

Full Length Article

Effect of different washing parameters on the fuel properties and elemental composition of wheat straw in water-washing pre-treatment. Part 2: Effect of washing temperature and solid-to-liquid ratio

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ARTICLE INFO

Keywords:

Leaching
Fouling
Corrosion
Biomass pre-treatment
Biomass composition
Agricultural residues

ABSTRACT

The present work is the second part of a study conducted to evaluate the effect of basic parameters on the efficiency of water washing pre-treatment. As per the results of Part-1, large sizes and shorter washing durations are favourable for industrial applications, yet low to moderate fouling and corrosion can be expected from them on combustion. The aim of the present study was to further improve the efficiency of the washing pre-treatment for rather short washing durations (5 and 10 min) and a large feedstock size (3 cm) by optimizing the temperature and solid-to-liquid (S:L) ratio. The washing temperatures considered were 20 °C, 40 °C, 60 °C, and 80 °C, while the S:L ratios considered were 1:15, 1:20, 1:30, 1:40, and 1:50. Fuel composition, heating values, energy loss, and fouling and slagging propensity were evaluated. Increasing the washing temperature resulted in the greater removal of ash (25–37%), K (42–55%), Cl (60–81%), S (32–61%), Mg (52–68%), N (17–25%), P (11–37%), and Ca (14–29%). On increasing the S:L ratio, improvement in the removal of ash (27–35%), Cl (73–84%), S (41–59%), and N (21–40%) was also observed. For practical applications, an S:L ratio of 1:15 was found adequate compare to higher S:L ratios. The washing of 3 cm sized wheat straw for 10 min at 40 °C with a 1:15 S:L is recommended for industrial applications, as it shows the least fouling propensity and energy loss.

1. Introduction

With their ample availability and carbon neutrality, short rotation crops are considered important renewable energy sources. Due to its high and clean energy potential, countries including the USA, UK, China, Germany, Canada, Sweden, and Finland are trying to integrate bio-energy into government strategies for energy generation and transportation [1]. However, the composition of short-term crop residues such as wheat straw, rice straw, cotton stalk, miscanthus, switchgrass etc., often restricts their utilization for energy production in thermo-chemical conversion processes. Potassium (K), Sodium (Na), nitrogen (N), sulphur (S), calcium (Ca), chlorine (Cl), phosphorus (P), and magnesium (Mg) are important plant nutrients, and they are often present in plants in considerable amounts [2–5]. Quantities of these macro- and micronutrients often lead to technical difficulties in biomass combustion, such as fouling, slagging, agglomeration, corrosion, and ash-related issues, which were already discussed in detail in Part 1 of this study. Washing pre-treatment can be used to improve the fuel composition of agricultural residues, as it significantly improves the fuel

properties and reduces the corrosion, fouling, and slagging propensity of the fuel by removing ash and water-soluble salts of K, Na, Cl, N, and S. Consequently, the emissions and corrosion, fouling, and slagging propensity of the biomass are largely reduced, while the heating values and combustibility of the fuel are simultaneously improved [5–11] (Table S1).

Even though the washing pre-treatment is quite effective for improving the fuel quality of various agricultural residues, it still requires certain process modifications before being utilized on an industrial scale. Longer washing durations and smaller sample sizes have been commonly used in earlier studies, as they result in the better removal of troubling elements (K, Na, Cl, S, N, P, Ca) (Table S1). However, longer washing durations lead to higher mass and energy losses (Table S1). Additionally, longer washing durations require a larger washing apparatus and can lead to low daily production of the treated feedstock. The economic feasibility and profitability of the pre-treatment may then suffer. Smaller sample sizes (<1 cm) are difficult to pelletize [12], require extra energy for milling [13], and demand sophisticated and/or costly filtering equipment to prevent feedstock loss while separating the

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biomass from the water. Thus, a smaller size may lead to higher operational and waste-water treatment costs. Short washing durations and larger sample sizes are highly favourable for the industrial-scale washing pre-treatment process. However, the outcomes of Part 1 of the present study showed that washing for shorter durations (<10 min) with a larger sample size (>1 cm) may cause low to moderate fouling and corrosion problems during combustion. Further research and modifications are therefore required to utilize washing for practical purposes.

Some researchers have tried to enhance the efficiency of the washing pre-treatment by altering various washing parameters, but such studies are still very limited. From the literature review it was found that the effectiveness of the pre-treatment significantly affected by the basic washing parameters: washing duration, sample size, washing temperature [7], biomass-to-water ratio/solid-to-liquid ratio (S:L) [14], and pressing [15] (Table S1). However, the effect of these parameters was not mentioned in-depth in the available body of knowledge, and this information is vital for understanding and modifying the washing pre-treatment. The effects of the washing duration and sample size were explained in detail in Part 1 of the present study. Deng et al. [7] evaluated the effect of water temperature on the washing of six different agricultural residues at 30 °C, 60 °C, and 90 °C. Higher temperatures resulted in better ash, Si, and K removal, while there was fluctuation in the removal trends of Cl, S, N, Ca, and P when compared to washing at 30 °C. Ma et al. [14] evaluated the effect of increasing the S:L in wheat straw washing at two data points, which resulted in improvements in calorific values and fouling and slagging propensity. However, when compared to 1:10, negligible-to-poor removal was seen for ash and troubling elements at 1:50. Jenkins et al [10] tried to soak wheat and rice straw for 24 h with 1:70 S:L ratio at room temperature and found up to 68%, 97%, 67%, 77%, 52% removal of K, Cl, Na, S and ash respectively. Saddawi et al [16] tried to wash 4 different biomass including wheat straw with with 1:16 S:L ratio with relatively longer washing time (6 h) and found up to 54% K, 100% Cl, 92% Na and 12% Ca removal. From the scarce literature available on the modification of the washing pre-treatment, published studies [7,10,11,14,16,17] have considered only a few data points (1–3 values) for each washing parameter (all data points from these studies mentioned in Table S1). These studies are good for initial assessment, but insufficient for practical and large-scale applications. Basic washing parameters must be studied thoroughly and systematically to further improve the technical and economic feasibility of the washing pre-treatment for industrial use. As short washing durations and larger sample sizes are beneficial for practical and industrial applications, detailed knowledge and larger datasets related to these parameters are crucial but still missing from the literature. In addition, no past studies were found related to the effects of washing durations and the sample size on the washing process, nor were there any on the industrial applicability and challenges associated with the washing pre-treatment. Furthermore, even though raising the washing temperature and S:L ratio results in better washing efficiency, their effect on short washing durations is yet to be determined.

Based on the findings of Part 1 of the present study, short washing durations and larger sample sizes are beneficial for industrial applications, as they show considerable improvements in the fuel properties and the fouling, slagging, and corrosion propensity of the wheat straw. However, they still require further modifications, as the straw may cause fouling and corrosion issues due to its considerable alkali and chlorine content after washing for shorter durations. In the present study (Part 2), we tried to improve the effectiveness of the washing pre-treatment for short washing durations (5 min and 10 min) and a larger sample size (3 cm) by varying the washing temperature and S:L ratio. A total of 20 washing experiments were conducted and analysed to evaluate changes in different compositions, heating values, energy loss, and fouling, slagging, and corrosion propensity. At the end of the article, some recommendations are provided for the industrial applicability of the results, and further prospects for improving the washing pre-treatment are

discussed.

2. Materials and methods

The wheat straw used in the present study was collected from fields in Lempäälä, Pirkanmaa region, Finland. The original wheat straw contained about 4% moisture (M), and it was used for the washing experiments as received. During the preliminary testing, it was found that an S:L below 1:15 would not fully submerge the 3 cm sample, potentially leading to inconsistent results after washing. So, a minimum 1:15 S:L was used for all temperature variations in the washing experiments. In all the washing experiments, 6 g of 3 cm sized wheat straw was used. To evaluate the effect of the washing pre-treatment on wheat straw for small durations and a larger sample size, the temperature was varied from 20 °C to 80 °C (Table 1). The temperature variations during the experiments were conducted inside a temperature-controlled incubator using water at the specific temperature set for the experiment. To study the effects of the S:L ratio, it was varied from 1:15 to 1:50 (Table 1). After washing, excess water was squeezed from the biomass by manual pressing. The biomass was then dried overnight at 103 ± 2 °C. After the removal of moisture from the samples, they were left to absorb moisture at room temperature for 24 h [7]. The samples were then stored in tightly sealed containers and utilized for the different analyses. All analytical methods, the data analysis, and the calculation of mass yield, energy yield, element removal, base-to-acid (B/A) ratio, and slagging index (S_i) were done by following the same methodology as mentioned in Part 1 of the present study (shown in Table 2 and also included in supplementary material for greater detail). As the S content in the wheat straw samples was found very low to be detected by the CHNS-O analyser, the S content (wt%) of the ash was used for assessment. To minimize the error due to variation in the untreated feedstock composition, all analyses for the unwashed wheat straw were repeated three times. The standard deviation for the analyses was found within acceptable range of error. To check the reliability of the results obtained from the washing experiments, five experiments were repeated randomly: 10 min washing at 40 °C and 60 °C, 5 min washing at 40 °C and 60 °C, and 10 min washing with a 1:15 S:L ratio. The discrepancy between experimental data was found to be within experimental uncertainty (shown in supplementary material maximum SD shown with the data in Tables 3 and 4).

3. Results and discussion

3.1. Effect of temperature variation on fuel properties after the washing pre-treatment

Based on the results of the washing experiments (Tables 3 and 4), it is clear that washing has a high impact on all fuel properties. In addition, the washing temperature has a direct impact on the composition of the wheat straw (Figs. 1 and 2). When compared to washing at 20 °C, increasing the washing temperature has a faster effect on the fuel

Table 1
Various parameters for different washing experiments.

Parameter Varied	Washing parameters used in experiment				Reading points for batch experiment
	S:L ratio	Sample size	Temperature	Washing time	
Temperature	1:15	3 cm	–	5 min	20 °C, 40 °C, 60 °C, 80 °C
Temperature	1:15	3 cm	–	10 min	20 °C, 40 °C, 60 °C, 80 °C
S:L ratio	–	3 cm	20 °C	10 min	1:15, 1:20, 1:30, 1:40, 1:50

Table 2
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	HHV (MJ/kg) = 0.3491C + 1.1783H + 0.1005S – 0.1034O – 0.0151N – 0.0211A	[18]
Inorganic composition of ash	Thermo Scientific™ Niton XL3t GOLDD+	X-ray fluorescence (XRF)	–
Fouling prediction	–	Base-to-acid ratio (B/A) = $\frac{K_2O + Na_2O + CaO + MgO + Fe_2O_5 + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2}$	[19]
Slagging prediction	–	Slagging Index (Si) = $\frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \times 100$	[8]

Table 3

Proximate (wt%), ultimate (wt%, db), heating value, mass loss, and energy loss analysis of the washed wheat straw in terms of temperature and S:L variation (nd = not detectable).

Washing time	Temp/ S: L	M	VS	FC	Ash	C	H	N	S	O	HHV (MJ/kg)	Mass yield (in %)	Energy yield (in %)	EC (µS/cm)
original sample		4.32	70.14	16.01	9.53	44.02	5.81	0.48	0.13	40.03	17.88	–	–	–
5 min	20 °C	4.34	72.79	15.38	7.47	45.21	5.76	0.41	nd	41.16	18.15	96.16	97.38	760
5 min	40 °C	4.05	73.44	15.34	7.17	45.47	5.73	0.40	nd	41.23	18.20	95.91	97.42	1015
5 min	60 °C	3.99	73.47	15.90	6.64	45.48	5.77	0.38	nd	41.72	18.22	95.83	97.43	1270
5 min	80 °C	3.98	73.60	15.72	6.70	45.63	5.77	0.42	nd	41.49	18.28	95.14	97.07	1877
10 min	20 °C	4.01	73.45	15.68	6.86	45.19	5.71	0.39	nd	41.85	18.02	95.99	96.74	1150
10 min	40 °C	4.40	73.68	15.31	6.61	45.49	5.73	0.38	nd	41.8	18.16	95.68	96.95	1300
10 min	60 °C	4.18	73.63	15.44	6.76	45.48	5.78	0.38	nd	41.61	18.24	94.94	96.62	1550
10 min	80 °C	3.57	74.37	15.70	6.36	45.81	5.78	0.40	nd	41.65	18.36	94.45	96.75	1888
10 min	1:15	2.48	74.00	16.39	7.13	44.87	5.79	0.37	nd	41.84	18.00	94.26	94.70	1170
10 min	1:20	2.11	74.37	16.01	7.50	44.90	5.69	0.41	nd	41.50	17.92	92.23	92.24	924
10 min	1:30	2.17	74.76	16.03	7.03	45.11	5.72	0.34	nd	41.80	18.01	94.10	94.59	730
10 min	1:40	2.18	75.22	15.99	6.61	45.10	5.76	0.31	nd	42.22	18.02	94.24	94.78	535
10 min	1:50	2.18	74.89	15.88	7.04	44.92	5.69	0.31	nd	42.05	17.88	93.85	93.65	415
Max St. dev.	–	0.13	0.24	0.41	0.08	0.17	0.02	0.02	–	–	0.07	0.13	–	111

Table 4

Ash composition (wt%) and the different indices of the investigated samples.

Washing time	Temp/ S:L	K	Cl	Si	Fe	Ca	Mg	P	S	Na	Al	Mn	Ti	B/A	S _i
org sample		16.32	10.88	28.61	1.11	1.66	4.99	1.91	0.55	0.13	0.32	0.06	nd	0.90	78.66
5 min	20	12.61	5.77	37.95	0.83	1.85	3.15	2.26	0.50	nd	0.34	0.07	nd	0.54	86.69
5 min	40	11.20	3.53	41.22	0.88	1.86	2.77	1.88	0.39	nd	0.32	0.08	nd	0.45	88.21
5 min	60	12.59	5.32	40.51	0.95	1.79	3.01	1.79	0.45	nd	0.33	0.12	nd	0.49	87.57
5 min	80	11.70	3.58	42.34	1.12	1.87	2.55	1.85	0.36	nd	0.32	0.14	nd	0.45	88.42
10 min	20	12.24	4.77	36.96	0.74	1.88	2.69	1.92	0.50	nd	0.36	0.10	nd	0.52	87.46
10 min	40	11.08	3.63	44.40	1.32	1.83	2.38	2.36	0.39	nd	0.46	0.19	nd	0.42	88.91
10 min	60	11.47	3.55	42.64	1.05	1.84	2.50	2.24	0.36	nd	0.32	0.11	nd	0.44	88.78
10 min	80	11.62	2.98	43.23	1.08	2.03	2.67	2.03	0.34	nd	0.38	0.11	nd	0.45	88.21
10 min	1:15	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
10 min	1:20	11.68	3.36	39.93	1.08	1.80	2.19	2.30	0.38	nd	0.29	0.10	nd	0.47	88.72
10 min	1:30	12.85	3.13	36.37	1.00	1.92	3.01	1.76	0.40	nd	0.34	0.10	nd	0.56	85.96
10 min	1:40	13.68	3.70	37.34	1.06	1.93	2.87	1.99	0.44	nd	0.36	0.11	nd	0.57	86.44
10 min	1:50	11.11	2.45	42.66	1.05	1.97	3.00	2.16	0.33	nd	0.32	0.11	nd	0.45	87.63
MaxSt. dev.	–	0.09	0.08	0.27	0.09	0.02	0.14	0.11	0.03	–	0.08	0.01	nd	0.02	1.11

composition, which can be seen in Table 4 and Fig. 2. A continuous improvement in volatile solids (VS) was seen for both 5 and 10 min when increasing the washing temperature. The ash content of the washed wheat straw was also decreased continuously from 9.53% to 6.70% and from 9.53% to 6.36% for 5 and 10 min, respectively. When increasing the temperature from 20 °C to 80 °C, about 3.2–6.1% of additional ash removal was observed. Consequently, higher washing temperatures result in a 1.5–1.8% improvement in carbon content compared to the original sample. However, compared to 20 °C, the increment in the concentration of carbon (C) was small, while ash removal was much higher (27–37%). This means that the loss of organic matter is also higher when washing at a higher temperature, which has also been reported in earlier studies [7,20]. This could be the effect of

the increased leaching of some organic acids, sugars, inorganic species, and waxes from the biomass at higher temperatures [7,21,22], which were earlier sparingly soluble at room temperature. Hydrogen (H) content shows continuous improvement, while the continuous decrement in oxygen (O) content was seen at higher temperatures with a washing time of 10 min. As the C and H content in biomass increased on raising the washing temperature, an increment in HHV was seen for the samples washed for 5 min (0.05–0.14 MJ/Kg higher) and 10 min (0.14–0.34 MJ/Kg higher) compared to those washed at 20 °C. Due to the higher ash removal and organic loss, a significant and continuous increase in mass loss was observed at higher temperatures. However, as the improvement in HHV was also significant, energy loss in washing at 40 °C and 60 °C shows even lower energy loss when compared to 20 °C.

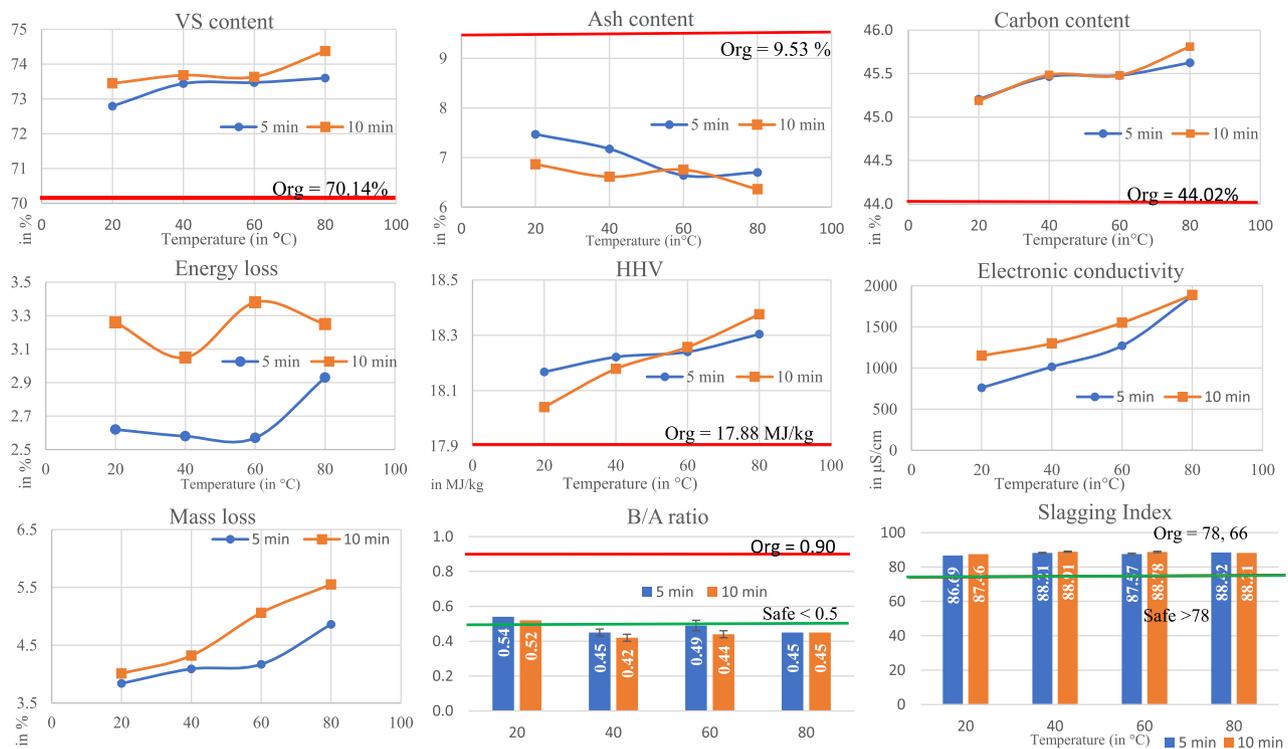


Fig. 1. Effect of temperature variation on the washing pre-treatment: (a) VS content, (b) ash content, (c) carbon content, (d) energy loss, (e) HHV, (f) electronic conductivity, (g) mass loss, (h) B/A ratio, and (i) slagging index.

Thus, to obtain the maximum benefit in terms of improving the fuel quality with a lower energy loss, a washing pre-treatment for 10 min at 40 °C can be adopted for industrial applications.

An increment in the removal of N and S was observed on raising the washing temperatures. For S, continuous improvement in removal was seen upon increasing the temperature; 1.7–1.8 times more removal was observed at 80 °C (57–61%) compared to 20 °C (32–37%). Greater removal at higher temperatures could be the result of the additional leaching of organic and inorganic compounds, such as Ca and Fe sulphates, due to higher water temperatures. For S removal, the trends visible in the present study are different compared to those of Deng et al. [7]. This could be the outcome of using shorter washing times, where the solubility increases as water temperatures increase and not all the water-soluble S has leached into the water within 10 min. For N, a slight increase in removal was observed on increasing the temperature to 60 °C (2.8–5.7% more removal). The trends for C, H, O, N, and S can also be used as indicators to estimate the effectiveness of the washing pre-treatment, as already shown in Part 1. Looking at the various trends for C, H, O, N, and S (Table 3), it can be concluded that increasing the temperature rapidly increases the efficiency of the washing pre-treatment. Additionally, after looking at these trends, much lower alkali and chlorine can be expected in the treated feedstock compared to the original biomass and the biomass washed at 20 °C.

Increasing the washing temperature results in better removal of K, Cl, S, Mg, P, and Ca, which can be evaluated from the electronic conductivity (EC) values of the leachate. EC of leachate rises in line with increasing washing temperatures, which could be the result of the greater leaching of some inorganic and organic species from the wheat straw. Increasing the washing temperature results in 7–10% better removal of K for 5 min of washing and 5–7% better removal of K for 10 min of washing (Fig. 2) when compared to washing at 20 °C. The higher removal of K and Cl could be the result of the better leachability of the elements into the water due to higher solubility at high temperatures. Some of the K and Cl also forms weak complexes with the organic matrix of the plant, which could possibly be broken down and leached into the

water upon washing with warmer water [7,23]. This could be another possible reason behind the better removal of K and Cl at higher temperatures compared to washing at 20 °C. Higher removal of K was also found by Deng et al. [7], where the washing time was much longer compared to the present study. One interesting outcome from the temperature variation is that even after increasing the washing temperature by 40 °C, a less than 2% increment was seen in K removal. So, washing for 10 min at 40 °C should be sufficient to remove a substantial amount of K, which was earlier only achieved after washing for 30–60 min at 20 °C. For Cl, up to 13.5% and 18% better removal was achieved for 10 min and 5 min, respectively, compared to 20 °C. To achieve such high removal values for Cl, wheat straw needs to be washed for at least 60 min, as illustrated in Part 1. However, by increasing the temperature, high removal of K and Cl can be achieved even at lower washing times, which could be highly beneficial for practical applications. Besides the greater removal of K and Cl, 3–13% greater removal of Ca and 3–26% greater removal of P was observed at higher washing temperatures. This could be the result of the increased leaching of some weakly attached Ca and P species from the biomass structure and soluble species into the water at higher temperatures, such as Ca oxalate, Ca malate, Ca nitrate, K phosphate, and phytate. P and Ca are highly important macronutrients for plants, and they are present in considerable amounts.

They are vital for the transfer and storage of energy and genetic information, and for cell membrane rigidity, respectively [2,4,24,25]. During epigenesis, Ca and P are precipitated as different compounds, of which some are water soluble (K_3PO_4 , Na_3PO_4 , $Ca(NO_3)_2$, $C_4H_4CaO_5$, $CaCl_2$); some are sparingly soluble ($CaC_2O_4 \cdot xH_2O$, $CaCO_3$, $CaSO_4$, Ca phytate, $FePO_4$), and some are insoluble ($CaSiO_3$, Ca-K-Al silicates, $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$) [3,21,24,25]. Increasing the washing temperature increases the solubility of water-soluble and sparingly soluble Ca and P compounds, resulting in the higher removal of these elements compared to washing at 20 °C.

Lower B/A and S_i were found in the wheat straw washed with water at higher temperatures. Even though after washing the original wheat straw sample at 20 °C, its B/A ratio was reduced by almost half, it was

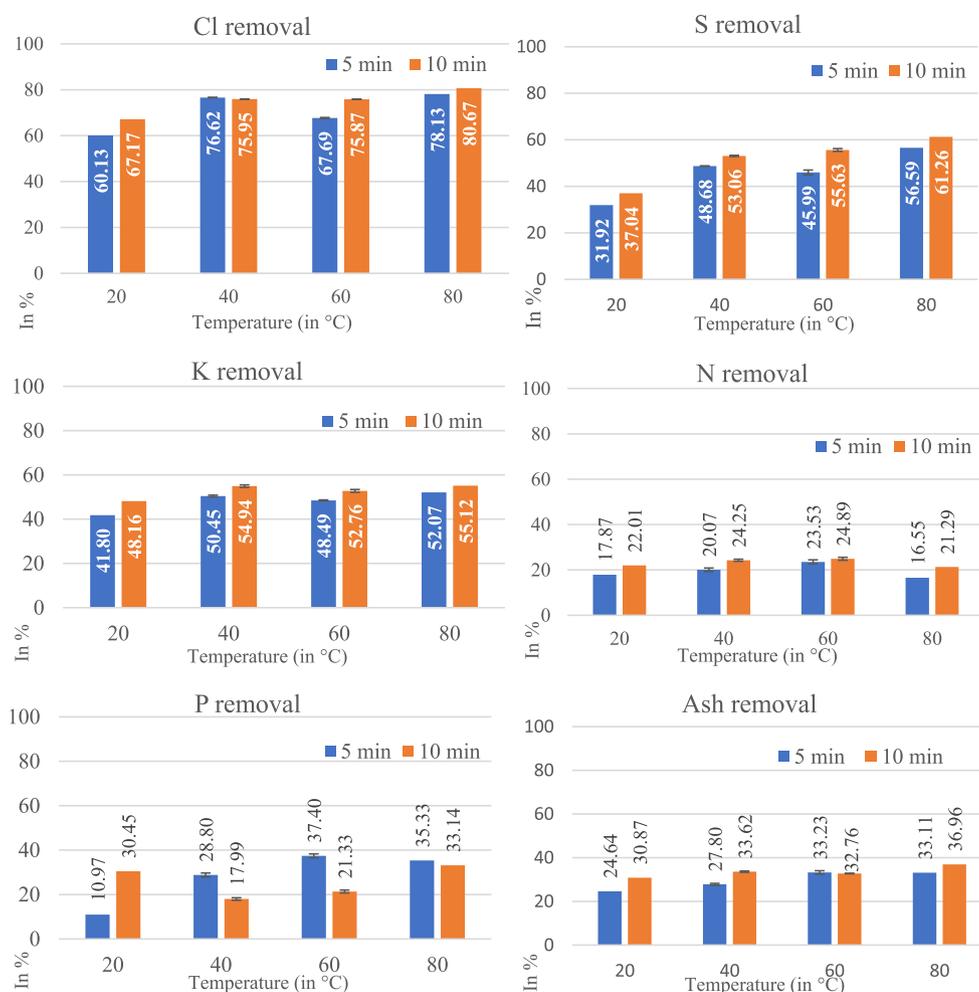


Fig. 2. Effect of temperature variation on the washing pre-treatment on removal of (a) chlorine, (b) sulphur, (c) potassium, (d) nitrogen, (e) phosphorus, and (f) ash.

higher than 0.5, which may cause low to medium fouling in boilers [8]. However, on increasing the temperature, the B/A fell below 0.5 with washes lasting both 5 min and 10 min (Fig. 1). The improvement in all the indexes is the result of the high removal achieved for K, Ca, and P at higher washing temperatures compared to 20 °C. Continuous improvement in the removal of Cl and S was also observed on raising the washing temperature, which means fewer issues related to corrosion, fouling, and agglomeration can be expected from the treated wheat straw. The lowest corrosion propensity can be expected from the sample washed at 80 °C, as it shows the highest Cl and S removal. Even though washing at 80 °C results in the highest K, S, Cl, and ash removal, it was interesting to find that the samples washed for 10 min at 40 °C had the lowest B/A and S_i among all the samples – even those washed at higher temperatures (60 °C and 80 °C) and with greater S:L ratios (1:20–1:50). As it shows the least fouling propensity, a lower water heating requirement, the second-highest ash, K, Cl, and N removal, and lowest energy loss compared to the other washing temperatures considered during the experiments, 40 °C can be adopted for practical and industrial-scale pre-treatment.

3.2. Effect of S:L variation on fuel properties after the washing pre-treatment

Like temperature, increasing the S:L ratio also directly influences the effectiveness of the washing pre-treatment. When increasing the amount of water in the washing experiments, an increment in VS was seen that was even higher than that found with washing at a higher temperature. Except for 1:20, ash removal increased as the S:L ratio increased.

Compared to unwashed wheat straw and other S:L values, the highest ash removal (34.6%) was achieved at the 1:40 S:L ratio. Similar ash removal was achieved after washing the wheat straw for 180 min (Part 1) and washing for 10 min at 40 °C and 80 °C. The higher ash removal could be the result of less competition between inorganic species leaching into the water due to the higher water quantity. Compared to the results of the present study, Ma et al. [14] found both similar and contradicting results for ash removal upon increasing the S:L from 1:10 to 1:50 under soaking and continuously stirring conditions, respectively. As a higher S:L and washing time both result in greater ash removal, their combined effects seem to show even greater ash and alkali removal. This could be the possible reason behind the greater ash removal in earlier studies [7,10,14,22] that used a higher S:L ratio (1:20–1:80) and longer durations (3–24 h).

Slight increment in C and O contents were observed on increasing the S:L ratio, which could be a result of the high ash removal. Negative to negligible improvement was seen in HHV, while mass loss remained higher for all S:L values, especially for 1:20 S:L. Consequently, a higher energy loss (0–2.5% more than 1:15) was observed on increasing the S:L, which is least for the 1:15 S:L ratio (5.2%). One major benefit of raising S:L in the washing pre-treatment is the higher removal achieved for N and S. Higher removal was observed on increasing S:L ratio up to 1:50, at up to 12.6% for N and 18.2% for S. On using the 1:15 S:L ratio, such a removal rate was only achieved after washing the wheat straw for 30–60 min. This means that by increasing the S:L ratio, the washing duration can be reduced without compromising the removal efficiency for N and S. The reason behind the high removal of N and S from the

biomass matrix could be reduced competition between various soluble organic and inorganic species due to the higher dilution ratio. High removal of N and S was achieved in the present study even with a short washing time, and this is comparable with the results of Ma et al. [14], even though they washed wheat straw for much longer durations (180 min).

Better removal was observed for Cl, Ca, P, S, and N upon increasing the S:L ratio in the washing pre-treatment. Some 4–11% better removal was achieved for Cl upon increasing the S:L ratio compared to 1:15. Cl leaching is influenced by the competitive leaching of other ions, such as NO_3^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^- [7,26]. This competition reduces on increasing the dilution ratio, which may be the main reason behind the improved leaching of Cl at higher S:L ratios. With a washing time of 10 min, the highest removal of Cl (84.4%) was achieved at 1:50 S:L. Similar removal was only achieved after washing for either 60 min or washing for 10 min at 80 °C.

Due to the higher removal of S and Cl on increasing the S:L, a lower corrosion risk can be expected from the treated wheat straw samples (Fig. 3). K removal was not much affected by the dilution ratio, and its removal with 10 min of washing remains somewhat similar even after increasing the dilution ratio fivefold. Similar findings were also reported by Ma et al. [14], where an insignificant change was also observed for K on increasing the S:L from 1:10 to 1:50. For Ca, 5.8–12.1% better removal was achieved on increasing the S:L. Even though increasing the S:L resulted in the greater removal of Cl, Ca, S, N, and ash, the effect of S:L on the fouling and slagging propensity was negligible to negative. At 1:30 S:L and 1:40 B/A, the ratio is even higher than 0.5, which means there may be considerable fouling problems upon boiler combustion. At 1:15, 1:20, and 1:50 S:L, the B/A was just below 0.5, which means some fouling in the boilers. Even though for the washing cases slagging propensity is low, increments in S_i were observed for 1:30 and 1:40, which is inappropriate when considering washing as a pre-treatment.

3.3. Optimal parameters for washing and suggestions for industrial scale washing pre-treatment

The results from both Part 1 and 2 of the present study indicate that the washing pre-treatment substantially improves the composition and fuel quality of wheat straw. Based on results it is clear that the washing duration, biomass size, washing temperature, and S:L have a significant impact on the efficiency of the washing pre-treatment. For industrial applications, these parameters can be varied to improve the pre-treatment affectability and for cost reduction. As per the results of the present study, longer durations of washing small-sized wheat straw shows the maximum improvement in fuel properties and fouling tendency. However, longer washing durations also lead to various complications, such as the lower per day production of treated feedstock and the requirement for a bigger reactor to meet the high demand for the treated biomass. This may result in lower productivity and/or higher capital and operational costs. Moreover, longer washing times lead to higher mass loss with a slight improvement in HHV, resulting in higher energy losses, as observed in Part 1 [27] and shown in Table S1. Furthermore, even after increasing the washing duration fivefold beyond 10–30 min, less than 10% more removal was achieved for ash, K, Cl, N, S, and Ca. Therefore, increasing the washing time beyond 30 min may not be feasible when comparing the energy input and improvement in the feedstock quality. When considering feedstock size for the washing pre-treatment, a smaller sample size (<1 cm) shows better improvement in fuel quality compared to larger sizes (Part 1). However, a smaller feedstock size requires a lot of extra energy in grinding [13], and it is difficult to pelletize [12], also leading to higher mass and energy losses in washing when compared to a larger feedstock size (>1 cm). Furthermore, small-sized biomass is difficult to separate from water and requires complex separating equipment, which may result in extra capital and operational costs.

For the abovementioned reasons, a short washing duration and large sample size seem to be beneficial for industrial applications. Based on the results of the present study, a washing time of <30 min and a sample

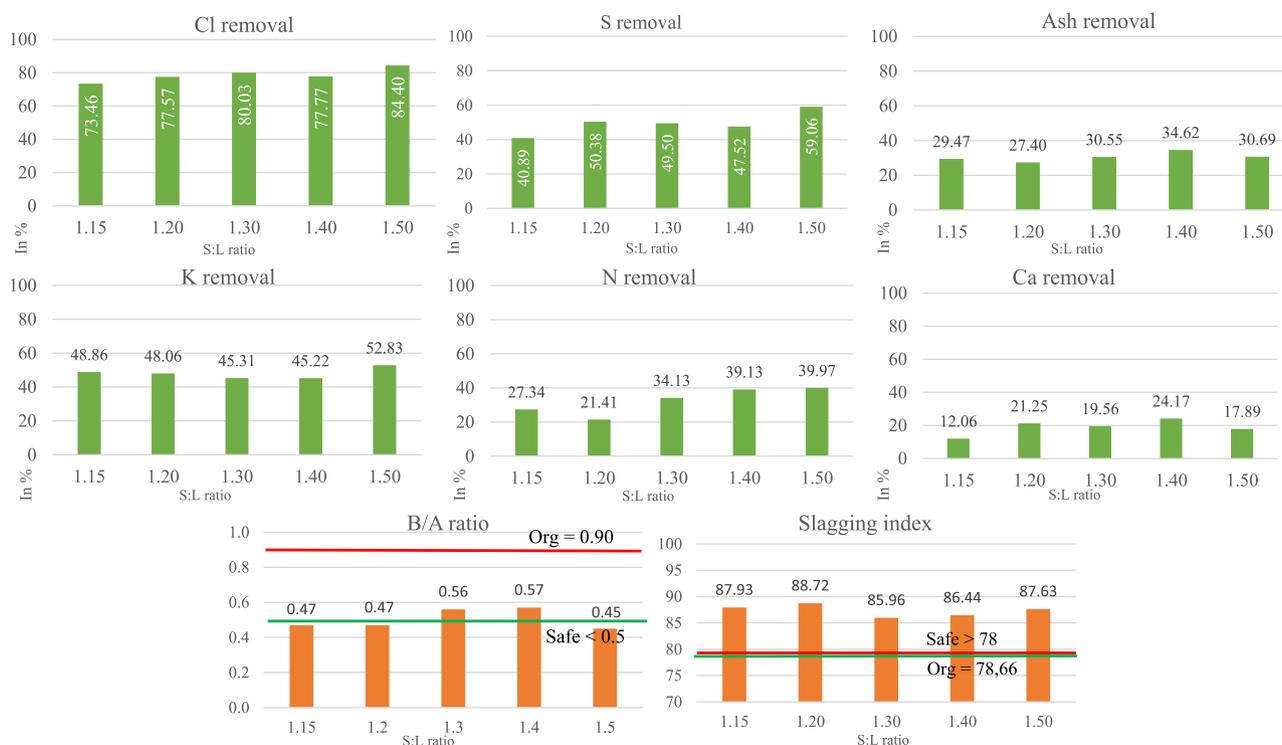


Fig. 3. Effect of solid-to-liquid (S:L) ratio variation on (a) chlorine removal, (b) sulphur removal, (c) ash removal, (d) potassium removal, (e) nitrogen removal, (f) calcium removal, (g) B/A ratio, and (h) slagging index.

size of ≥ 1 cm can be used, as they also show substantial improvement in fuel properties and composition. Reductions in the fouling, slagging, and corrosion propensity and improvements in fuel quality can be achieved with short washing times and larger sizes by raising the washing temperature and S:L, as shown in the present study. However, higher S:L ratios and washing temperatures require more water and extra energy for heating. Furthermore, greater energy loss was also observed at higher temperatures. For such reasons, wheat straw can be washed for 10 min at 40 °C with a 1:15 S:L ratio, as this showed the least energy loss and fouling propensity among all temperature variants. An S:L of 1:15 should be used for washing, as greater S:Ls show a higher fouling propensity and may result in extra costs and a larger environmental footprint due to the high water demand of the process. So, as per the results of the present study, 3 cm sized wheat straw samples washed for 10 min at 40 °C with a 1:15 S:L ratio is recommended for industrial applications. For washing biomass at the power plant, cooling water from the condenser can be used, as it ranges from 30 °C to 50 °C. If higher washing temperatures are needed, they can be achieved by heating water using the excess heat resulting from the steam extracted from the turbine [7].

As most of the studies published earlier on the washing pre-treatment have only considered longer washing durations (>30 min) and with a higher S:L ratio ($>1:20$), their results are not directly comparable to the present study. Furthermore, very few studies have provided recommendations for optimal washing parameters for lab or industrial-scale washing. Deng et al. [7] recommend washing of biomass for 3 h with high water temperature and 1:80 S:L ratio. Similar to the findings of the present study, they also found higher removal of ash, K and Cl with temperature increment. Ma et al. [14] recommend washing for 3 h with higher S:L ratio (1:50 S:L ratio) as it shows better improvement in fuel properties on increasing S:L ratio which was also observed in the present study. A recent study published on water washing of rice husk by Bandara et al., [28] recommend washing for 15 min with 50 °C, 1:80 S:L ratio and size 1 mm. Compare to these studies removal found in present study for K, Cl, S, P and ash was found slightly to considerably less (0–30%). Even though removal of the troubling elements in the present study is relatively less compare to past studies, B/A and S_i values are still low which means fewer problems related to fouling and slagging. Possible reason behind less removal of the ash and troubling elements in the present study may be the higher amount of water used (1.5 to 6 time more), smaller biomass size (5–300 times small), and/or longer washing durations (18–36 times more). But utilizing such high amounts of water, shredding to very small sizes and washing for longer periods may not be economically and environmentally feasible for industrial processes as earlier mentioned in the present section. In that aspect, present shows sufficient improvement in the fuel properties of the wheat straw with much lower washing time and water requirement.

3.4. Limitations and further scope of the washing pre-treatment

Washing is an effective and uncomplicated pre-treatment method to improve fuel quality, but certain issues need to be resolved when using washing in larger applications. The large quantities of wastewater resulting from the pre-treatment could be a challenge, as the water cannot be disposed directly due to the considerable organic and inorganic impurities [22,29]. Therefore, treatment of this wastewater is important in order to reuse and/or dispose of the wastewater. Jenkins et al. [29] have tried to treat the washing leachate using reverse osmosis, while Yu et al. [22] have identified various organic and inorganic compounds present in the leachate, thus providing a fairly good initial idea about its nature. However, in order to manage and treat the wastewater efficiently, detailed characterization of the leachate is essential, which is still missing from the literature. The treatment of wastewater may result in extra costs, which may reduce the economic feasibility of the washing pre-treatment. To overcome these extra costs, the recovery of product or reuse of wastes can be applied, as the

wastewater has some nutrient and product value due to the presence of S, N, K, and P [7,10]. To evaluate such different prospects, detailed wastewater characterization is essential, and it is currently under research at our laboratory. Another issue with washed feedstock is the high moisture content, which limits its direct use in boilers and also causes some handling issues. However, problems related to high moisture content can be resolved by drying using hot stack gases [7], air-drying, or utilizing waste heat from the plant.

The present study shows the in-depth effects of different parameters on the washing process and how they can be used to increase the washing efficiency. The practical applicability of washing for industrial processes was also considered in this study. However, there are many further opportunities to improve the applicability of the washing process in industrial applications. One is washing the biomass in multiple steps, where each step consists of short washing durations. Even though single-step washing significantly improves the biomass quality, a certain amount of fouling and corrosion can still be expected from the treated feedstock due to the considerable alkali and chlorine left in the biomass and the lower reliability of the indexes [8,21]. Depending on the boiler-type and configuration, the boilers may have a lower tolerance to alkali and chlorine content, in which case more intensive biomass pre-treatment is required than single-step washing. In such cases, multiple-step washing may be a solution that might possibly result in a more significant improvement in fuel quality. For this reason, multiple-step washing needs to be explored further. The authors are presently working on washing in multiple steps, and the present study could serve as a basic study for enhancing the washing pre-treatment. From the results of the present study, it is clear that the washing of wheat straw is a two-stage process. However, proper kinetic study and modelling is still required to clearly understand the elemental removal phenomenon and to modify the washing pre-treatment.

4. Conclusion

Short washing durations and a larger feedstock size are favourable for practical and industrial-scale implementation of the washing pre-treatment. However, these parameters still require further modification, as low to moderate fouling, corrosion, emission and ash-related issues in boilers still remains a challenge. In the present study, the effect of the washing temperature and S:L ratio on the efficiency of washing was evaluated for short washing durations (5 and 10 min) with a larger sample size (3 cm). Based on the outcomes of the present study, the following conclusions can be drawn:

1. Washing temperature has a very high impact on all the fuel properties. On increasing the washing temperature, improvements in C, HHV, and the fouling, corrosion, and slagging propensity were observed for the wheat straw, while a higher removal of Cl, S, K, N, Ca, P, and ash was also observed. The least amount of fouling and slagging can be expected when washing the wheat straw for 10 min at 40 °C and 80 °C, as these temperatures showed the highest removal of troubling elements with a lower energy loss.
2. The S:L ratio also has a direct impact on the washing efficiency, and increasing it resulted in an even higher removal of Cl, S, ash, and N compared to lower S:L ratios. However, on comparing the fouling and slagging propensity of the sample washed at a higher S:L ratio, a negative to slight improvement was observed. Thus, a 1:15 S:L ratio seems sufficient for practical applications, as it shows high washing efficiency, the smallest water footprint, and reduced wastewater treatment costs.
3. A longer washing duration and smaller feedstock size may lead to several complexities and extra costs when applied on an industrial scale. As per the results of the present study (Parts 1 and 2), a larger sample size and shorter washing duration also result in high washing efficiency, which can be further improved by increasing the washing temperature. For industrial applications, the washing of 3 cm sized

wheat straw for 10 min at 40 °C with a 1:15 S:L is recommended for the washing pre-treatment.

- To further improve the feasibility and efficiency of the washing pre-treatment for industrial applications, further research work is still required on the characterization and treatment of wastewater and stepwise washing. For future research purposes, the present study will be a valuable contribution for understanding, exploiting, and modifying the washing pre-treatment for wheat straw and other herbaceous residues.

Funding

The present work was carried out as part of the doctoral school of industrial invocation (DSII) at Tampere University. This work was funded by Tampere University and Valmet Technologies Oyj, which are also collaborator in this research project.

CRediT authorship contribution statement

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

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.

Acknowledgements

The authors would like to acknowledge Maria Goossens and Anubhuti Bhatnagar for their help in the preparation of the manuscript and suggestions for improving the overall experimental study. The authors also like to express our gratitude to Tuomo Hilli and Mikko Varonen from Valmet for their help in development of the methodology and arranging feedstock for the washing experiments. We would also like to express our gratitude to Pasi Arvela, Essi Sariola-Leikas, and Henrik Toivanen for their support in the analysis of the treated feedstock.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2021.120209>.

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