Effect of basic washing parameters on the chemical composition of empty fruit bunches during washing pretreatment: A detailed experimental, pilot, and kinetic study

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HIGHLIGHTS

• Effect of washing time, temperature, and S:L ratio were studied in detail.
• Upto 98% Cl, 80% S, 77% K, 67% ash, and 63% N removal was seen after washing.
• High time and temperature values shows much lower fouling and corrosion propensity.
• Leaching of ash, K, Cl, N, and S follows second-order kinetics.
• Washing for 10 min at 50 °C with 1:15 S:L ratio is recommended for EFB.

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Oil palm
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ABSTRACT

The present study aimed to evaluate the effect of basic washing parameters on the chemical composition of empty fruit bunches of oil palm (EFB) and to determine the optimal parameters for large-scale applications of washing pre-treatment. Three basic washing parameters were studied in detail: washing duration, temperature, and solid/liquid (S:L) ratio. The leaching kinetics of ash and troubling elements such as K, Cl, N, and S were also evaluated with respect to washing time. About 82–98% Cl, 64–80% S, 38–77% K, 34–67% ash, and 24–63% N removal was noted after washing EFB, which follows a second-order leaching kinetics on increasing washing duration. Two pilot washing tests were also conducted to evaluate the effectiveness of the pre-treatment on a large scale, which showed similar trends as the laboratory results. The recommended EFB washing conditions for large-scale applications are 10 min washing with a 1:15 S:L ratio at 50 °C.

1. Introduction

Palm oil is currently the most produced and exported vegetable oil in the world. Due to its high demand, palm tree plantations and palm-oil processing is a large industry in tropical countries such as Indonesia, Malaysia, Thailand, Colombia, and Nigeria (Mahlia et al., 2019). As a by-product, palm-oil processing industries also generate about 50 million tonnes of empty fruit bunches (EFB) annually (Abelha et al., 2020). Such high amounts of EFB are a major challenge for palm oil mills due to limited storage, usability, and greenhouse gas emissions (Anyah et al., 2018). One possible solution to the problem is to utilize EFB for centralized or decentralized energy production or for valuable product recovery. However, the chemical composition of EFB often restricts its valorisation in thermochemical processes such as combustion,
pyrolysis, and gasification. EFB is rich in nutrients such as potassium (K), chlorine (Cl), sulphur (S), nitrogen (N), sodium (Na), potassium (P), magnesium (Mg), and calcium (Ca) (Anyaoha et al., 2018; Tan et al., 2018). The higher alkali, Cl, and S content in EFB leads to severe alkali-induced fouling and slagging, fluidised-bed agglomeration, corrosion, and lower ash-fusion temperatures during combustion and gasification (Hupa et al., 2017; Jenkins et al., 1996; Link et al., 2012; Niu et al., 2016). Depending on the growing condition, EFB may contain up to 1.65% N and 1.06% S. Such high amounts are not environmentally favourable for combustion due to elevated NO\(_x\) and SO\(_x\) emissions (Anyaoha et al., 2018; Hupa et al., 2017; Karlström et al., 2017). Si, Ca, Mg, and P are also present in considerable amounts in EFB, mostly adhered to the organic structure of the biomass (Vassilev et al., 2010). Together with alkali metals, these elements form low melting eutectics (\(<700\,^\circ\mathrm{C}\)), which lead to intense slagging and agglomeration (Hupa et al., 2017; Niu et al., 2016). To mitigate the above-mentioned complexities and to maximise the valorisation of EFB, pre-treatment of EFB is crucial.

Due to operational simplicity, high removal of troubling elements (TE), and lower energy losses, washing pre-treatment hold a special place amongst the other pre-treatment methods. The washing pre-treatment results in high removal of soluble TEs, especially K, Na, S, and Cl, hence reducing the fouling, slagging, and corrosion propensity of the feedstock (Garcia-Maraver et al., 2017; Jenkins et al., 1998, 1996; Singhal et al., 2021a). Washing also results in an increment in the ash fusion temperatures of biomass (by 200–500 °C) and a reduction in harmful emissions during combustion due to the removal of Cl, S, and N (Deng et al., 2013; Jenkins et al., 1996). Due to the high removal of K, Na and Cl in washing pre-treatment, better quality and higher yield of bio-oil were observed in pyrolysis by several researchers (Cen et al., 2019; Deng et al., 2013). Also, as a result of high removal of TEs after washing, washed biomass results in higher CO\(_2\) and H\(_2\) content in gasification with fewer deposition-related issues (Link et al., 2012). Furthermore, the removal of ash cations (K\(^+\), Ca\(^{2+}\), Mn\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\) and Zn\(^{2+}\)) is beneficial for increasing the efficiency of the enzymatic hydrolysis process (Bin and Hongzhang, 2010). So, as water-washing results in higher removal of ash and TEs, it can be useful for improving the overall efficiency of second-generation biorefineries producing bioethanol (Cheng et al., 2020). Studies published on the washing of different biomasses, such as straw (Deng et al., 2013; Singhal et al., 2021b), wood (Liaw and Wu, 2013; Werkelin et al., 2010), grass (Gudka et al., 2016), and husk (Bandara et al., 2020), show the high removal of ash (5–75%), Cl (40–90%), Na (15–90%), Na (30–100%), and Ca (0–25%) on washing. Such studies on the washing of EFB are very limited in the available body of knowledge. A few researchers have tried to improve the effectiveness of the washing pre-treatment by modifying different washing parameters. Lam et al. (2014) studied the effect of time and temperature variation on EFB washing. They found up to 36% removal of ash, which follows second-order kinetics and shows the best removal at 120 min. Tan et al. (2018) focused on the removal of K by varying the washing time (30–120 min), solid-to-liquid ratio (S:L) (1:10–1:20), and temperature (28–60 °C). They found 73–89% K removal, which improved on increasing all three basic washing parameters. Chin et al. (2015) found 45–73% reduction in the Ca, Mg, and P content in EFB on washing.

The above-mentioned studies have shown that washing is beneficial, and its effectiveness is directly influenced by the four basic parameters, i.e. washing duration, biomass size, washing temperature, and S:L ratio. However, in almost all these washing studies, the effects of basic washing parameters were studied for only 2–3 data points, which is insufficient to draw any conclusion or trend. An in-depth analysis of the effects of the basic washing parameters is crucial for understanding the washing process and for further modification, which is yet to be done. Also, for improving the EFB composition, the main focus of the past washing studies was limited to ash and K removal. The removal of other TEs, such as Cl, S, and N, were not studied, while Na, Mg, P, and Fe were not studied in-depth during the washing pre-treatment. Lam et al. (2014) have studied the leaching kinetics of the ash content of EFB. However, the leaching kinetics of TEs in the washing pre-treatment have not been studied before, neither for EFB nor for any other agricultural residues. For large-scale washing operations, short washing durations are highly favourable, as they require smaller reactor sizes, provide adequate productivity, and lower mass and energy losses (Singhal et al., 2021a). However, only a few studies have examined the effect of washing using short washing durations (Bandara et al., 2020; Lam et al., 2014; Singhal et al., 2021b), of which, studies on EFB are even more scarce. The effect of washing temperature and S:L ratio is also yet to be determined for short washing durations, especially for EFB. Although several studies showed that washing is highly effective for improving biomass fuel quality, these studies were mainly based on laboratory-scale testing. Large-scale pilot testing of the washing pre-treatment is still yet to be accomplished, which is crucial for upsaling the washing process.

The aim of the present study was to examine in detail the effect of water-washing pre-treatments on the fuel properties and elemental composition of EFB. To study the effect of washing duration on EFB fuel composition, the washing time was varied from 2 min to 180 min. In addition, the leaching kinetics of K, Cl, N, S, and ash were determined with respect to washing time. As short washing durations are more favourable for practical applications, the impact of S:L ratio and water temperature on the chemical composition were studied in detail for short washing durations. To evaluate the effectiveness of the washing pre-treatment on a large scale, pilot tests were also performed. A total of 20 laboratory experiments and two pilot-scale washing tests were conducted. The washed EFB samples were analysed for proximate and elemental composition, heating values, and energy loss, as well as corrosion, slagging, and fouling behaviour. Based on the results, recommendations for large-scale washing applications are provided at the end of the article.

2. Materials and methods

2.1. Sample preparation and laboratory experiments

The EFB used in the present study originated from Kapar, Malaysia, and were transported to Tampere, Finland. As-received EFB contain about 51% moisture. For all the laboratory washing experiments, EFB samples were first reduced to a size of 3–5 cm and then dried overnight at 104 ± 2 °C. Before using it for washing experiments, the oven-dried sample was left in an open atmosphere (at 22 °C) for 24 h. For all the washing duration and temperature variation experiments, 7 g of the sample was used with 105 ml of water (maintaining S:L ratio of 1:15). For the S:L ratio variation experiments, the amount of water used is mentioned in Table 1. All the washing experiments were done in a temperature-controlled incubator with 100 rpm mixing (image of the

<table>
<thead>
<tr>
<th>Parameter altered</th>
<th>Washing parameters used for the experimentation</th>
<th>Reading points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing duration</td>
<td>1:15</td>
<td>2 min, 5 min, 10 min, 15 min, 30 min, 180 min</td>
</tr>
<tr>
<td>Washing temperature</td>
<td>20 °C</td>
<td>20 °C, 40 °C, 50 °C, 60 °C, 80 °C</td>
</tr>
<tr>
<td>S:L ratio</td>
<td>1:15, 1:20, 1:50</td>
<td>1:15, 1:20, 1:50</td>
</tr>
<tr>
<td>Temperature – Pilot testing</td>
<td>25 °C, 45 °C</td>
<td>1:20</td>
</tr>
</tbody>
</table>

Table 1 Experimental test matrix for washing experiments performed in the present study.
equipment included in supplementary material). A small plastic breaker (150 ml) was used as a washing vessel where biomass and water were mixed. For high-temperature washing experiments, water used in washing was preheated to the required temperature. During washing, temperature was maintained by adjusting the temperature inside the incubator for the required experiment. After washing for the dedicated washing duration, wet biomass was separated from the leachate and dried overnight at 104 ± 2 °C. The wet EFB sample contained about 67–71% moisture. After drying, the washed samples were left in open environment to absorb moisture for 24 h (Deng et al., 2013; Singhal et al., 2021b). After that, the samples were marked and stored tightly for further analysis. The leachate resulting from each washing experiment was collected separately and used for evaluating electrical conductivity (EC).

Parallel to the washing experiments, an error analysis was also done to test the reliability of the process. As fluctuations in smaller washing durations were higher than the longer duration (Singhal et al., 2021b), each 5-min and 10-min washing experiment were repeated thrice. Average values were used in the present study where standard deviation on the graphs were the maximum possible error values, which were shown in the supplementary material. Maximum error observed in the removal of different elements were <2.6% for ash removal, <0.63% for Cl removal, <1.98% for N removal, <1.61% for K removal, <1.74% for S removal, <1.01% for P removal, <2.05% for Mg removal, <2.14% for Ca removal and <0.01 for Alkali index value. As the difference between the removal efficiencies of the respective elements at different washing durations, temperature, and S:L ratio (shown in Fig. 1) were much higher than the error value, all the results are shown in Fig. 1 and Table 3-4 are significant.

Fig. 1. Effect of different washing parameters on the removal of troubling elements and alkali index (a) effect of time; (b) and (c) effect of washing temperature; (e) and (f) alkali index.

A. Singhal et al.
2.2. Pilot testing

The pilot-testing experiments were performed at the Valmet R&D centre in Tampere, Finland. Two washing tests were conducted where EFB were washed for 10 min at 25 °C and 45 °C (Table 1). A rotary drum reactor was used for washing 12 kg of EFB in each experiment with a rotation of 30 rpm (diameter: 1.5 m; width: 0.34 m; figures included in supplementary material). During washing approximately one-third of the reactor was filled with the mixture of water and biomass. After washing, leachate was separated from the feedstock by opening the drainage valve in the reactor situated on the periphery. Washed EFB left in the reactor was collected for further analysis. From each washing experiment, five wet biomass samples were taken from different depths and mixed. The collected samples were sent for drying and further analysis.

2.3. Analytical methods and data analysis

All the untreated and washed EFB samples were analysed for composition (proximate, ultimate, and elemental), heating value, mass and energy loss, and slagging and fouling propensity. The analytical methods and formula used in the present study are included in Table 2. The ultimate composition of EFB samples was determined on a dry basis by using an Elemental Analyser (Table 2). The S content of the EFB samples was too low to be detected by the elemental analyser, so the removal of S was calculated using the S content of the ash. For proximate, ultimate, and HHV analysis, all the samples were analysed in triplicate. HHVs were calculated using the proximate and ultimate composition data by using the relation provided by Channiwala and Parikh (2002):

$$\text{HHV (MJ/kg)} = 0.3491C + 1.1783H + 0.1005S - 0.0151N - 0.0211A$$

(1)

where C, O, H, N, S, and A are the carbon, oxygen, hydrogen, nitrogen, sulphur, and ash content in the biomass, respectively (wt.% on dry basis).

The mass and energy yield of all washing cases were calculated by using:

$$\text{Mass yield} = \left( \frac{m_o}{m_w} \right) \times 100\%$$

(2)

$$\text{Energy yield} = \left( \frac{\text{HHV}_{mf} \times m_o}{\text{HHV}_{ar,mf}} \right) \times 100\%$$

(3)

where $m_w$ and $m_o$ are the sample’s weight before and after washing, and $\text{HHV}_{ar,mf}$ and $\text{HHV}_{ar,mf}$ are the HHV of the original and washed samples (moisture-free basis).

The relation provided by Deng et al. (2013) was used for calculating the removal efficiency of various elements:

$$R_x = \left( 1 - \frac{m_w}{m_o} \times R_o \right) \times 100\%$$

(4)

where R is the removal efficiency, x is the removed element, and $R_o$
and \( r_w \) are the mass fractions of the respective elements in the original and washed samples, respectively.

After drying, the pilot washed EFB samples were analysed for proximate and elemental composition using the methods mentioned in Table 2. To determine the inorganic content, samples were digested with \( \text{HNO}_3 \) and \( \text{HF} \) in a controlled microwave oven and analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Table 2).

2.4. Fouling and slagging predictions

To predict the fouling and slagging propensity of the washed and unwashed fuel, two empirical relations were used in the present study, i.e., Alkali index (AI) and Cl.

Alkali index (AI) = \( \frac{F_{\text{ash}} (\text{K}_2\text{O} + \text{Na}_2\text{O})}{\text{HHV}} \)  

Here \( F_{\text{ash}} \) is the mass fraction of the ash in the feedstock (on a dry basis), \( \text{HHV} \) is expressed in GJ/kg, and \( \text{K}_2\text{O} \) and \( \text{Na}_2\text{O} \) are the mass fractions of \( \text{K}_2\text{O} \) and \( \text{Na}_2\text{O} \) in the ash. AI < 0.17 means probable fouling, while AI > 0.34 means fouling is certain to occur (Gudka et al., 2016).

For Cl (wt.%) in the biomass, there is an extremely high slagging risk if > 0.5; a high slagging risk if 0.3–0.5; a medium slagging risk if 0.2–0.3; and a low slagging inclination if < 0.2 (Garcia-Maraver et al., 2017).

2.5. Leaching kinetics

The leaching kinetics of K, Cl, S, N, and ash were examined in the present study with respect to washing time. Using experimental results, first- and second-order kinetics models were tested using data-fitting method to understand the leaching phenomenon and to determine the leaching rate of different troubling elements from the biomass. The leaching process was assumed to proceed as:

\[
\text{Untreated EFB}_{(s)} + \text{distilled water}_{(l)} \rightarrow \text{Leached compounds (water-soluble organic and inorganic compounds)}_{(aq)} + \text{treated EFB}_{(s)}
\]  

(6)

It was assumed that the leaching of organic and inorganic species was irreversible (Ho et al., 2005; Lam et al., 2014). The differential equations used for first- and second-order kinetics to study the leaching of different elements are as follows:

\[
\frac{dC_t}{dt} = k(C_{\text{sat}} - C_t) \quad \text{[First-order model]} 
\]  

(7)

\[
\frac{dC_t}{dt} = k(C_{\text{sat}} - C_t)^2 \quad \text{[Second-order model]} 
\]  

(8)

where \( k \) is the leaching rate constant, \( C_{\text{sat}} \) is the saturated concentration (g/L) of the respective element in the leachate, and \( C_t \) is the concentration of the respective element in the leachate at time \( t \) (in min). After applying boundary conditions from \( C_t \) (at \( t = 0 \) min) to \( C_t = C_t \) (at \( t = t \) min), the integration of the differential equations gives:

\[
C_t = C_{\text{sat}} \left(1 - \text{e}^{-kt} \right) \quad \text{[First-order model]} 
\]  

(9)

\[
C_t = \frac{ktC_{\text{sat}}^2}{1 + ktC_{\text{sat}}} \quad \text{[Second-order model]} 
\]  

(10)

3. Results and discussion

Before and after the washing pre-treatment, the fuel composition of EFB was analysed thoroughly, as detailed in Tables 3 and 4, and illustrated in Figs. 1 and 2. As per the results, it was observed that washing greatly affects the proximate and elemental composition of EFB. In general, the washing pre-treatment results in high removal of Cl (<98%), K (<77%), S (<81%), N (<64%), Fe (<62%), and Mg (<40%). Consequently, reduced fouling, slagging, and corrosion can be expected from the fuel after pre-treatment. High ash removal (<67%) and

<table>
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<tr>
<th>Washed for</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>Cl</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>SO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>Al</th>
<th>Cl</th>
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<td>Raw</td>
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<td>15.11</td>
<td>9.77</td>
<td>3.27</td>
<td>4.04</td>
<td>1.74</td>
<td>9.30</td>
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<td>0.20</td>
<td>0.02</td>
<td>0.77</td>
<td>0.79</td>
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<td>27.30</td>
<td>4.19</td>
<td>12.35</td>
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<td>2.19</td>
<td>2.69</td>
<td>5.72</td>
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<td>0.02</td>
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<td>2.47</td>
<td>10.73</td>
<td>5.64</td>
<td>1.98</td>
<td>3.52</td>
<td>6.53</td>
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<td>0.00</td>
<td>0.03</td>
<td>0.40</td>
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</tr>
<tr>
<td>10 min</td>
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<td>22.13</td>
<td>1.47</td>
<td>10.82</td>
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<td>1.77</td>
<td>3.15</td>
<td>7.94</td>
<td>1.63</td>
<td>0.00</td>
<td>0.03</td>
<td>0.36</td>
<td>0.05</td>
</tr>
<tr>
<td>15 min</td>
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<td>20.68</td>
<td>0.95</td>
<td>13.24</td>
<td>7.17</td>
<td>1.80</td>
<td>3.51</td>
<td>8.60</td>
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<td>0.00</td>
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</tr>
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<td>0.94</td>
<td>13.24</td>
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<td>1.74</td>
<td>3.53</td>
<td>9.00</td>
<td>1.60</td>
<td>0.00</td>
<td>0.03</td>
<td>0.28</td>
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<td>6.59</td>
<td>1.76</td>
<td>4.15</td>
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<td>1.60</td>
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<td>0.03</td>
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<td>3.15</td>
<td>7.94</td>
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<td>0.03</td>
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<td>2.03</td>
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<tr>
<td>10 min 60°C</td>
<td>42.86</td>
<td>19.81</td>
<td>1.43</td>
<td>16.14</td>
<td>7.57</td>
<td>1.69</td>
<td>3.90</td>
<td>9.29</td>
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<td>0.27</td>
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<td>10 min 80°C</td>
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<td>19.20</td>
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<td>1.65</td>
<td>4.53</td>
<td>9.60</td>
<td>1.68</td>
<td>0.00</td>
<td>0.03</td>
<td>0.24</td>
<td>0.03</td>
</tr>
<tr>
<td>10 min – 1:15</td>
<td>34.98</td>
<td>22.13</td>
<td>1.47</td>
<td>10.82</td>
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<td>1.77</td>
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<td>7.94</td>
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<td>13.22</td>
<td>7.00</td>
<td>1.96</td>
<td>4.39</td>
<td>6.33</td>
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<tr>
<td>10 min – 1:30</td>
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<td>1.57</td>
<td>0.00</td>
<td>0.03</td>
<td>0.32</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4

Effect of washing on the EFB ash composition (wt.%) (colour code: Red – high fouling and slagging; Blue – Medium; Green – Low).
increment in volatile (\(\leq 3\) wt%), C (\(\leq 2\) wt%), H (\(\leq 0.3\) wt%), and HHV (\(\leq 0.9\) MJ/kg) were also noted after washing. Due to the leaching of some soluble organic and inorganic compounds, a slight mass loss (\(\leq 7.2\)%) and energy loss (\(\leq 4.9\)%) was also noted after washing.

3.1. Effect of washing time on biomass composition

Washing duration had a very high impact on the fuel composition, which can be clearly seen in Fig. 1. Continuous improvement in the proximate, ultimate, and elemental composition of EFB was noted on increasing the washing duration. This change was high and quick for the short washing durations (<15 min). On increasing the washing time, continuous increments in volatile content and ash removal were noted, although this change was greatly reduced after 30 min (Figs. 1 and 2). In just 2 min, 34% ash removal was noted, which further increased to 53% upon washing for 180 min. This high removal of ash was a result of the intensive leaching of some soluble inorganic compounds and the removal of extraneous material such as dust, dirt, rust, etc. The ash removal found in the present study is higher (4–16% more) than most of the past washing studies (Abdullah and Sulaiman, 2013; Lam et al., 2014; Rahman et al., 2015). This could be the result of the higher amount of leachable inorganic and extraneous species present in the EFB used for the present case.

As a result of the continuous removal of ash, steady increments in C (\(\leq 1.8\) wt%), H (\(\leq 0.2\) wt%), and HHV (<0.8 MJ/kg) were seen. This increment was rapid up to 10 min, and it was negligible after 15 min (Please see supplementary material). For O content, a sudden increment (1.75 wt%) was noted when the EFB was washed for 2 min. After that, it continuously decreased on raising the washing duration, though it remained higher than the O content in the raw EFB. Increments in C, H,
HHV, and O content were also noted in past washing studies (Gong et al., 2019; Rahman et al., 2015), but these studies did not illustrate this increment in detail nor did they explore the dependency of these parameters on washing time. A certain mass loss was noted after washing, which is even higher than the ash removed. This means some water-soluble organic compounds were also leached from the EFB during washing. Leaching of some water-soluble organic compounds, such as sugars, organic acids, and waxes, was noted in past studies after washing feedstocks such as straw, wood, husk, bark, leaves, and fibrous feedstocks (Long et al., 2020; Vassilev et al., 2014; Yu et al., 2014). As C, H, and HHV values also increased on raising the washing duration, the energy yield still remains higher even after washing (>95%). As no mass and energy yield values were reported in the past EFB washing studies, the energy and mass loss reported in the present study cannot be compared. However, compared to other washing studies conducted on other feedstocks (3.2–17.12%; Deng et al., 2013; Ma et al., 2018, 2017; Singhal et al., 2021a, 2021b) and pre-treatment methods (torrefaction, SE, HTC, acid washing: 16–60%; Chen et al., 2013; Chen et al., 2017; Ma et al., 2018; Madanayake et al., 2017), energy losses in the present case are much lower (<4.9%).

On increasing the washing duration, a continuous reduction in N and S content was observed. The removal up to 10 min (37% N and 74% S) was very high, but it stagnated after 30 min (55% N and 77% S removal). A considerable amount of N and S exists in biomass as mobile water-soluble ions, such as NO₃⁻ and SO₄²⁻ (Vassilev et al., 2012, 2010). These mobile species are leachable in higher amounts on washing, which is the reason behind such a high removal of N and S during washing. Not many washing studies report removals of N and S, especially from EFB. However, on evaluating the ultimate analysis results of the washing studies conducted on other feedstocks (Deng et al., 2013; Ma et al., 2017; Rahman et al., 2015; Singhal et al., 2021a), N and S removal found were comparable to the present study (0–46% N and 30–70% S removal). As washing results in high removal of N and S, washed EFB would be favourable for combustion applications, as washed EFB results in lower NOₓ and SOₓ emissions.

Similar to N, S, and ash, a continuous removal of K and Cl was also seen on increasing the washing duration. Among all the elements, the highest removal was achieved for Cl, i.e. 97%. In just 5 min of washing, up to 90% Cl and 50% K was removed, which increased up to 97% and 65%, respectively on increasing washing duration. Most of the K (40–90%) and Cl (25–100%) present in the biomass exists as mobile K⁺ and Cl⁻ ions, which are highly water soluble (Vassilev et al., 2010; Zevenhoven et al., 2012). Due to their high leachability, such high removal of K and Cl was noted after washing EFB. Almost all the Na was removed after washing for 2 min. As K, Na, and Cl are the main elements behind fouling, corrosion, and slagging, much less of these issues can be expected from washed EFB. Compared to past EFB washing studies (Chin et al., 2015; Tan et al., 2018), the K removal achieved in the present study was 11–15% less. This may be due to the higher S:L ratio (>1:20) used in past studies for washing with either a higher stirring intensity (340–520 rpm) or mechanical dewatering (at 2800 rpm) after washing, which directly influences the removal of inorganic species. The removal of Cl was not mentioned in any EFB washing studies, though a high removal of Cl (20–95%) was noted in studies published in the washing of different types of straws (wheat straw (Deng et al., 2013; Singhal et al., 2021a), rice straw (Deng et al., 2013; Jenkins et al., 1996), and wood (Deng et al., 2013; Liaw and Wu, 2013; Zevenhoven et al., 2012)). Among the other elements, the removal of Mg (<40%) and Fe (<59%) was also noted, which further increased for Mg on increasing the washing duration (included in supplementary material). In general, Fe is present in biomass in very small amounts, and it is incorporated into the biomass structure, which does not leach in water, especially in such high quantities (Vassilev et al., 2012; Zevenhoven et al., 2012). However, about 50–60% removal of Fe was noted after washing, which remains almost consistent regardless of washing duration. Most probably Fe was present in the raw biomass as an external impurity that may adhere to wet EFB during transportation and/or storage and be removed during washing.

As per the alkali index (AI) and Cl, high levels of fouling, slagging, and corrosion can be expected from the untreated EFB. However, after washing for just 2 min, a large improvement was noted for Cl, while after 10 min the AI showed the likelihood of moderate fouling. The improvement in the indexes is the result of the high removal of inorganic elements such as K and Na. Although a three-fold improvement was seen in AI after washing for 3 h (Fig. 1), moderate fouling can still be expected from the washed EFB as per the AI. However, while examining AI, one important fact should be considered that it was originally developed for coal (Niu et al., 2016). The cut-off values of the AI may not be directly applicable for lignocellulosic feedstocks due to disparities in the fuel composition (Niu et al., 2016; Vassilev et al., 2015, 2010). As the AI does not consider the effect of elements such as Cl, S, and Ca content, it often leads to overestimations for biomasses (Zevenhoven et al., 2012). Therefore, instead of emphasising cut-off values, more priority should be given to the trends in the indexes. S and Cl are the main facilitators for the volitation of K, Na, Ca, and Mg during combustion (Itupa et al., 2017). So, due to the high removal of Cl (<97%) and S (<80%) together with Na (<100%) and K (<65%), much less fouling, slagging, and corrosion should be expected for the washed EFB.

3.2. Leaching kinetics of troubling elements

As per the kinetics study results, K, Cl, S, N, and ash all followed the second-order leaching kinetics. The r², Csat, and k values for each of the elements are shown in Fig. 2. The second-order kinetic model (r² between 0.960 and 0.999) was a better fit to the experimental data than the first-order kinetics for all the parameters. Similar to the trend seen in the previous section, the concentration of the elements and the soluble ash compounds in the leachate continuously increased with the washing time. The rate of leaching for all the elements was very high for short washing durations (<15 min), especially for K, S, and Cl. After 30 min of washing, an almost negligible rise in the concentration was noted for all the elements. Lam et al. (2014) also found a similar trend in the leaching of soluble ash content in EFB, where the ash also follows the second-order kinetic model. No such study was found that includes the leaching kinetics of TEs for EFB on washing. However, for mallee wood, Liaw and Wu (2013) have shown that K and Cl follow second-order leaching kinetics. For inorganic elements, the second-order leaching model confirms that there are two phases in the overall leaching process. In the first phase, maximum leaching takes place over a very small duration (<10–15 min), which is a result of the intense dissolution and scrubbing of inorganic species and extraneous materials (Ho et al., 2005). In the second phase, the leaching is much less and occurs very slowly, which can be explained by two approaches. First, this could be a result of the diffusion of residual inorganic species in the EFB, which is affected by the concentration of the inorganic species in the leachate (Ho et al., 2005). Second, this slower leaching could be facilitated by water-soluble organics, which also leach during washing. Part of the inorganic elements, such as K, Na, S, N, Mg, Ca, P, etc., are bounded to the organic matrix which does not leach into the water (Vassilev and Vassileva, 2019; Zevenhoven et al., 2012). However, leached organic compounds (organic acids and sugar) facilitate the removal of such weakly-bound and acid-soluble inorganic species, which is very slow but persistent (Liaw and Wu, 2013), as can also be seen in the previous section (Figs. 1 and 2). Both phenomena most likely happen in parallel in the second phase of the leaching. Another finding that can be deduced from the Csat is that K and Cl were leached in the highest amount. Nevertheless, the overall rate of leaching is much faster for S and Cl compared to other elements.

3.3. Effect of washing temperature and S:L ratio

Among all the basic washing parameters, washing temperature showed the highest impact on the fuel composition, while the S:L ratio...
showed the least (Fig. 1). On increasing the washing temperature and S:L ratio, an increment in ash removal and volatiles content was observed, which can be seen in Fig. 1 and Table 1. As the trends found in 5- and 10-min washing cases were similar, only the results for 10 min washing are reported in the manuscript. The results of 5 min washing with a higher temperature and S:L ratio are shown in the supplementary material. The highest ash removal was noted at 80 °C (51.4%), though it was only marginally higher than the removal seen at 50 °C (49.2%). About 5% more removal in ash content was noted on raising the S:L ratio from 1:15 to 1:20, which then reduced slightly on further increasing the ratio to 1:50. A reduction in ash content was also observed in Lam et al., 2014 (<37%) and Rahman et al., 2015 (<33%) on increasing the washing temperature, though the removal in these studies was lower compared to the present case (<51.4%). The high removal of ash could be the result of the higher diffusion and solubility of inorganic species due to increased water temperature and reduced competition between ions for leaching. Due to this high ash removal, a continuous increment in C and H was noted on increasing the washing temperature (for both 5 and 10 min) and S:L ratio. Consequently, the HHV of washed EFB also increased slightly (<0.6 MJ/kg). Due to the increased HHV and consistent organics loss, energy yields were as high as 99.99% and 99.38% at 80 °C and a 1:50 S:L ratio were seen, respectively (Table 3).

In general, the highest removal of troubling elements and ash was noted at higher temperatures (60–80 °C), while not much improvement in inorganic composition was noted even after raising the S:L to 1:50. Higher removal of S and N was seen on increasing the water temperature, though trends were not continuous for N. Up to 74–80% S and 54–57% N was removed in just 10 min at high temperatures (50–80 °C), which is even more than for washing 180 min. Consequently, washing at greater temperatures is more beneficial for higher N and S removal. About 12% extra removal of N was seen on increasing the S:L from 1:15 to 1:20; after that it remains unchanged. N and S removal were not reported in any past EFB washing studies. However, in some other biomass washing studies (using herbaceous and woody biomass), higher removal was noted for N (0–47%) and S (30–100%) at higher temperatures (>60 °C) (Deng et al., 2013; Singhal et al., 2021a).

Continuous and substantial removal of K was noted on increasing the washing temperature (Fig. 1). Up to 68% of K removal was seen at 80 °C after washing for just 10 min. It was 13% higher compared to room temperature washing and even 3% more than the EFB sample washed for 180 min. About 3.5% extra removal of K was noted on increasing the S:L ratio. An increment in K removal was also seen in Lam et al. (2014) and Tan et al. (2018) on increasing the washing temperature. While similar to the present study, no significant increment in the removal of K was seen in Tan et al. (2018) on raising the S:L ratio beyond 1:20. Higher K removal could be the result of the enhanced diffusion and solubility of K compounds (KCl, KNO3, K2SO4, K3PO4, etc.) on increasing the washing temperature. Cl removal was already very high at room temperature (94%), and <3% increment in Cl removal was noted after increasing the temperature and S:L ratio up to 80 °C and 1:50 respectively. The highest Cl removal in the present study was noted for the sample washed for 10 min at 50 °C (98%).

Due to the high ash and alkali metal removal, a continuous reduction in AI was seen after washing. At higher washing temperatures (>40 °C) and S:L ratios (>1:20), the AI values were lower than 0.34, which means low to medium fouling can be expected from washed EFB. Cl was already very low, which even further improved at higher washing temperatures. So, as per the indexes and the higher removal of inorganic compounds, much lower fouling, slagging, harmful emissions, agglomeration, and corrosion can be expected from the EFB washed at a high temperature and S:L ratio with short washing durations. As per the results, it was confirmed that washing at higher temperatures is more effective than washing for much longer durations. Thus, for practical and industrial applications, washing at higher temperatures (50–80 °C) with a short washing time (<15 min) should be preferred. Also, a smaller S:L ratio (1:10–15) should be preferred for practical applications, as a higher S:L ratio will result in more wastewater.

3.4. Pilot testing of EFB washing

After the experimental studies, two washing experiments were replicated on a larger scale for upsampling the washing approach. The results of the pilot testing and their comparison are shown in Fig. 3 and supplementary material. The trends that were earlier noted in the lab experiments were also seen in the pilot testing. Similar to the experimental results, a reduction in ash content and an increment in C, H, O, and HHV values were also noted after the pilot testing. These values were comparable to the findings of the experimental studies. Similar to lab-scale washing, a high removal of K, Cl, N, S, and ash were also found in the pilot-scale washed EFB, which further increased on raising the washing temperature. So, one can conclude from both the pilot scale and laboratory results that washing is an effective pre-treatment approach, and it can be replicated on a larger scale. On comparing the laboratory and pilot washing results, an interesting trend was discovered. The removal of K, N, Mg, and ash was significantly higher in the pilot washed EFB compared to the lab-scale washing. Furthermore, a high removal of Ca (27–32%) and P (72–73%) was also noted in the pilot testing, which was not seen in lab-scale washing. There could be two explanations behind higher removal of K, Mg, Ca, and P in pilot testing results. First, the S:L ratio used in the pilot testing was 1:20, while in the lab-scale washing experiments, the S:L ratio was 1:15. As shown in the previous section, on increasing the S:L from 1:15 to 1:20, extra removal of K, N, and ash was noted. The second possible explanation could be the breaking of the biomass structure due to intense mixing. Although the rpm used in pilot testing was low (30 rpm), but the wet biomass tumbled over and over from the height of 1–1.2 m in the water continuously for 10 min. This constant impact may possibly partially break the EFB surface and internal structure from several places, which improves the percolation and mixing of the fluid inside the biomass. Most of Ca (<60%) and part of P (<20%), Mg (<50%) and K (10–20%) is loosely to moderately adheres to the organic matrix (Hawkesford et al., 2012) which does not leach in high amounts on simply washing or soaking (Deng et al., 2013; Singhal et al., 2021b; Zevenhoven et al., 2012). However, due to breaking of structure and better water percolation, these elements adhered to the organic matrix now leached into the biomass which were negligible in the laboratory experiment. As a result, much higher removal of K, Ca, Mg and P was noted in pilot testing compared to lab-scale washing results. Consequently, much lower ash content was also noted in pilot-scale washed EFB.

3.5. Recommendation for industrial applications and further scope

As per the results, it can be clearly noted that washing is a highly effective pre-treatment method for improving biomass composition. As per the pilot testing results, washing can be effectively replicated for larger industrial applications with high pre-treatment efficiency. Washing time and temperature had a very high effect on the fuel properties and elemental composition, which can be used to improve washing efficiency for large-scale operations. Longer washing durations show a higher pre-treatment efficiency, but for industrial applications, a short time (<15–20 min) is more favourable (Singhal et al., 2021a). As 15 min of washing results in the high removal of troubling elements
(97% Cl, 62% K, 48% S, 48% ash, 47% N, and 30% Mg removal) and shows a comparable efficiency to washing for 180 min, it can be used for practical applications. To further improve the removal efficiency of troubling elements, the washing temperature can be further increased for short washing durations. The best pretreatment results were noted on washing EFB for 10 min at 80 °C, which was even better than washing for an extra 170 min at 20 °C (Fig. 1). However, the hot water required even more energy to increase the temperature, which may lead to extra costs. For that reason, 50 °C should be used for washing, as it shows a similar efficiency as 80 °C with 99.5% of the energy yields and a lower fouling, corrosion, and slagging propensity. Even though increasing the S:L ratio results in a higher washing efficiency, the improvement seen was only marginal (<5% except for N removal). Higher water quantities result in more wastewater, which is expensive to treat for larger operations and easily leads to higher capital and operational costs. Furthermore, the higher water requirement will increase the environmental and water footprint of the system, which is not sustainable for water-limited regions. Thus, a 1:15 S:L ratio is sufficient for large-scale applications, while 1:20 can be used for smaller applications due to better efficiency. Consequently, for the best washing pre-treatment efficiency for EFB, 10 min washing at 80 °C with a 1:15 S:L ratio is recommended, for better energy efficiency, EFB can be washed at 50 °C as well.

Even though the washing pre-treatment is a simple method to enhance biomass fuel quality, issues such as wastewater and the higher moisture content of the washed biomass still require further attention. Jenkins et al. (1996) and Deng et al. (2013) suggest that washing leachate can be used for irrigation. However, Vassilev and Vassileva (2019) and Long et al. (2020) found alarming amounts of toxic heavy metals and organic compounds in the washing leachate of some biomasses. For that reason, a detailed wastewater characterisation study on washing leachate is crucial, which is yet to be determined. Another issue is the high moisture content of the washed biomass (40–70%), which is problematic for direct combustion applications. Though by using mechanical pressing (Cui et al., 2015) and hot-stock gases (Singhal et al., 2021a) the moisture content can be reduced, further work is still required in this area.

4. Conclusion

The effect of basic washing parameters (washing duration, S:L ratio, and water temperature) was determined in-depth on the fuel composition of EFB. On increasing all three washing parameters, continuous removal of troubling elements and improvement in fuel quality was noted. Up to 98% Cl, 80% S, 77% K, 67% ash, 63% N, and 40% Mg removal was noted after washing EFB. The leaching of K, Cl, N, S, and ash follows second-order kinetics on increasing washing duration. The results of the pilot testing validate the high effectiveness of the washing pre-treatment on a larger scale. For practical applications, washing for 10 min with a 1:15 S:L ratio at 50 °C is recommended for EFB.

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Abhishek Singhal: Conceptualization, Methodology, Investigation, Software, Formal analysis, Writing - original draft, Visualization, Data curation, Resources. Maria Goossens: Conceptualization, Methodology, Software, Formal analysis, Visualization, Data curation, Writing - review & editing. Jukka Konttinen: Methodology, Project administration, Resources, Supervision, Validation, Writing - review & editing. Tero Joronen: Methodology, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing - review & editing.

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.
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Appendix A. Supplementary data

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