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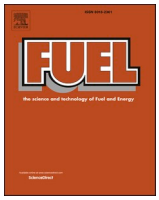

Monitoring of bed material in a biomass fluidized bed boiler using an electronic tongue

T. Leffler [a,*], M. Eriksson [c], B. Leckner [b], F. Lind [b], F. Winquist [c], P. Knutsson [a]

[a] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-41 296 Gothenburg, Sweden
[b] Department of Space, Earth and Environment, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden
[c] Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

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ABSTRACT

The thermal conversion of biomass fuel mixes in fluidized beds can cause agglomeration. To counteract agglomeration, bed material is gradually exchanged with virgin bed material, and this results in increased disposal of used bed material. Furthermore, the bed material exchange represents a costly option, as it involves a cost for virgin bed material, for landfill, and for unplanned downtime of the plant.

This paper presents a novel method for the evaluation of bed material quality: the electronic tongue (ET). Evaluation of bed material quality can contribute toward decreasing the cost of unnecessary exchanges of bed material. The proposed method was tested on bed material sampled on an almost daily basis from a commercial fluidized bed boiler during several months of operation.

A two-electrode ET was used for the evaluation of the bed material quality. The analysis relied on pulsed voltammetry measurements and multivariate data analysis with Principal Component Analysis (PCA). The results suggest that it is possible to follow bed material changes and that the ET, after further development, may be used to optimize the material flows connected to the bed material. Further research is being conducted to optimize the ET's performance and its application in monitoring bed material.

1. Introduction

Fluidized Bed (FB) technology is one of the preferred methods for thermal conversion of solid fuels, including biomass. Biomass contains a relatively low amount of ash that can be used as bed material in contrast to, for example, coal. Therefore, the FB boiler used in this investigation was fed with extraneous bed material. The conventional bed material for FB combustion of biomass is silica sand. The main drawback of silica sand is that it readily reacts with alkali compounds released during the conversion of biomass. This leads to the formation of a sticky layer on the bed particles, eventually resulting in bed agglomeration. Visser et al. [1] identified two types of bed agglomeration: coating-induced (Type 1) and melt-induced (Type 2) agglomeration. Type 1 agglomeration occurs when the gas-phase ash components from the biomass fuels form a uniform coating on the bed particles. Once the accumulated coating layer has reached a certain thickness and temperature, there is risk of neck formation, which initiates agglomeration between bed particles. Type 2 agglomeration occurs when molten ash particles interact with bed particles functioning as glue, binding the bed particles together. The most common agglomeration in FB boilers is coating-induced agglomeration (Type 1).

Sintering of the bed can be mitigated by feeding additives to the bed. Traditionally, this is achieved by co-combustion, like in one of the largest biomass-fired CFB boilers in the world, the 550 MW_{th} boiler in Alholmen, Finland, where the operators claim that the bed sinters if operated with wood waste only. However, during normal operation, peat is employed as an additional fuel, and then no sintering takes place as the mineral components of the peat ash prevent agglomeration. To meet the current goals of reducing the use of fossil fuels, the addition of such fuels cannot be readily applied. Instead, the addition of an alternative bed material to silica sand can be used as a solution. Such bed materials, for instance kaolin and some waste materials like blast furnace slag, were investigated [2] and were found to have the desired effect. Some alternative bed materials (e.g., ilmenite) tend to reduce the impact of agglomeration by lowering the levels of potassium, absorbing it inside the particles, and avoiding sintering [3,4]. Despite the possibilities of co-firing and the addition of dedicated bed material, the conventional way of avoiding sintering is often preferred, i.e., the

* Corresponding author.
E-mail address: letomas@chalmers.se (T. Leffler).

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premature renewal of the bed material at regular intervals. The bed materials are chosen depending on the ash content in the fuel and on the process operation conditions. Even though agglomeration is avoided, the regular exchange of bed material implies an additional cost for the plant owners and results in increased material waste flows that must be managed. The material flows, both in terms of fresh bed material and the generated bottom ash, can be unnecessarily high if the bed material is extracted prematurely. Therefore, getting an indication of the state of the bed material would help to determine the minimum rate of exchange of bed material. Schouten and van den Bleek [5] developed a method to detect changes in the fluidization behaviour that was used with good results by Chirone et al. [6]. The method helped predict bed agglomeration in two reactors burning biomass fuel with different scales. Another method that allows to follow the state of the bed material is based on monitoring the bed material temperature with a reproducibility of ± 5 °C [7], which could be an indicator of ongoing agglomeration and could be used for decision-making concerning the exchange of the bed material. Even though theoretically possible, commercial plants are not using the described methods for the indication of bed material exchange. This is most likely due to the complexity of the process as well as to insufficiencies in the information regarding fluidization and the process temperature that do not completely describe the complex phenomenon taking place in the plant.

In recent decades there has been an increased interest in multisensor systems for the monitoring of complex systems, such as electronic tongues (ETs), which have been evaluated with a multivariate method such as Principal Component Analysis (PCA) [8]. Multisensor systems are based on the measurements of properties, such as the quality, the condition, and the progression of a process rather than a single chosen parameter. These systems involve a large number of non-specific sensors with overlapping selectivity profiles instead of single sensors with specific selectivity. Different techniques for ETs have been described in the literature, e.g., potentiometry using ion-selective electrodes, using lipid/polymer membranes or voltammetry [9]. Among these technologies, voltammetry is the preferred choice when ruggedness and simplicity are required, which is the case with agglomeration, and thus this is the technology of choice for the present study.

The ET used in this investigation was based on pulsed voltammetry with two working electrodes of platinum and rhodium, respectively, which is a standard choice, allowing different catalytic properties and providing long-term stability for a variety of applications. These noble and catalytic metals have different catalytic properties, so each working electrode may produce a unique signal pattern. To measure chemical information, the bed material was placed in deionized water under stirring and the ET measured the so-obtained leachate. The collected information, in terms of measured current responses, was post-processed with PCA [10,11]. PCA is a multivariate technique that reduces the number of variables in a data set in a standardized way to preserve as much of the information as possible. Principal component 1 represents the direction that captures the largest part of the variance in the data set and principal component 2 is the second direction, orthogonal to the first, that captures the second largest part of the variance, and so on. An ET, developed at Linköping university [12,13], was used in an earlier feasibility study [14] on bed material samples (1–7) collected from the circulating fluidized bed (CFB) at Chalmers—see Fig. 1. Samples 4–7 are presented in consecutive order, marked by the arrows in Fig. 1. The rest of the samples were taken at different occasions. Sample 4 was obtained after the boiler had been running on a fuel mix of bark, refuse-derived fuel (RDF), and sewage sludge. Sample 5 was taken one week after Sample 4, when the boiler was running on wood chips over the weekend. The experiment continued for another 9 days. Later Samples (6–7) were obtained during a boiler stop. The bed material samples collected from the circulating fluidized bed (CFB) at Chalmers University of Technology showed that the leachable compounds detected by the ET allowed to group the samples in different clusters, representing different bed material states. The present study is a continuation of the development of

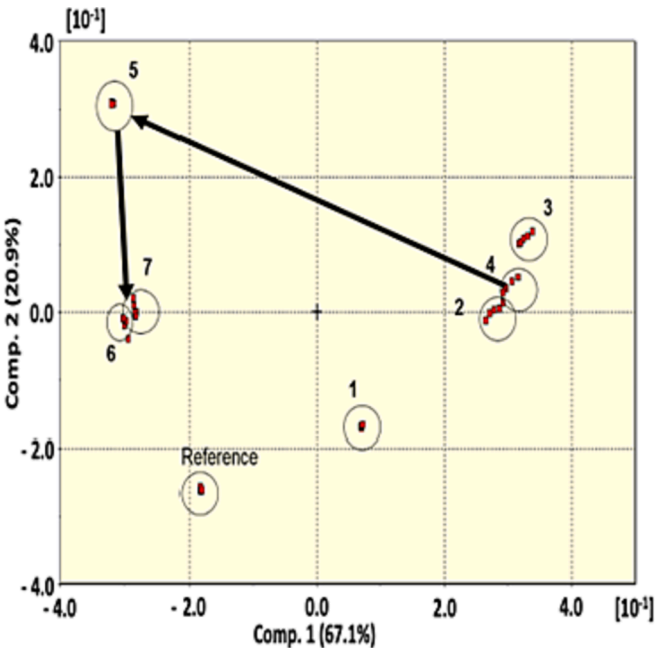

Fig. 1. Results from the pre-study with the electronic tongue: Reference is deionized water without sand; 1. Virgin sand (S36); 2. Bed sample from combustion of wood chips; 3. Bed sample from combustion of wood chips and straw; 4. Bed sample from wood chips combustion in the middle of the firing season; 5. Bed samples from combustion of wood chips mixed with bark, RDF (refuse-derived fuel), and sewage sludge after one week; and 6. and 7. agglomerated bed sample a few days after sample 5 was taken. (Comp. 1 and Comp. 2 are the principal components (PCs) and the percentage values are the percentage of the total variance explained by the respective PC).

the ET as a method for bed material status screening, where the aim is to evaluate that changes in the bed material can be followed over time and to subsequently determine when the bed material needs to be replaced to avoid bed agglomeration. Furthermore, the study investigates the application of the methodology on a commercial fluidized bed boiler under normal operation conditions.

2. Material and methods

2.1. Equipment and materials

The Swedish energy company Vattenfall AB owns and operates the 105 MW_{fuel} combined heat-and-power plant, Idbäcksverket, where the test was carried out. Biomass, consisting of demolition wood received from trucks (from the Nordic countries) and ships (from Central Europe), wood chips, and bark, was used as fuel. The plant was operated as a bubbling fluidized bed (BFB) producing 40 kg/s steam at 140 bar (g) and 540 °C. The furnace bottom has a cross-sectional area of 9.3 × 5.3 m. The height from the lowest part of the fuel inlet to the furnace bottom is approximately 1.5 m. Fig. 2 shows the lower part of the furnace, where eight thermocouples (T8121– T8128) were placed in an oval configuration about 30 cm above the air distributor nozzles. The pressure gauges, P-left, and P-right, measuring the bottom bed pressure, can also be seen in Fig. 2.

The boiler was operated in three modes: high load between 11th of December 2019 and 20th of February 2020, a transition from high load to low load between 25th of February 2020 and 14th of April 2020, and low load between 18th of April 2020 and 6th of June 2020. On 6th of June 2020, the boiler was stopped for annual maintenance. The three operational modes reflect the heating demand from the household sector. Table 1 describes the date and type of fuel mix for each boiler mode during the experiment.

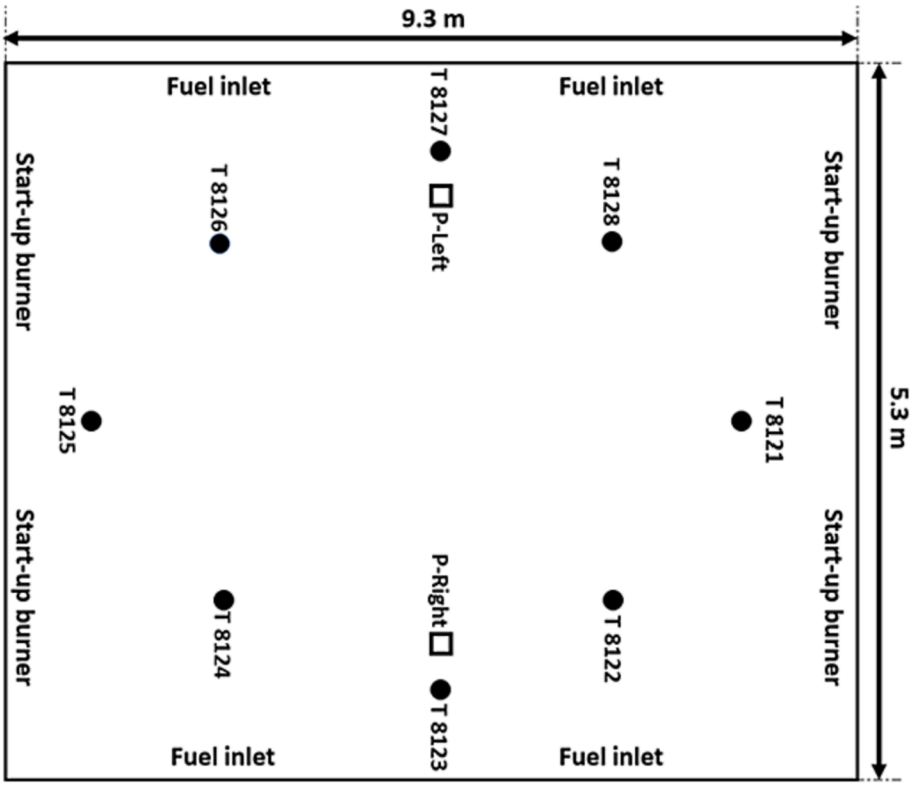

Fig. 2. The bottom part of the furnace, indicating the location for the eight thermocouples T8121–T8128 (dots) and the two pressure gauges (squares), measuring the bottom pressure of the bed—see Fig. 4.

Table 1
Date and fuel mix for the different boiler modes.

Boiler mode	Date	Fuel
High load	11th of December 2019 to 20th of February 2020	Demolition wood received from trucks (50 %) and ships (50 %). Three days of 100 % wood chips during the weekend before the stop.
Transition high → low load Low load	25th of February 2020 to 14th of April 2020 18th of April 2020 to 6th of June 2020	Demolition wood received from trucks (50 %) and ships (50 %). Demolition wood received from trucks (20 %), ships (50–70 %), and bark (10–30 %)

The calculated average amount, standard deviation (stdv.), maximum (max.), and minimum (min.) of the fuel ash components received from trucks and ships during the measurement campaign are shown in Table 2 as well as ash data for bark and wood chips. The ash data for bark and wood chips were supplied by the plant (stdv., max., and min. values were not available) while the data for demolition wood received from trucks and ships were from a standard fuel analysis carried out by Eurofins (SFS-EN ISO 16968:2015 (Al, Ca, Fe, K, Mg, Na, P, Si and Ti) and SS-EN 15408:2011 (S and Cl)).

The total mass of bed material in the system was around 120 tons. Upon start on 11th of December 2019, all the bed material was replaced with silica sand (particle size distribution: 0.354–2.800 mm) BASKARPSAND® B1-2. Two further changes to the bed material were made: at the end of February 2020, when two thirds of the bed material were replaced, and in the middle of April 2020, when two thirds of the bed material were replaced again.

The feed of fresh bed material was at a relatively stable flow of around 3 kg/MWh, while the removal of the rejected bed material fluctuated around 6 kg/MWh from December 2019 to mid-April 2020. At the end of the firing season, the removal of the rejected bed material

Table 2
Average fuel ash composition on Ds (dry substance) during the test.

Type of fuel	Al	Ca	Cl	Fe	K	Mg	Na	P	S	Si	Ti	[mg/kg Ds]
Demolition	334	2517	727	516	615	379	529	117	418	3107	82	Mean
wood received	129	685	1699	410	216	85	227	162	156	1874	54	Stdv.
from trucks	640	4300	9600	2400	1700	620	1000	940	900	9300	230	Max.
	150	1700	120	180	480	250	290	52	200	550	17	Min.
Demolition	536	4220	862	1270	714	544	812	112	644	5952	125	Mean
wood received	200	1680	323	1069	157	133	339	33	243	4937	64	Stdv.
from ships	1000	7800	1600	5000	1100	850	1400	210	1020	19000	240	Max.
	270	2200	490	410	390	350	430	64	270	1200	23	Min.
Bark	600	7900	200	340	1600	580	200	360	300	3000	26	
Wood chips	434	4654	200	296	1843	580	174	461	400	3093	21	

was increased to around 8 kg/MWh. This increase could be due to the incineration of bark, which contains high amounts of certain ash components, in combination with the normal fuel mix of demolition wood. Fig. 3 shows the boiler's steam load, the feed of fresh bed material, and the removal of the rejected bed material during the campaign.

Fig. 4 shows the measured temperatures and the pressures at the bottom of the bed during the experiment. This data represents valuable bed parameters for the monitoring of the status of the bed—see Fig. 2 for locations. The bed temperature fluctuates less when the boiler is operated on a low load in contrast to the fluctuation at a high load. The two stops from 21st to 24th of February 2020 and from 15th to 17th of April 2020 were planned stops for cleaning, while the third stop from 22nd to 23rd of April 2020 was unplanned, caused by a tube leakage in the economizer. The bed pressure increased toward the end of the firing season. Fig. 4 also shows two minor temperature drops toward the end of January (Temp_8121) and at the beginning of February (Temp_8123), which indicates a disturbance in the bed. After the larger temperature drop shown in Fig. 4 at around 10th of February (Temp_8124), a cleaning stop was scheduled. Fig. 3 shows that, concomitant with an increased input feed of fresh bed material as well as an increased removal of rejected bed material, the boiler load was reduced to combat the bed disturbance.

2.2. Bed material and ash flows

Fig. 5 presents an overview of the input of fuel ash and fresh bed material (silica sand), the recirculation loop of the bed material passing the storage silo for recirculated bed material (see Fig. 6) and the output of fly- and bottom ashes. It should be noted that the silos for storage, reject, and recirculated bed material are not included in Fig. 5 but can be seen in Fig. 6. The recirculated bed material was sieved to remove larger ash particles and agglomerates (directed to a reject silo—see Fig. 6) before it re-entered the furnace. The storage silo for recirculated bed material had a capacity of 60 tons but, during operation, the average mass of bed material stored in the silo was 40 tons. The storage silo for fresh bed material had a capacity of 50 tons. The reject silo had a capacity of 80 tons.

During the experiment, which was carried out between 11th of December 2019 and 6th of June 2020, the plant operators collected 147 bed samples that were analyzed by the ET. Each sample had a mass between 0.4 and 0.8 kg. The bed samples were extracted from the storage silo of recirculated bed material, where the recycled bed material was kept once the larger ash particles and agglomerates had been removed by sieving—see Fig. 6. The bed material was sampled in Point 4—shown in Fig. 6. The flow of fresh bed material (2) was on an average 3 kg/MWh of burned fuel. The fresh bed material was mixed with the fuel (3) before it entered the furnace. Bed material continuously left the furnace through its bottom for the removal of larger ash particles and agglomerates in the sieve (shown as the "screen" in Fig. 6). Fly ash left the system via (1), while the rejected bed material, larger ash particles, and agglomerates (bottom ash), left the system via the reject silo (5). The turnaround time of the recirculated bed material stored in the recirculation silo was approximately 24 h depending on load.

2.3. Bed material characterization

2.3.1. ET measurements

The ET set-up used in this experiment consisted of five parts shown in Fig. 7 (left): a sensor probe, a relay box, a potentiostat, an interface, and a computer [14]. The sensor probe contained two working electrodes of platinum and rhodium, respectively, with a purity of 99.9 % (Fig. 7, left, shows three electrodes but only two were used). The electrode diameter was 1 mm. The electrodes were placed in a stainless-steel tube (length 100 mm, diameter 15 mm), embedded in dental material (Filtec, The 3 M Company, USA). The stainless-steel tube served as the counter electrode in the voltametric measurements. The relay box was connected to the electrodes, the potentiostat, and the interface. The potentiostat applied a voltage signal (Fig. 7, top right) to the sensor probe and simultaneously measured the current response (Fig. 7, bottom right). The interface connected the relay box, the potentiostat and the computer. The computer, connected to the interface, controlled the measurements and stored the measured data. For the ET measurements, 40 ml of deionized water from a Milli-Q System was used to extract chemical substances from 10 g of the sampled bed material. The solution was then analysed by the ET with pulsed voltammetry under magnetic stirring. As shown in Fig. 7 (top right), the applied voltage pulses were both positive and negative and had different amplitudes (0, 0.7, -1.0, 0, -0.5, 0, -0.2, 0, 0, 0.2, 0, 0.5, 0, 0.7 and 0 V). This is a standard pulse train used for exploratory measurements. The first 2 pulses (+0.7 and -1.0 V) are carried out to regularly perform an electrochemical cleaning of the

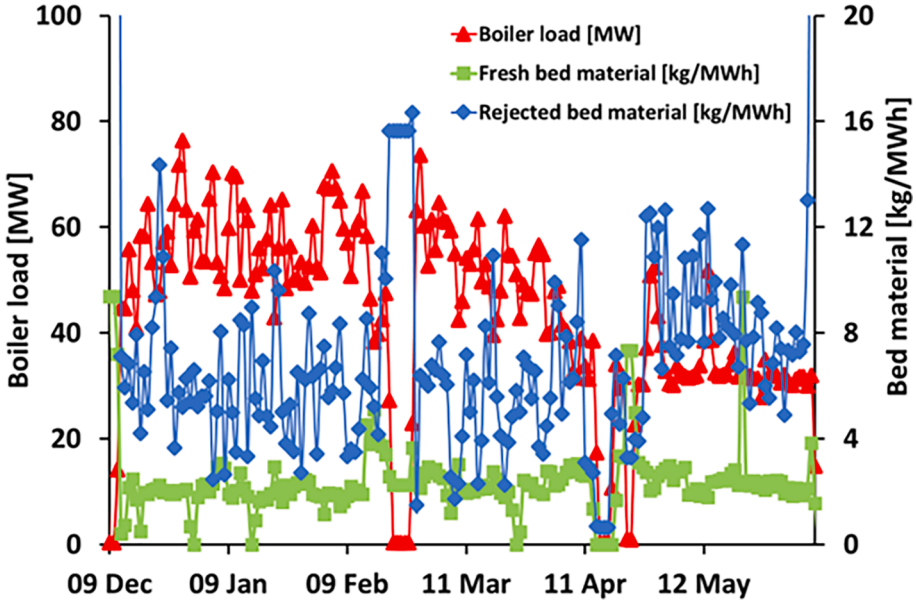

Fig. 3. The load (steam power: red triangles), the feed of fresh bed material (green squares), and the removal of rejected bed material (blue diamonds) during the experiment. (For interpretation of the colour references in this figure legend, the reader is referred to the web version of this article.)

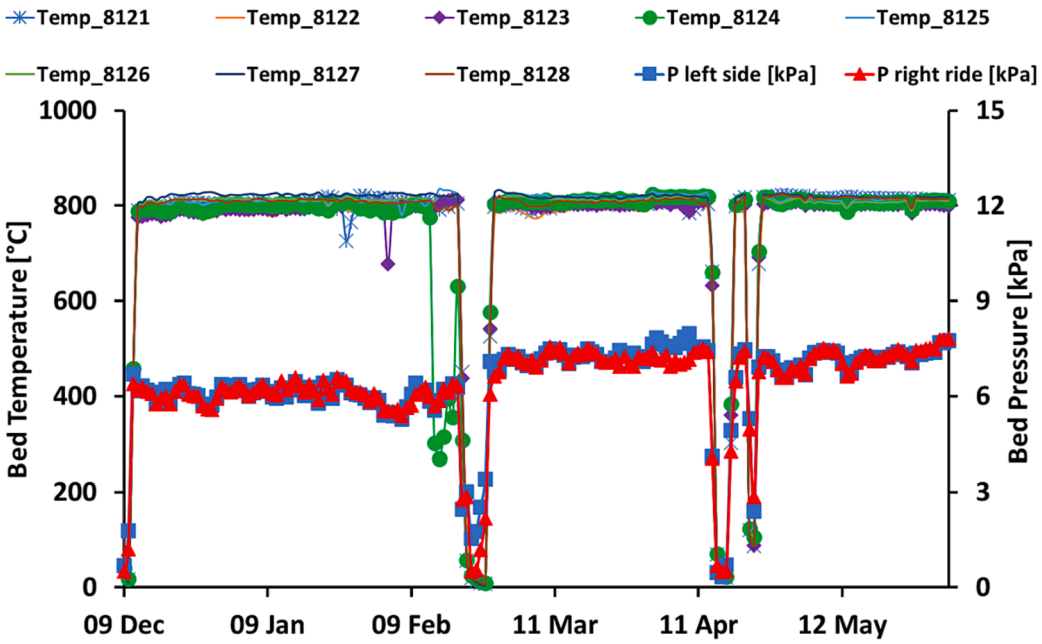

Fig. 4. Bed temperature (upper curves) and bed pressure (lower curves) during the experiment.

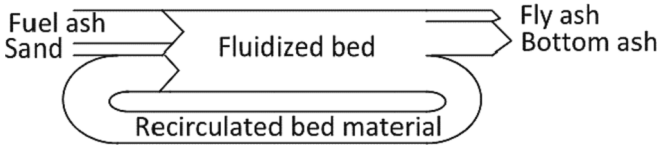

Fig. 5. Overview of the material flows studied during the experiment.

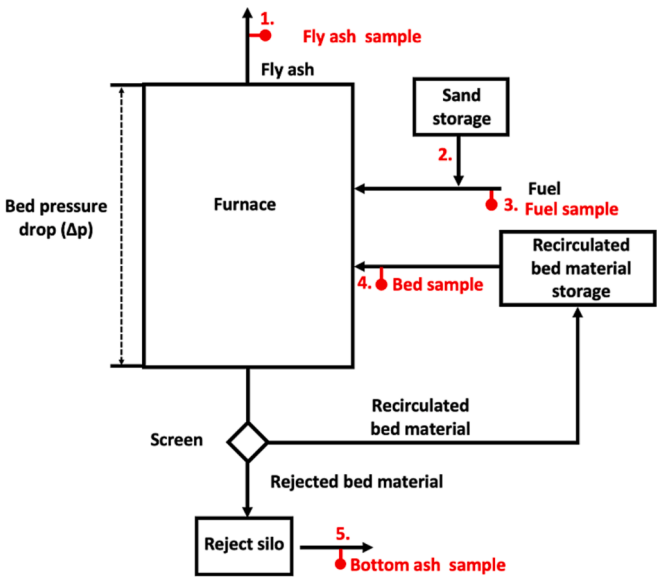

Fig. 6. Overview of input, output, and recirculated material flows during the investigation. The scheme shows the five material sampling points.

working electrode surface but may also be used for evaluation purposes. The remaining pulses (- 0.5 to +0.7 V) are used to find the optimum pulse(s) for the samples at hand, e.g., in the case of redox currents triggered by a certain voltage, or pulses generating features (by "picking up a combination of compounds") better than other pulses (in terms of sensitivity, selectivity, and stability). The current response signals measured by the ET were sampled 5 times in each pulse (4.0 ms between the samples), which generated 15 × 5 = 75 response variables from each electrode as shown in Fig. 7 (bottom right). The marked variables Pt_12 and Rh_11 in Fig. 7 (bottom right) were separately used in part of the evaluation. In the transient part, the current response depends both on the conductivity of the solution, on the redox-active compounds, and on the diffusion properties of the detected molecules [12,13], potentially providing useful information about the bed samples. One measurement cycle consisted of 150 (75 × 2) variables: 75 variables for each electrode. One bed sample analysis with the ET consisted of 600 measurement cycles and took about 3.5 min to complete. The PCA technique was used for the post-data evaluation of the variables of the two electrodes (2 × 75) on the collected samples [10,11]. The ET is equipped with three working electrodes (Pt, Ir, Au), but we chose to use only the Pt and Ir electrodes in the evaluation in this study.

2.3.2. *Inductively coupled plasma optical emission spectroscopy (ICP-OES)*

The ICP-OES technique was used on the leachate prepared in the laboratory from four different bed samples after the measurement campaign. Bed sample 3 (from 12th of December 2019), bed sample 34 (from 13th of January 2020), bed sample 72 (from 2nd of March 2020) and bed sample 137 (from 25th of May 2020) were chosen for ICP-OES measurements. Bed samples 3 and 34 were collected, respectively, at the beginning and in the middle of the high load. Bed sample 72 was collected in the beginning of the transition from high load to low load. Bed sample 137 was collected at the end of the low load period when bark was added to the fuel mix.

3. Results and discussion

3.1. *ET results*

The current responses of the ET were evaluated in two different ways: 1) the maximum response value (absolute value) which occurs for the -1.0 V voltage pulse, was measured as illustrated in Fig. 7 (bottom right) where the variables Pt_12 and Rh_11 are defined. The response for these variables strongly correlates with the conductivity of the water containing the bed material sample. These results are shown in Fig. 8 (**a**) and Fig. 9 (**a**). 2) PCA analysis of all variables. In this way variations in both conductivity, redox activity, catalytic properties and diffusion may

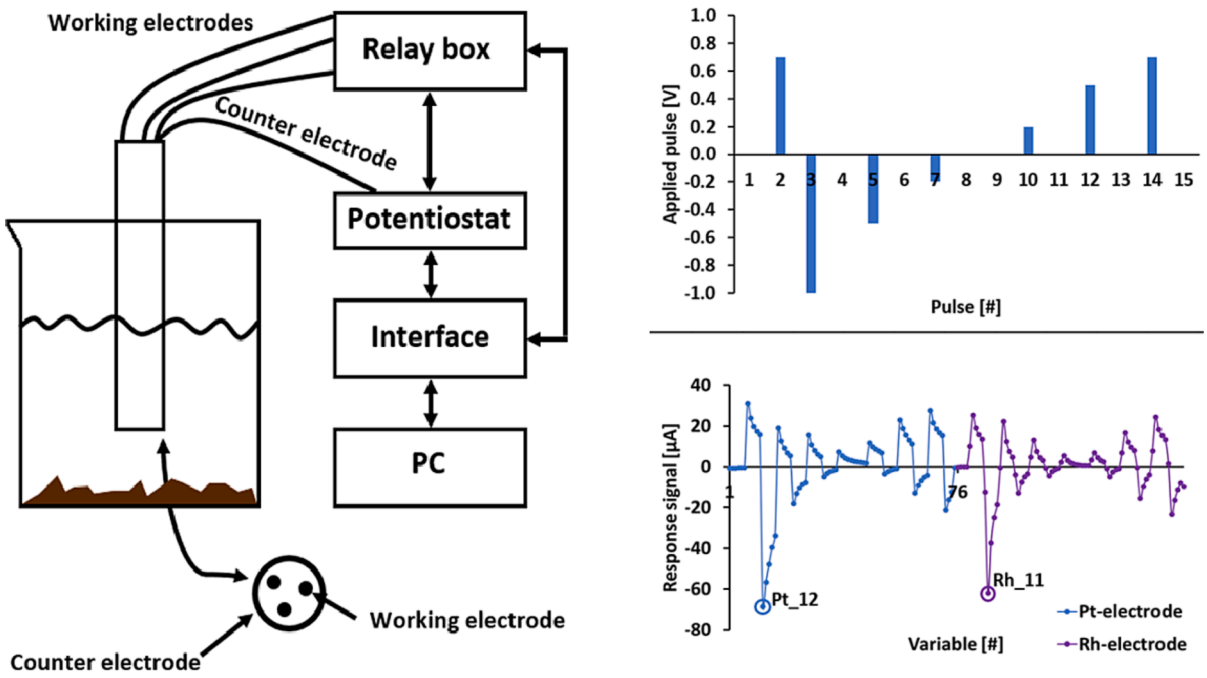

Fig. 7. Main hardware components of the electronic tongue (left). Type of pulsed train applied (top right) to the electronic tongue during the measurements (pulses 1, 4, 6, 8, 9, 11, 13, and 15 had zero amplitude) and their response signal for the Pt and Rh electrodes (bottom right).

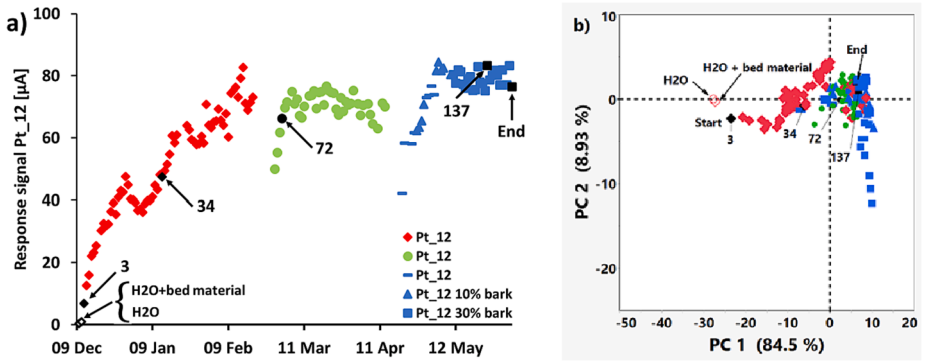

Fig. 8. Response signal from variable Pt_12 of the Pt electrode (a). The PCA performed on all response signals from the electronic tongue's platinum electrode (b). The axes are the principal components 1 and 2 and the percentage numbers are the percentage of the total variance explained by PC1 and PC2, respectively. The numbers 3, 34, 72 and 137 denote bed samples where leachate was analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy.

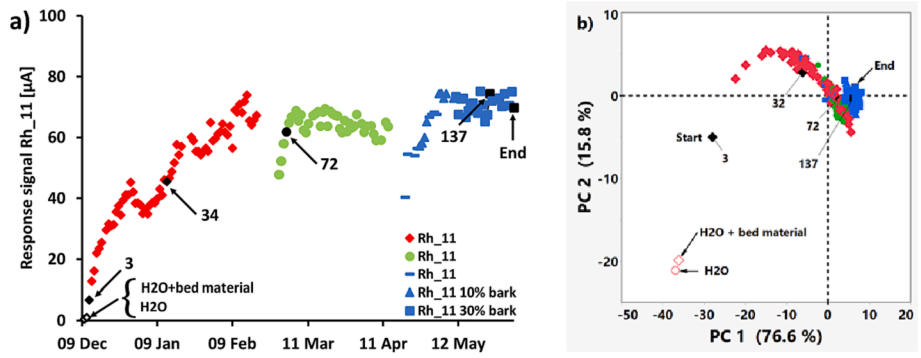

Fig. 9. Response signal from variable Rh_11 of the Rh electrode (a). PCA performed on all response signals from the electronic tongue's Rh electrode (b). The axes are the principal components 1 and 2. The numbers 3, 34, 72 and 137 denote bed samples where leachate was analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy.

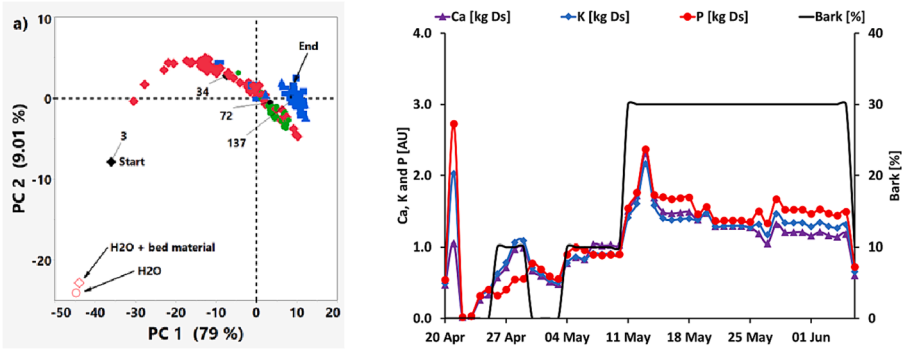

Fig. 10. PCA performed on the response signals from the electronic tongue's two electrodes (Pt and Rh). The axes represent the principal components 1 and 2. 3, 34, 72 and 137 denote bed samples where leachate was analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy. (a). Relative fuel ash components are shown as a function of time during spring and early summer. The black curve shows the mass percentage of bark in the input fuel (vertical scale to the right).

be captured. These results are presented in Fig. 8 (**b**), Fig. 9 (**b**) and Fig. 10 (**a**).

In Fig. 8, Fig. 9 and Fig. 10**(a)** different markers and colors are used for the three different operation modes of the boiler (discussed in section 2.1). The red diamonds represent data from the high load period, the green circles represent the transition from high to low load and the blue markers represent the low load period (see Table 1). The low load period is further divided into periods with 0 % bark (blue rectangles) 10 % (mass) of bark (blue triangles) and 30 % of bark (blue squares).

3.1.1. *Platinum electrode results*

When the boiler was started on 11th of December 2019, after a maintenance stop, the bed material consisted of clean silica sand. The samples from the first day gave nearly no ET response for the variable Pt_12, as seen in Fig. 8 (**a**). This is expected since for deionized water the current is negligible due to the low conductivity. Furthermore, for clean silica sand no compounds contributing to an increased conductivity were neither expected nor extracted. The ET response signal thereafter increased with time until a cleaning stop was necessary on 21st of February 2020. This result indicates that chemical compounds contributing to an increased conductivity (e.g., Ca, K, and Na) accumulate on the sand particles. The accumulated amount increases with boiler operation time and also the amounts of such compounds extracted from the particles into the water at the time of the ET measurements are increasing.

During the cleaning stop between 21st and 24th of February 2020, two thirds of the bed material was replaced by clean silica sand. A reduction of the ET response was observed for the first sample after the cleaning stop. This sample is from 28th of February 2020, so the boiler had been running for a couple of days before sampling resumed. In this case, the ET response approached a steady state value, close to the value observed before the cleaning stop after just a couple of days. This suggests that the new sand becomes contaminated more quickly when a relatively large portion of the old sand has already been contaminated.

From 15th to 17th of April 2020 a second cleaning stop was necessary. Also at this cleaning stop two thirds of the bed material were replaced by clean silica sand. Similarly to the previous stop, the ET response signal was initially reduced, but quickly approached a large value again which was somewhat higher than before the cleaning stop. The first sample after this stop is from 20th of April 2020, so at this time the boiler had also been running for a couple of days before sampling was resumed.

Fig. 8 (**b**) shows the PCA plot of the response signal with all the variables of the Pt electrode that were used in the evaluation. The increase of the signal in Fig. 8 (**a**) is in Fig. 8 (**b**), observed mainly as an increase along PC1, so the trend of the signal shown starting at the left and moving toward the right (red–greenblue markers) in Fig. 8 (**b**) mainly relates to the conductivity increase observed in Fig. 8 (**a**). Part of the red, green, and blue data coincide in a common cluster corresponding to the markers with high signal in Fig. 8 (**a**). Some of the data, however, show a clear deviation along PC2 (blue squares). This occurred during the mixing with 30 % bark. There is also a variation in the behavior of PC2 during the high load operation (red diamonds).

3.1.2. *Rhodium electrode results*

Fig. 9 (**a**) shows the response signal from variable Rh_11. A similar trend, but with slightly lower signal strength to that of Pt_12, is observed. The PCA for Rh, Fig. 9 (**b**), is, however, different from that of Pt, particularly in the PC2 direction. The PC2 part of the variance of the Rh data (15.8 %) is also higher than that of the Pt data (8.93 %). Furthermore, the low load data (blue markers) is much more concentrated for the Rh data, which is interpreted as a larger sensitivity to changes in the fuel properties (and ash elements from the burned fuel) for the Pt electrode than for the Rh electrode.

3.1.3. *Collective evaluation of both electrodes and ash analysis*

Fig. 10 (**a**) shows a PCA plot, where all variables in the response signals ($2 \times 75 = 150$ variables) from both electrodes (Pt and Rh) were included in the PCA. The figure shows a clearer separation of the blue cluster group at the end of the measurement campaign compared to the PCA plots of the individual electrodes. This indicates that using two electrodes together in the evaluation may give more information than that provided by the separate electrodes. This separated cluster group occurred when bark was introduced in the fuel mix, which indicates that there must be something in this fuel mix that caused the separated cluster group, which was enhanced when both electrodes were combined. It thus appears that the ET can detect a change in the chemical composition of the fuel mix as well as changes in the bed material.

The observation of the separate (blue) cluster group in Fig. 10 (**a**) triggered an extra investigation of the ash components when bark was included in the fuel mix. The average of each ash component in the fuel mix from 11th of December 2019 to 19th of April 2020 was calculated. Each ash component from 20th of April to 6th of May 2020 was divided with its previously calculated averaged value. The results from these calculations are presented in Fig. 10 (**b**). It is noticeable that Ca, K, and P increased, and that they started to increase when bark became a part of the fuel mix, especially when the amount of bark was 30 % of the fuel mix. This extra amount of bark in the fuel mix could be the reason for the observed cluster group in Fig. 9 (**b**) and Fig. 10 (**a**). Further analysis of the liquid solution from the bed samples with dedicated measuring equipment is needed to verify this assumption.

3.2. *ICP-OES results*

Leachate from bed samples 3, 34, 72 and 137 showed an increasing concentration of Ca, from 5 ppm (bed sample 3) to 35 ppm (bed sample

137). A constant concentration of 20 ppm Si was measured in all bed samples. Lower concentration (less than 1 ppm) of Mg and Na were measured in all samples. Al, Fe, Mn, P and S could be detected and were expected to be less than 0.1 ppm. Unfortunately, no signal from K could be measured by ICP-OES.

3.3. General discussion

This study generated a lot of bed material samples, which could be further evaluated by means of sintering tests where the agglomeration temperature is determined and correlated to the signal received from the ET. The signal from the ET could also be used to determine which of the bed material samples should be further analyzed with for example scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX or EDS). This is because the signal is an indication that the bed material sample has changed. To incorporate SEM/(EDX or EDS) is also motivated by the results from the ICP-OES measurement since only Ca could be measured in larger amounts.

It should be pointed out that the ET technique has been tested for the first time in this study for detecting signs of bed materials agglomeration, which means that there is always room for improvement. For example, when changing the duration of the applied pulses to the ET, short pulses are used when the focus is on conductivity while longer pulses are used when the redox phenomena are of interest. This research has also indicated that the cluster separation becomes clearer when an extra electrode is included in the PCA evaluation. It might be worth incorporating a few more noble metal working electrodes to improve it even further—e.g., compare the PCA plots in Fig. 8 (**b**) and in Fig. 10 (**a**).

At this stage it is not clear how often a bed sample needs to be extracted from the boiler to give valuable information about the bed material status. However, judging from the results in Fig. 8 (**a**) and Fig. 9 (**a**) it is hypothesized that once per day is a reasonable sampling rate.

4. Conclusions

This investigation has demonstrated that an ET can be used to detect changes in the bed material over time in a BFB boiler as well as deviations in the fuel-ash composition. The ET measurements seem to pick up an accumulation of Ca in the bed material and could, furthermore differentiate between combustion of pure demolition wood and a mix of demolition wood and bark, and this differentiation can be represented as a separation in a PCA plot.

The working electrodes of platinum and rhodium show different response patterns in their PCA plot when each electrode is evaluated separately. However, this study suggests that it would be more favourable to include both electrodes in the PCA evaluation instead of conducting an individual PCA evaluation because this achieves a clearer separation.

The presented results have provided valuable information for further studies to characterize and to determine the agglomeration tendency of the bed material. For example, the signal from an ET could be correlated with the agglomeration temperature determination carried out in the laboratory. Another example would be to correlate the signal from an ET with SEM/(EDX or EDS) to study the mechanism for layer build-up on the bed particles.

CRediT authorship contribution statement

T. Leffler: Writing – original draft. **F. Lind:** Writing – original draft. **B. Leckner:** Writing – original draft. **F. Winquist:** Writing – original draft. **M. Eriksson:** Writing – original draft. **P. Knutsson:** Writing – original draft.

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.

Data availability

Data will be made available on request.

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References

[1] Visser HJM, van Lith SC, Kiel JHA. Biomass ash-bed material interactions leading to agglomeration in FBC. J Energy Resour Technol Trans Asme 2008;130(1).
[2] Davidsson KO, Åmand LE, Steenari BM, Elled AL, Eskilsson D, Leckner B. Countermeasures against alkali-related problems during combustion of biomass in a circulating fluidized bed boiler. Chem Eng Sci 2008;63(21):5314–29.
[3] Corcoran, A., Lind, F., Thunman, H., Knutsson, P., Leachability of potassium from ilmenite used as bed material during OCAC, in 23rd International Conference on Fluidized Bed Conversion. 2018: Seoul, Korea.
[4] Corcoran A, Knutsson P, Lind F, Thunman H. Mechanism for migration and layer growth of biomass ash on ilmenite used for oxygen carrier aided combustion. Energy Fuel 2018;32(8):8845–56.
[5] Schouten JC, van den Bleek CM. Monitoring the quality of fluidization using the short-term predictability of pressure fluctuations. AIChE J 1998;44(1):48–60.
[6] Chirone R, Miccio F, Scala F. Mechanism and prediction of bed agglomeration during fluidized bed combustion of a biomass fuel: Effect of the reactor scale. Chem Eng J 2006;123(3):71–80.
[7] Öhman M, Nordin A. A new method for quantification of fluidized bed agglomeration tendencies: a sensitivity analysis. Energy Fuel 1998;12(1):90–4.
[8] Winquist F, Olsson J, Eriksson M. Multicomponent analysis of drinking water by a voltammetric electronic tongue. Anal Chim Acta 2011;683(2):192–7.
[9] Winquist F, Bjorklund R, Krantz-Rülcker C, Lundström I, Östergren K, Skoglund T. An electronic tongue in the dairy industry. Sens Actuators B 2005;111–112: 299–304.
[10] Bro R, Smilde AK. Principal component analysis. Anal Methods 2014;6(9): 2812–31.
[11] Wold S, Esbensen K, Geladi P. Principal component analysis. Chemom Intel Lab Syst 1987;2(1):37–52.
[12] Winquist F. Voltammetric electronic tongues – basic principles and applications. Microchim Acta 2008;163(1):3–10.
[13] Winquist F, Krantz-Rülcker C, Lundström I. Electronic tongues. MRS Bull 2004;29 (10):726–31.
[14] Leffler, T., Winquist, F., Lind, F., Knutsson, P., Multisensor System to Predict Bed Agglomeration During Fluidised Bed Combustion, in Nordic Flame Days. 2019: Turku, Finland.