<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Combustion and Flame*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

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

Qu, Z., Holmgren, P., Skoglund, N., Wagner, D R., Broström, M. et al. (2018)
Distribution of temperature, H₂O and atomic potassium during entrained flow biomass
combustion: coupling in situ TDLAS with modeling approaches and ash chemistry
Combustion and Flame, 188: 488-497
<https://doi.org/10.1016/j.combustflame.2017.10.013>

Access to the published version may require subscription.

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

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-141456>

Distribution of temperature, H₂O and atomic potassium during entrained flow biomass combustion – coupling in situ TDLAS with modelling approaches and ash chemistry

Zhechao Qu^{a,1,†}, Per Holmgren^{a,†}, Nils Skoglund^{a,b}, David R. Wagner^{a,2}, Markus

Broström^a and Florian M. Schmidt^{a,*}

^a Thermochemical Energy Conversion Laboratory (TEC-Lab), Department of Applied Physics and Electronics, Umeå University, SE-901 87 Umeå, Sweden

^b Energy Engineering, Department of Engineering Sciences & Mathematics, Luleå University of Technology, SE-971 87 Luleå, Sweden

*corresponding author, E-mail address: florian.schmidt@umu.se,

Phone number: +46-90-7867611

Abstract

Tunable diode laser absorption spectroscopy (TDLAS) is employed for simultaneous detection of gas temperature, water vapor (H₂O) and gas-phase atomic potassium, K(g), in an atmospheric, research-scale entrained flow reactor (EFR). In situ measurements are conducted at four different locations in the EFR core to study the progress of thermochemical conversion of softwood and Miscanthus powders with focus on the primary potassium reactions. In an initial validation step during propane flame operation, the measured axial EFR profiles of H₂O density-weighted, path-averaged temperature, path-averaged H₂O concentration and H₂O column density are found in good agreement with 2D CFD simulations and standard flue gas analysis. During biomass conversion, temperature and H₂O are significantly higher than for the propane flame, up to 1500 K and 9%, respectively, and K(g) concentrations between 0.2 and 270

¹ Present address: Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany.

² Present address: Oregon State University - Cascades, 1500 SW Century Dr. Bend, OR 97702.

[†] Equally contributing.

ppbv are observed. Despite the large difference in initial potassium content between the fuels, the $K(g)$ concentrations obtained at each EFR location are comparable, which highlights the importance of considering all major ash-forming elements in the fuel matrix. For both fuels, temperature and $K(g)$ decrease with residence time, and in the lower part of the EFR, $K(g)$ is in excellent agreement with thermodynamic equilibrium calculations evaluated at the TDLAS-measured temperatures and H_2O concentrations. However, in the upper part of the EFR, where the measured H_2O suggested a global equivalence ratio smaller than unity, $K(g)$ is far below the predicted equilibrium values. This indicates that, in contrast to the organic compounds, potassium species rapidly undergo primary ash transformation reactions even if the fuel particles reside in an oxygen-deficient environment.

Keywords: Tunable diode laser absorption spectroscopy (TDLAS); atomic potassium; entrained flow reactor; biomass combustion; thermodynamic equilibrium calculations; computational fluid dynamics (CFD).

1. Introduction

Entrained flow powder combustion and gasification are efficient technologies for production of heat, power and transport fuel from coal and biomass [1, 2]. As a consequence of the current interest in renewable, CO₂-neutral energy sources, the share of biomass in the fuel feedstock increases, and so does the demand for improved process efficiency and fuel-flexibility, which, in turn, requires a better understanding of thermochemical biomass conversion [3]. Research- and pilot-scale entrained flow reactors (EFRs) that resemble industrial systems with high heating rates and short residence times [4] are valuable tools to investigate fuel conversion [5] and ash formation [6, 7], and to improve process modelling by validation of kinetic models [8, 9] and computational fluid dynamics (CFD) simulations [10, 11]. If equipped with optical access windows, such droptube reactors allow studying the progress of fuel conversion online via in situ measurements in the reaction zone.

Important physical and chemical parameters for characterization of biomass combustion and gasification comprise gas temperature and velocity, the concentrations of major (CO₂, CO, CH₄, H₂, H₂O, O₂) and minor (e.g. SO₂, HCl, NO_x) species as well as gaseous alkali compounds (K, Na, KOH, NaOH, KCl), hydrocarbons, tars and soot. Compounds containing potassium (K) and sodium (Na) are of particular interest, as they can participate in various ash-forming reactions and thereby influence the ash properties and extent of operational problems, such as slag build-up and corrosion due to material interactions [7, 12], agglomeration [13, 14], and particle formation [15, 16]. Detailed knowledge of the alkali release forms and ash transformation reactions is needed to improve numerical models, identify suitable parameters for process optimization and control, and mitigate operational and environmental issues. During

devolatilization, high amounts of atomic potassium, $K(g)$, may be present due to direct release or decomposition from larger molecules [7, 17-19]. The problematic K-containing species in the flue gas, $KOH(g)$ and $KCl(g,s,l)$, are likely formed through secondary ash transformation reactions consuming $K(g)$ [3]. Thus, knowing the conditions in the reactor, the initial $K(g)$ concentrations could be an indicator for K release, and the decay rate of $K(g)$ could be a measure of how fast other K-containing compounds are formed.

Assessment of the conditions in an EFR is today mainly based on invasive and extractive analytical methods. Temperature is usually measured with thermocouples (TCs), which respond slowly, have to be cleaned or replaced frequently and may be unreliable at high temperatures and soot concentrations due to radiative heat transfer. Suction pyrometers offer improved performance as the TC is shielded from radiation, but the other drawbacks remain. Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled to mass spectrometry (GC-MS) are employed to analyze the gaseous conversion end products found at the exhaust and in the flue gases. Particulate matter can be collected using total dust filters or impactor sampling systems and analyzed offline to e.g. estimate the amount of potassium in the solid phase. However, empirical data describing changes in gas composition in the reaction zone are scarce. In situ real-time process monitoring is especially important for the alkali reactants, which are difficult to quantify accurately with extractive techniques.

Non-intrusive in situ measurements in EFRs can be performed using optical techniques, such as shadowgraphy for particle size and velocity [20], tunable diode laser absorption spectroscopy (TDLAS) for gas composition (atoms and small molecules) and temperature [21], and excimer laser induced fluorescence (ELIF) to determine total concentrations of alkali metals [22]. Laser absorption spectroscopy enables fast, selective

and accurate quantitative measurements without calibration procedures. Robust TDLAS setups have been applied in larger plants for analysis of temperature and major species in syngas and flue gas [23, 24], and are suitable for measurements in the harsh and sooty environments of EFR reactor cores [24-27]. The technique has also been used for detection of atomic potassium in entrained flow coal combustion [28] and biomass gasification [27].

Typical TDLAS implementations provide path-averaged data and thus cannot account well for unknown temperature or species distributions along the line-of-sight. Moreover, the accuracy depends on how well the absorption path length is known. Inhomogeneous conditions may occur close to the fuel inlet of an EFR where the particles are entrained at the center and gas mixing is poor. Strategies to handle inhomogeneous conditions with TDLAS and map out distributions from line-of-sight data include tomography [29] and multi-line detection with advanced post-processing using regularization methods [30]. Another approach is to couple the experimental results to (two-dimensional) CFD simulations [31, 32]. Once validated, e.g. using the path length-independent column density [32, 33], the simulations can provide more detailed information regarding, temperature, major species and particle distributions. A prediction of the distribution of K species in the EFR, is, however, difficult with currently available computational power, as it would require multi-phase CFD simulations that involve a large number of fuel particles, the main ash-forming elements as well as the corresponding chemical reactions.

In laminar EFRs with low particle Stokes number, the volatiles released from the fuel particles travel close to the remaining solid char during burn-out, which allows for continuous interaction between ash-forming elements, carbonaceous matrix and other

gaseous compounds originating from the same particle. This provides the possibility to compare experimental data with global thermodynamic equilibrium calculations (TEC) at certain locations (temperatures) [17, 34]. A comparison of TEC results with K(g) concentrations measured in the reaction zone can indicate whether the fuel conversion and ash transformation reactions are close to, or have reached, equilibrium.

In this work, a recently developed TDLAS sensor was used to measure gas temperature, H₂O(g) and K(g) in situ at four different locations of an entrained flow reactor core during combustion of propane and two different types of biomass, with the aim to study the fuel conversion. To aid interpretation of the TDLAS data, temperature and H₂O measurements were first validated during propane flame (PF) operation by comparison to 2D CFD simulations as well as TC and FTIR data. Thermochemical conversion of softwood and Miscanthus powders was then investigated in situ in terms of residence time. The obtained K(g) concentrations were compared to equilibrium calculations performed as a function of oxygen-to-fuel equivalence ratio at the TDLAS-measured temperatures and H₂O concentrations. Implications for release and primary reactions of K compounds are discussed.

2. Experimental setup and methods

2.1 Entrained-flow reactor

The research-scale, atmospheric EFR was made of an electrically heated 2 m tall steel (Sandvik 253MA, EN1.4835) tube with an inner diameter of 10 cm (measured at room temperature). Optical access port tubes with a length of 35 cm and inner diameter of 1.3 cm were installed on each side of the EFR at 3, 13, 70, 127 and 184 cm distance down from the fuel inlet. The port tubes and attached quartz windows were flushed with nitrogen

(0.1 L/min per tube) to prevent intrusion of reactor gases and window fouling. The fuel feeding system (K-Tron, K-CL-SFS-KT20, Switzerland) consisted of a loss-in-weight feeder, an entrainment cone, and a McKenna-style flat-flame burner (Holthuis & Associates, USA). The burner had a central tube with 0.6 cm inner diameter for biomass powder supply, an inner annular flat-flame and an outer annular protective dry air shroud inlet (40 L/min) to prevent wall-particle collisions. The burner and fuel inlet were water cooled (2 L/min). A premixed propane/air fuel (with air-to-fuel equivalence ratio of 1.12 and total flow rate of 20.75 L/min) was used for the flat flame to ensure high particle heating rates. The Reynolds number calculated for the gas flow was ~ 300 , well within the laminar regime for a tube ($Re < 2300$). Two stacked electrical clamshell furnaces were used to keep the surface temperature of the reactor wall close to 1273 K. The distance between the heaters and the reactor steel tube was approximately 10 cm, and the small gap between the heater sections (heater gap) above Port 4 tube was bridged with insulation material. A photograph and a schematic drawing of the EFR system, including the TDLAS setup, are shown in Fig. 1.

Fig. 1. Photograph (a) and schematic drawing (b) of the research-scale EFR at Umeå University. P – Port; PD – photodetector. The drawing also shows burner geometry, optical ports, TDLAS setup implementation and FTIR sampling point. Ports 2-5 were used in the experimental campaign.

2.2 Biomass fuel feedstock

The biomass feedstock used in this study included a woody-type fuel consisting of a blend of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris* L.), henceforth called softwood (SW), and *Miscanthus x giganteus*, a herbaceous energy crop (MC). These two fuels differ heavily in composition and ash content (Table 1). The amount of K(g) observed during thermochemical conversion of SW and MC can thus be expected to differ accordingly, but also depends on the other ash-forming elements that determine which ash transformation reactions take place. The average fuel feeding rate was set to 200 g/h for both fuels, corresponding to 100 mg K/h for SW and 556 mg K/h for MC.

Table 1. Physical and chemical fuel properties of softwood (SW) and Miscanthus (MC), including the lower heating value (LHV).

Parameter	Unit	SW	MC
LHV	MJ/kg dry	18.9	17.9
Moisture	wt % receiv.	2.8	5.5
Ash content	wt % dry	0.42	3.2
C	wt % dry	50.07	47.58
H		6.2	5.8
N		0.042	0.24
O		43.5	44.8
Main ash-forming elements			
K	mg/kg dry	499	2780
Na		29.9	87.1
Ca		904	1110
Mg		136	480
Fe		46.7	233
Al		76.6	191
Si		308	10100
P		47.5	298
S		56.3	343
Cl		23	239

2.3 Tunable diode laser absorption spectroscopy

Simultaneous real-time detection of H₂O, temperature and K(g) in one beam path was achieved by combining two existing TDLAS instruments previously applied and validated in flat-flames [35], single pellet conversion experiments [19, 36] and pilot-scale entrained flow biomass gasification [27]. Calibration-free scanned wavelength modulation spectroscopy (CF-WMS) at 1398 nm provided path-averaged H₂O concentrations and H₂O density-weighted, path-averaged gas temperature [35, 36], whereas direct absorption spectroscopy (DAS) at 769.9 nm was used to obtain path-averaged K(g) concentrations [19]. The laser beams were combined with the help of an optical fiber coupler (Newport, F-CPL-B12355), and, after passing the EFR, separated

again employing a beam splitter for subsequent detection with suitable photodetectors (Fig. 1b).

Gas temperature was assessed calibration-free and independently of the absorption path length by two-line thermometry on H₂O transitions with line strength maxima around 1100 K and linear line strength temperature dependence in the range 1200–1800 K [36]. The latter allowed determination of the H₂O density-weighted, path-averaged temperature even in the presence of temperature and species non-uniformities [33]. The obtained temperature was then used to calculate the species column densities or, assuming a certain path length, the concentrations. The detection limit for H₂O at 10 cm path length was 0.1% and the measurement uncertainties were estimated to 25 K and 0.5% H₂O for temperature and water vapor, respectively [36]. The K(g) sensor was designed to allow operation under optically thick and partially opaque conditions, which enabled a dynamic range of 10⁶, from 40 parts per trillion by volume (pptv)·cm to 40 parts per million by volume (ppmv)·cm, while the measurement uncertainty could be up to 20% at high absorbance. The line strength temperature dependence of the D₁ potassium transition is weak, exhibiting a change of about 40% in the interval 1000–1800 K.

At each optical port and for each fuel type (propane flame, SW, MC), the three parameters were monitored for about 15 minutes under steady state combustion conditions. During this measurement sequence, absorption spectra were acquired using laser scan rates of 80 Hz for CF-WMS and 200 Hz for DAS. Assuming that the EFR operated at steady state, an average of 10 spectra was then saved at time intervals of 2–10 s to enable the long measurement time period. Following temperature and concentration evaluation, the average over one sequence was taken as data point

representing the prevailing operating conditions (port and fuel type). The nitrogen flow applied to the optical port tubes helped to maintain an optical path length close to the inner diameter of the EFR, which was estimated to 10.5 cm at 1273 K, based on the thermal expansion properties of the steel. At Port 1, the uppermost optical access port, light transmission was severely disturbed by unconverted solid fuel particles entering the EFR and falling through the laser beam such that, in this study, with the employed laser scan rates, reliable measurements could not be performed at this port.

2.4 Complementary analytical instrumentation

In situ particle image velocimetry (PIV), also referred to as shadowgraphy, of the fuel particles falling through the reactor was realized using a LaVision ParticleMaster system (Imager SX 4M CCD camera) and a long distance microscope QM1 (LDM) [20]. Silhouette images of suspended particles were captured to determine parameters such as particle velocity and size [37]. The observed average particle velocity at a given optical port was taken as the approximate velocity that prevailed between that and the preceding port (or the fuel inlet for Port 1). The average residence time was then calculated stepwise by dividing the distance between two consecutive ports with the corresponding particle velocity. Particle diameter and velocity allowed calculation of the average particle Reynolds number (Re_p) and Stokes number (Stk), where $Re_p < 10$ indicates a laminar flow around the particle and $Stk < 1$ implies that the particle follows the gas flow. At Ports 2-5, the average Re_p and Stk were $\ll 1$ for both fuels, which supports the assumption of entrained flow. The largest 5% of the observed particles (based on diameter) had $Re_p > 10$ and $Stk > 1$ at Ports 2-3 for SW, and at Ports 2-4 for MC, indicating the occasional presence of particles large enough to disrupt the entrained flow.

Radial and axial temperature profiles were measured with a Type S thermocouple that had a weld point diameter of 0.6 mm. In addition, a portable FTIR instrument (Gasmet DX-4000) equipped with a ZrO_2 -cell for O_2 measurement was used to determine the flue gas composition (O_2 , CO_2 , H_2O , CO) at the exhaust.

2.5 Two-dimensional CFD simulations

Two-dimensional numerical simulations of the EFR system (excluding optical ports) with the burner operated on the propane/air mixture were carried out for different reactor core diameters using Fluent (Ansys Fluent 17.0). The gas flow was simulated using a k - ϵ model with non-equilibrium wall functions [38, 39]. The inner EFR diameter was initially set to 10.5 cm, taking the expected thermal expansion into account. An axisymmetric geometry with ~157000 cells and a fine mesh along the walls and centerline was chosen to describe the reactor tube. PF combustion was modelled employing non-adiabatic probability density function tables of 20 species, with the rich flammability limit for propane in the fuel stream set to 0.1. The effect of radiation on the gas phase was incorporated using a domain-based, weighted-sum-of-gray-gases model, and radiation from surfaces was accounted for by a discrete ordinates approach [40]. All surfaces were ascribed an emissivity coefficient of 0.7. Since measurements of flat-flame burner and shroud inlet surface temperatures were not available, a one point temperature calibration was performed using the temperature measured by TDLAS at Port 2. The wall temperatures were approximated by a polynomial function based on measured TC values corresponding to the wall at Port 1, and TDLAS measurements from Port 2 to Port 5.

From the full 2D simulation, the column density of H_2O at each port was calculated as

$$N_{H_2O} = \sum_{k=1}^n (w_k c_k), \quad (1)$$

where k is the mesh cell number with values from 1 (EFR center) to n (adjacent to EFR wall), w is the radial width of cell k , and c_k is the H_2O mole fraction in the cell. The average H_2O concentration was then determined by dividing the column density with the sum of the radial widths of all cells according to

$$\bar{C}_{H_2O} = N_{H_2O} / \sum_{k=1}^n w_k. \quad (2)$$

The H_2O density-weighted path-averaged temperature was obtained from the simulation using

$$\bar{T}_{H_2Ow} = \sum_{k=1}^n (w_k c_k T_k) / \sum_{k=1}^n (w_k c_k), \quad (3)$$

where T_k is the simulated temperature in cell k .

2.6 Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations were carried out for the conditions at Ports 3 and 5 as a function of O_2 -to-fuel equivalence ratio (λ) using FactSage 7.0 [41] and the databases FactPS, FToxid-SlagB (MC), FToxid-SlagD (SW) and FTsalt-SaltB. The concentrations of all 14 elements provided in Table 1 as well as the moisture content were used as fuel composition input for SW and MC. The average temperatures determined by TDLAS at the respective ports were used in the calculations, so that the effect of fuel particle burnout and changes in O_2 partial pressure during conversion could be used as variables to describe the partial pressure of $K(g)$. Initial calculations were performed for the PF case to determine the oxidizing atmosphere available to the fuel particles, and the resulting gas stream was exported and used as O_2 carrier stream in the calculations for SW and MC. The shift from an oxygen-deficient (gasification) to

an oxygen-rich (combustion) environment occurs at λ equal to one. This is a coarse representation of the local conditions for the burning fuel particles, but provides global equilibrium predictions for the concentrations of various gaseous potassium compounds.

3. Results and discussion

A summary of the results obtained in this work is presented in Table 2. The table shows the average gas temperature, H_2O and atomic potassium measured by the TDLAS sensor at the different optical ports and operating conditions, as well as the corresponding results for temperature and H_2O obtained by the 2D CFD simulations.

The TDLAS-measured temperature at Port 2 was used as calibration point for the numerical simulations. Temperature in units of Kelvin and column density in units of $\% \cdot \text{m}$ were determined independently of the absorption path length. The concentration values in units of % and parts per billion by volume (ppbv) are given for a path length of 12 cm, which was identified as the most likely effective path length (see section 3.2 and Fig. 3). Since the actual fuel feeding rate was found to vary significantly (up to 50 g/h) [42], and the only source of potassium was the biomass, the K(g) values were normalized to an average fuel feeding rate of 200 g/h. At Port 5, still unconverted, burning fuel particles led to occasional high K(g) concentration outliers, which caused a non-normal distribution of K(g) . For that reason, the median (instead of the average) K(g) values are given for this port.

Table 2. Summary of the experimental (TDLAS) and numerical (2D CFD) results per optical port and operating condition (EFR mode). PF-propane flame; SW-softwood; MC-Miscanthus. Measurement uncertainties of TDLAS-derived temperatures and H_2O concentrations are around 25 K and 0.5% H_2O , respectively.

Parameter	Unit	Method	EFR mode	Port 2	Port 3	Port 4	Port 5	FTIR exhaust
Temperature	[K]	TDLAS	PF	1314	1228	1228	1268	
		2D CFD	PF	1314	1226	1234	1260	
		TDLAS	SW	1473	1400	1305	1316	
			MC	1477	1472	1301	1314	
H ₂ O(g)	[%]	TDLAS	PF	6.6	5.0	4.6	4.7	4.7
		2D CFD	PF	6.7	4.9	4.8	4.8	
		TDLAS	SW	8.3	8.1	7.7	7.6	
			MC	8.4	9.2	7.3	7.4	
H ₂ O(g)	[%·m]	TDLAS	PF	0.79	0.60	0.56	0.57	
		2D CFD	PF	0.80	0.58	0.57	0.57	
K(g)	[ppbv]	TDLAS	SW	88	50	23	1.7	
			MC	101	80	6.3	0.2	

3.1 Propane flame CFD simulations

Figure 2 displays the simulated temperature and H₂O distributions in the EFR during propane flame operation assuming an inner EFR diameter of 10.5 cm (expected diameter at 1273 K).

Fig. 2. (a) 2D Fluent simulation of gas temperature and H₂O distributions in the PF-operated EFR. (b) Simulated radial temperature profiles at Ports 2, 3 and 5 (solid lines) together with TC-measured profiles (solid markers). (c) Simulated radial H₂O profiles at Ports 2, 3 and 5.

Close-ups on the regions around the port locations (indicated by arrows) are shown for clarity. For both temperature and H₂O, steep gradients are present at Port 2, since the hot propane combustion products are concentrated at the EFR center, while the cold shroud gas resides near the reactor wall. At Ports 3-5, the gases are well mixed, leading to more uniform conditions across the reactor tube.

Simulated radial temperature and H₂O profiles (lines) are shown for some of the ports in Figs. 2b and 2c, respectively. The temperature profiles are compared to TC measurements (markers), which capture the general shape, but, at Port 2, agree poorly with the simulations. This suggests that, even with thin-wire S-type TCs, a small weld point and in the case of PF combustion without biomass, TC measurements are unreliable in environments with complex radiation balance. Radiation effects and temperature and species gradients probably play an even larger role when firing biomass, especially in the gasification regime, when soot particles can form deposition layers on the TC junction, increasing its emissivity [43].

3.2 Reactor gas temperature and H₂O(g) – propane flame

Figure 3 presents a comparison between measured and simulated axial temperatures (Fig. 3a) and H₂O profiles (Figs. 3b-d) as a function of reactor length for the PF-operated EFR. In Fig. 3a, the average temperature measured by TDLAS at each port is shown together with the corresponding TC data (radial average and center temperature, see Fig. 2b) as well as the average H₂O density-weighted, centerline and maximum axial temperature profiles (lines) extracted from the 2D simulation for an EFR diameter of

10.5 cm. Fig. 3b displays the TDLAS-measured path-averaged H_2O levels together with average and maximum axial H_2O profiles from the simulation. The H_2O concentration quantified by FTIR at the exhaust is shown for comparison. In Fig. 3c, experimental and simulated H_2O results assuming optical path lengths of 10.5, 11 and 12 cm are compared. Finally, Fig. 3d presents the TDLAS-measured column density together with the column density obtained from the 2D CFD simulations for EFR diameters of 10.5, 11 and 12 cm. In all four figures, the error bars represent the measurement uncertainties stated in section 2.3.

The TDLAS results fit well to the simulated temperatures beyond Port 2. The steep decrease in temperature between Ports 2 and 3 is due to the mixing of hot flue gas with the colder shroud gas. Around Ports 3 and 4, the temperature is lower than the nominal heater temperature (1273 K), likely because heat is not efficiently transferred to the EFR as a consequence of the heater gap and the 10 cm distance between the heaters and the reactor tube. Approaching Port 5, the temperature rises again as the wall is fully exposed to the heating elements. The small difference between experimental results and simulated center, maximum and H_2O -weighted temperatures suggests that TDLAS gives a good estimate of the temperature in the hot EFR center, where most of the water resides. Cooler water vapor near the walls, even in low concentrations, may, however, bias the TDLAS results as the maxima of the H_2O employed transitions lie around 1100 K [36]. Due to radiative heat transfer to the water-cooled burner, the TC average and center values do not accurately represent the gas temperatures at Port 2, even in the absence of soot and ash particles. At Ports 3-5, for laminar flow and homogenous conditions, both TDLAS and TC results are reliable and agree to within 25 K.

Fig. 3. Comparison between TDLAS data and 2D CFD simulations as a function of reactor length of the PF-operated EFR. (a) Axial temperature profiles, (b) axial H₂O concentration profiles, (c) H₂O concentration profiles for EFR diameters of 10.5, 11 and 12 cm, (d) experimental H₂O column density compared to simulated column density for the different EFR diameters. The error bars represent the TDLAS measurement uncertainties.

The TDLAS-measured H₂O concentrations in Fig. 3b indicate an axial profile shape similar to the simulated average H₂O profile, but the absolute concentrations are somewhat higher than the model prediction and the exhaust FTIR data. The discrepancy may partly stem from uncertainties in the spectroscopic parameters of the H₂O transitions, but are most likely due to a systematic error in the assumed absorption path length. In the upper part of the reactor, the maximum simulated H₂O is considerably higher than the TDLAS-derived concentration, owing to the prevailing inhomogeneous conditions.

The effect of a change in absorption path length of up to 1.5 cm (or 14% of the initial EFR diameter) on the experimental and simulated H₂O concentrations is illustrated in

Fig. 3c. The 2D simulations show only a minor dependence on the EFR diameter due to slight differences in chemistry and flow dynamics. On the other hand, as expected according to Beer-Lambert's law in the optical thin limit, the concentrations determined by TDLAS change linearly with path length. A good agreement with 2D CFD is observed for a path length of 12 cm. This observation is confirmed by looking at the path length-independent TDLAS column density (Fig. 3d), which again agrees well with the simulated column density for an EFR diameter of 12 cm. Here, the simulated column density shows a strong dependence on the EFR diameter, because the same average water vapor concentration is observed over a larger domain. Since the actual EFR diameter must be close to 10.5 cm, this indicates that the hot gases slightly (by less than 1 cm) penetrate the optical access port tubes. Deviations could mean that tube diameter or penetration depth varied slightly from port to port, probably dependent on local temperature or gas velocity.

Overall, in the PF case, a very good agreement between experiment and simulation was achieved under homogeneous conditions (Ports 3-5). In the upper, heterogeneous, part of the EFR (Ports 2), the comparison can give an idea about the actual temperatures and species distributions. The difference between TDLAS and simulated maximum H_2O (Fig. 3b) may give an indication of the diameter of the entrained reaction zone in the center of the EFR.

3.3 Gas temperature and $\text{H}_2\text{O(g)}$ in the biomass-fed reactor

Average TDLAS temperatures and H_2O concentrations measured in the EFR at the four optical ports during conversion of SW and MC are shown as a function of particle residence time in Fig. 4, calculated as outlined in section 2.4. For comparison, the values obtained during PF combustion (Fig. 3) are also displayed. The H_2O data are evaluated

for a path length of 12 cm. Due to the large variations in fuel feeding and resulting changes in O_2 -to-fuel equivalence ratio [42], corresponding fluctuations were also observed in the measured parameters. Therefore, in contrast to Fig. 3, here, the error bars represent the standard deviations of these fluctuations, which were largest at Port 3.

Fig. 4. Average TDLAS-measured gas temperatures (a) and H_2O concentrations (b) during SW and MC combustion in the EFR, displayed as a function of particle residence time. The error bars show the standard deviations of the fluctuations due to variations in the fuel feeding rate.

At all ports, both temperature and H_2O were higher than in the PF case. Temperature increased by up to 200 K at the upper ports and around 50 K at the lower ports, whereas H_2O increased by 2-5%. This is reasonable given the added heating value, moisture and bound hydrogen from the biomass. Devolatilization occurred around Ports 2 and 3, which was visually confirmed by looking into the EFR through the optical ports tubes, where burning fuel particles could be observed. The differences between the fuels were largest at Port 3. As opposed to the PF case, during biomass combustion, the flow entrainment and thus the temperature and H_2O gradients were more severe and probably extended down to Port 4. Temperature is less affected, since water-weighted,

but the average H_2O represents global conditions and may underestimate the water concentrations close to the biomass.

3.4 Gaseous atomic potassium in the biomass-fed reactor

The average/median K(g) concentrations measured by TDLAS at each port during combustion of SW and MC are displayed as a function of residence time in Fig. 5a. The values are given for an absorption path length of 12 cm and are corrected for changes in the average fuel feeding rate observed in the different experimental runs. The error bars represent the maximum measurement uncertainty stated in section 2.3. Despite the much higher initial potassium content in MC (Table 1), only slightly higher K(g) concentrations were observed compared to SW at Ports 2 and 3, and even lower values than for SW at Ports 4 and 5.

Fig. 5. (a) Average TDLAS-measured K(g) concentrations at Ports 2-5 as a function of residence time for SW and MC combustion in the EFR. Error bars represent the estimated measurement uncertainty. (b) Real-time TDLAS data for all three parameters measured at Port 5 during SW conversion. Occasional fluctuations due to variations in feeding rate (and λ) can be observed even at this port.

Similar to what was observed for temperature and H_2O , fluctuations due to variations in the fuel feeding rate (and λ) were also observed for K(g) , even at Port 5, as evident from Fig. 5b, which displays a few minutes of online data for all three parameters

recorded during SW combustion. Here, the fuel feeding system was turned on at 230 s. A stable base K(g) level of around 2 ppbv was then established and a correlation between K(g) and temperature could be observed. The extent of the fluctuations was probably not fully resolved since, in this work, a relatively low overall data acquisition time (varying between 2-10 s) was employed. While the fluctuations led to normally distributed K(g) concentrations at Ports 2-4, the occasional outliers in K(g) concentration at Port 5 due to high K(g) in the vicinity of not yet fully converted, burning fuel particles (also observed visually when looking into the EFR through the optical port) caused a non-normal distribution. Thus the median values were considered more representative for Port 5.

As for H₂O(g), and as was evident from the 2D CFD simulations of the water vapor distribution in the PF-operated EFR, the average/median K(g) concentrations represent the global conditions and may underestimate the local concentrations. In the vicinity of the fuel particles entrained in the EFR center, local temperature and K(g) could be higher and the path length smaller (but difficult to define).

3.5 Atomic potassium – comparison to equilibrium calculations

Thermodynamic equilibrium calculations were performed for both fuels for the conditions at Ports 3 and 5 using the TDLAS-measured temperatures given in Table 2. Figure 6 presents the calculated dominant gas phase K compounds and water vapor as a function of O₂-to-fuel equivalence ratio at each of the ports, together with the experimental average (or median for Port 5) K(g) mole fractions, marked at a lambda that was matched to the measured H₂O concentration. Fuel-rich conditions were assumed at Port 3, whereas an oxygen-rich atmosphere was supposed at Port 5. In general, shifting towards lower lambda can be interpreted as moving axially higher up

in the EFR as well as radially closer to the entrained fuel particles. The TEC-predicted and measured $K(g)$ mole fractions can be compared since the equilibrium was calculated taking the biomass, the propane flame products and the shroud gas into account. This provides the average partial pressure of $K(g)$ at the given average port temperature, which corresponds to the average $K(g)$ concentrations determined by TDLAS.

The error bars on the experimental $K(g)$ values in Fig. 6 show the standard deviations and recorded maxima as a result of the overall concentration variations that were mainly caused by fluctuations in fuel feeding and λ , as exemplified in Fig. 5b. Note that the maximum $K(g)$ values are generally associated with a higher temperature and, therefore, cannot directly be compared to equilibrium calculated at the average temperature. Evidently, the fluctuations were largest during devolatilization (at Port 3), but occasional peaks were observed at Port 5. For λ s around one (at constant PF and shroud combustion), an increase in fuel supplied to the system, shifts the equivalence ratio to lower values, which dramatically increases $K(g)$, much more than what can be explained by changes in temperature or optical path length.

Fig. 6. Thermodynamic equilibrium values of K compounds and water vapor for SW (a, b) and MC (c, d) for Ports 3 and 5, plotted as a function of lambda and calculated using the TDLAS-measured temperature at the respective port. The blue dots indicate the measured H₂O concentration, to which the measured K(g) concentrations (red star markers) were matched. The errors bars represent the standard deviations and maxima due to fuel feeding fluctuations.

The equilibrium calculations revealed several key parameters affecting the amount of K(g) for these fuels at the conditions prevalent in the EFR. Firstly, as opposed to KOH(g) and KCl(g), the predicted amount of K(g) changes significantly with lambda, in particular around stoichiometric conditions, and is much higher in gasification mode ($\lambda < 1$) than in combustion mode ($\lambda > 1$). Secondly, K(g) increases with temperature at any given lambda. Thirdly, in the combustion regime, the amount of K₂SO₄(g) formed increases, which directly decreases the amount of K(g) in the system. However, K₂SO₄ may be over-predicted in TEC as its production is strongly affected by the oxidation from SO₂(g) to SO₃(g), which can be slow [44, 45]. Finally, the interaction with other ash-forming elements is very important for K(g). Although the MC used in

this study contains 5.5 times more potassium than SW (Table 1), lower mole fractions of $K(g)$ are predicted by TEC for this fuel.

From Table 1 it is evident that the SW ash has a clear deficit of Lewis base forming elements (Si, P, S, Cl) compared to Lewis acid forming elements (K, Na, Ca, Mg, Fe, Al) [46], which directly affects the ratio between $KOH(g)$ and $KCl(g)$ (Fig. 6). For example, little chlorine is available in SW to form $KCl(g)$, whereas much larger amounts of $KCl(g)$ compared to $KOH(g)$ are predicted for MC in the combustion regime. Thus, while the potassium in SW is probably bonded in alkali carbonates at temperatures lower than those observed in the EFR it will to a large extent be released as $K(g)$ at elevated temperatures. The lower amount of $K(g)$ predicted and measured for MC at the end of the conversion (Ports 4 and 5) may partly be explained by secondary ash transformation reactions consuming $KOH(g)$ to bond K in silicates (including slag), phosphates, or sulphates, which pushes the equilibrium for $K(g)$ to lower concentrations.

At Port 3, devolatilization was still ongoing and λ was probably below unity as indicated by the low experimental H_2O concentrations. The fact that, for both SW and MC, the measured amounts of $K(g)$ were much lower than those predicted by TEC at $\lambda < 1$ suggests that primary ash transformation reactions have taken place to produce $KOH(g)$, possibly reacting further through secondary reactions to form other K-containing compounds [3]. This conclusion holds even though TDLAS may somewhat underestimate the local $K(g)$ and H_2O concentrations, as discussed above. At Port 5, the calculated and measured $K(g)$ values were in excellent agreement for both SW and MC, suggesting that even the secondary and tertiary ash transformation reactions [3, 46] affecting $K(g)$ were close to – or at – global equilibrium. The slightly higher experimental value for MC could be related to slow oxidation reactions (SO_2 oxidation to SO_3 for

subsequent formation of sulphates) and possibly the somewhat slower alkali silicate forming reactions.

The measured $K(g)$ concentrations and temperature profiles also provide information regarding the fuel burnout. As evident from Table 2 and Figs. 4 and 5, MC combustion first (at Port 3) results in higher $K(g)$ concentrations and temperatures than observed for SW conversion. Towards Port 4, $K(g)$ then drops sharply to 6.3 ppbv for MC, whereas for SW the compound decreases linearly to 23 ppbv at similar temperatures. This confirms the TEC prediction of lower $K(g)$ in MC conversion and suggests faster burnout for this fuel.

The in situ TDLAS measurements of $K(g)$ during combustion of the two different fuels in the EFR have provided empirical support for, and valuable new information on, the conceptual model for ash transformation reactions [3], which was developed and investigated primarily using extractive techniques. Importantly, it has been shown in this work, that global equilibrium models may overestimate $K(g)$ at reducing conditions, which is probably related to different reaction rates for the inorganic and organic matrices, as has previously been suggested in the literature [3]. TEC assumes that all reactants are available for reaction, which is not true during a real fuel particle conversion. Overall, the results presented here support the assumption that $K(g)$ rapidly undergoes primary ash transformation reactions to form KOH or KCl even if the global atmosphere for the fuel particles exhibits a λ smaller than unity. It cannot be stated with certainty that KOH and KCl are at equilibrium levels, even at port 5, without further empirical studies.

This information was obtainable only by in situ measurements of $K(g)$ with the fuel particle in close proximity to the flue gases, where a global equilibrium could be

established. In cases where the fuel particle is separated from the gas phase, e.g. in grate fired combustion, it is still reasonable to assume that $K(g)$ undergoes primary reactions quickly and then interacts with other ash-forming elements through secondary reactions close to the fuel bed. The current work also demonstrates the importance of accurate in situ measurements of process parameters, such as temperature and major species, in addition to alkali compounds in fuel conversion studies.

In future investigations, it will be beneficial to be able to conduct measurements even closer to the fuel inlet, quantify carbon-containing species, and determine the degree of fuel conversion and total K release by established experimental methods. CFD simulations that include biomass particles and potassium reactions can improve our understanding of the local conditions experienced by the fuel. Without doubt, in situ detection of other potassium species, such as $KOH(g)$ and $KCl(g)$, is of great importance to track the secondary ash transformation reactions and assist the development of kinetic models.

4. Conclusions

In this work, a first step has been taken towards investigating potassium chemistry in situ during thermochemical conversion of powdered biomass in settings resembling industrial facilities. By comparison with 2D CFD simulations and standard gas analysis, the suitability of TDLAS for calibration-free measurements of average temperature and species concentrations in the hot reaction zone of an atmospheric entrained flow reactor was confirmed. Absolute concentrations of elemental potassium were for the first time detected in an EFR core during biomass combustion. Only small differences in $K(g)$ were observed between softwood and Miscanthus along the EFR. At the end of the reactor,

the measured K(g) concentrations were in excellent agreement with thermodynamic equilibrium. The fact that, in the upper part of the EFR, K(g) was significantly lower than predicted by TEC for reducing conditions points to inorganic ash-transformation occurring faster than organic reactions. Although K(g) changes significantly around stoichiometric conditions, the most important factor determining the concentrations of gaseous K compounds in general is the fuel composition, especially the concentrations of the other ash-forming elements. The combination of laser-based diagnostics and modelling approaches has the potential to provide unique insights into fuel conversion and ash-related chemistry.

Acknowledgements

The work was financially supported by the Swedish Energy Agency (36160-1), the Kempe Foundations (JCK-1316), the Swedish Gasification Center, and the Swedish strategic research program Bio4Energy.

References

- [1] L.D. Smoot, P.J. Smith, Coal combustion and gasification, Springer Science & Business Media, New York, 2013.
- [2] F. Weiland, H. Hedman, M. Marklund, H. Wiinikka, O. Öhrman, R. Gebart, Pressurized oxygen blown entrained-flow gasification of wood powder, *Energ Fuel* 27 (2013) 932-941.
- [3] D. Boström, N. Skoglund, A. Grimm, C. Boman, M. Öhman, M. Broström, R. Backman, Ash transformation chemistry during combustion of biomass, *Energ Fuel* 26 (2012) 85-93.
- [4] M.-K. Bahng, C. Mukarakate, D.J. Robichaud, M.R. Nimlos, Current technologies for analysis of biomass thermochemical processing: a review, *Anal Chim Acta* 651 (2009) 117-138.
- [5] K. Umeki, K. Kirtania, L. Chen, S. Bhattacharya, Fuel particle conversion of pulverized biomass during pyrolysis in an entrained flow reactor, *Ind Eng Chem Res* 51 (2012) 13973-13979.
- [6] A.J. Damoe, P.A. Jensen, F.J. Frandsen, H. Wu, P. Glarborg, Fly Ash Formation during Suspension Firing of Biomass: Effects of Residence Time and Fuel Type, *Energ Fuel*, (2016).

- [7] C. Ma, M. Carlborg, H. Hedman, J. Wennebro, F. Weiland, H. Wiinikka, R. Backman, M. Öhman, Ash formation in pilot-scale pressurized entrained-flow gasification of bark and a bark/peat mixture, *Energ Fuel* 30 (2016) 10543-10554.
- [8] C. Dupont, L. Chen, J. Cances, J.-M. Commandre, A. Cuoci, S. Pierucci, E. Ranzi, Biomass pyrolysis: Kinetic modelling and experimental validation under high temperature and flash heating rate conditions, *Journal of Analytical and Applied Pyrolysis* 85 (2009) 260-267.
- [9] S. Halama, H. Spliethoff, Numerical simulation of entrained flow gasification: Reaction kinetics and char structure evolution, *Fuel Process Technol* 138 (2015) 314-324.
- [10] L. Álvarez, M. Gharebaghi, M. Pourkashanian, A. Williams, J. Riaz, C. Pevida, J. Pis, F. Rubiera, CFD modelling of oxy-coal combustion in an entrained flow reactor, *Fuel Process Technol* 92 (2011) 1489-1497.
- [11] T. Kolb, M. Aigner, R. Kneer, M. Müller, R. Weber, N. Djordjevic, Tackling the challenges in modelling entrained-flow gasification of low-grade feedstock, *J Energy Inst* 89 (2016) 485-503.
- [12] D. Nordgren, H. Hedman, N. Padban, D. Boström, M. Öhman, Ash transformations in pulverised fuel co-combustion of straw and woody biomass, *Fuel Process Technol* 105 (2013) 52-58.
- [13] M.S. Bashir, P.A. Jensen, F. Frandsen, S. Wedel, K. Dam-Johansen, J. Wadenbäck, S.T. Pedersen, Ash transformation and deposit build-up during biomass suspension and grate firing: Full-scale experimental studies, *Fuel Process Technol* 97 (2012) 93-106.
- [14] S.B. Hansen, P.A. Jensen, F.J. Frandsen, B. Sander, P. Glarborg, Mechanistic Model for Ash Deposit Formation in Biomass Suspension Firing. Part 1: Model Verification by Use of Entrained Flow Reactor Experiments, *Energ Fuel* 31 (2017) 2771-2789.
- [15] A. Williams, J. Jones, L. Ma, M. Pourkashanian, Pollutants from the combustion of solid biomass fuels, *Prog Energ Combust* 38 (2012) 113-137.
- [16] S. Zellagui, G. Trouvé, C. Schönnenbeck, N. Zouaoui-Mahzoul, J.-F. Brilhac, Parametric study on the particulate matter emissions during solid fuel combustion in a drop tube furnace, *Fuel* 189 (2017) 358-368.
- [17] C. Ma, R. Backman, M. Ohman, Thermochemical equilibrium study of slag formation during pressurized entrained-flow gasification of woody biomass, *Energ Fuel* 29 (2015) 4399-4406.
- [18] S. Akbar, U. Schnell, G. Scheffknecht, Modelling potassium release and the effect of potassium chloride on deposition mechanisms for coal and biomass-fired boilers, *Combust Theor Model* 14 (2010) 315-329.
- [19] 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.
- [20] H. Tolvanen, L. Kokko, R. Raiko, Fast pyrolysis of coal, peat, and torrefied wood: mass loss study with a drop-tube reactor, particle geometry analysis, and kinetics modeling, *Fuel* 111 (2013) 148-156.
- [21] C.S. Goldenstein, R.M. Spearrin, J.B. Jeffries, R.K. Hanson, Infrared laser-absorption sensing for combustion gases, *Prog Energ Combust* 60 (2017) 132-176.
- [22] C. Erbel, M. Mayerhofer, P. Monkhouse, M. Gaderer, H. Spliethoff, Continuous in situ measurements of alkali species in the gasification of biomass, *Proceedings of the Combustion Institute* 34 (2013) 2331-2338.

- [23] H. Teichert, T. Fernholz, V. Ebert, Simultaneous in situ measurement of CO, H₂O, and gas temperatures in a full-sized coal-fired power plant by near-infrared diode lasers, *Appl Optics* 42 (2003) 2043-2051.
- [24] K. Sun, R. Sur, X. Chao, J.B. Jeffries, R.K. Hanson, R.J. Pummill, K.J. Whitty, TDL absorption sensors for gas temperature and concentrations in a high-pressure entrained-flow coal gasifier, *Proceedings of the Combustion Institute* 34 (2013) 3593-3601.
- [25] P. Ortwein, W. Woiwode, S. Fleck, M. Eberhard, T. Kolb, S. Wagner, M. Gisi, V. Ebert, Absolute diode laser-based in situ detection of HCl in gasification processes, *Exp Fluids* 49 (2010) 961-968.
- [26] R. Sur, K. Sun, J.B. Jeffries, R.K. Hanson, R.J. Pummill, T. Waind, D.R. Wagner, K.J. Whitty, TDLAS-based sensors for in situ measurement of syngas composition in a pressurized, oxygen-blown, entrained flow coal gasifier, *Applied Physics B* 116 (2013) 33-42.
- [27] A. Sepman, Y. Ögren, Z. Qu, H. Wiinikka, F.M. Schmidt, Real-time in situ multi-parameter TDLAS sensing in the reactor core of an entrained-flow biomass gasifier, *Proceedings of the Combustion Institute* 36 (2017) 4541-4548.
- [28] E. Schlosser, J. Wolfrum, L. Hildebrandt, H. Seifert, B. Oser, V. Ebert, Diode laser based in situ detection of alkali atoms: development of a new method for determination of residence-time distribution in combustion plants, *Appl Phys B-Lasers O* 75 (2002) 237-247.
- [29] C. Liu, L. Xu, J. Chen, Z. Cao, Y. Lin, W. Cai, Development of a fan-beam TDLAS-based tomographic sensor for rapid imaging of temperature and gas concentration, *Opt Express* 23 (2015) 22494-22511.
- [30] C. Liu, L. Xu, Z. Cao, Measurement of nonuniform temperature and concentration distributions by combining line-of-sight tunable diode laser absorption spectroscopy with regularization methods, *Appl Optics* 52 (2013) 4827-4842.
- [31] M. Simone, E. Biagini, C. Galletti, L. Tognotti, Evaluation of global biomass devolatilization kinetics in a drop tube reactor with CFD aided experiments, *Fuel* 88 (2009) 1818-1827.
- [32] I.A. Schultz, C.S. Goldenstein, J.B. Jeffries, R.K. Hanson, R.D. Rockwell, C.P. Goynes, Spatially resolved water measurements in a scramjet combustor using diode laser absorption, *Journal of Propulsion and Power* 30 (2014) 1551-1558.
- [33] C.S. Goldenstein, I.A. Schultz, J.B. Jeffries, R.K. Hanson, Two-color absorption spectroscopy strategy for measuring the column density and path average temperature of the absorbing species in nonuniform gases, *Appl Optics* 52 (2013) 7950-7962.
- [34] K. Froment, F. Defoort, C. Bertrand, J.M. Seiler, J. Berjonneau, J. Poirier, Thermodynamic equilibrium calculations of the volatilization and condensation of inorganics during wood gasification, *Fuel* 107 (2013) 269-281.
- [35] Z. Qu, R. Ghorbani, D. Valiev, F.M. Schmidt, Calibration-free scanned wavelength modulation spectroscopy-application to H₂O and temperature sensing in flames, *Opt Express* 23 (2015) 16492-16499.
- [36] Z. Qu, F.M. Schmidt, In situ H₂O and temperature detection close to burning biomass pellets using calibration-free wavelength modulation spectroscopy, *Applied Physics B* 119 (2015) 45-53.
- [37] P. Holmgren, D.R. Wagner, A. Strandberg, R. Molinder, H. Wiinikka, K. Umeki, M. Brostrom, Size, shape, and density changes of biomass particles during rapid devolatilization, *Fuel* 206 (2017) 342-351.

- [38] A.-h. Wang, J.-j. Cai, G.-w. Xie, Numerical simulation of combustion characteristics in high temperature air combustion furnace, *Journal of Iron and Steel Research, International* 16 (2009) 6-10.
- [39] B. Andersson, R. Andersson, L. Håkansson, M. Mortensen, R. Sudiyo, B. Van Wachem, *Computational fluid dynamics for engineers*, Cambridge University Press, Cambridge, U.K., 2011.
- [40] A.A. Aboje, J.I. Erete, K.J. Hughes, L. Ma, M. Pourkashanian, A. Williams, An investigation of methane and propane vertical flares, *J Energy Inst* 89 (2016) 793-806.
- [41] C. Bale, E. Bélisle, P. Chartrand, S. Decterov, G. Eriksson, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melançon, A. Pelton, FactSage thermochemical software and databases—recent developments, *Calphad* 33 (2009) 295-311.
- [42] A. Sepman, Y. Ögren, H. Wiinikka, Optical techniques for characterizing the biomass particle flow fluctuations in lab-and pilot-scale thermochemical systems, *Powder Technol* 313 (2017) 129-134.
- [43] H. Wiinikka, High temperature aerosol formation and emission minimisation during combustion of wood pellets, Luleå University of Technology, Luleå, Sweden, 2005.
- [44] K. Iisa, Y. Lu, K. Salmenoja, Sulfation of potassium chloride at combustion conditions, *Energ Fuel* 13 (1999) 1184-1190.
- [45] P. Glarborg, P. Marshall, Mechanism and modeling of the formation of gaseous alkali sulfates, *Combust Flame* 141 (2005) 22-39.
- [46] N. Skoglund, Ash chemistry and fuel design focusing on combustion of phosphorus-rich biomass, Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå University, Umeå, Sweden, 2014.