Investigation of leaching on the elemental composition of alternative fuels

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A R T I C L E   I N F O

A B S T R A C T

This study highlights the leaching process of biomass and food waste (FW), which reduces potassium and sodium content to more than 80% and improves its quality to be used as fuel. Alternative fuels with high water content, especially from FW and the palm oil industry, represent the majority of alternative resources in Malaysia. However, the combustion of these fuels often causes more ash-related problems such as fouling, slagging, and higher particle emissions compared to other fuel types. Water leaching is a pre-treatment process that has a great potential to alleviate the deposition problems caused by the thermal and chemical reactions of the biomass and FW elements during its combustion and thus increase their value. This study compared the fuel characteristics and water leaching effect to the selected fuels with specific water ratios for 5 minutes. Energy-dispersive X-ray spectroscopy (EDX) was used to determine water leaching effectiveness to compare the relative fuel composition after leaching. Leaching results were simulated using FactSage software to predict slag formation in treated and untreated samples during combustion at 650, 800, and 950°C. Simulated results show significant slagging formation reduction following the water leaching process onto the samples. Simulating the particulate and ash compositions paves the path to formulating strategic assessment techniques to reduce their emissions and slagging tendencies.

1. Introduction

The conventional use of fossil fuels for power generation has begun to shift towards alternative, renewable fuel sources such as biomass in the form of waste and residues from the agricultural or plantation industry (Piwowar and Dzikuć, 2016). Biomass includes (1) wood and woody biomass; (2) herbaceous and agricultural biomass; (3) aquatic biomass; (4) animal and human biomass wastes; (5) semi-biomass (contaminated biomass and industrial biomass wastes) such as municipal solid waste, refuse-derived fuel, sewage sludge, demolition wood, and other organic wastes; and their (6) biomass mixtures (Vassilev et al., 2017). Malaysia is one of the top exporting fuel pellets used for heat and power generation. Recently, it has been reported that Malaysia produced 168 million tons of biomass (Abdullah et al., 2019). Biomass in Malaysia, such as palm-based empty fruit bunches (EFB), has high alkali metal contents and is occasionally used to generate heat and power (Leffler et al., 2017; Lim et al., 2017; Mason et al., 2016; Yan et al., 2017).

Biomass is a complex heterogeneous mixture of organic matter (54 to 99%) and inorganic matter (0.1 to 46%) in solid and fluid phases with different content and origin (Vassilev et al., 2013). The organic component's main structural for biomass is cellulose, hemicellulose, and lignin; semi-biomass is more complex and complicated than natural biomass due to incorporating various non- biomass during the processing steps (Vassilev et al., 2013).

Significant associations related to the occurrence, content and origin of elements and phases were identified in natural biomass, and they include: (1) C–H (mainly as authigenic cellulose, hemicellulose, lignin and organic extractives); (2) Si– Al–Fe–Na–Ti (primarily as detrital silicates and oxyhydroxides, excluding authigenic opal); (3) Ca–Mg–Mn (commonly as authigenic oxalates and carbonates); and (4) N–K–S–P–Cl (usually as authigenic phosphates, sulfates, chlorides, and nitrates)

(Vassilev et al., 2010). The fundamental association of biomass elements is essential for systematic classification and indicator of sustainable biomass processing.

Food waste is new alternative biomass with low alkali metal content. A significant amount of food waste is available in landfills, and it is increasing over time. FW is the main component of MSW, and most of the time, it is sent to landfills. This problem arises due to the lack of applicable technologies to valorize food waste efficiently and adequately. Statistics show that almost half of the MSW generated daily is from food waste in Asian countries such as China, Singapore, and Malaysia (Leckner, 2015; Rahman, 2013; Zhang et al., 2015a; 2015b). FW has high water content and low heating value, and it is also mixed with other wastes in the landfill so much that it is hard to be separated (Tong et al., 2018).

Biomass and ash characterization involves complex and vast chemical compounds formation after thermal degradation, such as the combustion process. The biomass ash formation is due to the high-temperature combustion and mainly comprises of inorganic fraction of the biomass as organic compounds break down and become less solid after the process. These inorganics are ash-forming elements categorized as alkaline metal; K, Na, alkaline earth metal; Na, Ca, Mg, K, and silica, Si (Tabish et al., 2021). Other researchers listed more ash-forming chemical elements: Al, Ca, Cl, Fe, K, Mg, P, Na, S, Mn, Si, and Ti (Vassilev et al., 2017). Each type of biomass has its unique chemical composition and shall produce its biomass and ash characteristics. These elements shall increase the deposit formation, sintering, agglomeration, fouling, slagging, corrosion, abrasion and health and environmental related risk (Tabish et al., 2021; Vassilev et al., 2017). The formation of a hard and fused glassy layer which is corrosive and heat resistive after the ash melts and stuck on the boiler surface is not favorable to the energy player (Tabish et al., 2021). Thus, to reduce the inorganics deposit, the biomass must first be treated with a proper method such as water leaching, as studied in this paper.

Due to the complex composition of the biomass, the combustion of high ash content fuel causes several operational issues, such as high slagging, fouling propensities, and high particulate matter emissions. These issues are caused by high alkali metal content in the biomass, which devolatilize, nucleate, and condense to form hydroxide, chloride, and sulfate compounds (Niu and Tan, 2016; Subramani and Jayanti, 2011; Wu et al., 2016; Zhang et al., 2001). When the temperatures are high enough (depending on the alkali metal content), the alkali metal compounds form slags in the form of aluminosilicates (Paneru et al., 2016). Besides alkali metal, silica, alkaline earth metal, and other elements are the significant ash forming elements for biomass (Lateef et al., 2020; Tabish et al., 2021; Zafar et al., 2020); the combination of biomass inorganic and

organic ash can be as high as 20.1% (Vassilev et al., 2010). Another study reported that the ranges are 1 to 15%, depending on the type of biomass. The reduction of ash-forming elements could be made to the biomass using the leaching process (Lateef et al., 2020; Tabish et al., 2021).

Biomass leaching is a process of soaking biomass with selected reagents such as using water, acid, and bases (Lateef et al., 2020). The water leaching process is done by soaking biomass into the water with selected process conditions. The water leaching treatment is more economical; however, it is not an in-depth treatment method such as acid leaching. The biomass water leaching washes the biomass soluble chemical components. It can be integrated with the mechanical mechanism to reduce the processing time and increase the water penetration into the biomass. The efficiency and process duration of the treatment shall be decreased by shredding the biomass and increasing the biomass surface area. The deposition of slagging and fouling biomass during combustion is contributed by potassium (Deng et al., 2017; Zhang et al., 2015b). The composition of this element in biomass varies with the biomass type. In biomass, potassium is a free K+ion in a solution within xylem cells (Clery et al., 2018). Food waste has other problems, such as the source and texture of the material. The abundant FW biomass requires this waste to be disposed of properly. The combustion of this waste is feasible with a proper pre-treatment method. After the FW crushing and pressing process, the leaching pre-treatment can be done to increase the contact surface area and reduce the FW moisture content before the leaching pre-treatment. Depending on the reagent used in the study, water leaching of biomass and FW needs to be done in an optimized condition of the highest removal of inorganic slagging chemical elements/compounds. This study found that food waste ash is high in phosphorus and calcium. These elements may originate from chicken and fish bones inside the food waste. The effect of leaching as a form of pre-treatment method for biomass composition, samples were analyzed using energy dispersive X-ray spectrometry. The EDX analyses were done before and after the leaching process, and composition changes were investigated. FactSage 7.2 was used to simulate the combustion process and formation of slagging and fouling of the FW in this study. The EDX composition of the food waste was used as the software's input by focusing on the top elements from the EDX results for each sample. The leaching process has the potential to improve biomass's physical, thermal, and chemical properties as a fuel source and reduces the formation of slagging and fouling after the combustion process. Leaching also could be done to the biomass ashes to facilitate technological and environmental problems.

Leaching using acids has several benefits and problems. The advantage of biomass acid leaching is that it can dissolve and remove chemical components inside the biomass better than water leaching. The problem with acid leaching with a

more prolonged process time is (usually needs 2 to 4 hours (Lateef et al., 2020; Tabish et al., 2021). This condition will incur more costs for the commercial operation. It is reported that acid leaching has reduced the fuel's calorific value (Tabish et al., 2021; Zafar et al., 2020), making biomass more acidic, overreacting with biomass, taking a long time, and requiring a dedicated facility to do so. The fuel and wastewater will be acidic after the process. The wastewater requires good waste disposal governance and cannot flow into the river or standard water treatment system. Water leaching also has the same problem with its wastewater disposal; however, it is less harmful to the environment since this wastewater can be treated in a typical effluent pond after the process. The calorific value of the biomass becomes lower after certain types and concentrations of acid leaching may be due to the chemical reaction of biomass with acid, dissolving and reducing the biomass fibrous components (Zafar et al., 2020).

This study highlights the five-minute water leaching process to determine the reduction of the slagging elements before and after the combustion process. This paper discussed the water leaching process to selected biomasses and food waste (FW) to highlight the performance of water leaching and its chemical elements reduction such as alkali metal and other inorganic elements.

2. Research methodology

2.1. Sample preparation and experiment: Leaching pre-treatments

The biomass and food waste samples were collected, sorted, dried, and crushed to less than 10 mm. The selection was from canteen food waste, which was collected from TNB Research, Malaysia. Food waste was sorted into three types which are fish (FW F), chicken (FW C), and others (FW O). Biomass types used in this study were EFB 1, EFB 2, rice husk, coconut fiber, and banana leaf. All biomass is dried in the oven and crushed using the conventional dry grinder before the pre-treatment to increase the FW surface contact area, reduce the time and improve the water leaching penetration to the samples.

The water leaching pretreatment was conducted in a 2 L beaker with a magnetic stirrer. The leaching was done by manipulating the water ratio. In brief, the food waste or biomass sample was mixed with distilled water with a 1:2 to 1:10 sample-to-water ratio in the beaker. The specimens were then labeled with a number, for example, O2, F6, and C10, to show their water leaching ratio. The water and sample were mixed using a magnetic stirrer for 5 minutes. After that, the products were oven-dried at 150 °C. The samples were cooled and stored in a sealed container. Then it is sent to the lab for fuel characteristic and compositional analysis.

The five minutes is selected to understand the effect of the water leaching process on the chemical elements changes and formation of slagging, fouling, and ash compounds after the combustion process using simulation and experiment. Besides the quick process, five minutes is considered because of the practical aspect of adopting the water leaching process into the bioenergy power plant with lesser cost and energy requirement. The water leaching with five minutes is selected and suggested as practical shorter time duration for a continuous water leaching system, and for a more protracted process duration, it is suitable for the water leaching with batch system design. The justification for a faster leaching process rate is due to the biomass energy power plant's requirement to burn biomass in a high capacity. The commercialization of water-leached biomass requires a faster output with a lower cost. Reducing the cost can be done by using shredded, older biomass and less reagent. Shredded and more aged biomass are the typical conditions of biomass in agri-waste biomass for power generation.

2.2. Compositional analysis: EDX analysis and fuel characterization

The elemental analysis was performed using a scanning electron microscope (SEM) coupled to an energy dispersive X-ray spectroscope (EDX) that has a Bruker XFlash Beryllium 6/60 detector (8386 series). The X-ray spectra were acquired for 60s. EDX analyses were done for food waste samples before leaching, after leaching, and after combustion in a Carbolite chamber furnace. For biomass samples, the EDX analyses were only done to check the leaching effect.

Energy Dispersive X-ray diffraction is an analysis that can be used to study the chemical composition of any solid. EDX had been used to understand solid compositions such as ash and deposit (El-Zahhar et al., 2019). In this study, the EDX method is used to understand the relative comparison of solid fuel composition before and after the water leaching process to detect the compositional changes of the fuel. After the combustion of the FW, the ash is analyzed using the EDX to study the thermochemical effect of the chemical composition changes of the fuel into ash. The composition of ash is then determined using the EDX method to study the chemical composition. To further understand the ash simulation software is used to predict the ash formation of samples.

Proximate and ultimate analyses were made on the FW F, O, and C samples. Then the calorific values (lower heat value) of all the fuels were determined. Calorific values of FW samples were determined according to ASTM method D5865 by using a bomb calorimeter model Leco AC-600. The calorimeter was calibrated before the measurement.

For proximate analysis, it is typically assumed that the FW fuel consisted of two sources of carbon, volatile and fixed carbon. The moisture content, volatile matter and ash content analyses were done in accordance with ASTM method D5142 using Seiko TGA analyzer model 220U. Finally, the fixed carbon

was calculated by subtracting the sum of the percentage of volatile matter and ash content on a dry basis from a total of a hundred percent.

Carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) are the major chemical elements in fuel. The chemical analysis for FW samples is essential to calculate the material composition balance accurately. Thus, C, H, N, O, and S's content were determined by ultimate analysis conducted using the LECO Truspec Micro CHNOS analyzer.

2.3. Food waste combustion and FactSage simulation analysis

2.3.1. Food waste combustion

Dried raw and pre-treated food waste samples were combusted inside the AF1100 Carbolite chamber furnace reactor. Each sample was weighed to 5g and filled inside crucibles. The samples were heated to 650, 800, and 950°C for 60 minutes. When the combustion was complete, the products were

extracted from the reactor, weighed, and kept inside sample bottles before being used for subsequent analysis. Fig. 1 shows the samples before and after combustion in the Carbolite furnace chamber.

2.3.2. FactSage simulation: Chemical equilibrium calculation

The slag content was estimated using FactSage simulation. In this study, FactSage 7.2 was used to simulate the chemical reactions based on the Gibbs free energy minimization and thermodynamic equilibrium calculation. The amount of ash or slag produced was weighed and compared with that of the pre-treated samples. The simulation was performed using the Equilibrium module. For the Equilibrium module, the FactPS, FToxide, and Ftsalt databases were chosen for simulating the reactions of gas, liquid, and pure solid compounds. FT-Oxide-SLAGA and FT-SALTF functions were selected for the simulation of the chemical reaction.

Fig. 1: (Left) Dried Food waste from chicken, fish, and other samples. (Middle) Carbolite chamber furnace. (Right) ash/slag samples after combustion

The simulation is done using selected EDX data of pre-treated FW with a water ratio of 6 and 10. These simulated EDX data then were labeled as F and F(S) for FW fish simulation; O and O(S) for FW other simulation; C and C(S) for FW chicken simulation.

3. Results and discussion

3.1. Fuel characteristics

The ultimate, proximate, and calorific value analyses were done on the raw food waste to determine FW's potential as an alternative fuel source for power generation and compare it with other biomass characteristics in the literature. Leaching slightly impacted the characteristic analysis, such as proximate, ultimate, and calorific value analyses of the biomass (Novianti et al., 2015),

and was not analyzed in this study. Table 1 shows the comparison of the proximate analysis characterization of certain biomass types and FW.

Table 2 shows the comparison of proximate analysis and calorific value characterization of some biomass types and FW.

3.2. EDX result

The samples were prepared and leached into the water to see the compositional changes of the fuel. The samples were analyzed using before the heat treatment to understand the composition of the dry fuel.

Fig. 2 shows the FESEM/EDX results of the selected biomass for selected chemical elements. The EDX was analyzed relatively for each sample to check for the changes in the fuel's chemical

composition after water leaching. According to the fuel samples EDX spectrum, the particles mainly formed are mainly composed of oxygen and carbon, consistent with the elemental composition determined by CHNS analysis in Table 2. SEM images show that the FW and Agri-waste biomass samples are different in surface structure and condition. The surface structure of the biomass may influence the effect of the reduction of alkali metal after the water leaching process.

**Table 1**: Proximate analysis of biomass (NR: Not reported)

Biomass	Moisture content (Wt. %)	Volatile matter (Wt. %)	Fixed carbon (Wt. %)	Ash (Wt. %)
Fish (FW)	5.01	60.15	6.98	27.84
Other (FW)	6.68	54.85	21.36	17.10
Chicken (FW)	9.20	61.91	11.02	17.83
Meat (Cascarosa et al., 2011)	0.95	97.66	5.38	21.47
Bone meal (Cascarosa et al., 2011)	1.01	65.26	3.70	30.04
Tea waste (Ozyuguran et al., 2018)	NR	73.36	21.93	4.71
Rice straw (Huang et al., 2018)	9.32	79.22	12.27	8.51
Rice husk (Huang et al., 2018)	6.34	79.22	8.70	10.85
Sugarcane bagasse (Huang et al., 2018)	8.61	86.02	9.93	4.05
Pinewood (Zhang et al., 2015b)	NR	76.10	23.10	0.80
Wood pellet (Mason et al., 2016)	8.90	85.00	16.10	0.30
Empty fruit bunch (Novianti et al., 2015)	NR	NR	NR	4.90

Table 2: Ultimate analysis and calorific value of biomass (NR: Not reported)

Biomass	C (Wt. %)	H (Wt. %)	N (Wt. %)	S (Wt. %)	O (Wt. %)	Calorific value (MJ/kg)
Fish (FW)	43.70	6.79	6.87	0.39	42.25	18.54
Other (FW)	43.80	6.12	2.36	0.25	44.47	17.51
Chicken (FW)	44.40	7.35	4.96	0.38	42.91	19.40
Meat (Cascarosa et al., 2011)	42.53	6.64	9.05	0.00	NR	18.10
Bone meal (Cascarosa et al., 2011)	26.96	3.98	4.64	0.00	NR	9.50
Tea waste (Ozyuguran et al., 2018)	45.04	6.07	3.48	0.50	40.21	16.96
Rice straw (Huang et al., 2018)	45.76	6.22	0.52	NR	47.50	16.16
Rice husk (Huang et al., 2018)	43.98	5.94	49.68	NR	49.68	15.91
Sugarcane bagasse (Huang et al., 2018)	48.88	6.71	0.27	NR	44.15	16.92
Pine wood (Zhang et al., 2015b)	51.30	6.00	< 0.01	0.02	42.68	NR
Wood pellet (Mason et al., 2016)	49.20	6.00	0.10	NR	44.70	19.50
Empty fruit bunch (Novianti et al., 2015)	43.56	5.34	0.56	0.11	45.64	16.76

(a) Fish FW

(b) Chicken FW

(c) Plant based FW

(d) Banana leaves
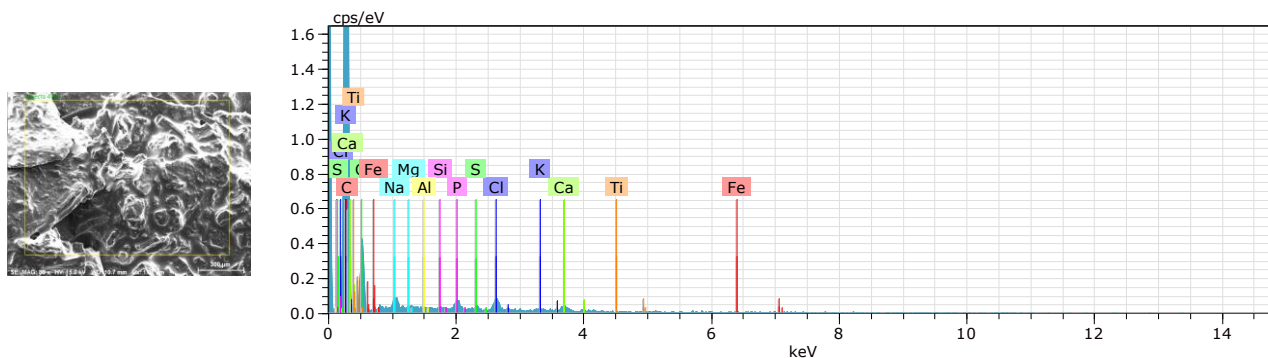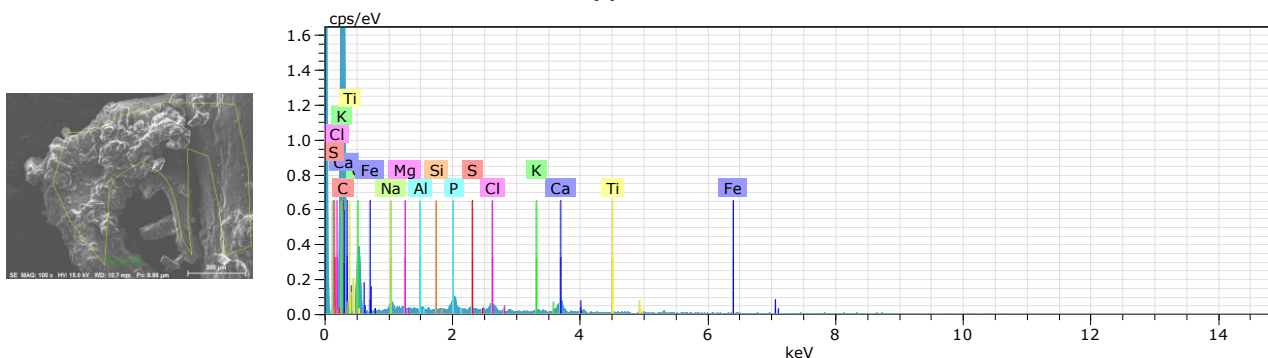
(e) Coconut Fibre

(f) Rice Husk

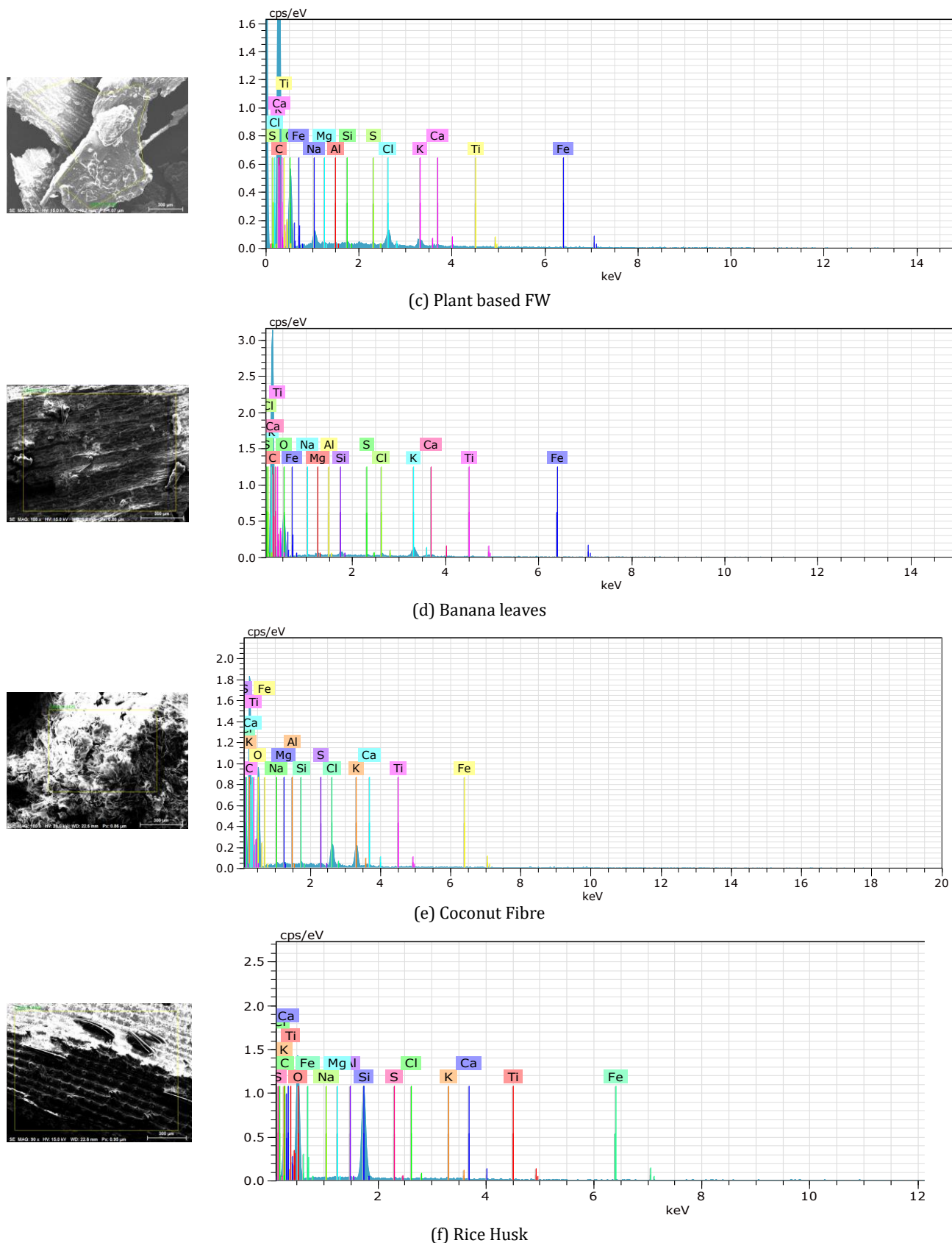**Fig. 2:** FESEM/EDX analysis of biomasses fuel (a) Fish FW, (b) Chicken FW, (c) Plant-based FW, (d) Banana leaves, (e) Coconut fiber, (f) Rice Husk

3.2.1. EDX Potassium and sodium reduction

Leaching pre-treatment alters the biomass and food waste chemical compositions, especially alkali metal contents (potassium and sodium). This condition will affect the combustion and the formation of slagging during the combustion process. The food waste chemical elements change is measured using the EDX analysis. The EDX analysis was performed to compare treated and untreated food waste. Table 3 shows the alkali metal composition changes of selected biomass in this

study. Fig. 3 shows the FESEM/ EDX results of K and Na reduction of the selected biomass. The EDX samples were analyzed for selected elemental composition.

Table 3: The composition changes of alkali metal K and Na

Sample	Raw K Wt. (%)	Leached K (Wt. %)	K (% reduction)	Raw Na (Wt. %)	Leached Na (Wt. %)	Na (% reduction)
EFB1	3.64	0.53	86	0.05	0.03	29
EFB2	2.91	0.33	89	0.06	0.03	39
Rice husk	0.18	0.03	83	0.07	0.00	100
Food Waste	0.36	0.06	82	0.52	0.02	95
Banana leaf	2.35	1.63	31	0.02	0.00	100

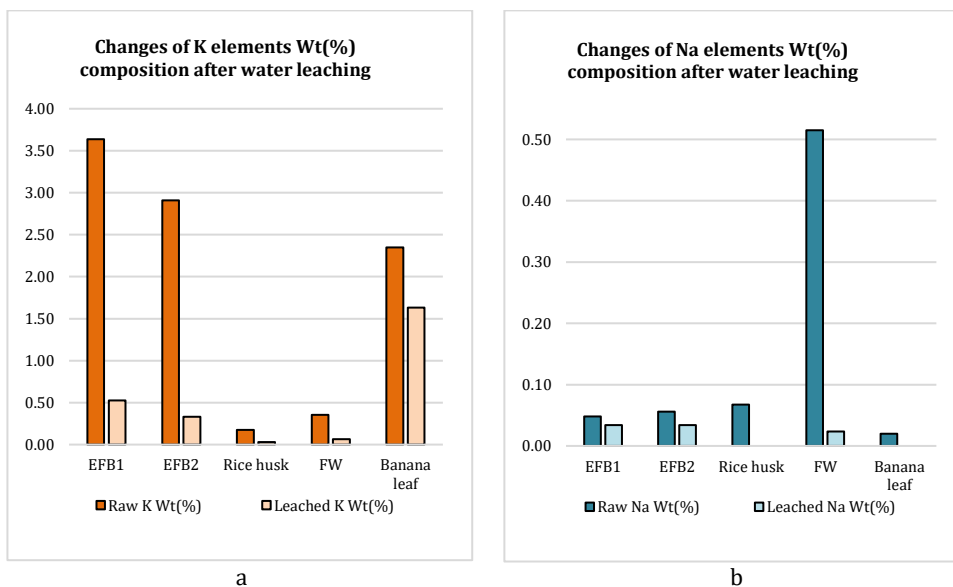a   b

Fig. 3: The composition changes of alkali metal (a) K and (b) Na after pre-treatment for several biomass samples

From Table 3 and Fig. 3, the raw EFB and raw banana leaves show the highest K content inside the fuel, and after water leaching the K, content is reduced in the range of 31 to 89%. The highest Na content appears for FW and after water leaching, the Na content reduced in the range of 29 to 100%. The

reduction of alkali metal may depend on the biomass surface structure and its chemical bonding of elements and compounds.

Fig. 4 shows an overview of (a) K and (b) Na removal after pre-treatment for several biomass samples.
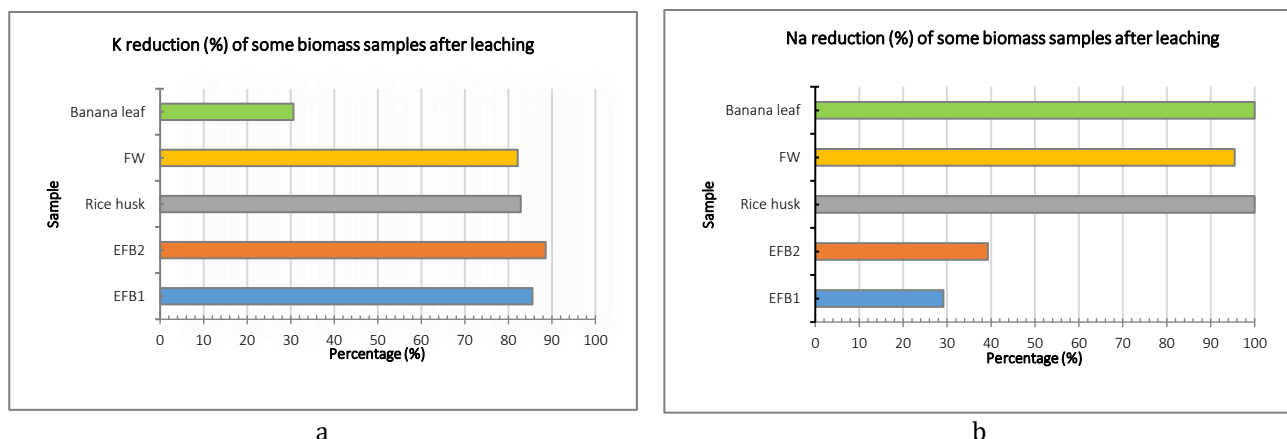

a   b

Fig. 4: Overview of (a) K and (b) Na removal after pre-treatment for several biomass samples

After leaching was done to the biomass and food waste, the EDX data were compared. Fig. 4 shows the comparison of K and Na reduction for several samples. For potassium, EFB showed the highest chemical element reduction, and for sodium, rice husk and banana leaf showed the highest reduction after the leaching process. The comparison shows

the effect of leaching. The chemical element reduction is significant; however, the changes in water ratio during leaching impacted the leaching pre-treatment performance. Fig. 5 shows the water ratio performance on the FW samples in terms of K and Na reduction after leaching pre-treatment.
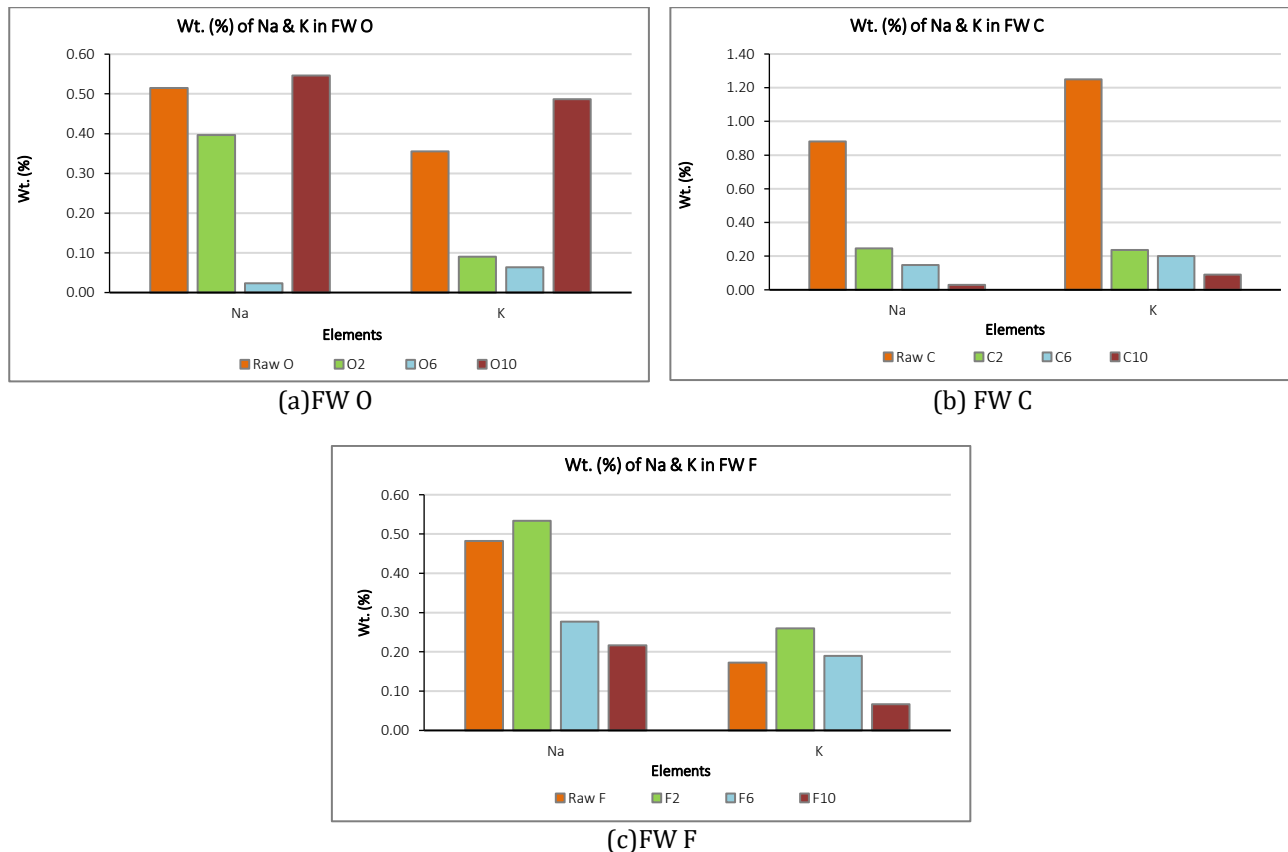
(a)FW O

(b) FW C

(c)FW F

Fig. 5: The weight percentage of Na and K in (a) FW O, (b) FW C, and (c) FW F

A detailed comparison of elements in the FW was made based on the leaching pre-treatment water ratio to determine the best water ratio for this study. The elements sodium and potassium were selected as the main elements in this study because of their high tendency to become slag after combustion. Potassium reduction ranges from 74.65% to 82.16% for FW O at the best leaching ratio of 6, ranges from 33.33% to 76.65% for FW C at the best leaching ratio of 10, and ranges from 26.76% to 81.22% for FW F at the best leaching ratio of 10. Meanwhile, sodium reduction ranges from 22.98% to 95.47% for FW O at the best leaching ratio of 6, ranges from 52.10% to 94.17% for FW C at the best leaching ratio of 10, and ranges from 46.28% to 57.93% for FW F at the best leaching ratio of 10.

For FW, the sodium content may link with sodium chloride (salt) during the cooking process. The high sodium content inside FW, especially in the plant-based FW, is impossible. This condition is because the higher sodium content is toxic for green plants (Dayton et al., 1999). This condition can also be seen when compared with Na content inside other biomass types with lower Na content (Vassilev et al., 2017). Protein sources for consumption, such as fish and seafood, have a certain amount of Na, usually low. For both K and Na, FW O showed the highest reduction and might be due to the structure of this FW, which is less fibrous and lignocellulosic compared with other palm-based biomasses. Among FW, more edible oil may increase adhesion on the FW C and FW F flesh and bones, which may happen because chicken and fish were served in this canteen as fried foods.

Most of the fluctuation in the EDX resulted from the inhomogeneous size of the food waste samples, although the size is limited to lower than 10 mm. In addition, leftover edible oil from FW reduces pre-treatment efficiency because oil is hydrophobic and is not water-soluble. Edible oil undergoes chemical reactions such as polymerization and oxidation during food cooking, which affect edible oil density and viscosity (Michalski et al., 1998). A study reports that adhesion is directly proportional to the edible oil's viscosity (Michalski et al., 1998).

3.3. FactSage simulation result

Part of the FW EDX data was used as the input for the FactSage simulation. These selected sets of treated samples were labeled as O(S), C(S), and F(S); and raw data is not labeled as O, C, and F. Table 4 shows the EDX data of the raw FW and treated FW which is used as input for FactSage simulation.

The elemental composition (weight percentage) for each sample in Table 4 was averaged over three readings with an average standard deviation range of 0 to 8.38%. FactSage 7.2 was used to simulate the oxidation of the FW. The elements mass was approximated by multiplying the weight percentage of the elements from Table 4 by 5 g and additional air gases, oxygen, and nitrogen were used as the Equilibrium module input according to the air to fuel ratio of 1 to 1. These elements are the commonly found elements in the biomass, which include C, O, Cl, Na, Ca, K, S, Ti, Si, Mg, Al, Fe, and P; sometimes, Mn and N are included in the list (Grimm, 2012; Vassilev et al., 2013; 2017).

The data analysis also included the treated FW from all the food waste types to compare the method's effectiveness to treat the FW. The results show the dominant form of calcium phosphate. It is predicted that the reaction of calcium, phosphorus, and oxygen is simplified into calcium oxide and phosphorus oxide, as shown in Eq. 1. This chemical reaction simulation simulates the formation of solid residue after the combustion using the thermodynamic equilibrium module with FactSage 7.2:
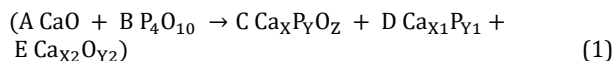
$$(A\ CaO\ +\ B\ P_4O_{10}\ \rightarrow\ C\ Ca_XP_YO_Z\ +\ D\ Ca_{X1}P_{Y1}\ +\ E\ Ca_{X2}O_{Y2}) \tag{1}$$

Table 4: EDX weight percentage of food waste chemical elements

Chemical Element	Samples (Wt. %)					
	O	O (S)	C	C (S)	F	F (S)
C	57.03	58.52	52.68	75.12	78.62	74.36
O	35.03	39.21	39.01	20.21	19.14	15.20
Cl	0.80	0.08	1.05	0.07	0.58	0.12
Na	0.52	0.02	0.88	0.03	0.48	0.22
Ca	4.89	1.25	3.06	2.88	0.34	6.43
K	0.36	0.06	1.25	0.09	0.17	0.07
S	0.19	0.27	0.40	0.07	0.09	0.14
Ti	0.05	0.04	0.00	0.01	0.02	0.00
Si	0.11	0.22	0.03	0.01	0.06	0.03
Mg	0.16	0.04	0.09	0.11	0.03	0.16
Al	0.03	0.07	0.15	0.00	0.10	0.09
Fe	0.16	0.04	0.02	0.03	0.05	0.15
P	0.70	0.17	1.37	1.39	0.31	3.04

Tables 5 and 6 list the simulated data products for all temperatures (650°C, 800°C, and 950°C) and FW types. This research's boundary temperature condition might affect the minerals slagging formation because certain mineral compounds have a higher melting temperature. The simulation predicted the formation of calcium phosphate for all temperature ranges, proven by other research works as one of the phases and minerals identified in biomass ash (Grimm, 2012; Vassilev et al., 2013). These compounds are dominant products of the ash/slag for treated samples. Besides, only samples from F(S) showed the formation of sodium (alkali metal) sulfate. Part of the simulation results showed the chemical formations of calcium sulfate and calcium oxide; however, these formations are not dominant and are not discussed in this paper.

From the FactSage equilibrium simulation, the formation of slag liquid in the forms of Na₂O, K₂O, CaO, Na₂S, K₂S, CaS, P₂O₅, and P₂O₃S₂ was only observed in raw samples. The treatment of FW removed elements (such as alkali metals) that contribute to the formation of slagging and fouling. Significant reduction of alkali metals after treatment, as shown in Table 3, supports the claim. Table 5 shows alkali metal compounds and some sulfate and slag liquid formed from the FW oxidation before the treatment. After the treatment, sulfate formation was reduced, no slag was formed, and almost no alkali metal was found except for a small amount in the treated fish sample, F(S) (Table 6). High concentrations of Cl and alkali metals (K and Na) in biomass have resulted from the rapid build-up of unmanageable deposits on the fired surfaces such as superheater and water wall (Niu and Tan, 2016). The leaching pretreatment can reduce the deposit effect before the combustion. Table 5 shows FactSage simulation results on ash/slag residue formation after the Combustion of raw FW.

Table 6 below shows FactSage simulation results on ash/slag residue formation after the Combustion of treated FW.

Table 5: Ash/slag formed from FW combustion equilibrium simulation in FactSage 7.2 (slag liq=slag liquid)

Other			Chicken			Fish		
650 °C	800 °C	950 °C	650 °C	800 °C	950 °C	650 °C	800 °C	950 °C
Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉	Slag liq	Slag liq	Na₂CaP₂O₇	Na₂CaP₂O₇	Slag liq
CaO	CaO	CaO	Na₂Ca₂P₂O₈	Ca₄P₂O₉	Ca₄P₂O₉	Ca₃P₂O₈	Ca₃P2O₈	CaSO₄
Na₂SO₄	Na₂SO₄	Na₂SO₄	K₃Na(SO₄)₂	K₃Na(SO₄)₂	Na₂SO₄	-	-	-
Na₃PO₄	Na₃PO₄	-	Ca₃P₂O₈	-	-	-	-	-
-	-	-	Na₂SO₄	-	-	-	-	-

Table 6: Ash/slag formed from treated FW combustion equilibrium simulation in in FactSage 7.2 (slag liq=slag liquid)

Other			Chicken			Fish		
650 °C	800 °C	950 °C	650 °C	800 °C	950 °C	650 °C	800 °C	950 °C
Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉	CaO	CaO	CaO	Ca₃P₂O₈	Ca₃P₂O₈	Ca₃P₂O₈
CaSO₄	CaSO₄	CaO	Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉	Ca₄P₂O₉
CaO	CaO	CaSO₄	-	-	-	CaSO₄	CaSO₄	-
-	-	-	-	-	-	Na₂SO₄	Na₂SO₄	-

Table 4 and FactSage simulation were used to predict the nitrates, chlorides, and phosphate compounds formation, which are formed during the combustion of biomass. Vassilev (2013) also reported the formation of compounds nitrates, chlorides, phosphate, macromolecules, and oxalate.

Simulation results literature and simulation results are shown in Tables 5, and 6 confirmed the chemical formation from these elements after the combustion. Both Tables 5 and 6 suggested that P, Ca, and O elements formed solid residue after combustion. Similarly, these elements are the top three elements found from the EDX analysis of all FW ashes.

Alkaline earth metal such as Mg was not listed as one of the ash deposit or slagging compounds in the simulated results. On the other hand, Ca solid compounds are one of the main products based on the simulated data. Ca and Mg fluctuated before and after the water leaching and did not present any trends after the pre-treatment was done on FW samples. Alkaline earth metals include K and Na, Si, Mg, and Ca. The Factsage simulation results do not suggest Mg and Si as the slag liquid compounds. Only elements Ca become slag liquid in the form of CaO and Cas are reported. Due to the simulation and experimental

From Table 6, the product of biomass ash did not produce any slagging compounds. However, there is a formation of Na_2SO_4 from the treated fish sample at 650 and 800°C. Na_2SO_4 or Thenardite is reported in another study (Vassilev et al., 2013). The Na compounds are not in the solid and liquid phase at 950°C.

CaO, $CaSO_4$, $Ca_3P_2O_8$, and $Ca_4P_2O_9$ solid ash is formed in the simulated treated samples in Table 6. The formation of calcium ash compounds from biomass combustion from other studies is CaO or lime (Grimm, 2012; Vassilev et al., 2013), $CaSO_4$ or anhydrite (Grimm, 2012; Vassilev et al., 2013), $Ca_3P_2O_8$ or Ca phosphates (Grimm, 2012; Vassilev et al., 2013) and $Ca_4P_2O_9$ or calcium phosphate (Gusiatin et al., 2020). Thus, the simulated results are related to other studies on the formation of calcium ash compounds after thermal treatment or combustion.

Biomass furnace temperature ranges from 900 to 1100°C depending on the furnace load. The temperature variations in this study (650 to 950°C) were used to compare the formation of the products by stages at an increasing temperature in the boiler furnace. By referring to Table 5, slag liquid is only formed at 800 and 950°C for raw chicken and raw fish samples using the equilibrium module calculation, respectively. At 650°C, no slag liquid is formed for all simulated models.

4. Conclusion

In this study, leaching pre-treatment showed a significant reduction in alkali metal contents of K and Na for both biomass and food waste. The amount of ash and slag of FW was also estimated using FactSage simulation and compared with the combustion experiments to understand the primary chemical reaction of FW during the combustion process. The alkali metal reduction in FW reduced the formation of slagging compounds in the simulated result. Both methods enable furnace operators to estimate the composition, alkali

content, and slag propensity, permitting sufficient time to adjust the furnace operating conditions correspondingly. The leaching treatment method has been proven to remove unwanted elements such as alkali metal from the FW, thus preventing slag and fouling formation.

FW fuel characteristics are comparable with other types of biomasses. The FW calorific value ranges from 17.5 to 19.4 MJ/kg, indicating FW could become good fuel for power generation. Incineration/boiler is recommended for pre-treated FW since it could reduce solid waste volume up to 80%–85% in a short time with minimum requirements. Reducing FW in the landfills will reduce the greenhouse gas (GHG) emissions to the air. Further studies are needed to investigate FW utilization so that this abundant source can be fully utilized and, at the same time, reduce the landfill effect on the environment.

Compliance with ethical standards

Conflict of interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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