



Full Length Article

Effect of different washing parameters on the fuel properties and elemental composition of wheat straw in water-washing pre-treatment. Part 1: Effect of washing duration and biomass size

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ABSTRACT

Washing pre-treatment significantly improves the fuel properties and composition of agricultural residues, though still requires further development before being applied on the industrial scale. So, to improve the efficiency of the washing pre-treatment, four basic parameters were modified in the present study, and presented in two separate and consecutive articles as Part 1: washing duration and biomass size; and Part 2: washing temperature and solid-to-liquid (S:L) ratio. In Part 1, to evaluate the effect of washing duration and sample size, three different sample sizes of wheat straw were used – 3 cm, 1 cm, and 0.05–0.08 cm, and each size was washed for 0 min, 2 min, 5 min, 10 min, 30 min, 60 min, and 180 min. The biomass composition, heating values, energy loss, and fouling and slagging propensity were evaluated for both treated and untreated samples. As a function of increasing the washing time and reducing the sample size, continuous improvements in fuel properties and fouling and slagging propensity were observed. Washing for longer durations shows best improvement in fuel properties, with a much lower fouling and slagging tendency due to the high removal of potassium (up to 68%), chlorine (up to 87%), sulphur (up to 74%), nitrogen (up to 46%), and ash (up to 39%). For biomass size, smaller sizes resulted in better washing efficiency, while larger sizes showed similar trends in washing. As shorter washing durations and a larger sample size are more favourable for industrial applicability and show considerable improvement, such cases were further modified by varying the temperature and S:L ratio (presented in Part-2).

1. Introduction

Biomass is mankind's oldest energy source, and it holds an important place among various renewable energy sources due to its carbon-neutrality over its life cycle. Among different biomass types, short-term rotation crops such as wheat straw, rice husk, sorghum straw, miscanthus, reed canary grass etc., are generated in very large quantities every year, and such large amounts lead to waste management issues. This often results in open field crop burning, which is a common practice in many parts of the world particularly in different part of south Asia and sub-Saharan Africa [1,2]. This problem can be reduced enormously by redirecting these agricultural residues into various energy and biofuel production activities. The sustainable utilization of agricultural residues is therefore an active area of interest, and many researchers, policymakers, and governments are working in this area. Among the various agricultural residues, there is a high motivation to utilize wheat straw in

different thermochemical processes, as wheat straw is amongst the most generated agricultural residues in the world (6×10^8 tons/annum) [3].

Even though agricultural residues have already been recognized as an alternative to solid fossil fuel, their composition often restricts their utilization in various thermochemical conversion technologies such as combustion, gasification, pyrolysis etc [4,5]. The root cause of the major problems in thermochemical processes is high alkali content of the agricultural residues, which leads to severe alkali-induced slagging, agglomeration, heat-exchanger fouling, and lower ash melting temperatures in boilers [5–8]. Sulphur (S) and chlorine (Cl) present in the biomass accelerate the volatilization of alkali metals and leads to severe corrosion and fouling issues in the boilers [6,7]. Due to the overuse of fertilizers in fields, many agricultural residues contain large amounts of nitrogen (N) and sulphur, which deteriorate the environmental quality due to elevated levels of NO_x and SO_x emissions [4]. In biomass combustion, silicon (Si), calcium (Ca), magnesium (Mg), and phosphorus (P)

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are not likely to cause fouling and agglomeration issues due to high melting points of the compounds they form in the combustion [8,9]. However, together with potassium (K), they form low melting eutectics (500–700 °C), which lead to severe fouling and slagging [6,7]. Several indexes, such as base-to-acid ratio (B/A), fouling index (F_i), slagging index (S_i), alkali index (AI), bed agglomeration index (BAI), S/Cl ratio, and slag viscosity index (S_r) are generally used to predict the fouling and slagging behaviours of different fuels [7,9–12]. As per these indexes, untreated wheat straw generally tends to show very high fouling behaviour upon combustion (B/A 1–1.5) (Table S1). However, it is important to mention that these indexes were originally developed for coal. For agricultural residues, their applicability may be limited due to different inorganic composition of biomass, mode of occurrence of inorganic species, combustion chemistry and exclusion of few problematic elements from the indexes compare to coal [7,13]. Exact values and cut-off values of these indexes may not be directly applicable for the agricultural residues as these values were originally derived for coal [13]. However, trends in some of these indexes may be utilized for evaluating the affectability of pre-treatment processes as they have been used in some of the recent studies [12,14]. As some herbaceous agricultural residues such as straw and grasses has higher Si content, indexes such as B/A, Si, Sr, AI can be used for predicting the fouling and slagging propensity in these fuels initially.

To avoid many technical and environmental complexities in the utilization of wheat straw for energy and biofuel generation, pre-treatment of the feedstock is vital. Some pre-treatment options are available to improve the fuel quality of agricultural residues, such as torrefaction, hydrothermal carbonization, and acid washing [15–18]. However, these processes result in high energy losses (30–65%) and high process complexities, which currently may not be economically and/or technically feasible for industrial applications [15,16,19–21]. Water washing could be a simple and feasible pre-treatment option to improve fuel quality, as it is a low-cost, operationally simple, and environmentally friendly process. Various chemical fractional studies conducted on different herbaceous agricultural residues shows that upto 40–90% K, 25–100% Cl, 15–90% sodium (Na), 15–95% S, and 0–25% Ca is water-soluble [9,22,23]. For wheat straw, based on the existing studies, a significant removal of troubling elements (K (54–93%), Na (13–67%), Cl (71–100%), S (30–100%)), and ash (24–80%) was found on leaching pre-treatment with a low to moderate energy loss of 2–17% [10,12,24–26]. Consequently, the fouling, corrosion, and slagging propensity of woody and herbaceous agricultural residues is significantly reduced with improvement in the combustion performance [4,12,24,25]. In addition, the ash-melting temperatures increase by 300–500 °C after washing, resulting in fewer issues related to ash fusion and alkali-induced slagging in combustion [10,25,27]. Due to lower fouling and slagging issues after washing, the need for additives such as lime, calcite, Kaolin, or Zeolite in combustion [7,28] is also reduced, resulting in operational cost savings. Washing with water also results in the high removal of Cl, S, and N from the biomass, which reduces acidic and harmful emissions during combustion [7,24,29,30]. Reason behind higher leaching of these element was their existence in the biomass as anions (Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , HPO_4^{2-}) and cations (K^+ , Na^+ , NH_4^+ , Ca^{2+} , Mg^{2+}) which readily leached into the water on washing [9,31,32]. Most existing washing studies mainly report the removal of K, Na, Cl, and S, while only a few studies report on the removal of N [12], Si [10], and the improvement in fouling and other indices [7,10–12,33]. Whereas removal of P, Ca, and Mg has not been mentioned in any of the past studies conducted on washing of wheat straw. However, for other biomasses it was found in few selective leaching studies [9,22] that about 5–75% P, 0–25% Ca and 5–60% Mg is water-soluble. Still, to clearly understand the effect of washing, special attention should be paid on the troubling elements (K, Na, Cl, S, N, P, Si, and Ca) that cause fouling, slagging, and emission issues [34].

For washing pre-treatment, most studies uses longer washing durations (3–20 hrs), which result in the high removal of troubling elements

(40–100%). However, longer washing durations result in higher mass (15–16%) and energy losses (2–17%; avg. 10%), which may lead to considerable feedstock and economic losses [10,12,20]. Furthermore, longer washing durations require a larger washing reactor and lead to lower productivity of treated feedstock per day, which directly affects the economic feasibility of the pre-treatment. So, for practical applications, a short washing time seems attractive if the treated feedstock causes fewer fouling, slagging, and emission issues. However, to the best of our knowledge, studies specifically focused on the effects of washing durations or short washing duration have not been reported in the literature. The literature review shows that besides the washing duration, feedstock shape and size also influence the effectiveness of the washing treatment (Table S1). However, the clear impact of feedstock size on the efficiency of the washing pre-treatment is yet to be established. To improve the technical and economic feasibility of the washing pre-treatment especially on the industrial scale, in-depth studies and experimental data sets for the basic washing parameters are required. Both are still missing from the available body of knowledge.

In the present study, the effect of washing pre-treatment was investigated in-depth on biomass fuel properties by varying four washing parameters: washing duration, sample size, washing temperature, and S:L ratio. In Part 1, the effect of washing duration and feedstock size on the washing pre-treatment are presented. As wheat straw is one of the major agricultural residues generated annually in huge amounts worldwide, it was selected for the present study. Batch leaching was chosen, as it results in the better removal of troubling elements and is more suitable for industrial applications than a continuous flow condition [32]. A total of 28 washing experiments were conducted in which three different samples sizes were tested for seven different washing durations to evaluate the improvement in biomass fuel properties and composition. The effect of both the washing parameters on the fuel properties and composition of wheat straw was evaluated in depth, including the fouling and slagging propensity of the fuel. In Part 2, the washing temperature and S:L were varied to improve the industrial applicability of the washing pre-treatment process; this is presented as a separate research article.

2. Materials and methods

2.1. Sample preparation and washing experiments

The wheat straw used in the present study was collected in August 2019 from the rural areas of Lempäälä, Pirkanmaa region, Finland. All washing experiments were done on an as-received basis in which the original sample contained about 4% moisture. For all washing experiments, 6 g of the sample and 90 ml of water was used, maintaining a 1:15 S:L ratio. All the washing experiments were done in temperature-controlled conditions with mixing (100 rpm). Three different wheat straw sizes were tested for the washing experiments: 3 cm, 1 cm, and 0.05–0.08 cm. The 3 cm (± 0.4 cm) and 1 cm (± 0.2 cm) size length were achieved with the help of scissors, while the 0.05–0.08 cm size was achieved using a micron-size shredder and sieves (pictures of different sample sizes and washing experiment included in [supplementary material](#)). Each sample size was washed for 2 min, 5 min, 10 min, 30 min, 60 min, and 180 min to study the effect of washing duration and biomass size. In addition, to study the impact of quick water spraying on wheat straw, one sample from each sample size was tested and labelled “0 min”. For the 0 min washing, 90 ml of water was poured within 3–5 s over the 6-gram sample, and the leachate was simultaneously removed from the bottom via artificially made holes in the base. The washing experiments with the 3 cm sample size were repeated thrice for reliability purposes, and the difference in the results was within an acceptable range of error (shown in [supplementary material](#)). After washing and filtration, all the samples were dried overnight at 103 ± 2 °C and then left to absorb moisture at room temperature for 24 h [10]. After this process, the samples were stored in tightly closed boxes for preservation and used for further analysis.

2.2. Analytical methods and data analysis

All washed samples were analysed for proximate, ultimate, high heating value (HHV), and elemental analysis. For the proximate analysis, moisture content was determined by air drying in an oven at 103 ± 2 °C, while volatile and ash content were determined by ASTM E872 – 82 (2006) and ASTM E1755 – 01 (2007) respectively (Table 1). Fixed carbon content was calculated by subtracting ash, volatile, and moisture from the total content. CHNS content (on dry basis) in the biomass was determined by using a Thermo Scientific™ Flash Smart™ Elemental Analyzer, and O content was calculated by the difference. As the S content in the wheat straw samples was found to be too low to be detected by the CHNS-O analyser, the S content in the ash was used to evaluate the S removal. All the samples were tested in triplicates for proximate analysis, ultimate analysis, and HHV analysis. Elemental composition in the ash was determined by X-ray fluorescence (XRF) using a Thermo Scientific™ Niton XL3t GOLDD + following ASTM D4326. HHV was calculated from the ultimate and proximate composition data by using the relation given by [35]:

$$\text{HHV}(\text{MJ/kg}) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{A} \quad (1)$$

Where C, H, S, O, N and A are carbon, hydrogen, sulphur, oxygen, nitrogen, and ash content in the biomass respectively (determined as mass percent on dry basis).

Mass and energy yield from the individual washing case were calculated by using the formulas:

$$\text{Mass yield} = \left(\frac{m_{\text{wash}}}{m_{\text{org}}} \right) \times 100\% \quad (2)$$

$$\text{Energy yield} = \left(\frac{\text{HHV}'_{\text{ar,mf}} \times m_{\text{wash}}}{\text{HHV}_{\text{ar,mf}} \times m_{\text{org}}} \right) \times 100\% \quad (3)$$

where m_{wash} and m_{org} are the weight of the sample after and before washing, and $\text{HHV}'_{\text{ar,mf}}$ and $\text{HHV}_{\text{ar,mf}}$ are the HHV of the washed and original sample calculated on the as-received and moisture-free basis.

To calculate the removal efficiency of various elements, the relation provided by [10] was used:

$$X_i = \left(1 - \frac{m_{\text{wash}} \times R_{\text{wash}}}{m_{\text{org}} \times R_{\text{org}}} \right) \times 100\%,$$

where X is the removal efficiency, i is representative of the removed element or constituent, and R_{wash} and R_{org} are the mass fraction of the respective elements or constituent in the washed and original sample.

2.3. Base-to-acid ratio and slagging prediction

In the present study, two empirical relations were used to predict deposition, fouling, and slagging related issues in the boilers which are base-to-acid (B/A) ratio [36], and slagging index (S_i) [11]. The formula

for the indexes is:

$$B/A = \frac{\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_5 + \text{P}_2\text{O}_5}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2} \quad (4)$$

for $B/A < 0.5$, very low fouling possibility; for $0.5 \leq B/A \leq 1$, medium fouling expected; and for $B/A > 1$, severe impact and fouling will definitely occur [36].

$$S_i = \frac{\text{SiO}_2}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}} \times 100 \quad (6)$$

For $S_i < 66$, extremely high slagging risk; $66 \leq S_i \leq 78$, medium slagging propensity; and $S_i > 77$, very low slagging propensity [11].

3. Results and discussion

Fuel properties and chemical composition are crucial parameters when selecting biomass for various thermochemical conversion processes and predicting the complex issues in such processes. The washing pre-treatment significantly affects almost all the fuel properties and inorganic composition of the wheat straw, which can be seen in Figs. 1 and 2. With water washing, a significant increment can be seen in volatiles (<5.1%), C (<4.5%), O (<2.3%), HHV (<0.48 MJ/Kg), and mass loss (<6.7%) compared to the original sample. While substantial decrease in ash content (<39%), troubling elements ($K \leq 68\%$; $Cl \leq 87\%$; $S \leq 74\%$; $N \leq 46\%$; $P \leq 45\%$), and fouling and slagging propensity was also observed after the washing pre-treatment. A certain amount of mass loss is inevitable in the washing pre-treatment, as water-soluble organic acids (lactic acid, acetic acid, propanoic acid, formic acid), sugars (glucose, mannose, xylose, arabinose), waxes, and inorganic species (K, Na, Cl, S, N, P, Mg) leach into the water from the biomass [37,38]. A high removal (35–100%) of K, Cl, S, and ash, as well as a considerable increment in volatile matter, C, O, HHV, mass loss, and energy loss, has also been reported in earlier studies (Table S1) on the washing pre-treatment of wheat straw [10,12,25,27,33].

3.1. Effect of washing duration on fuel properties

3.1.1. Effect on proximate ultimate composition, HHV, and mass loss

Based on the results presented in Tables 2 and 3 and Fig. 1, the washing time has clearly a very high impact on the fuel properties. Even after the quick spraying (0 min) of water, significant changes in the proximate, ultimate, and inorganic composition can be seen. A slight decrease in C and ash content was observed at short washing durations (Fig. 1), which could be the result of the quick leaching of some highly water-soluble organic and inorganic compounds into the water. Consequently, sudden mass loss and a fall in HHV was observed with short washing times. As the washing time increased over 2 min, there was a continuous increment in VM, C, H, O, HHV, and mass loss. Increasing the washing duration also improved the removal of ash, N, and S, and it increased the electrical conductivity (EC) of the leachate, indicating the removal of soluble salts and acids from the biomass (Table 2).

Due to the continuous removal of inorganic matter from the biomass

Table 1

Analytical methods used in the present study.

Analysis	Instrument used	Method/formula used	Reference
Proximate Analysis	Oven and Muffle furnace	ASTM E872 – 82 (2006) and ASTM E1755 – 01 (2007)	–
Ultimate Analysis	Thermo Scientific™ Flash Smart™ Elemental Analyzer	BS EN 15104:2011	–
High-Heating value (HHV)	Thermo Scientific™ Flash Smart™ Elemental Analyzer	$\text{HHV}(\text{MJ/kg}) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{A}$	[31]
Inorganic composition of ash	Thermo Scientific™ Niton XL3t GOLDD+	X-ray fluorescence (XRF)	–
Fouling prediction	–	Base-to-acid ratio (B/A) = $\frac{\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_5 + \text{P}_2\text{O}_5}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$	[32]
Slagging prediction	–	Slagging Index (Si) = $\frac{\text{SiO}_2}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}} \times 100$	[13]

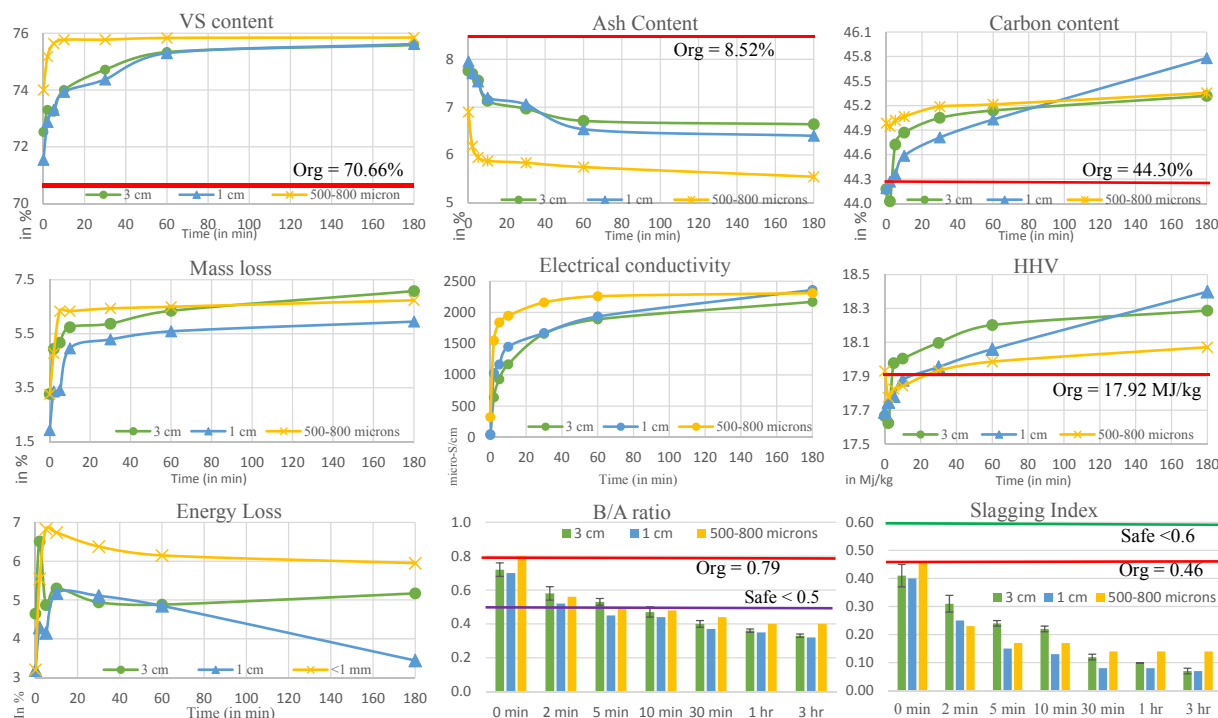


Fig. 1. Effect of time and size variation in the washing pre-treatment on (a) VS content, (b) ash content, (c) carbon content, (d) mass loss, (e) electrical conductivity of leachate, (f) HHV, (g) energy loss, (h) B/A ratio, and (i) slagging index.

with increasing washing time, a continuous decrease in ash content was observed. Even at 0 min, 8–22% ash removal was achieved, which further increased by 1.8–3.5 times after washing for 3 h (Figs. 1 and 2). This decrease in ash content tends to produce fewer problems related to ash and fouling and slagging [7]. The removal of ash found in the present study is comparable to some past studies, although it was relatively lower compared to some of them (Table S1). The greater ash removal in some of the other studies could be the result of a longer washing time (6–20 hrs; [10,25,38]), very small biomass size used for washing (280–900 μm ; [10,12]), higher washing temperature (30–90 $^{\circ}\text{C}$; [39]), or the high salt content in the sample [25]. Considerable removal of ash can also be noted at short time periods such as 5 min and 10 min, where the removal ranges from 14.6 to 34.6% and 19.7–35.4%, respectively.

On increasing the washing duration, a significant increase in C and O was observed, while a slight increase in H was also noted. This change could be the result of increment in lignocellulosic content within the biomass due to the high removal of soluble salts [12]. Due to the quick loss of some organics into the leachate at short washing times (0–2 min), an immediate but slight decrease in C and H content was noted. However, C and H have shown continuous improvement with increasing washing times and shown 1–1.5% and 0–1% higher values than the untreated sample after 3 h of washing, respectively. HHV was also found to follow the same trend as C and H, i.e. initially decreasing then continuously increasing with time. Even though HHV continuously improves with the longer washing durations, the increase in HHV is relatively small compared to the original value (<0.5 MJ/Kg) because of the inevitable mass loss. Due to the continuous removal of ash elements and organics when increasing the washing duration, mass loss was found to continuously increase for all sizes. Consequently, a small energy loss (3.2–6.7%) was observed after the washing pre-treatment. The mass loss was highest for the longer washing durations (1–3 hrs), which resulted in higher energy losses even though the HHV increased.

As N and S are important plant nutrients, depending on the growing conditions of the biomass, plants may uptake as high as 3.4% N and 2.2% S in their bodies from the environment [4,40]. Washing pre-treatment can effectively remove substantial amounts of N and S from

the agricultural residues. Even with the quick spraying of water, 6–25% and 10–23% removal was seen for N and S, respectively. With short washing times (<10 min), high removal of both S and N (6–62%) was observed, which further improved by 1.1–2.1 times and 1.7–7.5 times (depending on the sample size) after 3 h of washing. The removal of S and N in the present study was found to be relatively higher compared to past studies (Table S1). The reason behind the high removal of N and S could be the greater amounts of mobile and/or water soluble N and S compounds present in the biomass (e.g. NO_3^- , SO_4^{2-}) and the weakly bound compounds in the organic matrix, which leached into the water in higher amounts [8,32]. One observation that can be noted for both N and S is that near maximal removal was achieved after just 5 min of washing for the 0.05–0.08 cm sized samples, while 30 min of washing was needed for the 1 cm and 3 cm sized samples. This means that short washing times also show good removal efficiency for N and S, and they can be effectively utilized for practical applications, especially with smaller sample sizes.

3.1.2. Effect on inorganic elements and fouling and slagging propensity

In Fig. 2, the effect of the washing duration can be seen on the removal of different inorganic elements. During washing, the maximum removal for K and Cl was 67.5% and 87.3% respectively. Even at 0 min, 18–36% removal of Cl and 16–24% removal of K was observed, which escalates very quickly until 10–30 min for both. After that, the removal of both elements continued to increase, but the net increment remained <10% even after washing for an extra 150 min. Up to 34–53% removal of K and 61–81% removal of Cl was already achieved within 5–10 min of the washing. This quick and high removal of K and Cl at short washing times could be the result of the leaching of water-soluble K and Cl ions into the water, while the slow removal may be the result of weakly bound species removal via ion exchange [32]. K is mostly present in the biomass as the mobile K^+ ion and small amount of K is also attached to organic matrix [9]. Cl acts as the counter anion Cl^- in the biomass to stabilize cell potential, and it is often supplied together with K^+ or it forms weak complexes with the organic matrix [10,40].

As very small amounts of Na were present in the sample, its complete



Fig. 2. The effect of time and size variation in the washing pre-treatment on the removal of (a) chlorine, (b) sulphur, (c) potassium, (d) nitrogen, (e) phosphorus, (f) calcium, (g) silicon, and (h) ash.

removal was achieved within 2 min of washing. No past reference was found on the batch leaching of wheat straw or any other herbaceous residues, which correlates with washing time. However, a study conducted by Liaw and Wu [32] on mallee wood and leaf washing found similar trends as in the present study, i.e. high leaching of K, Na, and Cl within 5–10 min, while only a small improvement in removal was seen after 10 min. Most of the studies published on wheat straw use a longer washing time (3–20 hrs), which results in the high removal of K (54–93%), Na (13–92%), and Cl (71–100%) [10,12,22,25–27] (Table S1).

Nevertheless, the present study shows that a shorter washing time

also ensures the high removal of alkali metals and chloride. For example, 41–53% and 69–81% removal of K and Cl, respectively, was already achieved within 10 min of washing.

P, Mg, and Ca are present in smaller amounts in plants compared to other nutrients, yet they play an important role in plant growth [4,40–42]. Low to high removal of Ca (0–21%), P (0–45%), and Mg (22–71%) can be seen in the biomass after the washing pre-treatment (Figs. 2 and S2). Quick and effective removal of Mg can be seen in 10 min (58–63% removal), and further removal occurs with increasing washing duration (up to 71%). P shows slow but continuous removal on increasing washing time. Unlike other elements, Ca has shown variation

Table 2

Proximate, ultimate, heating value, mass loss, and energy loss analysis of the washed wheat straw on washing time and biomass size variation (nd = not detected).

Size	Washing time	MC (%)	VM (%)	FC (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)	HHV (MJ/kg)	Mass yield (%)	Energy yield (%)	Electrical conductivity ($\mu\text{S}/\text{cm}$)
Original biomass	–	4.01	70.66	16.81	8.52	44.3	5.81	0.47	0.05	40.79	17.92	–	–	–
3 cm	0 min	3.10	72.52	16.61	7.76	44.18	5.71	0.36	0.05	41.87	17.66	96.73	95.35	38
	2 min	2.48	73.30	16.52	7.70	44.03	5.75	0.42	nd	42.10	17.62	95.06	93.49	640
	5 min	2.50	73.23	16.71	7.56	44.72	5.79	0.41	nd	41.51	17.98	94.83	95.13	930
	10 min	2.48	74.00	16.39	7.13	44.87	5.79	0.37	nd	41.84	18.00	94.26	94.70	1170
	30 min	2.38	74.72	15.94	6.97	45.05	5.81	0.36	nd	41.81	18.10	94.13	95.06	1658
	1 hr	2.13	75.34	15.82	6.71	45.14	5.88	0.31	nd	41.96	18.20	93.65	95.12	1890
1 cm	3 hr	2.42	75.58	15.36	6.64	45.32	5.89	0.28	nd	41.87	18.29	92.92	94.83	2170
	0 min	3.74	71.54	16.76	7.96	44.19	5.71	0.45	0.05	41.59	17.69	98.07	96.81	50
	2 min	3.53	72.87	15.88	7.71	44.27	5.76	0.43	nd	41.83	17.75	96.64	95.71	1028
	5 min	3.36	73.30	15.80	7.54	44.36	5.77	0.38	nd	41.96	17.78	96.59	95.85	1166
	10 min	3.04	73.93	15.83	7.20	44.59	5.79	0.39	nd	42.04	17.88	95.04	94.82	1451
	30 min	2.80	74.37	15.77	7.06	44.81	5.78	0.31	nd	42.04	17.95	94.71	94.89	1671
0.05–0.08 cm	1 hr	2.62	75.30	15.55	6.54	45.03	5.82	0.30	nd	42.31	18.06	94.41	95.15	1935
	3 hr	2.88	75.62	15.10	6.40	45.78	5.83	0.27	nd	41.72	18.40	94.05	96.56	2360
	0 min	2.61	74.00	16.49	6.90	44.99	5.71	0.38	nd	42.03	17.93	96.74	96.80	325
	2 min	2.48	75.18	16.15	6.18	44.95	5.65	0.31	nd	42.91	17.78	95.22	94.45	1550
	5 min	2.67	75.64	15.75	5.95	45.02	5.68	0.27	nd	43.08	17.83	93.66	93.17	1840
	10 min	2.87	75.77	15.49	5.88	45.07	5.68	0.28	nd	43.10	17.84	93.66	93.26	1947
0.05–0.08 cm	30 min	2.82	75.78	15.58	5.84	45.19	5.71	0.29	nd	42.98	17.93	93.56	93.62	2160
	1 hr	2.69	75.84	15.73	5.75	45.22	5.75	0.27	nd	43.02	17.99	93.5	93.85	2260
	3 hr	3.10	75.85	15.51	5.54	45.36	5.78	0.27	nd	43.05	18.07	93.26	94.05	2310

Table 3

Ash composition (wt %) of the samples on washing time and biomass size variation.

Size	Washing time	K ₂ O	Cl	SiO ₂	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	Na ₂ O	Al ₂ O ₃	MnO	TiO ₂	B/A	S _i
Original biomass		15.91	10.51	31.33	0.72	1.59	4.92	1.90	0.58	0.11	0.32	0.08	nd	0.79	81.23
3 cm	0 min	15.26	8.70	32.51	0.74	1.54	4.38	1.63	0.57	0.03	0.30	0.08	nd	0.72	83.00
	2 min	12.84	5.23	38.09	0.86	1.93	4.16	2.32	0.54	nd	0.35	0.07	nd	0.58	84.57
	5 min	12.52	4.85	38.29	0.81	1.93	3.04	2.11	0.46	nd	0.31	0.09	nd	0.53	86.90
	10 min	11.83	4.09	40.86	1.01	2.07	2.54	1.98	0.46	nd	0.31	0.10	nd	0.47	87.93
	30 min	9.82	2.94	43.75	0.97	1.91	2.94	2.02	0.31	nd	0.36	0.09	nd	0.40	88.24
	1 hr	8.67	2.32	45.39	1.13	2.00	2.72	2.09	0.28	nd	0.35	0.11	nd	0.36	88.58
1 cm	3 hr	8.53	2.21	47.74	1.36	2.01	2.28	1.92	0.22	nd	0.39	0.15	nd	0.33	89.42
	0 min	14.48	9.46	31.76	0.52	1.59	4.06	1.79	0.57	0.02	0.35	0.06	nd	0.70	83.74
	2 min	11.64	4.45	38.05	0.72	1.80	3.73	1.99	0.48	nd	0.32	0.10	nd	0.52	85.90
	5 min	11.17	3.68	40.28	0.77	1.94	2.53	2.05	0.33	nd	0.30	0.09	nd	0.45	88.49
	10 min	10.88	2.52	41.20	0.81	1.83	2.55	2.07	0.31	nd	0.31	0.08	nd	0.44	88.82
	30 min	9.29	2.28	45.24	1.03	2.02	2.32	2.02	0.22	nd	0.29	0.10	nd	0.37	89.39
0.05–0.08 cm	1 hr	8.97	1.98	45.56	0.98	1.93	2.22	1.87	0.24	nd	0.32	0.12	nd	0.35	89.88
	3 hr	8.31	1.88	47.61	1.19	1.90	2.02	1.72	0.21	nd	0.33	0.14	nd	0.32	90.32
	0 min	15.53	8.57	29.90	1.03	1.67	4.22	1.83	0.57	nd	0.30	0.11	nd	0.80	81.21
	2 min	13.05	4.47	38.38	1.28	1.96	3.32	2.10	0.41	nd	0.34	0.14	nd	0.56	85.40
	5 min	12.45	3.84	40.49	0.88	2.01	3.03	2.09	0.34	nd	0.36	0.14	nd	0.50	87.25
	10 min	11.58	3.46	41.81	1.67	2.11	2.82	2.10	0.36	nd	0.33	0.15	nd	0.48	86.38
0.05–0.08 cm	30 min	9.86	2.94	41.01	1.46	2.12	2.90	1.92	0.32	nd	0.38	0.16	nd	0.44	86.36
	1 hr	8.68	2.32	42.06	1.37	2.10	2.84	1.90	0.35	nd	0.40	0.14	nd	0.40	86.95
	3 hr	8.53	2.21	42.67	2.46	2.08	2.76	1.72	0.35	nd	0.40	0.17	nd	0.40	85.39

in removal depending on the sample sizes and washing duration (Fig. 2). When increasing the washing time, the Si content in the washed sample continuously increased for the 1 cm and 3 cm sizes, but not for the 0.05–0.08 cm size, which is comparable to the Si removal found by Denge et al. [10]. On comparing the removal rate of various elements present in the biomass, the water washing of wheat straw can be divided into two stages. In the first stage, water-soluble components from the biomass, such as K, Cl, Na, N, S, Mg, and P, quickly leach (within 2–10 min) into the water with some organic acids and sugars. The leached organic compounds facilitate the further removal of these elements, which are loosely bound to the organic matrix and are slowly removed via ion exchange [10,32]. About 60% Ca, 18% Si, 50% Mg and 20% P in agricultural residues is in ion-exchangeable form [9] which can be partly removed by extended leaching duration. Longer washing times (>30 min) provide better removal due to extended leaching, especially for Ca

and P, which starts to show substantial improvement only after 10 min of washing. The above-mentioned two-stage behaviour can also be clearly noticed in the EC of the leachate (Fig. 1e). EC also shows a quick increase until 30 min of washing, but after that it shows only a small increment, even after washing for an extra 2.5 hrs. Similar trends in K, Cl, Ca, Mg, and EC were also seen by Liaw and Wu [32]. It can be noted that the removal of Si (7–25%), P (14–25%), Fe (10–34%), and Ca (9–18%) at 0 min is even higher than some samples washed for longer durations (supplementary material). This could be the result of the removal of dirt or extraneous compounds loosely attached to the straw surface that washed away with the leachate via the tiny holes present in the bottom of the apparatus. Considerable amounts of Si, Ca, P, and Fe are part of the plant structure, but some portions of these elements are detrital and/or of technogenic origin, which is present as dirt and/or extraneous materials [8,43].

As the washing pre-treatment shows the high removal of alkali metals, Cl, and S, a significant improvement in the fouling, corrosion, and agglomeration behaviour of the wheat straw can be expected. Due to the high B/A, untreated wheat straw is expected to cause medium to high fouling in the boilers. However, a continuous improvement in all the indexes can be seen with increasing washing time (Table 3 and Fig. 1). For longer washing times, a 1.8–2.5 times reduction in B/A values can be seen when compared to the untreated sample, which is the result of the higher removal of K, Mg, and P. Substantial improvement in B/A value was also observed in earlier studies after the washing of wheat straw, [11,12]. Even though slagging index (S_i) of the untreated wheat straw already has low slagging tendency, further improvement in the S_i value was observed after washing. High removal of S and Cl was also shown (up to 74% and 87%, respectively) through water washing, which reduces deposition, corrosion, and flue gas (SO_x and HCl) emission-related issues in wheat straw.

3.2. Effect of sample size on fuel properties after the washing pre-treatment

3.2.1. Effect on proximate ultimate composition, HHV, and mass loss

As per Tables 2 and 3 and Fig. 1, it is clear that the sample size directly influences the effectiveness of the washing pre-treatment. The 1 cm and 3 cm sized samples were found to behave very similarly, while the 0.05–0.08 cm sized sample showed relatively different effects on the fuel properties (Figs. 1 and 2). As mentioned in the previous subsection, the VM content of the biomass continuously increases upon extending the washing time. However, this increment is relatively higher and much quicker in the 0.05–0.08 cm samples compared to 1 cm and 3 cm samples (Fig. 1a). Ash removal in the small sample size was found to be 1.3–2.6 times greater compared to the larger sample sizes (1 cm and 3 cm). The maximum ash removal achieved for the 0.05–0.08 cm samples after washing for 3 h was 39.3%. However, 35.4% of the removal was already achieved after washing for just 10 min. For longer washing durations, the ash content seems to be directly proportional to the sample size (Fig. 1b). Continuous improvement in the carbon content was seen in all sample sizes when increasing the washing time. Nevertheless, improvement in the smaller sized sample was found to be the highest. This could be the result of higher ash removal in the smaller sample compared to the 1 cm and 3 cm samples. When looking at the trends presented in Table 2, it is clear that the increase in O and H content upon washing is directly proportional to the sample size used in the washing pre-treatment. As the smaller sized samples contains higher O content, lower H content, and similar C content compared to the 1 cm and 3 cm samples, consequently they shows the least improvement (0–0.3 MJ/Kg less) in HHVs while showing maximum energy loss (1–2.7% higher). Mass loss was also found to be higher in the smaller sized samples, which could be the result of high organic and ash element loss. The 1 cm and 3 cm samples showed similar trends upon increasing washing duration. The higher mass (15–16%) and energy loss (10.5–12.5%) in the small sized sample on washing was also observed in earlier studies as well [10,12,20] where the sample size was 900 μ m and < 800 μ m, respectively (Table S1).

With short washing times, the 0.05–0.08 cm sample showed much better and quicker removal of N and S compared to the 1 cm and 3 cm samples. For both N and S, near maximal removal in the smaller sized sample was achieved within 5 min of washing. After that, removal increased by only 1–3% for longer washing durations. For the 1 cm and 3 cm sized samples, the removal of both N and S continuously increased as the washing time increased until it became similar or higher than that for the 0.05–0.08 cm sample (Fig. 2). Therefore, for the effective removal of N and S, washing for 5 min seems sufficient for small-sized wheat straw, while for the 1 cm size, 30 min seems to be adequate. In comparison to the findings of the study by Ma et al. [12] which used a sample size \sim 0.9 mm for washing, the removal of N was similar, but the removal of S was higher in the present study.

3.2.2. Effect on inorganic elements, B/A, and slagging propensity

In Fig. 2, the effect of size can be seen on the removal of different inorganic elements. One clear trend is notable in most of the elements, such as K, Cl, Mg, N, S, and Ca: the smaller sized sample (0.05–0.08 cm) shows significant to high removal of all of these species within just 5–10 min of washing. Furthermore, the 1 cm and 3 cm sized samples again seem to behave very similarly, i.e. showing continuously better removal on increasing washing time, but much slower compared to the 0.05–0.08 cm sample. EC of the leachate supports the trends found for the different sample sizes (Fig. 1e). In most of the cases, the small sized sample shows the highest removal of the inorganic species, which is most likely the result of better diffusion and higher reactivity with the water [44]. For a particular washing time, it is clearly visible that the 0.05–0.08 cm sample (\leq 67.5%) shows better removal of K compared to the 1 cm (\leq 63.1%) and 3 cm (\leq 61.2%) samples. Maximum removal for Cl was similar for all the sizes, ranging between 84.8% and 87.3%, means irrespective of the size, Cl shows high removal with longer washing times ($>$ 10 min). With a shorter washing duration, high removal in the smaller size was evident in both K and Cl, which is 10–20% higher than for the 1 cm and 3 cm sizes. However, for longer washing durations, all sizes show similar removal of K and Cl.

Significant removal of Ca was only observed for the smaller size, while for 1 cm and 3 cm, the removal started to appear after 30 min of washing. For P, the highest removal was also shown in the smaller sized biomass, about 2–3 times higher at shorter washing durations and 1.3–2 times higher at longer washing durations when compared to the 1 cm and 3 cm sized samples. Si removal was seen only in the 0.05–0.08 cm sized sample, and it remains at a similar level even after washing for 3 h. High removal in the smaller sized sample for Si, P, and Ca could be the result of the better reaction of the biomass with water, which shows significantly higher and quicker removal of soluble compounds during short washing times. While higher removal at longer washing durations could be the result of ion exchange, in which the smaller sized sample shows the best removal compared to the other sizes. A similar removal of P and Si was also observed in smaller sized wheat straw washing in Ma et al. [12] and Denge et al. [10] respectively.

B/A ratio for the smaller sized samples was slightly higher than in the larger sample sizes, which is the effect of Si removal and the slightly higher content of Ca and Mg compared to other sizes. Maximum reduction in B/A was seen for the 1 cm sample washed for 3 hrs (0.32), which was only slightly lower than that for the 3 cm sample (0.33). Fuels having a B/A value of $<$ 0.5 are expected to cause very low fouling, which was already accomplished after washing the smaller sized sample (0.05–0.08 cm) for 10 min and the 1 cm and 3 cm samples for 5 min. Hence, a short washing duration with a larger sample size can also be utilized for practical purposes, as low energy is required for milling the larger sizes, and they are also easy to pelletize [45].

The results from the present study indicate that longer washing times ($>$ 30 min) and smaller sample sizes ($<$ 1 cm) lead to the maximum improvement in the fuel properties. However, the results from the present study also indicate that even at lower washing times (5–10 min) and higher sample sizes (1–3 cm) sufficient improvement in the removal of ash and troubling elements (K, Cl, S, N, P, Ca), B/A ratio, and fouling propensity can be achieved. A lower washing time and a larger sample size provide some benefits over a smaller size and longer washing times, such as lower mass and energy loss (0–1.7% more), a lower energy requirement for cutting, [16] reduced operation time with a high treatment rate/productivity, easier separation of the biomass from the water, easier handling and transportation, [46] efficient palletization, [45] etc. Thus, to uphold the operational and economic feasibility for industrial application, a short washing duration and larger sample size are highly favoured. However, the efficiency of the short washing time and larger sample size still require further improvement, as they may still cause some fouling and corrosion issues during combustion. One important point should be scrutinized when analyzing fouling and slagging indexes that all these indexes were originally developed for

coal. So, they may not be accurate for biomass, as they may overestimate the fouling and slagging tendency of biomass by not taking ash removal and the effect of certain elements into consideration [7,11]. As B/A values for the samples washed for short durations are very close to the cut-off i.e. 0.5 and still contain 3–5% Cl in the ash, some fouling and corrosion can be expected even after washing. Even though accuracy of these indexes may not be accurate but then still can be used to observe fouling and slagging trends in the washed biomasses [13]. As K and Cl are the main elements behind fouling, slagging and corrosion issues, their removal from the biomass will definitely reduce such problems in the boilers. As washing pre-treatment result into high removal of troubling elements on increasing time and reducing size, much lower fouling and corrosion issues can be expected from the washed wheat straw compare to the untreated sample. Also, as the temperature [10] and S:L ratio [12] has a considerable impact on washing efficiency, they can be utilized to further modify the washing process. Thus, in Part 2 of the study, the efficiency of the washing pre-treatment was improved for short washing times (5 and 10 min) and a larger size (3 cm) by increasing the washing temperature and S:L ratio.

4. Conclusion

In the present study, the effect of water washing on fuel properties was evaluated in-depth by altering the washing duration and sample size. Their effect on the washing pre-treatment was missing from the literature, and evaluating these factors is crucial for the basic understanding and modification of the pre-treatment to enable its implementation on a larger scale. Based on the results and various novel trends obtained in the present study, the following conclusions can be drawn:

1. Washing was shown to have a high impact on the fuel properties and the fouling and slagging propensity. After washing, a significant increment in the content of VS ($\leq 5.2\%$), C ($\leq 1.8\%$), and O ($\leq 2.3\%$), and a slight improvement in HHVs (≤ 0.5 MJ/kg) and H ($\leq 0.1\%$) was observed. Simultaneously, the high removal of ash ($\leq 39\%$), Cl ($\leq 87\%$), S ($\leq 74\%$), Mg ($\leq 71\%$), K ($\leq 68\%$), N ($\leq 46\%$), P ($\leq 45\%$), and Ca ($\leq 29\%$) was also noted.

2. Washing time has a high impact on the fuel properties of wheat straw. Even at 0 min, i.e. quick spraying, significant improvement in fuel properties and composition was observed. Continuous removal of ash and troubling elements (K, Cl, S, N, P, Ca), as well as improvement in C, HHV, and fouling and slagging propensity was observed as the washing duration increased, with the best results generated using a longer wash duration (60–180 min). Furthermore, substantial removal of troubling elements was observed during lower washing durations (≤ 10 min). Up to 53% K and 81% Cl removals were achieved on washing for just 10 min, while simultaneously the fouling propensity improved from severe (B/A 0.79) to low fouling (B/A 0.32–0.40). As per various novel trends evaluated in the study, washing seems to be a two-step process. In the first step, quick leaching of water-soluble inorganic and organic matter (in < 10 min) was observed, while in the second step, much slower leaching of loosely bound elements and some soluble matter was observed.

3. Feedstock size also directly influences the efficiency of the washing pre-treatment. The smaller sample size (0.05–0.08 cm) shows the most rapid improvement in fuel properties and composition. With longer washing durations, the removal of the main troubling elements and improvement in fouling tendency were found to be similar for all sample sizes (61–67% K, 85–87% Cl, 63–74% S, and 45–46% N removal, and 0.3–0.4B/A). The smaller sample size shows in general a slightly better improvement in fuel properties in relatively shorter wash durations (10–30 min). However, the 1 cm and then 3 cm samples were found to show the best improvement in fouling (B/A 0.32–0.33) and slagging propensity (89–90), while simultaneously showing a high increment in HHV (18.3–18.4 MJ/kg) and the least energy losses (3.4–5.2%).

4. Short washing durations and a larger sample size are favourable for industrial applications and result in considerable improvement in post-wash fuel properties and composition, so these conditions can be selected for practical applications. However, they require further modifications, as they may cause low to moderate fouling in combustion, which is shown in Part 2 (separate article) of the study by varying the washing temperature and S:L ratio.

CRedit authorship contribution statement

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