, KOH, K₂CO₃ and K₂SO₄ (not shown due to extreme concentrations) to the reactor operated with air at 900 °C.

delivered alkali loading in the CO₂ experiments due to the reduced atomizer flow (Section 2). However, the suppression of KOH(g) is substantially stronger than expected from this effect alone and is consistent with rapid carbonate formation already upstream of the reactor: CO₂ readily dissolves into the atomized KOH droplets and converts KOH to (bi)carbonate/carbonate during atomization and transport, producing K₂CO₃-rich particles that PF-TDLAS cannot detect. The K₂CO₃(s) persists to higher temperatures (~650–700 °C) compared to KCl and KOH according to [22] and TECs, where the latter also show conversion to KOH(g) above 850 °C when water is sufficiently present (a byproduct from aerosol formation). As discussed in Section 3.1, the air-case CFD shows that the temperature at the sampling location is likely significantly below 900 °C, and additional radiative heat transfer in the CO₂-case may further modify this local thermal history, see Sec. S3 in SI. The low KOH(g) measured by PF-TDLAS is therefore interpreted as a combined effect of carbonate formation and incomplete conversion of carbonate-rich particles to KOH(g) under the local thermal history. This is also reflected in the high measured total K by SID, where the large error bars reflect increased temporal variability associated with operation in a mixed particle–gas regime. Under these conditions, coexisting phases lead to increased temporal variability in the SID signal (see Fig. S5), which is also seen during the particle-to-gas transition between 700 and 800 °C in Fig. 3. PF-TDLAS also detects a smaller KCl(g) signal during KOH seeding in all atmospheres, consistent with chlorine “memory” from reactor/probe surfaces. The SID total-K again decreases when shifting from air to N₂, strengthening the argument that the air-N₂ offset reflects differences in aerosol generation/transport and/or SID response and reactor/sampling losses rather than KCl-specific chemistry.

3.5. Seeding chemical dependence

The influence of seeding chemistry shows how compound-dependent thermochemistry and surface reactivity interact with the transport and sampling effects identified above. To further explore these effects, K₂CO₃ and K₂SO₄ were investigated in addition to KCl and KOH. Fig. 6 shows measurements of K species concentrations for each seeding chemical in air at 900 °C, each with a total K solvent concentration of 0.4 M (on K atom basis) in the atomizer.

A clear variation in measured K species concentrations can be observed. The PF-TDLAS shows similar trends during KCl and KOH seeding as observed before (Fig. 4). In the case of K₂CO₃ seeding, the measured KOH(g) concentration is similar (10% lower) to that observed during KOH seeding. The K₂CO₃ aerosols are expected to be fully vaporized above 650 °C [22] and according to TECs they can be converted into KOH(g) above 740 °C when water is present. During K₂SO₄ seeding, the PF-TDLAS system detects no gaseous K, as expected since K₂SO₄ aerosols remain in particulate form at these temperatures and even gaseous compounds would take the form of K₂SO₄(g) in this environment. The SID total K measurements agree with the PF-TDLAS and earlier results (Fig. 4) for KCl and KOH seeding. High total K concentration is observed during K₂CO₃ seeding, indicating that the K₂CO₃ is not fully converted to KOH despite TEC predictions, and that SID can measure all chemical forms of alkali (not only KCl and KOH detected by PF-TDLAS). For K₂SO₄ seeding, the SID reports around 180 ppm total-K, which is why the corresponding measurement point is not shown in Fig. 6, showing that the alkali resides in particulate form at these temperatures (as expected with a 900 °C evaporation threshold [22]) and

the particles experience low alkali losses prior to sampling. However, the high total-K concentrations during K_2CO_3 and K_2SO_4 seeding should be interpreted cautiously. The SID current during K_2CO_3 seeding is only moderately higher ($\approx 70\%$) than for KOH, indicating comparable alkali flux. The much higher reported concentrations arise from salt-specific calibration curves, where SID sensitivity to carbonates and sulfates is substantially lower than for KCl and KOH (Fig. S3 in SI). Consequently, a given ion current corresponds to a significantly larger inferred mass concentration when using K_2CO_3 or K_2SO_4 calibration curves, see Sec. S2. This effect is more pronounced for K_2SO_4 : although the measured current (~ 1100 nA) is lower than for particulate KCl and KOH (~ 6600 – 8300 nA), the weak sulfate calibration yields an apparently very high concentration. Therefore, K_2CO_3 and K_2SO_4 results should be interpreted qualitatively, demonstrating compound-dependent SID response and the presence of non-PF-TDLAS-detectable potassium, rather than as precise absolute concentrations.

Across all conditions, the trends are explained by coupled phase partitioning, transport/surface losses, spatial non-uniformity, and chemistry-dependent transformations. The particle-to-gas transition is governed by the local thermal history of the aerosol jet rather than the nominal reactor temperature. Once volatilized, gaseous potassium is rapidly lost to surfaces, while particles are transported more efficiently. Spatial non-uniformity further affects the diagnostics differently: PF-TDLAS provides a line-of-sight average, whereas SID samples locally. Chemistry further modifies the signals through carbonate formation in CO_2 , stronger KOH reactivity, and chlorine-memory-driven KCl formation. Together, this framework explains the behavior across temperature, concentration, atmosphere, and seeding chemistry.

3.6. Status and outlook

In conclusion, both methods provide a clear, concentration-dependent response for gaseous K and operate in the same order of magnitude even at very low seeding loadings. PF-TDLAS provides in situ, path-averaged speciation of KCl(g) and KOH(g) and SID indicates the amount of total K that survives transport to an extraction point and further to the instrument. This combined view is essential for interpreting alkali behavior in high-temperature systems where evaporation, chemistry, and transport are tightly coupled. The work extends the very limited prior literature on coordinated optical/SID alkali measurements by providing a framework for interpreting discrepancies between extractive and in situ diagnostics under realistic, non-uniform reactor conditions. Given the applications of PF-TDLAS and SID as diagnostic tools, these findings argue for paired deployment, as individual limitations of the techniques can be complemented when used together, e.g., gas species-selectivity and particle phase inclusion. Alternatively, CFD or TEC-informed corrections may be necessary if only one technique is used. Although this study focuses on potassium, the framework is in principle extendable to other alkali metals, such as NaOH and NaCl [24]. SID is broadly sensitive to alkali metals with appropriate calibration, while PF-TDLAS can be extended to any species where suitable photo-fragmentation wavelengths, fragment-detection transitions, and available laser sources exist. Several design and operating changes can mitigate bias: (1) avoid jet impingement by relocating or angling the aerosol inlet, (2) reduce or redirect purges tangentially, (3) use multi-hole/annular SID probes to approximate a path average, (4) quantify trace Cl⁻ to interpret speciation during KOH seeding, and (5) ensure correct MFC settings when changing gas atmospheres, and (6) extend CFD to CO_2 operation using appropriate radiation models.

4. Conclusions

This work demonstrates a synergistic PF-TDLAS and SID methodology for potassium measurements in a high-temperature, alkali-seeded reactor, interpreted with CFD and TECs. Reactor operating temperature, gas atmosphere (air, N_2 , CO_2), and the amount and chemical form of

injected potassium (KCl, KOH, K_2CO_3 , K_2SO_4), were varied to study phase partitioning, speciation, and losses. Key conclusions include:

- The combined diagnostics resolve the particle-to-gas transition and show that the effective evaporation threshold is governed by local jet heating and mixing rather than the reactor temperature, explaining deviations from TEC.
- Once volatilized, most potassium is removed by surface interactions in the reactor and sampling system. This loss is amplified for gas-phase K due to rapid diffusion, while particles are transmitted more efficiently.
- CFD shows persistent radial non-uniformity, causing reactor wall losses to impact PF-TDLAS and SID unequally: PF-TDLAS, being path-averaged through the core, reports higher gas-phase concentrations than point-sampled SID, which also suffers probe/line losses.
- Atmosphere and chemistry effects are separable with paired diagnostics. In CO_2 , PF-TDLAS and SID together show that changes in measured alkali can reflect both delivery/transport differences and chemistry-driven phase partitioning. During KCl seeding, reduced gas-phase KCl and total-K are consistent with lower delivered loading, whereas during KOH seeding CO_2 shifts potassium toward carbonate-rich particles, strongly suppressing KOH(g) while total-K remains elevated and more variable.
- Despite systematic offsets, both diagnostics show repeatable trends, scale consistently with injected alkali, and quantify potassium in the sub-ppm to ppm range with excellent sensitivity.

Across all conditions, the observations are explained by a unified framework combining phase partitioning, transport and surface losses, spatial non-uniformity, and chemistry-dependent transformations. The two diagnostics are therefore complementary rather than interchangeable: PF-TDLAS constrains in situ gas-phase speciation, while SID captures total-K gas and particle contributions. Together, they provide a more reliable basis for interpreting alkali behavior and extend the very limited prior literature on coordinated optical/SID alkali measurements by establishing a transferable framework for reconciling discrepancies between extractive and in situ diagnostics under combustion-relevant conditions.

CRedit authorship contribution statement

Viktor Andersson: Conceptualization, Investigation, Methodology, Software, Formal analysis, Visualization, Writing - Original Draft. **Emil Thorin:** Conceptualization, Project administration, Investigation, Methodology, Formal analysis, Software, Writing - Review & Editing. **Thomas Allguren:** Writing - Review & Editing, Supervision. **Klas Andersson:** Conceptualization, Writing - Review & Editing, Supervision, Funding acquisition. **Florian M. Schmidt:** Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition.

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.

Acknowledgements

This work is supported by the Swedish Energy Agency and European Union (P2021-00128), the Swedish Energy Agency (P2022-00189), the Kempe Foundations (JCK-1316), and the Swedish Strategic Research Environment Bio4Energy (B4E3-TM-3-05).

Supplementary materials

Supplementary material associated with this article can be found, in

the online version, at doi:10.1016/j.proci.2026.106578.

References

- [1] Y. Niu, H. Tan, S.e. Hui, Ash-related issues during biomass combustion: alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures, *Prog. Energy Combust. Sci.* 52 (2016) 1–61.
- [2] Z. Wang, S. Liu, W. Weng, Y. He, M. Aldén, Z. Li, Alkali metal release in thermochemical conversion of biomass and coal: optical measurements and modeling, *Prog. Energy Combust. Sci.* 100 (2024) 101131.
- [3] W. Wang, R. Lemaire, A. Bensakhria, D. Luat, Review on the catalytic effects of alkali and alkaline earth metals (AAEMs) including sodium, potassium, calcium and magnesium on the pyrolysis of lignocellulosic biomass and on the co-pyrolysis of coal with biomass, *J. Anal. Appl. Pyrolysis* 163 (2022) 105479.
- [4] E. Thorin, A. Sepman, Y. Ögren, C. Ma, M. Carlborg, J. Wennebro, M. Broström, H. Wiinikka, F.M. Schmidt, Quantitative real-time in situ measurement of gaseous K, KOH and KCl in a 140 kW entrained-flow biomass gasifier, *Proc. Combust. Inst.* 39 (2023) 1337–1345.
- [5] V. Andersson, J.B.C. Pettersson, T. Allguren, P. Knutsson, K. Andersson, Alkali uptake, release, and speciation in fluidized beds using oxygen carriers, *Energy Fuel* 39 (2025) 3280–3294.
- [6] D. Gall, J. Viljanen, I. Gogolev, T. Allguren, K. Andersson, Alkali monitoring of industrial process gas by surface ionization—Calibration, assessment, and comparison to In situ laser diagnostics, *Energy Fuel* 35 (2021) 20160–20171.
- [7] V. Andersson, A.H. Soleimanislim, X. Kong, F. Hildor, H. Leion, T. Mattisson, J.B.C. Pettersson, Alkali-wall interactions in a laboratory-scale reactor for chemical looping combustion studies, *Fuel Process. Technol.* 217 (2021) 106828.
- [8] W.C. Hinds, *Aerosol Technology - Properties, Behavior and Measurement of Airborne Particles*, Wiley, New York, 1999.
- [9] V. Andersson, Y. Ge, X. Kong, J.B.C. Pettersson, A novel method for on-line characterization of Alkali release and thermal stability of materials used in thermochemical conversion processes, *Energies* 15 (2022) 4365.
- [10] M. Inc., Gas correction factors for thermal-based mass flow, in, <https://www.mks.com/n/gas-correction-factors-for-thermal-based-mass-flow-controllers>.
- [11] T. Sorvajärvi, J. Toivonen, Principles and calibration of collinear photofragmentation and atomic absorption spectroscopy, *Appl. Phys. B* 115 (2014) 533–539.
- [12] Z. Qu, E. Steinvall, R. Ghorbani, F.M. Schmidt, Tunable diode laser atomic absorption spectroscopy for detection of potassium under optically thick conditions, *Anal. Chem.* 88 (2016) 3754–3760.
- [13] E. Thorin, F.M. Schmidt, TDLAS-based photofragmentation spectroscopy for detection of K and KOH in flames under optically thick conditions, *Opt. Lett.* 45 (2020) 5230.
- [14] E. Thorin, K. Zhang, D. Valiev, F.M. Schmidt, Simultaneous detection of K, KOH, and KCl in flames and released from biomass using photofragmentation TDLAS, *Opt. Express* 29 (2021) 42945.
- [15] M. Hagström, K. Engvall, J.B.C. Pettersson, Desorption kinetics at atmospheric pressure: alkali metal ion emission from hot platinum surfaces, *J. Phys. Chem. B* 104 (2000) 4457–4462.
- [16] K. Davidsson, K. Engvall, M. Hagström, J. Korsgren, B. Lönn, J. Pettersson, A surface ionization instrument for on-line measurements of Alkali metal components in combustion: instrument description and applications, *Energy Fuels* 16 (2002).
- [17] K.H. Kingdon, A method for the neutralization of electron space charge by positive ionization at very low gas pressures, *Phys. Rev.* 21 (1923) 408–418.
- [18] D. Gall, C. Nejman, T. Allguren, K. Andersson, J.B.C. Pettersson, A new technique for real-time measurements of potassium and sodium aerosols based on field-reversal surface ionization, *Meas. Sci. Technol.* 32 (2021) 075802.
- [19] K. Möller, L. Holmlid, Desorption of cesium from pyrolytic graphite basal surfaces with strongly non-equilibrium behaviour, *Surf. Sci.* 163 (1985) L635–L640.
- [20] F. Stienkemeier, M. Wewer, F. Meier, H.O. Lutz, Langmuir–Taylor surface ionization of alkali (Li, Na, K) and alkaline earth (Ca, Sr, Ba) atoms attached to helium droplets, *Rev. Sci. Instrum.* 71 (2000) 3480–3484.
- [21] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack, I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, M.A. Van Ende, Reprint of: factSage thermochemical software and databases, 2010–2016, *Calphad* 55 (2016) 1–19.
- [22] D. Gall, M. Pushp, K.O. Davidsson, J.B.C. Pettersson, Online measurements of alkali and heavy tar components in biomass gasification, *Energy Fuel* 31 (2017) 8152–8161.
- [23] V. Andersson, X. Kong, H. Leion, T. Mattisson, J.B.C. Pettersson, Gaseous alkali interactions with ilmenite, manganese oxide and calcium manganite under chemical looping combustion conditions, *Fuel Process. Technol.* 254 (2024) 108029.
- [24] Y. Dai, W. Weng, R. Zhong, S. Liu, Y. He, Z. Wang, Quantitative measurement of atomic sodium in combustion environments using tunable laser absorption spectroscopy, *Opt. Lett.* 50 (2025) 6550.