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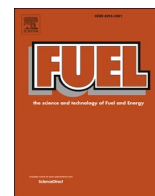
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Full Length Article

Impact of the blending of kaolin on particulate matter (PM) emissions in a biomass field-scale 250 kW grate boiler

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ABSTRACT

The aim of the study was to investigate the impact of adding kaolin on the partitioning of chemical elements in the particulate matter (PM) when virgin and waste woody biomass fuels were fired in a 250 kW grate boiler. A comprehensive analysis of the chemical compositions of the PM has been conducted, including alkali and non-volatile species, size-fractionated mass concentrations and micromorphology images. The results showed that the PM emission levels were significantly decreased by approximately 70–76 % and 60–66 % after the addition of kaolin to virgin wood (VW) and grade A recycled wood (RW), respectively, which inhibited the partitioning of the alkali species into fine and ultrafine PM. On the other hand, the concentration of the non-volatile elements, SiO₂ and Al₂O₃, significantly increased in the PM emissions after the addition of kaolin due to the adhesion and aggregation of particulates between airborne kaolin and the fine and ultrafine PM. Moreover, the addition of the kaolin at 1.55 wt% showed comparable effects with that at 2.5 wt% on the chemical composition of PM emission. Furthermore, the SEM morphology suggested that KCl salts were diminished after the addition of the kaolin. These findings demonstrate the practicality of adding kaolin to mitigate PM emissions and their impacts in actual biomass combustion scenarios.

1. Introduction

Particulate matter (PM) emissions generated from combustion sources, such as boilers, must be significantly addressed. This is due to the negative impacts of particulate matter emissions on cardiovascular and respiratory health [1,2]. The concentrations of alkali metals, chlorine, and sulphur in the fuel have been observed to significantly impact the formation of PM emissions during biomass combustion [3–5]. Indeed, the release of alkali metals is recognized as a significant factor in the formation of PM in biomass combustion systems. Fine PM emissions were due to the presence of the aerosols in the flue gas [6–8]. Previous research indicates that numerous trace metals, such as Na, K, S, and Cl, tend to accumulate in the fly ash, while elements classified as non-volatile, such as Ca, Fe, Al, Mg, Si, P, and Mn, predominantly remain in the bottom ash [9]. Trace metals present in the fine particles can

substantially contribute towards their hazardous properties. Generally, to reduce PM emissions, electrostatic precipitators (ESPs) have been widely used in the boiler to separate the ultrafine and fine particles in the flue gas [10–13]. However, these particulate collectors are less efficient in eliminating intermediate particle size ranges 0.2 and 1 μm [14]. To address these problematic PM issues, various approaches have been attempted to enhance the efficiency of dust collectors, but they often come with high costs [15–17]. The use of additives aims to reduce PM emissions during combustion at a lower cost [18].

To address the multifaceted challenges in boiler operations, various additives, including bauxite, diatomaceous earth, calcium oxide, and kaolin, have been recommended to concurrently mitigate both the formation of deposits and the emissions of particulate matter [19–21]. A recent study by Nowak et al. [22] reported that reductions of sodium, potassium, sulphur and chlorine were observed in the aerosols when

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adding coal fly ash into a pulverised wood fuel combustor. However, the usage of coal fly ash as an additive will be restricted in the future due to the decision by the European Union to discontinue the usage of coal combustion for power generation [22]. Therefore, the growing research interest in kaolin has been emerged compared to coal fly ash due to its better sorption capacity, and it is considered the most viable option for future industrial use [18]. The findings by Davidsson et al. [23] concluded that kaolin is a successful absorbent for potassium under firing conditions. There are two pathways to reduce fine PM by using kaolin: i) kaolin reduces the formation of fine particles by trapping gaseous alkali substances, primarily potassium salts, such as KCl, K₂SO₄ and KOH/K₂CO₃; and ii) PM was captured through collision and aggregation by certain products of kaolin that melted and formed liquidus substances during the high-temperature combustion [24].

Previous studies in this field evaluated the performance of kaolin addition to various types of fuels on the PM emissions in laboratory, pilot and commercial scale furnaces. For example, Xu et al. [18] reported that there was a reduction in the PM_{2.5} emission when coal was co-fired with kaolin in a 1000 MW coal-fired power station. Furthermore, the addition of kaolin will lead to the formation of alkali aluminosilicates which enhance the capture of the PM through aggregation and collisions [18]. Tissari et al. [25] found that the addition of 5 wt% kaolin to oat grains reduced the emissions of alkali metals but increased the PM emissions of incomplete combustion in a 20 kW pellet burner. A recent study by Wang et al. [26] observed that the aerosol fraction of total ash shows a slight reduction when kaolin or coal fly ash was introduced. Rebbling et al. [27] concluded that the addition of kaolin into the woody biomass reduced the concentration of alkali metals (K and Na) in PM emissions in a 40 kW grate boiler. Cheng et al. [28] attempted to modify the kaolin by phosphoric acid treatment to enhance the chemical reactivity of the kaolin in a small scale vertical fixed-bed boiler. According to their findings, a substantial decrease in the PM_{0.2} emissions was observed when cornstalk was co-fired with kaolin treated with phosphoric acid.

Although numerous studies have been conducted to investigate the impact of kaolin on the PM emissions during biomass firing in a small scale < 100 kW, it is not certain whether the same is valid for biomass firing with kaolin addition in a field scale > 100 kW (*scale characterization based on BEIS report*) [29]. This is because, in a field scale furnace, biomass and mineral particles may experience significantly higher heating rates, reaching higher temperatures and more vigorous fragmentation compared to bench-scale reactors, leading to increased mineral matter released into the fly ash [18]. Moreover, the feed rate in the field scale will be much higher compared to the lab scale. As a result, more mineral matter such as non-volatile elements, alkali and alkali earth elements are released from the biomass during combustion. These elements become part of the fly ash, which is the fine particulate residue that is carried along within the flue gas. In the present, there is limited research with a focus on well-defined chemical elements partitioning in the PM emissions especially on the silica content. Most of the publications have discussed the silica content in coarse fly ash (>10 µm), while data of the silica content in aerosols form (PM < 10 µm) have not well understand due to the lack of appropriate analysis methods in determining the silica. It has been confirmed that the silica and its partitioning play a critical role in ash deposition issues in the biomass boiler [30,31]. Therefore, it is significant to understand how kaolin additives affect the silica partitioning in PM emissions of field scale combustor. Moreover, the kaolin consists of high amount of silica content and adding the kaolin may increase the excess of silica in the biomass boiler. To the best of author knowledge, five papers on the control of particulate matter emissions from biomass combustion by adding kaolin have been published in the past 5 years. The comparison of main content and research gaps of these literatures is listed in Table 1 [24,26,27,32,33].

To address this gap, kaolin was blended at two different dosages (1.55 wt% and 2.5 wt%) into a virgin and a waste type woody biomass, which were virgin wood and grade A recycled wood in a 250 kW grate

Table 1

The comparison of main content of five papers published within the past five years.

Authors	Main content and research gaps
Gehrig et al. [32]	A set of pelletized of spruce mixtures blended with kaolin to investigate the PM reduction (potassium mainly) in 12 kw biomass boiler. It was mentioned Si and Al were increased in boiler ash due to kaolin, however, limited quantitative analysis on the chemical partitioning of Si, Na, Ca, Mg in PM emissions.
Nowak et al. [24]	Investigation of the impact of the alkali upon capture efficiency in a 6 kW electric heated furnace where beech wood was co-fired with kaolin. Limited observation on the chemical elements partitioning in ultrafine PM.
Wang et al. [26]	To conduct a quantitative testing of the reaction between kaolin and coal fly ash and volatile K-salt species, which are produced during the combustion of biomass in an entrained flow reactor. Lack of analysis and discussion on the chemical compositions in ultrafine PM.
Höfer et al. [33]	CaHPO ₄ and kaolin were used to investigate the PM reduction (focus on potassium) of wood straw blend in 8 kW boiler. Lack of explanation of chemical elements partitioning consist of non-volatile (Si & Al), alkali earth metals (Ca & Mg) and sodium.
Rebbling et al. [27]	The kaolin reduces the volatile alkali species which is K and Na in a 40 kW grate boiler of woody biomass combustion. Limited explanation on the silica formation in the PM emissions.

boiler. The aim of the present work is to investigate the impact of kaolin addition to woody biomass fuels on the partitioning of chemical elements (Si, K, Na, Al, Ca, Mg) within particulate matter (PM) emission. In addition, the impact of two dosages of kaolin on reducing alkali and non-volatile species in PM emissions from the combustion of these fuels was investigated. A comprehensive analysis of mass concentration based on particle size distribution (PSDs), elemental compositions and morphology of the PM have been conducted. The detailed discussion on this topic enabled an understanding to be provided that will benefit industrial users and researchers of optimizing and improving the performance of biomass fired boilers. Moreover, this research provided further insights into optimising kaolin dosage for the reduction of alkali and non-volatile species in PM emissions from these fuels, paving the way for future studies.

2. Experimental setup

2.1. Combustion test rig

The combustion testing was conducted at the Translational Energy Research Centre (TERC) using a 250-kW biomass fuels, and capable of handling dry, as well as, wet fuels with high residual moisture content (up to ~60 %). The fuel was fed onto the grate by a series of augers connected to the feeding system from the biomass silo. To ensure the kaolin powder would mix homogeneously with the fuel, the kaolin feeding system was installed directly to the transfer auger, as shown in Fig. 1. The fuel feeding rate was set at 50.2 kg/hr. The combustion air consisted of two streams of primary air blown in from under the grate and two streams of secondary air blown in from the side walls above the grate (Fig. 1). The fuel feeding rate and the air (primary and secondary) were kept constant for each fuel mixture case to achieve the required oxygen concentration in the flue gas which was at 12–13 %. The flue gas from the combustion chamber passed through the inner tubes of the heat exchanger. Sampling of particles and emissions took place after the heat exchanger. The ESP was installed after the multi cyclone to remove fine particles in the flue gas before being discharged through the chimney by the flue gas fan.

2.2. Kaolin-fuel mixture preparation

The kaolin employed in this study was fine milled powder (70 % of particles < 1 µm and 4 % of the particles at 8 µm). Kaolin (K) at two

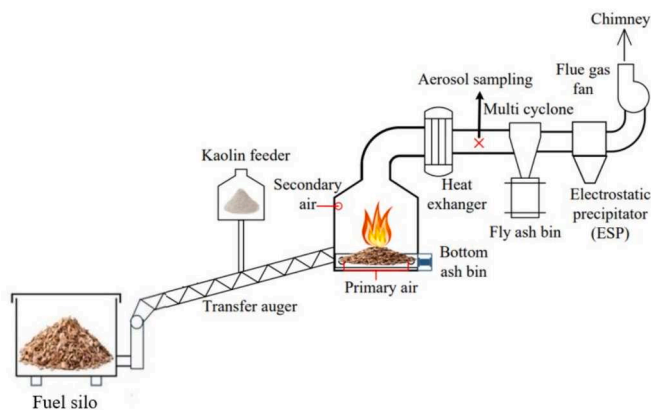


Fig. 1. Conceptual sketch of the 250 kW grate boiler combustion system in the TERC facilities.

different dosages (1.55 wt% & 2.5 wt%) were blended with two woody biomass fuels, virgin wood and grade A recycled wood which create 6 fuel mixtures, i.e. VW (pure virgin wood); VWK1.55 (VW + 1.55 wt% K); VWK2.5 (VW + 2.5 wt% K); RW (pure recycled wood); RWK1.55 (RW + 1.55 wt% K); and RWK2.5 (RW + 2.5 wt% K). The ratios of kaolin were selected based on the work by Nowak et al. [22], who suggested that the ratio between the kaolin additive and the fuel should be lower than the ratio used with coal fly ash (<3.22 wt%). In this study, the minimum ratio of the kaolin addition was set at 1.55 wt%, as this corresponded to the lowest feed rate capability of the screw feeder. The composition of the two different types of fuels and kaolin are shown in Table 2. The kaolin additive is made up of mostly silica (48 %) and alumina (36.5 %). It also contains potassium, however about 3 and 5 times less than the virgin wood and recycle wood, respectively.

2.3. PM emissions sampling and analysis

At the start of each experiment, the grate boiler was operated for 3 h to preheat the furnace and establish a stable operating condition before commencing the sampling. The VW and RW firing measurements were replicated 3 times, while those for VWK1.55, VWK2.5, RWK1.55 and RWK2.5 were repeated two times due to the fuel availability. The PM sampling consisted of a PM₁₀ cyclone, a Dekati ediluter, a Dekati low pressure impactor (ELPI+), a pressure gauge, and a vacuum pump. The sampling setup can be seen in the Fig. 2. The flue gas flowrate of 10 L/min was drawn from the central part of the flue duct using a stainless-

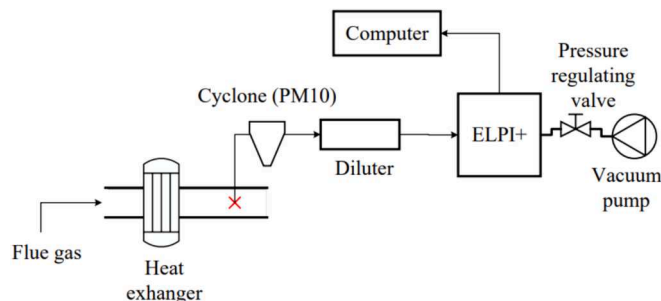


Fig. 2. Schematic diagram for the PM (aerosols) setup using Dekati instruments.

steel probe with a diameter of 10 mm and directed through a PM₁₀ cyclone to remove particles with aerodynamic diameters larger than 10 μm . Next, the samples were diluted using an ejection diluter (Dekati® eDiluter™) to provide a homogeneous and stable sample flow throughout the entire measurement system. The total dilution ratio (DR) used was 25. The flue gas was sampled through the 14 stages (with size ranges of 10 nm – 10 μm) of the impactor to assess the number and mass concentrations of particles based on discrete size distributions. The samples were grouped based on PM₁₀ (1 μm < PM₁₀ $\leq$ 10 μm), PM₁ (0.1 μm < PM₁ $\leq$ 1 μm) and PM_{0.1} ($\leq$ 0.1 μm). To prevent the condensation of acidic gases and agglomeration of wet particles, the sampling probe, cyclone, ELPI+, and the connecting tubes were all heated to a temperature of 180 °C. The duration of each measurement lasted for at least two hours to collect a representative quantity of the PM samples. The aerosol particles were collected through polycarbonate membrane treated with a high temperature grease (Apiezon-H). The PM samples collected by the polycarbonate membrane were digested with a microwave, assisted with HNO₃ and H₂O₂, and analysed with the inductively coupled plasma mass spectrometry (ICP-MS) to investigate the concentration of the element compositions which were SiO₂, Al₂O₃, CaO, K₂O, MgO and Na₂O. To ensure data consistency, the average of a minimum of three samples including one from each of the 3 repetitions for each fuel mixtures were ascertained to determine the elemental concentrations via ICP-MS. The micromorphology of the samples was observed using a scanning electron microscope (SEM) after coating them with a thin layer of gold to enhance conductivity.

3. Results & discussion

3.1. Effect of the addition of kaolin on the PM emissions in the grate boiler

The effect of kaolin blending on particulate emissions, specifically, PM₁₀, PM₁ and PM_{0.1} were measured in all the experiments. The mass of particle size distributions (PSDs) for virgin wood and grade A recycled wood cases are shown in Fig. 3(a) (The mass concentration of particulates were illustrated in Tables 3 and 4 of the Appendix section for comparison between PM₁₀, PM₁, and PM_{0.1}). The reduction efficiencies of kaolin on size-fractionated PM were computed using the formula suggested by Xu et al. [18], with the results being illustrated in Fig. 3(b). Most of the mass concentrations of the aerosols captured between 1–10 μm with kaolin has lowered the emissions levels for both fuel blends. The addition of the kaolin significantly decreased the amount of PM in the virgin wood cases. The mass concentrations of PM_{7.33-10} decreased from 3,039 $\pm$ 90 mg/Nm³ to 1,010 $\pm$ 27 mg/Nm³ and 694 $\pm$ 33 mg/Nm³ under the experimental conditions, resulting in a 66.7 % and 77.2 % of PM reduction efficiency for the VWK1.55 and VWK2.5 cases, respectively. On the other hand, the yield of the PM was also found to be significantly reduced in the grade A recycled wood when adding kaolin. As can be seen from Fig. 3(a), the mass concentrations of PM_{7.33-10} decreased from 4,380 $\pm$ 103 mg/Nm³ to 2,123 $\pm$ 60 mg/Nm³ and 1,803 $\pm$ 57 mg/Nm³, corresponding to a 51.5 % and 58.9 % in the reduction efficiency after

Table 2

Chemical compositions of the fuels and additive.

Content (as received)	Unit	VW	RW	Kaolin, K
Moisture	%	10.90	16.40	–
Ash	%	1.20	1.60	–
Volatile	%	74.60	69.70	–
Fixed carbon	%	13.30	12.90	–
C	%	45.33	41.24	–
H	%	5.63	5.18	–
O	%	36.64	35.30	–
N	%	0.11	0.25	–
S	%	< 0.02	0.02	–
Cl	%	0.05	0.01	–
SiO ₂	%	33.00	23.30	48.00
Al ₂ O ₃	%	2.40	7.30	36.50
Fe ₂ O ₃	%	3.10	4.20	0.02
TiO ₂	%	3.30	0.50	0.68
CaO	%	22.20	23.30	0.07
MgO	%	3.10	4.30	0.30
Na ₂ O	%	4.10	2.60	0.10
K ₂ O	%	5.80	9.00	1.65
P ₂ O ₅	%	1.20	2.00	–
SO ₃	%	1.80	10.10	–

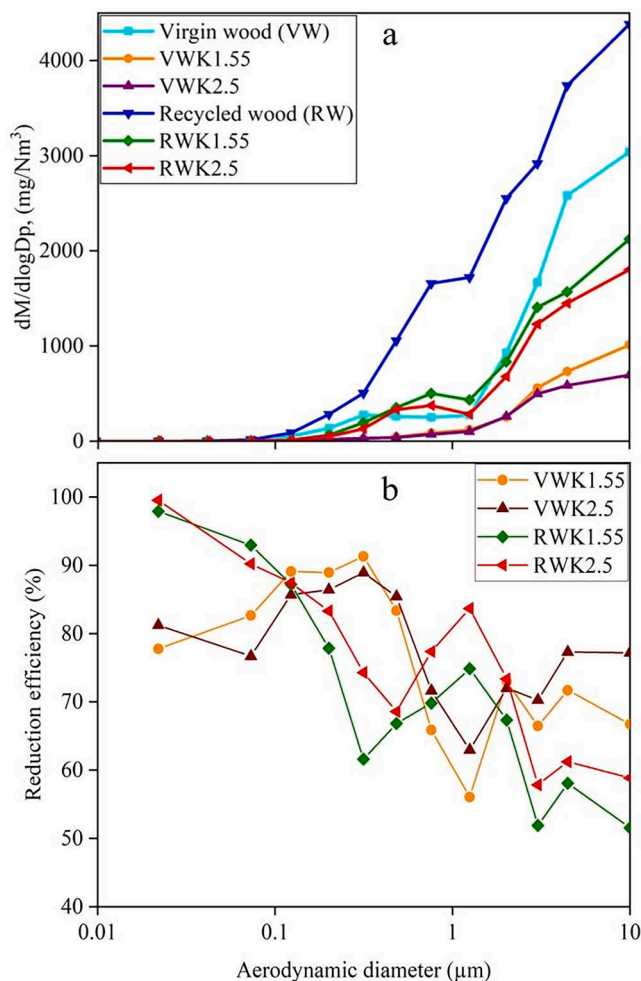


Fig. 3. (a) PSDs of mass concentrations of the virgin wood and recycled wood cases in fine fly ash by Dekati ELPI+; (b) PM reduction efficiency of kaolin at two different dosages for virgin wood and recycled woods.

addition of kaolin ratio at 1.55 wt% and 2.5 wt%, respectively. Overall, the addition of kaolin into the VW and RW were able to reduce the PM emissions by at least ~ 60 %.

3.2. Effect of the addition of kaolin on the chemical element partitioning of the PM

The element concentration analysis of the PM emissions are illustrated in Figs. 4 and 5 for the virgin wood and grade A recycled wood case studies respectively. The motivation is to investigate the partitioning of alkali species and non-volatile elements concentrations in the submicron region by ICP-MS analysis. Results in Fig. 4 illustrated that the fine and ultrafine PM had a high content of non-volatile elements species, such as SiO₂ and Al₂O₃ in the virgin wood case studies. The SiO₂ and Al₂O₃ were increased in PM_{0.1}, PM₁ and PM₁₀ after blending with kaolin for both dosages tested. These observations are posited to be associated with the adhesion, aggregation or agglomerated of airborne kaolin with the ultrafine PM, as the kaolin used comprised of 48 wt% SiO₂ and 36.5 wt% Al₂O₃. Potassium was found at 21.22 ± 0.26 wt% in the VW ash samples and this amount dropped significantly after the addition of kaolin at 1.55 wt% and 2.5 wt%. The use of kaolin also reduced the release of sodium by ~65 % for virgin wood when adding kaolin. This is in agreement with the study by Rebbling et al. [27], who found that the addition of kaolin reduced the release of potassium and sodium by ~46 % and ~80 %, respectively. This phenomenon can be explained through the simplified alkali sorption reaction as described in

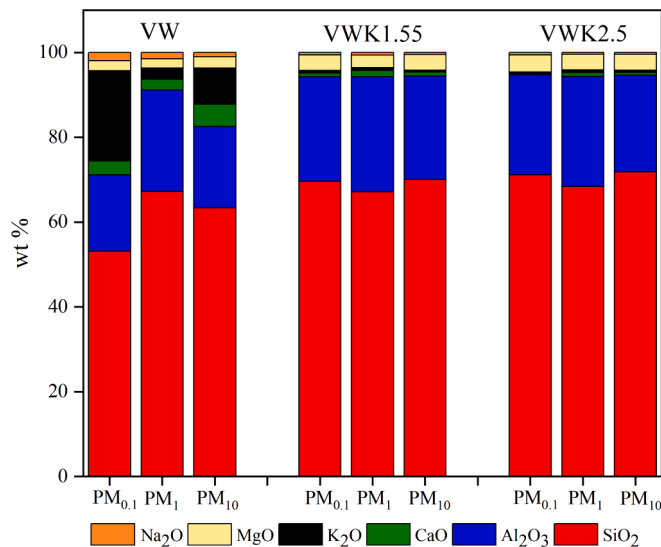


Fig. 4. Chemical compositions of the PM (normalized to 100%) when kaolin was added to virgin wood by ICP-MS analysis.

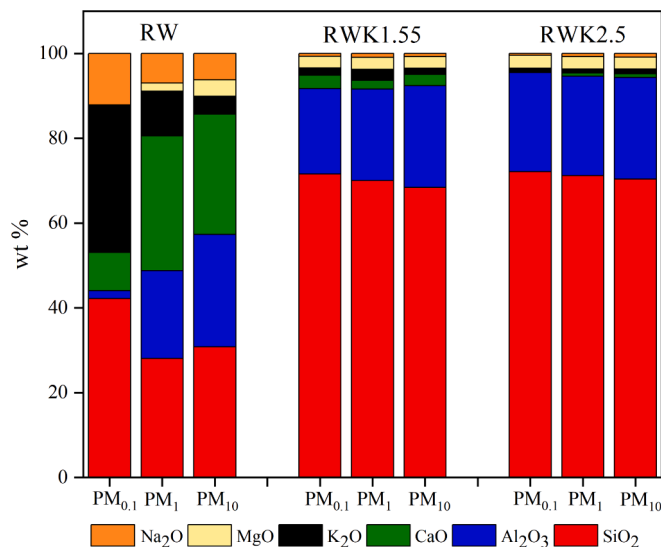
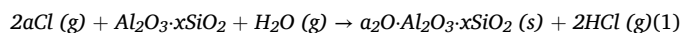


Fig. 5. Chemical compositions of the PM (normalized to 100%) when kaolin was added to grade A recycled woods by ICP-MS analysis.

the Eq. (1) [34–37]:



where $a = Na, K$.

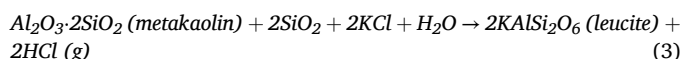
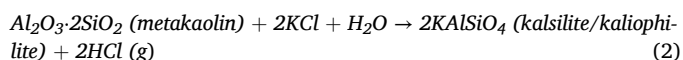
CaO and MgO were also observed in all fuel mixtures of PM samples, which indicated a contribution from heterogeneous condensation, agglomeration and coalescence to particles growth during the PM formation [38]. The magnesium level was found to slightly increase after blending the virgin wood with the kaolin. The amount of magnesium present in all the size-fractioned PM was below 4 wt% for all the VW mixtures. The CaO was found to decrease in PM₁₀ from 5.25 ± 0.12 wt% (VW), to 0.90 ± 0.01 wt% and 0.69 ± 0.01 wt% for VWK1.55 and VWK2.5, respectively. According to Ninomiya et al. [39] and Wei et al. [40], kaolin at specific addition ratios, would interact with calcium and promote the formation of a molten phase which potentially remain on the bed to form slag. During the combustion process, the volatile species of K, Cl, and S are prone to exist in the gas phase [41], and therefore the residual ash is mainly composed of non-volatile species, such as Ca, Si,

Mg, and Al [42]. These are in line with the XRD results, which indicate the existence of $(\text{Ca}_2\text{MgSi}_2\text{O}_7)$ and SiO_2 [42]. According to Chen et al. [43], a certain amount of K is also found in the residual ash, which could be due to the formation of K-containing carbonates and/or silicates and this was validated by Yang et al. [42] which found the existence of $\text{K}_2\text{Ca}(\text{CO}_3)_2$. The elemental and phase composition of the residual ash changed significantly when kaolin was added to the woody biomass. It is clear that Si and Al played a major role and the large silicates ($\text{Ca}_2\text{MgSi}_2\text{O}_7$, KAlSiO_4 , $\text{Ca}_2\text{Al}_2\text{SiO}_7$) exist in the residual ash. Kaolin undergoes dehydroxylation at 585°C [44], releasing water and forming amorphous *meta*-kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The produced *meta*-kaolinite could react with alkali metal containing species to form various aluminosilicates at temperatures between 700°C and 900°C [45,46], such as KAlSiO_4 (kalsilite), KAlSi_2O_6 (leucite) and K feldspar, thus by reducing K, reducing the formation of PM [44]. The formation of KAlSiO_4 in the residual ash validates this assumption [42].

For the recycled wood, SiO_2 was found to increase from 30.78 ± 0.83 wt% in RW to 68.41 ± 0.75 wt% and 70.35 ± 0.68 wt% in the PM_{10} size fraction, after being added with kaolin at dosages of 1.55 wt% and 2.5 wt%, respectively. In addition, there are no significant change in SiO_2 after the addition of kaolin for both dosages in PM_1 and $\text{PM}_{0.1}$. The high amount of CaO was found in the PM_1 at 31.85 ± 0.54 wt%, potentially due to the following reasons. First, CaO in the RW blends, primarily formed as organic-bound, was exposed to reducing atmosphere and high combustion temperatures. It is crucial to monitor the bed condition due to the primary air being supplied from underneath of the bed as shown in Fig. 1. Any ash related issues such as agglomeration, clinkers and slagging formed on the bed will result in localised spots with limited oxygen available for the combustion (strong reducing atmosphere). Second, in an actual furnace, biomass and mineral particles may undergo significantly higher temperatures and more vigorous fragmentation compared to bench-scale reactors, leading to increased mineral matter release into the fly ash. However, CaO was remarkably reduced to 2.08 ± 0.03 wt% and 0.76 ± 0.01 wt% for the 1.55 wt% and 2.5 wt% cases, respectively. These observations show that kaolin and *meta*-kaolin, reacted with calcium-containing compounds, effectively binding these elements to the additive's particles [47,48]. The MgO was increased from $\text{PM}_{0.1}$ to PM_1 and then to PM_{10} in the RW case. The MgO increased in $\text{PM}_{0.1}$ and PM_1 after the addition of kaolin while the amount of magnesium in PM_{10} is slightly lower compared to without kaolin in RW cases. The utilization of kaolin resulted in a reduction of

approximately 90 % in the release of sodium, as determined by a weighted average, when kaolin was added to grade A recycled wood at 1.55 wt% dosage. However, no difference has been observed when adding 2.5 wt% dosages of the kaolin. This is speculated to be due to the increases in the alkaline dosages from 1.55 wt% to 2.5 wt% becoming inefficient in the chemisorption of the sodium.

Moreover, the amount of K_2O was found to be the highest which was 34.56 ± 0.43 wt% in the aerosols from the RW case. This is a very interesting and important finding where the amount of potassium was considered high at particle sizes $< 0.1 \mu\text{m}$. This observation aligns with the Energy Dispersive Spectroscopy (EDS) results presented in Fig. 6 for $\text{PM}_{0.48}$, where it revealed high concentrations of K and Cl. Fernandes and Costa [49] suggested that these particulate matters predominantly consist of potassium chlorides which have a low melting temperature of 770°C and the presence of sodium would further decrease the melting point [42]. According to Yang et al. [42], the alkali metal compounds that melted are prone to form gas phase in the form of chloride and alkali metal vapor during the combustion process. These alkali salts in a gaseous state can condense on cooler surfaces when the ambient temperature is lower than their melting point resulting in the formation of submicron particles via heterogeneous condensation and homogeneous nucleation [38,50]. Furthermore, the K_2O was significantly reduced in the PM emissions after the addition of kaolin, as shown in Fig. 5. This shows the good capability of the kaolin to adsorb alkali metals in the flue gas. Also, this is supported by the studies of Sommersacher et al. [51] where the K-release has been successfully reduced by about 18 % in the experiment blending kaolin and spruce in a small reactor. The EDS analysis in Fig. 6 also proves that the kaolin reduced the formation of fine particles by trapping gaseous alkali substances, primarily potassium salts such as KCl. When kaolin is heated to temperatures above 450°C , it decomposes and transforms into metakaolin [52,53]. Then, metakaolin can capture the gaseous K-species by reacting with KCl to form K-aluminosilicate and releasing HCl into the gas phase. This reaction can be expressed as follows [54,55]:



On the other hand, from Fig. 6(a–b), illustrating the morphology

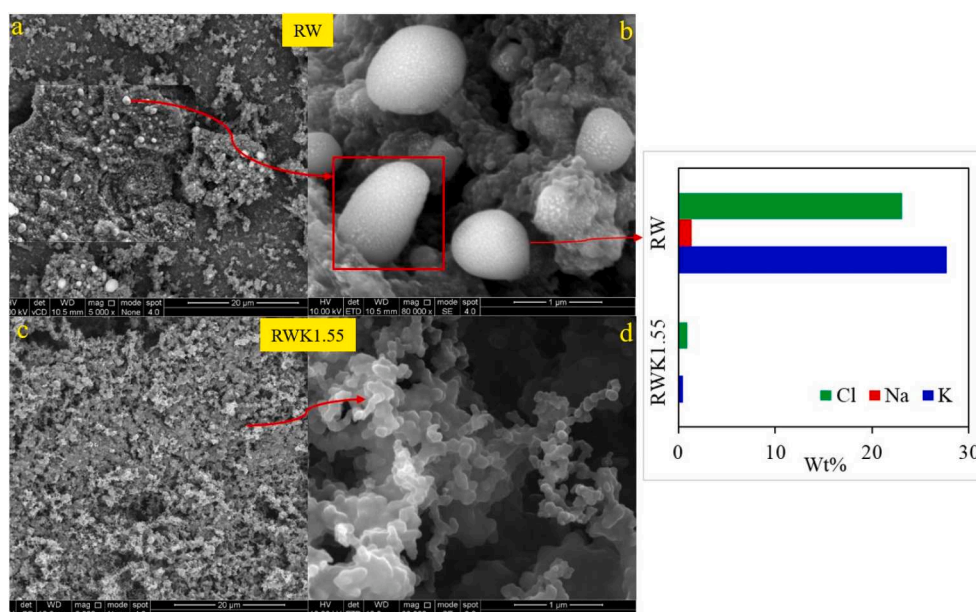


Fig. 6. (a–d) Micromorphology of the $\text{PM}_{0.48}$ (particles collected on the 7th stage of ELPI+) observed by SEM-EDS.

images of RW samples at $PM_{0.48}$, it can be clearly seen that KCl salts (white cylindrical shape) were formed during the combustion of RW. However, the KCl salts were significantly reduced and their visibility in Fig. 6(c–d) is diminished after added kaolin to RW at 1.55 wt% dosages. This direct morphology confirmed that the introduction of kaolin could enhance the capture of the ultrafine PM by the molten coarse PM [18]. A significant portion of the PM appeared to be agglomerated, as indicated in Fig. 6(b and d). The formation of the large structures may have arisen through processes such as agglomeration on the particles, interactions with the grease, as well as instances of particles rebounding (bounce-off) or undergoing re-entrainment from higher ELPI + cascade stages [56]. Agglomerates frequently exhibit porosity and possess a low effective density, leading to size of aerodynamic diameter smaller than apparent [56]. Moreover, Hindsgaul et al. [57] studied particles generated from biomass gasification through SEM and concluded that sizable agglomerates had reached to the lower stages of the cascade impactor. Thus, these explained our finding on the agglomerated particles appeared in $PM_{0.48}$ morphology as shown in the Fig. 6 (b and d).

4. Conclusions

Overall, this study aimed to provide understanding to the industrial users and researchers on the impact of kaolin addition to woody biomass fuels on the partitioning of the chemical elements of fine and ultrafine particulate matter (PM) emissions. The highest particle mass concentrations were observed at $PM_{7.33-10}$ for both fuel mixture cases with kaolin. Kaolin demonstrated an effective reduction in the formation of fine and ultrafine PM through vapor and liquidus capture, achieving a minimum of 60 % mass concentrations of PM reduction when injected to VW and RW fuels. The addition of kaolin resulted in reduced alkali species in PM emissions for both fuel mixtures, indicating kaolin's efficacy as a gaseous substance adsorbent in flue gas. The presence of CaO and MgO in all fuel blend samples suggested contributions from heterogeneous condensation, agglomeration, and coalescence to particle growth during PM formation. Moreover, the concentration of non-volatile elements significantly increased after adding kaolin, attributed to the high SiO_2 and Al_2O_3 content in the ultrafine kaolin powder. This result implies the importance of future works to explore the influence of kaolin particle size on PM emissions, encompassing both non-volatile components and alkali elements.

In addition, the influence of kaolin on alkali species reduction and the increase in non-volatile elements demonstrated comparable effects at concentrations of both 1.55 wt% and 2.5 wt%. Consequently, it is

strongly advised that future studies explore into the impact of kaolin concentrations below 1.55 wt% to understand the influence of additive concentration on PM emissions. This research underlined the effective mitigation of PM emissions in a field-scale grate boiler through the injection of kaolin with woody biomass fuels. Future investigations could explore the incorporation of kaolin into other types of biomass fuels to prevent the introduction of excessive aluminosilicate additives, preserving optimal boiler conditions. The findings from this study lay the groundwork for subsequent research aimed at determining optimal dosages for kaolin addition to wood-based biomass fuels.

CRediT authorship contribution statement

Nik Nor Aznizam Nik Norizam: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **János Szuhánszki:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation. **Ihab Ahmed:** Writing – review & editing, Supervision, Methodology, Data curation. **Xin Yang:** Writing – review & editing, Supervision. **Derek Ingham:** Writing – review & editing, Supervision, Project administration. **Kris Milkowski:** Methodology, Data curation. **Abdulaziz Gheith:** Methodology, Data curation. **Andy Heeley:** Writing – review & editing, Supervision, Data curation. **Lin Ma:** Writing – review & editing, Supervision, Project administration. **Mohamed Pourkashanian:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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Appendix

Particle size distribution (PSDs) ranges:

$1\ \mu m < PM_{10} \leq 10\ \mu m$.

$0.1\ \mu m < PM_1 \leq 1\ \mu m$.

$PM_{0.1} \leq 0.1\ \mu m$.

Table 3
Mass concentration of particulate matter for virgin wood mixtures.

PSDs	Fuel Mixture	Mass concentrations (mg/Nm ³)
PM_{10}	VW	8490 ± 130
	VWK1.55	2672 ± 84
	VWK2.5	2136 ± 56
PM_1	VW	973 ± 43
	VWK1.55	173 ± 13
	VWK2.5	165 ± 20
$PM_{0.1}$	VW	10.08 ± 0.48
	VWK1.55	2.18 ± 0.13
	VWK2.5	2.46 ± 0.12

Table 4
Mass concentration of particulate matter for recycled wood mixtures.

PSDs	Fuel Mixture	Mass concentrations (mg/Nm ³)
PM ₁₀	RW	15305 ± 306
	RWK1.55	6359 ± 172
	RWK2.5	5442 ± 136
	RW	3584 ± 143
PM ₁	RWK1.55	1117 ± 56
	RWK2.5	894 ± 40
	RW	16.86 ± 0.81
	RWK1.55	1.14 ± 0.05
PM _{0.1}	RWK1.55	1.60 ± 0.07
	RWK2.5	

References

[1] Brunekreef B, Holgate ST. Air pollution and health. *Lancet* 2002;360(9341): 1233–42.

[2] Pope CA, Dockery DW. Health effects of fine particulate air pollution: lines that connect. *J Air Waste Manag Assoc* 2006;56(6):709–42.

[3] Lamberg H, Tissari J, Jokiniemi J, Sippula O. Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials. *Energy Fuel* 2013;27(11):7044–53.

[4] Christensen KA, Stenholm M, Livbjerg H. The formation of submicron aerosol particles, HCl and SO₂ in straw-fired boilers. *J Aerosol Sci* 1998;29(4):421–44.

[5] Kortelainen M, Jokiniemi J, Nuutinen I, Torvela T, Lamberg H, Karhunen T, et al. Ash behaviour and emission formation in a small-scale reciprocating-grate combustion reactor operated with wood chips, reed canary grass and barley straw. *Fuel (Guildford)* 2015;143:80–8.

[6] Werther J, Saenger M, Hartge E-U, Ogada T, Siagi Z. Combustion of agricultural residues. *Prog Energy Combust Sci* 2000;26(1):1–27.

[7] Szemmelveisz K, Szűcs I, Palotás Á, Winkler L, Eddings E. Examination of the combustion conditions of herbaceous biomass. *Fuel Process Technol* 2009;90(6): 839–47.

[8] Fagerstrom J, Nazelius I-L, Gilbe C, Bostrom D, Ohman M, Boman C. Influence of peat ash composition on particle emissions and slag formation in biomass grate co-combustion. *Energy Fuel* 2014;28(5):3403–11.

[9] Becidan M, Todorovic D, Skreiberg Ø, Khalil RA, Backman R, Goile F, et al. Ash related behaviour in staged and non-staged combustion of biomass fuels and fuel mixtures. *Biomass Bioenergy* 2012;41:86–93.

[10] Xu, M., D. Yu, H. Yao, X. Liu, and Y. Qiao. *Coal combustion-generated aerosols: Formation and properties*. Proceedings of the Combustion Institute, 2011. **33**(1): p. 1681-1697.

[11] Yao Q, Li S-Q, Xu H-W, Zhuo J-K, Song Q. Studies on formation and control of combustion particulate matter in China: a review. *Energy* 2009;34(9):1296–309.

[12] Liu X, Xu Y, Zeng X, Zhang Y, Xu M, Pan S, et al. field measurements on the emission and removal of PM_{2.5} from coal-fired power stations: 1. case study for a 1000 MW ultrasupercritical utility boiler. *Energy Fuel* 2016;30(8):6547–54.

[13] Jaworek A, Krupa A, Czech T. Modern electrostatic devices and methods for exhaust gas cleaning: a brief review. *J Electrostat* 2007;65(3):133–55.

[14] Jena MC, Mishra SK, Moharana HS. Effect of particle size on collection efficiency of ESP and RABH: a case study. *Aerosol Sci Eng* 2019;3:75–87.

[15] Wang C, Liu X, Li D, Si J, Zhao B, Xu M. *Measurement of particulate matter and trace elements from a coal-fired power plant with electrostatic precipitators equipped the low temperature economizer*. Proc Combustion Institute 2015;35(3):2793–800.

[16] Gallego-Juárez JA, Riera-Franco De Sarabia E, Rodríguez-Corral G, Hoffmann TL, Gálvez-Moraleda JC, Rodríguez-Maroto JJ, et al. Application of acoustic agglomeration to reduce fine particle emissions from coal combustion plants. *Environ Sci Tech* 1999;33(21):3843–9.

[17] Xu Y, Liu X, Cui J, Chen D, Xu M, Pan S, et al. Field measurements on the emission and removal of PM_{2.5} from coal-fired power stations: 4. PM removal performance of wet electrostatic precipitators. *Energy Fuel* 2016;30(9):7465–73.

[18] Xu Y, Liu X, Wang H, Zeng X, Zhang Y, Han J, et al. Influences of In-furnace kaolin addition on the formation and emission characteristics of PM_{2.5} in a 1000 MW coal-fired power station. *Environ Sci Technol* 2018;52:8718–24.

[19] Rizeq R, Shadman F. Alkali-induced agglomeration of solid particles in coal combustors and gasifiers. *Chem Eng Commun* 1989;81(1):83–96.

[20] Öhman M, Nordin A. The role of kaolin in prevention of bed agglomeration during fluidized bed combustion of biomass fuels. *Energy Fuel* 2000;14(3):618–24.

[21] Steenari B-M, Lindqvist O. High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite. *Biomass Bioenergy* 1998;14(1):67–76.

[22] Nowak Delgado R, de Riese T, Johne P, Fendt S, Spliethoff H. Impact of coal fly ash addition on combustion aerosols (PM_{2.5}) in pilot- and full-scale pulverized wood combustion: a comparative study. *Energy Fuels* 2022;36(22):13665–77.

[23] Davidsson KO, Steenari BM, Eskinsson D. Kaolin addition during biomass combustion in a 35 MW circulating fluidized-bed boiler. *Energy Fuels* 2007;21(4): 1959–66.

[24] Nowak Delgado R, Bieli P, de Riese T, Fendt S, Spliethoff H. Influence of additive surface area degradation on fine particle formation during biomass pulverised-fuel combustion. *Fuel (Guildford)* 2023;338:127247.

[25] Tissari J, Sippula O, Kouki J, Vuorio K, Jokiniemi J. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. *Energy Fuels* 2008;22(3):2033–42.

[26] Wang G, Poulsen JNF, Poulsen SNF, Jensen PA, Frandsen FJ. Influence of kaolin and coal fly ash addition on biomass ash deposition in an entrained flow reactor. *Fuel (Guildford)* 2022;313:123041.

[27] Rebbling A, Fagerström J, Steinvall E, Carlborg M, Öhman M, Boman C. Reduction of alkali release by two fuel additives at different bed temperatures during grate combustion of woody biomass. *Energy Fuels* 2019;33(11):11041–8.

[28] Cheng W, Zhu Y, Shao Ja, Zhang W, Wu G, Jiang H, Hu J, Huang Z, Yang H, Chen H. Mitigation of ultrafine particulate matter emission from agricultural biomass pellet combustion by the additive of phosphoric acid modified kaolin. *Renew Energy* 2021;172:177–87.

[29] James Thomas, S.C.a.I.S., *Measurement of the in-situ performance of solid biomass boilers*. 2018.

[30] Nik Norizam NNA, Yang X, Ingham D, Szuhánszki J, Yang W, Rezende J, et al. An improved index to predict the slagging propensity of woody biomass on high-temperature regions in utility boilers. *J Energy Inst* 2023;109:101272.

[31] Sippula O, Lamberg H, Leskinen J, Tissari J, Jokiniemi J. Emissions and ash behavior in a 500kW pellet boiler operated with various blends of woody biomass and peat. *Fuel* 2017;202:144–53.

[32] Gehrig M, Wöhler M, Pelz S, Steinbrink J, Thorwarth H. Kaolin as additive in wood pellet combustion with several mixtures of spruce and short-rotation-coppice willow and its influence on emissions and ashes. *Fuel* 2019;235:610–6.

[33] Höfer I, Huelsmann T, Kaltschmitt M. Influence of Ca- and Al-additives on the pollutant emissions from blends of wood and straw in small-scale combustion. *Biomass Bioenergy* 2021;150:106135.

[34] Wu, H., G. Wang, P.A. Jensen, F.J. Frandsen, and P. Glarborg. Reactive additives for alkali capture in biomass combustion. in 27th International Conference on the Impact of Fuel Quality on Power Production and the Environment. 2018.

[35] Wu H, Bashir MS, Jensen PA, Sander B, Glarborg P. Impact of coal fly ash addition on ash transformation and deposition in a full-scale wood suspension-firing boiler. *Fuel* 2013;113:632–43.

[36] Wang L, Hustad JE, Skreiberg Ø, Skjevraak G, Grønli M. A critical review on additives to reduce ash related operation problems in biomass combustion applications. *Energy Procedia* 2012;20:20–9.

[37] Kerscher F, Spliethoff H. Alkali removal with mineral sorbents – Part I: Sorption capacity and reaction kinetics. *Powder Technol* 2021;390:190–6.

[38] Yang W, Zhu Y, Cheng W, Sang H, Yang H, Chen H. Characteristics of particulate matter emitted from agricultural biomass combustion. *Energy Fuel* 2017;31(7): 7493–501.

[39] Ninomiya Y, Wang Q, Xu S, Mizuno K, Awaya I. Effect of additives on the reduction of PM_{2.5} emissions during pulverized coal combustion. *Energy Fuel* 2009;23(7): 3412–7.

[40] Wei B, Wang X, Tan H, Zhang L, Wang Y, Wang Z. Effect of silicon–aluminum additives on ash fusion and ash mineral conversion of Xinjiang high-sodium coal. *Fuel* 2016;181:1224–9.

[41] Boström D, Skoglund N, Grimm A, Boman C, Öhman M, Broström M, et al. Ash transformation chemistry during combustion of biomass. *Energy Fuels* 2012;26(1): 85–93.

[42] Yang W, Zhu Y, Cheng W, Sang H, Xu H, Yang H, et al. Effect of minerals and binders on particulate matter emission from biomass pellets combustion. *Appl Energy* 2018;215:106–15.

[43] Chen X, Kong L, Bai J, Dai X, Li H, Bai Z, et al. The key for sodium-rich coal utilization in entrained flow gasifier: the role of sodium on slag viscosity-temperature behavior at high temperatures. *Appl Energy* 2017;206:1241–9.

[44] Kosminki A, Ross DP, Agnew JB. Reactions between sodium and kaolin during gasification of a low-rank coal. *Fuel Process Technol* 2006;87(12):1051–62.

[45] Arvelakis S, Jensen PA, Dam-Johansen K. Simultaneous thermal analysis (STA) on ash from high-alkali biomass. *Energy Fuel* 2004;18(4):1066–76.

[46] Vassilev SV, Baxter D, Vassileva CG. An overview of the behaviour of biomass during combustion: Part II. ash fusion and ash formation mechanisms of biomass types. *Fuel* 2014;117:152–83.

[47] Gale TK, Wendt JO. In-furnace capture of cadmium and other semi-volatile metals by sorbents. *Proc Combust Inst* 2005;30(2):2999–3007.

- [48] Chen D, Liu X, Wang C, Xu Y, Sun W, Cui J, et al. Effects of H₂O and HCl on particulate matter reduction by kaolin under oxy-coal combustion. *Energy Fuel* 2017;31(6):6455–62.
- [49] Fernandes U, Costa M. Particle emissions from a domestic pellets-fired boiler. *Fuel Process Technol* 2012;103:51–6.
- [50] Niu Y, Tan H, Hui Se. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Prog Energy Combust Sci* 2016;52:1–61.
- [51] Sommersacher P, Brunner T, Obernberger I, Kienzl N, Kanzian W. Application of novel and advanced fuel characterization tools for the combustion related characterization of different wood/kaolin and straw/kaolin mixtures. *Energy Fuels* 2013;27(9):5192–206.
- [52] Wang MR, Jia DC, He PG, Zhou Y. Influence of calcination temperature of kaolin on the structure and properties of final geopolymer. *Mater Lett* 2010;64(22):2551–4.
- [53] Wang G, Jensen PA, Wu H, Frandsen FJ, Sander B, Glarborg P. Potassium capture by kaolin, part 2: K₂CO₃, KCl, and K₂SO₄. *Energy Fuel* 2018;32(3):3566–78.
- [54] Tran K-Q, Iisa K, Steenari B-M, Lindqvist O. A kinetic study of gaseous alkali capture by kaolin in the fixed bed reactor equipped with an alkali detector. *Fuel (Guildford)* 2005;84(2):169–75.
- [55] Tran QK, Steenari B-M, Iisa K, Lindqvist O. Capture of potassium and cadmium by kaolin in oxidizing and reducing atmospheres. *Energy Fuel* 2004;18(6):1870–6.
- [56] Gustafsson E, Strand M, Sanati M. Physical and chemical characterization of aerosol particles formed during the thermochemical conversion of wood pellets using a bubbling fluidized bed gasifier. *Energy Fuel* 2007;21(6):3660–7.
- [57] Hindsgaul C, Schramm J, Gratz L, Henriksen U, Bentzen JD. Physical and chemical characterization of particles in producer gas from wood chips. *Bioresour Technol* 2000;73(2):147–55.