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A review of the mitigation of deposition and emission problems during biomass combustion through washing pre-treatment.

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Abstract

Pre-treatment of biomass via washing has shown to reduce the ash deposition and air-borne emissions. Particle size and temperature are important parameters to consider when washing biomass. Washing removes the problematic chemical species like K Na, Ca, Mg, Fe, Cl, S and P from the biomass. Hot water washing improves the removal efficiency of these metals, therefore increasing the ash melting temperatures. Removal of S and Cl reduce acid gases formation and hence corrosion in boilers and associated environmental impact.

Keywords: biomass, ash, air-borne emissions, washing, temperature, ash-melting.

Highlights:

There is significant reduction in ash content after washing.

Problematic elements during combustion such as; K, Cl and S are removed

Hot water washing accelerates the removal of chemical species from biomass.

Washing can be a positive solution to utilising waste wood for power generation.

1. Introduction

Biomass, especially in the form of white wood pellets, has become an internationally traded fuel for the growing needs of the bioenergy industry. In many of the industrialised countries, the UK included, bioenergy has become embedded in Government strategies for reducing greenhouse gas emissions from electricity, heat and transportation [1]. A major and growing market is white wood pellets for electricity generation, particularly for co-firing with coal in large coal boilers, or for situations such as complete conversion of coal units to biomass. White wood pellets are desirable for a number of reasons: pelletisation improves the volumetric energy content of the biomass and lowers the cost and carbon emissions associated with transportation and handling; regularly shaped pellets can be handled more easily than chip; energy requirements are lower for milling pellets to small particle size for pulverised fuel boilers; white wood pellets have standardised specifications [2] and so can meet the stringent requirements of the utility companies to minimise issues of deposition and corrosion. The main elements of concern are chlorine, sulphur, and alkali metals, as well as nitrogen, because of its impact on NO_x emissions. Pellets for non-industrial use (i.e. fuel for

smaller appliances for domestic, small commercial and public sector building installation) are covered by EN 14961-2 [3] This is sub-divided into three main classes: Class A1- covers pellets manufactured from virgin timber and chemically untreated wood residues and is low in ash, nitrogen and chlorine. It consists of virgin sawdust from the stem wood (bark removed) or untreated timber. Class A2 is similar to A1 but with slightly higher ash, nitrogen and chlorine levels and largely consists of tree chippings, including bark. Class B covers pellets containing some proportion of chemically treated and used wood with heavy metal content below specified threshold levels and uses recycled wood. Class C is not suitable for these applications and is contaminated by paint or preservative. It must be burned in industrial plant.

Whilst the supply of wood chips is on an internationally traded basis the recycled wood is more on a local supply basis. The quantities available are quite considerable and in the UK is about one Mty^{-1} of waste wood which is suitable as a fuel. Previously most of the pre-treatment of biomass via washing has been done for agricultural residues but further studies are now being conducted on woody biomass. In order to tackle the deposition and corrosion problems, biomass is pre-treated using various technologies to improve its properties. This paper reviews the pre-treatment of biomass via washing.

2. Biomass Properties

2.1 Biomass Composition

Tables 1 summarises some typical ranges of compositions for different types of biomass. It is clear that there can be wide variation, and this depends not only on the type of biomass, but also on other factors such as, the geographical location and soil type, the age of the wood and the amount of wood and bark in woody biomass. In the case of agricultural residues from some industrial processes; the amount of shells, husks and pits and the way in which the crops are processed also influence their composition [4]. Work on energy crop agronomy has shown that inorganics can also vary with fertilizer treatment and time of harvest, as well as the part of the biomass (leaf, stem etc) [5-10].

2.2 Ash composition and deposition problems during combustion

Typical ash compositions are given in Tables 2-4 for different biomass. In Tables 2 to 4, the slagging and fouling indices have been calculated by the authors of this paper. The major elements are the essential minerals for plant growth and include Si, Ca, K, Al, Fe, Mg, Ti, Na, P and S. Essential minor minerals make up the trace elements of the biomass, although some also arise through contamination. Waste wood can pose unique problems because of potential contamination from paint, plastic and preservatives (the latter affecting the copper chromium and arsenic concentrations (CCA)). Table 5 indicates typical levels of trace metals in a selection of biomass.

Table 1 Ultimate analysis of various biomass and solid waste fuels [11]

Fuel Sample	Ultimate analysis (db)							Proximate analysis (a.r. or db)			
	C	H	N	S	Cl	O	HHV	Moisture	Ash	Volatile matter	Fixed carbon
Woody											
Eucalyptus (Grandis)	48.33	5.89	0.15	0.01	-	45.13	19.35	-	0.52	-	16.93
Pine chips	52.8	3.1	0.5	0.09	-	40.5	21.2	-	6	72.4	21.6
Sawdust	49.8	6	0.5	0.02	-	43.7	19.83	-	1.1	84.6	14.3
Sawdust	46.9	5.2	0.1	0.04	-	37.8	18.14	-	2.6	76.2	13.9
Spruce bark	53.6	6.2	0.1	0.1	0.03	40	21.57	-	3.2	73.4	23.4
Spruce wood	52.3	6.1	0.3	0.1	0.01	41.2	20.95	-	0.5	81.2	18.3
Energy Crops											
Miscanthus	48.4	6.3	0.3	0.1	0.13	43.3	19.6	11.5	2.8	66.8	15.9
Poplar	50.2	6.1	0.6	0.02	0.01	40.4	19.02	9.2	2.7	84.8	12.5
Reed canary grass	46.87	6.01	0.39	-	<0.3	40.66	17.15	-	5.4	76.28	14.34
Switchgrass	46.94	6.27	0.43	-	<0.3	43.26	17.82	-	4.62	73.05	15.16
Willow	49.9	5.9	0.6	0.07	0.01	41.8	19.6	13.6	1.7	82.2	16.1
Agricultural Residues											
Alfalfa Stems	47.2	6	2.7	0.2	0.5	38.2	18.7	9.3	5.3	78.9	15.8
Almond Shells (dry)	49.3	6	0.8	0.04	0.01	40.6	19.5	7.8	3.3	76	20.7
Barley Straw	49.4	6.2	0.7	0.13	0.27	43.6	19.75	-	5.3	76.2	18.5
Pistachio Shells(dry)	50.2	6.3	0.7	0.2	0.01	41.1	18.2	-	1.4	81.6	17
Rice Husks	38.8	4.8	0.5	0.05	0.1	35.5	15.8	4	20.3	63.5	16.2
Rice Straw	38.2	5.2	0.9	0.2	0.6	36.3	15.1	9	18.7	65.5	15.9
Switchgrass	46.7	5.8	0.8	0.2	0.2	37.4	18.1	13.3	9	76.7	14.3
Wheat Straw	44.9	5.5	0.4	0.2	0.2	41.8	17.9	9.7	7	75.3	17.7
Imported residues											
Olive Cake	52	6.9	1.6	0.2	0.2	29.4	23	6.4	10.4	66.3	16.9
Olive Pits (dry)	52.8	6.7	0.5	0.05	0.04	38.3	21.6	6.1	1.7	82	16.3
Palm Kernel	46.4	6.1	38.1	2.8	0.2	38.1	19.8	5.9	3.5	80.3	10.3
Sugar Cane Bagasse	48.6	5.9	0.2	0.04	0.03	42.8	19	10.4	2.4	85.6	12
Wastes											
Animal Waste	43.4	5.7	4.5	0.6	-	41.1	-	-	-	-	-
Cardboard	42.2	5.6	0.2	0	*	44.8	14.5	5	6.8	82.1	6.02
Copy paper	40.8	5.7	0.21	0	*	46.6	13.8	4	6.4	79.4	10.1
HDPE	85.4	11.4	0.1	0	-	-	45.2	0.1	0.1	83.5	16.3
LDPE	84.1	12.2	0	0	-	-	45.7	1.1	0.3	98.4	0.2
Magazine paper	35.5	4.6	0.45	0	*	36	12.3	2.1	23	66.7	8.2
Meat and bonemea	43.4	6.4	9.2	0.4	0.3	-	15.5	6	20	64	10
Newspaper	44.1	5.6	0.17	0	*	40.7	15.9	5.4	8.9	76.9	8.75
Polyamide (PA)	62.7	9.7	10.7	0	-	5.1	32.6	0	0	100	0
Polycarbonate (PC)	74.1	5.5	0.2	0	-	6.5	32.2	0	0	100	0
Polyethylene (PE)	85.7	14.3	-	-	-	-	44.6	0.1	0.1	97.3	2.5
Polyethylene-terephthalate (PET)	62.8	4.3	0.07	-	-	32.8	23.2	0.1	0	97.6	2.3
Polypropylene (PP)	84.4	-	0.3	0	-	-	39.1	0.2	7.6	85.9	6.3
Polystyrene (PS)	90.7	7.7	0.05	0	-	1.5	42	1.2	6.5	83.4	8.9
Polyvinyl chloride (PVC)	35.9	4.4	0.1	0	56.7	-	18.1	0.99	10.4	79.1	9.6
RDF 1	51.3	7.5	0.8	0.21	0.6	29.7	23.1	6.9	41.5	44.6	7
RDF 2 (proximate, dry)	56.3	4.7	1.7	0.13	0.6	20.2	22.4	5.2	52.8	42.6	4.6
Recycled paper	41.9	5.5	0.27	0	*	39.5	15.2	7.5	11.9	75.8	4.81
Scrap tyres	85.9	8	0.4	1	0.1	2.3	40	0.8	2.4	66.5	30.3
Sewage Sludge 1 (dry)	52	6.3	6.3	3.1	0.12	32.1	21.7	6.8	32.4	59.2	8.4
Sewage Sludge 2	44.7	7.2	6.8	2.3	-	39	18.6	12.2	22.5	57	8.3
Sewage Sludge 3	55.3	7.8	9.8	1.4	-	25.8	24.6	-	-	-	-
Tetra Pak	48	6.3	0.08	0	0.09	39	18.5	1.3	16.1	71.9	10.7

a.r As received basis

db dry basis

*Range of 0.1-10%; average value ~ 2% for the paper content of MSW

Table 2 Example of ash compositions and ash melting characteristics of some woody biomass

	Pine [12]	Pine chips [13]	Spruce wood [13]	Spruce bark [13]	Eucalyptus [12]	Willow wood [14]	Hybrid Poplar [14]	Poplar [12]
Ash composition (%)								
SiO ₂	52	68.18	19.3	6.13	41	2.35	5.9	2.8
Al ₂ O ₃		7.04	9.4	0.68		1.41	0.84	
TiO ₂		0.55	0.1	0.12		0.05	0.3	
Fe ₂ O ₃		5.45	8.3	1.9		0.73	1.4	
CaO	13	7.89	17.2	72.39	18	41.2	49.92	33
MgO	4.5	2.43	1.1	4.97	4.2	2.47	18.4	3.7
Na ₂ O	1.9	1.2	0.5	2.02	1.9	0.94	0.13	0.14
K ₂ O	7.9	4.51	9.6	7.22	8.7	15	9.64	18
SO ₃		1.19	2.6	1.88		1.83	2.04	
P ₂ O ₅		1.56	0.1	0.12		7.4	1.34	
Slagging and fouling indices								
Alkali index (kg alkali/GJ)		0.16	0.02	0.14		0.14	0.14	
Base to acid ratio		0.28	1.27	12.77		15.84	11.29	
Base percentage (%)		21.48	36.7	88.5		60.34	79.49	
Ash fusion temperatures (°C)								
Deformation	1190				1160	lapses at 1190		>1400
Hemisphere	1220				1190			>1400
Flow	1280				1230			>1400

Table 3 Example of ash compositions and ash melting characteristics of some herbaceous biomass and straws

	Miscanthus [15]	Switchgrass [14]	Switchgrass [14]	Reed canary grass [14]	Wheat straw [14]	Barley Straw [16]	Barley straw [13]	Rape straw [13]
Ash composition (%)								
SiO ₂	33.8	61.3	65.18	75	55.32		50.78	40.8
Al ₂ O ₃	0.35	0.85	4.51	0.37	1.88		0.67	5.45
TiO ₂	0	0.09	0.24		0.08		0.08	0.29
Fe ₂ O ₃	0.31	0.93	2.03	0.04	0.73		0.95	2
CaO	6.2	16.5	5.6	9.13	6.14		9.89	30.68
MgO	6.55	2.82	3	1.95	1.06		2.87	2
Na ₂ O	0.73	0.75	0.58	0.25	1.71		1.39	0.44
K ₂ O	37.9	2.76	11.6	2.87	25.6		28.18	13.45
SO ₃	5.54	2.56	0.44	1.82	4.4		2.22	2.67
P ₂ O ₅	2.01	3.27	4.5	4.09	1.26		2.97	2.22
Slagging and fouling indices								
Alkali index (kg alkali/GJ)	0.26	0.09	0.6	0.1	1.07		0.79	0.32
Base to acid ratio	1.51	0.38	0.33	0.19	0.62		0.84	1.04
Base percentage (%)	51.7	23.76	22.81	14.24	35.24		43.28	48.57
Ash fusion temperatures (°C)								
Deformation	920				850	925		
Hemisphere	1070				1120	n/a		
Flow	1110				1320	1100		

Table 4 Example of ash compositions and ash melting characteristics of some residues and wastes

	Sugar cane bagasse [12]	PKE [4]	Olive residue A [4]	Olive residue C [4]	Sunflower [12]	Sunflower shell [17]	Sunflower husk [13]	Sawdust [13]	Furniture waste [18]	Forest residue [18]
Ash composition (%)										
SiO ₂	46.61	16.51	21.1	67.4	11	29.3	23.66	26.17	57.62	17.78
Al ₂ O ₃	17.69	0.87	1.94	2.74		2.9	8.75	4.53	12.23	3.55
TiO ₂	2.63	n/a				0.1	0.15	0.4	0.5	0.5
Fe ₂ O ₃	14.14	5.7	2.14	5.29		2.1	4.27	1.82	5.63	1.58
CaO	4.47	11.9	15.44	19.49	17	15.8	15.31	44.11	13.89	45.46
MgO	3.33	11.51	5.78	5.25	3.8	6.1	7.33	5.34	3.28	7.48
Na ₂ O	0.79	0.41	0.47	0.35	0.55	1.5	0.8	2.48	2.36	2.13
K ₂ O	0.15	21.43	31.04	4.41	24	35.6	28.53	10.83	3.77	8.52
SO ₃	2.08	n/a	n/a	n/a		1.3	4.07	2.05	1	2.78
P ₂ O ₅	2.72	n/a	n/a	n/a		4.8	7.13	1.82	0.5	0.44
Slagging and fouling indices										
Alkali index (kg alkali/GJ)	0.06	0.48	1.57	0.69		0.78	0.45	0.07	0.1	0.2
Base to acid ratio	0.36	2.93	2.38	0.5		1.89	1.73	2.08	0.41	2.99
Base percentage (%)	22.88	50.94	54.87	34.79		61.1	56.24	64.58	28.93	65.17
Ash fusion temperatures (°C)										
Deformation		1070	1080		740			1270		
Hemisphere		1140	1350		1360			1410		
Flow		1180	1360		1390			1430		

Table 5 Inductively Coupled Plasma-Mass Spectrometry ICP-MS determination of trace elements in a selection of biomass (expressed as ppm, on as received basis) [11]

Trace elements (ppm db)	Olive residue	Hazeln ut shell	Cotton residue	Wood-			Sewage Sludge	Waste wood Typical Range	Recommendation for quality sorted waste wood
				Straw (ar)	bark (ar)	RDF			
As	0.72	0.29	0.12	< 0.10	0.44	5	10		
Be	14.7	18.2	2.27	< 0.10	0.07				
Cd	0.017	0.04	0.022	< 0.15	0.2	<1	2	0.3-3.0	<1.0
Co	0.527	0.38	0.472			<2	3		
Cr	8.98	1.82	2.23	2.49	26	8	62		
Cu	15.3	7.9	11.3	3.16	87.3	35	829		
Fe									
Hg				0.009	0.034	<2	<2	Up to 0.4	<0.3
Li	0.776	0.118	0.136						
Mn	26.2	106.3	17.1	20.4	414				
Mo	0.25	0.13	1.61	0.42	1.26				
Ni	5.1	1.97	2.8	0.9	10	2	32		
P	907	146	7361						
Pb	3.24	3.53	1.22	2.64	3.06	50	211	50-400	<100
Sb	0.144	0.066	0.028						
Se	<0.18	<0.18	<0.18	< 0.20	< 0.80				
Sn	0.616	0.11	1.455						
Tl	0.016	<0.003	<0.003	0.002	0.086				
V	2.91	1.05	5.3	0.82	2.81				
Zn	14.8	22.8	32.2	30.9	150	85	567	200-1200	<200

ppm parts per million
a.r as received
db dry basis

The impact of the different mix of inorganics in biomass compared to typical coal ash composition is well documented (e.g. [12-14]). Different elements have different volatility; particularly volatile are the alkali chlorides. Gas phase reactions can lead to alkali sulphates, and these together with the chlorides are key species responsible in slagging, fouling and corrosions. Different ash chemistry leads to liquid or sticky ash particles with also form furnace deposits.

Biomass ash often has a low melting temperature leading to slagging and fouling, depending on the temperature and site that deposition occurs. Slagging is associated with the fusion and sintering of ash particles in the high temperature (radiative sections) of the boiler. Particles entrained in the flue gas impinge on boiler tubes and walls and can adhere depending upon the state of the particle and the surface in question. If either the particle or the surface is molten or sticky then the particle sticks by inertial impaction [15]. The temperature at which the ash softens is determined from the ash fusion test, and some measurements of this are given in Tables 2-4. Initial deposition rate is slow onto the clean and relatively cool surface, but it increases as the surface deposit gets thicker and the outside surface temperature increases. The base/acid ratio ($R_{b/a}$) is also a good indication of the ash fusibility and some values of this are also given in Tables 2-4. In the $R_{b/a}$, b indicates the sum of the basic oxides in the ash while a indicates the sum of the acidic oxides in the ash. It is given by

$$R_{b/a} = \frac{\%(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})}{\%(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)} \quad (1)$$

The correlation between ash melting temperature and base-acid ratio for coal tends to be parabolic with a minimum of 0.75. The ratio is less well validated for biomass fuels, but it is likely that the eutectic appears at lower base/acid ratio values [16]. Thus, normally a low melting temperature ash would have a $R_{b/a}$ of 0.4-0.6 [17]. Phosphorus is not included in the $R_{b/a}$ ratio since it was developed for coals originally (with low P content).

While considering the slagging in boilers, Fe_2O_3 in the fly ash is considered to be basic [16] but in the concrete industry it is considered to be acidic. In the case of biomass ash, the concentration of Fe_2O_3 is fairly low and hence has no significant effect on the slagging in boilers.

The alkali metals volatilise at low temperatures forming gaseous chlorides, hydroxides and sulphates dependent upon the temperature of the gas phase [19, 20]. The fate of these gas phase species is multifaceted: They can deposit onto small ash particles making a sticky coating at high temperature and encouraging these particles to stick to furnace walls and superheater tubes. The deposits can become very thick such that a temperature gradient forms across them and the deposits start to form different sintered, strong phases which are very difficult to remove, and lower the efficiency of the boiler [12, 15]. The alkali vapours might pass to the convective section of the boiler where they condense and foul the heat exchanger tubes. This can result in corrosion, as redox reactions shuttle chloride through the scale layer of the boiler tubes which then reacts with the steel [12]. Some alkali vapours may pass through the furnace entirely and form aerosol particles which are not as efficiently captured by dust removal systems.

Other indices [21], also derived from correlations of coal ash behaviour, include the slagging index, R_s , and the ratio-slag viscosity index S_i .

$$R_s = \%S(dry) \left(\frac{B}{A} \right) \quad (2)$$

Here $R_s < 0.6$ indicates low slagging propensity, $R_s = 0.6-2.0$ indicates medium slagging propensity, $R_s = 2.0-2.6$ indicates high slagging risk, and $R_s > 2.6$ indicates extremely high slagging risk.

$$S_i(\%) = \left(\frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \right) \times 100 \quad (3)$$

A high ratio-slag viscosity index indicates a high viscosity and therefore a low risk of slagging. Indicators are as follows: $S_i > 72$ = low slagging risk; $72 \geq S_i > 65$ = medium slagging risk; $S_i \leq 65$ = high slagging risk.

Fouling is ash deposition in the convective section of the boiler and can be indicated by the alkali index (AI):

$$AI = \frac{1}{GCV} F_{ash} (F_{K_2O} + F_{Na_2O}) \quad (4)$$

Where GCV is expressed in $GJkg^{-1}$, F_{ash} is the mass fraction of ash in the fuel (dry basis), and F_{K_2O} and F_{Na_2O} are the mass fractions of K_2O and Na_2O in the ash. It has been suggested that above $0.17 \text{ kg alkali } GJ^{-1}$ fouling is probable, and above $0.34 \text{ kg } GJ^{-1}$ fouling is virtually certain to occur (12). Some calculated fouling indices are also given in Tables 2-4, and Fig 1 displays some of these also.

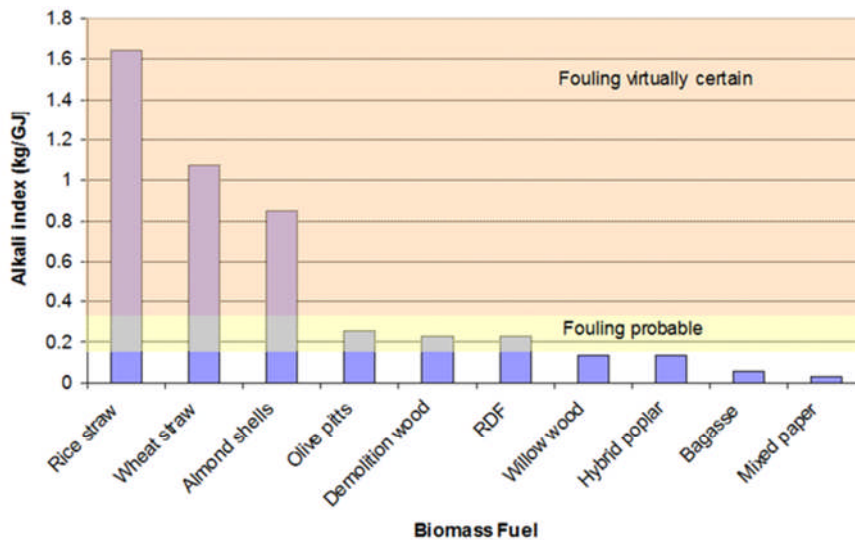


Fig 1 Calculated alkali indices of some biomass fuels

The Fouling Index is given by:

$$F_u = \frac{B}{A}(Na_2O + K_2O) \quad (5)$$

Where $F_u < 0.6$ = low fouling risk, $0.6 < F_u \leq 40$ = high fouling risk, $F_u > 40$ extremely high sintering tendencies are implied [21].

The ash fusion test is a standard test developed to describe the melting behaviour of biomass ashes. A test piece made from a prepared ash is heated at constant rate and with continuous observation. Four characteristic temperatures are recorded from changes in the test piece shape, namely the shrinkage temperature (ST), deformation temperature (DT), hemisphere temperature (HT) and flow temperature (FT).

3. Biomass Emissions before and after pre-treatment

3.1 Emissions from Biomass Combustion

Biomass contains volatile trace metals which can also pass to the flue and be emitted to atmosphere. This is a particularly important consideration for Waste Incineration Directive (WID) compliant plant where fuels might have higher levels of heavy trace metals. Trace metals are classified according to their volatility as indicated in Fig 2. There is overlap between the groups, and some studies report different partitioning to others. This is not surprising since partitioning is influenced by chemical interactions as well as operating conditions. E.g. chlorine increases volatility of trace metals through the formation of metal chlorides.

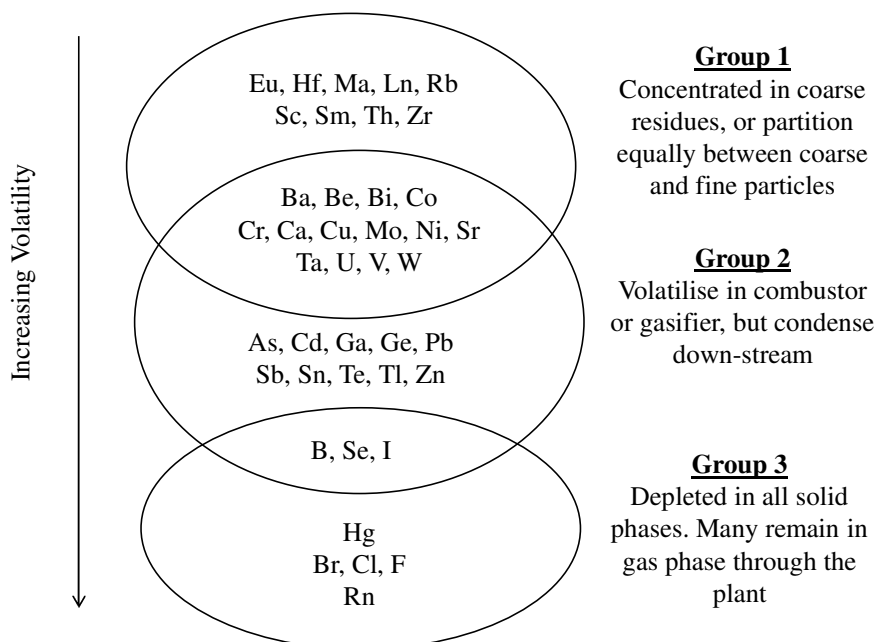


Fig 2 Classification of trace elements by their partitioning into groups of different volatility during combustion and gasification (Adapted from [22])

Apart from inorganic emissions, organic emissions can be of concern, particularly for small scale boilers [23]. Biomass degrades, upon heating to produce volatiles and tars which can react further to produce polyaromatic hydrocarbons (PAH) and soot. This can proceed by a number of routes depending upon the temperature, residence time and the local stoichiometry. During the combustion of the biomass both pyrolysis and oxidative pyrolysis of the biomass components occurs with the release of tars and vapours. The initial products obtained are a function of the composition of the biomass, the water content and the level of excess air. The extent of incomplete combustion and hence the level of the emissions can be controlled by the design features ensuring mixing of the fuel and air [24]. If the temperature is low (below $\sim 700^{\circ}\text{C}$) as might be the case in small cook stoves and units based on smouldering combustion, and there is poor mixing then compounds in the bottom half of Figure 2 dominate in the smoke. At higher temperature (above $\sim 900^{\circ}\text{C}$) which would be the case in larger domestic combustors and industrial furnaces, emissions of pyrolysis products decrease and compounds in the top half of Fig 2 become more dominant.

3.2 Approaches to mitigate deposition/emission problems

A number of approaches have been explored to mitigate the deposition/corrosion and emission problems during combustion. These include:

1. The use of blends to modify ash behaviour and help retain volatile metals in the ash. This approach has also been used to adjust the S/Cl ratio to help limit corrosion [25].
2. The use of additives that seek to change the chemical composition of the ash and so the melting temperature, and potential for release of volatile components. Typical additives are Al-Si-based (e.g. kaolinite), S-based (e.g. ammonium sulphate), P-based, or Ca-based [26].
3. Lowering the concentration of key elements before the fuel enters the boiler to mitigate the ash and emission problems using pre-treatment methods. This can be done by pre-treatment via washing in order to upgrade low-grade biomass for heat/electricity generation.

Inorganics in biomass can be categorised into four groups [17]:

1. Dissolved salts that are precipitated during the drying process and include the anions and cations dissolved in the plant fluids, typically, K^+ , Na^+ , Ca^{2+} , Cl^- , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} . These salts can be redissolved and removed during water washing.
2. Organically-bound matter that are mainly metal cations that are associated with the organic polymers and include K, Na, Mn, Ca, Mg, Fe, and Al. These are capable of undergoing ion exchange in ammonium acetate solutions; Sulphur and nitrogen are associated with organic matter via covalent bonds, such as in amino acids, proteins etc. These are insoluble or only slightly soluble in water solutions. Phosphorus can be present in organic forms which may be partly soluble in acids. Chlorine may be present in organic form, especially in waste-derived fuels containing PVC.
3. Included minerals that are mineral naturally deposited during the plant growth. They include silica and different calcium oxalates. These have typically low solubility in water, but the calcium salts become more soluble in acid solutions.
4. Excluded minerals that arise from soil and foreign particles attached to the biomass. Soil material will not dissolve easily although may rinse off the fuel. This category also includes contaminants associated with waste wood, which might include PVC,

paints, glues, and preservatives. The inorganics associated with these contaminants have varying solubility depending upon their form.

There is extensive literature concerned with leaching/washing of biomass. Several authors have been interested in characterising the inorganics based on their ease of leaching using successive treatment in water, ammonium acetate and finally acid. Different pH solvents leach different groups of inorganics in a process known as selective leaching [27] There has been some success in ranking fuels in terms of their likelihood to form deposits based on the amount of easily leached (generally volatile) species [28].

Table 6 summarises some of the literature concerning leaching of different elements in water. Miles [29] also categorised inorganics into four types:

1. Refractories (Si, Ti, Al) with little or no solubility.
2. Alkali and alkaline earth elements (Na, K, Ca, Mg) with varying degrees of solubility
3. Non-metallic elements (Cl, S, P)
4. Iron

Miles and his team studied a wide range of fuels at three different laboratories following identical procedures (16 h, hot water). Fuels included almond hulls, almond shells, urban waste wood fuel blended with wheat straw, urban wood fuel blended with almond shells, olive pits, rice straw, switchgrass, non-recyclable paper and wheat straw. They found that the refractory group (Si, Ti, Al) are essentially insoluble in all the fuels investigated. The alkali metals are highly soluble in water and the authors propose that this indicates a high mobility and susceptibility to vaporisation during combustion. 50-90% of the potassium was leached through water washing of the “clean fuels”. Less potassium (~35%) was removed from the non-recyclable paper, which may be a consequence of the form it is in (i.e. clays in the glossy print). In general, sodium was removed in slightly lower percentages and there was more variability depending on fuel type. In most fuels studied, at least 40% of the sodium was leached by water washing. The alkaline earth metals (Ca, Mg) are less soluble in water, with Mg being leached to a greater extent than Ca in all fuels studied. Most fuels exhibited < 20% Ca removal, the exceptions being almond hulls (~40%) and wheat straw (~30%). Mg leaching was more variable; almond hulls, almond shells, rice straw and wheat straw all showed a high (nearly 50%) removal of Mg, and other fuels were generally less than 20% removal.

Non-metallic elements (Cl, P and S) were also investigated and results are summarised in Table 6. % removal was strongly dependent on fuel type. Chlorine was easily removed by water washing from all the fuels except non-recyclable paper (25% removed). Sulphur is present in trace amounts in most fuels but was generally found to be in soluble form in wheat straw, rice straw, almond hulls and almond shells. Lower solubility was seen for the sulphur in the woody biomass fuels. Phosphorus showed high solubility (>50% removed) from the agricultural residues and straws. Less (<25%) was removed from the urban waste wood.

Saddawi et al also studied leaching in water at room temperature for four chipped fuels (Miscanthus, wheat straw, willow, and eucalyptus) [30]. Similar findings were reported – i.e. alkali metals and chloride show high solubility. Magnesium is more soluble than calcium, but both are less easy to remove than the alkali metals. The efficiency of removal of phosphorus and sulphur appears to be very fuel dependent.

The group at Abo Akademi University have also been very active in this area and have published a number of studies [e.g. [17, 31]]. General conclusions are that potassium, sodium, chloride and phosphorus show high potential for water leaching from woody biomass (spruce, pine, birch and aspen) and agricultural residues (straws, bagasse, seeds, hulls etc.). Some calcium and magnesium can also be leached.

Specific studies on the effect of water temperature on leaching appear to be limited. Deng and co-workers [32] studied six biomass fuels, wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood and rice hull. These were soaked in water for 3 h at 30, 60 or 90°C and analysed for ash composition before and after treatment. The results, summarized in Table 7, indicate that a positive effect is observed with increasing temperature; ash weight percent decreases for all fuels as the water temperature increases. This appears to mostly arise from the removal of silica from the biomass since the efficiency of removal of this species appears receptive to elevated water temperature. The highly soluble inorganics, K and Cl are removed in high percentages at all water temperatures, but higher temperature was more advantageous for the wood fuel studied, where a significant improvement in K (from 70% to 85% removed) and a small improvement in Cl removal is observed. It is likely that the K and Cl are so soluble and accessible in the grassy biomass and residues that higher temperature produces no added benefit. Also, it should be noted that small particle sizes of fuels were used and this is likely to improve efficiencies of removal also. The effect of temperature may be more marked for larger particle sizes, but this is an area for further study.

Jenkins [27] did the early work on the influence of washing on the inorganics in straws. Their results are summarised in Table 6 and in Fig 3. Other fuels were investigated but only results for wheat straw and particularly rice straw are reported in detail. Even just spraying of the rice straw was seen to give rise to a 40-50% reduction in K, P, and Cl and a 20% reduction in Na. Soaking produced dramatic results for both rice straw and wheat straw with 80-90% removal of Cl, Na, P, and K observed together with a 70% reduction in S content. Surprisingly, very similar results were observed for rain-washed rice straw after 65mm of cumulative rain fall.

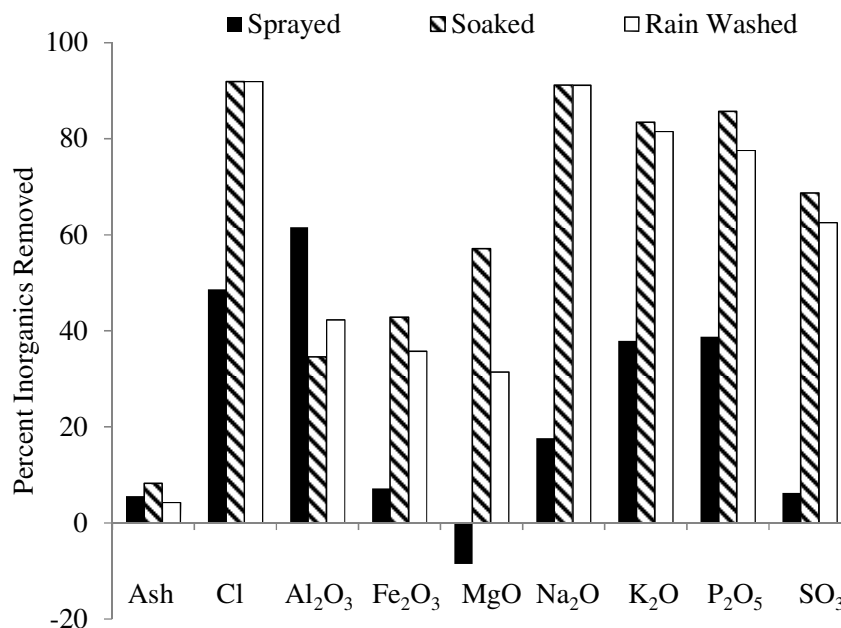


Fig 3 Influence of different washing approaches on the inorganics in rice straw [27].

Fig 3 indicates the reduction in chlorine after water washing. This together with the results summarised in Table 6 indicate the high solubility of chlorine and ease of removal by water washing most biomass. Since chlorine content is almost monotonically related to HCl emission during combustion, it is clear that water washing will be beneficial for HCl emissions and significantly reducing chlorine-mediated corrosion.

There have been few studies of the influence of time on the leaching process. Liaw and Wu [33] used a batch reactor at room temperature to leach *Eucalyptus Loxophleba* (mallee) samples (150-250 μm) and monitored for sodium, potassium, magnesium calcium and chloride as a function of time. Results were compared with a continuous flow reactor system and are summarised in Figure 4 and Table 6. Greater than 90% removal of potassium, sodium and chloride were observed within the first few minutes, equilibrium appears to be reached in less than 5 minutes.

Chromated Copper Arsenate (CCA) - contaminated wood: Chromium, copper and arsenic contamination in waste wood arises from preservatives used to give high durability to fences, decking, poles etc. by protecting insect and fungus attacks. Eventually, this wood makes its way into the waste wood stream, and can lead to leaching and dispersion if it is disposed of in landfills [34-36]. Furthermore combustion of CCA-treated wood risks the release of volatile metals into the atmosphere and/or leaching of these metals from the resulting ash [37-39]. Most studies (e.g. [40], Table 6) have found these elements to be highly mobile and can be leached through water washing. Often this is followed by approaches for capturing the leached elements from the leachate for disposal. Clearly, pre-treatment via water washing is expected to have very positive impacts on the emission of volatile trace metals from the flue during combustion. However, if the wood is high in these elements then remediation approaches for the leachate will need to be considered [40].

Table 6 Success of leaching on % removal of different inorganic elements

Fuel	Species	Solvent	Temp, Time	Size	% removed	Ref
Range of urban wastes, agricultural residues, wood, grasses and straws	Si, Ti, Al	Water	Hot plate, not boiling, 16 h, soaked	<60 mesh	Very low or not soluble	[29]
Range of urban wastes, agricultural residues, wood, grasses and straws	K, Na, Ca, Mg	Water	Hot plate, not boiling, 16 h, soaked	<60 mesh	50-90% K, 10-90% Na, 5-35% Ca, 5-60% Mg	[29]
Range of urban wastes, agricultural residues, wood fuels, grasses and straws	Cl, S, P	Water	Hot plate, not boiling, 16 h, soaked	<60 mesh	30-100% Cl, 0-95% S, 10-80% P	[29]
Range of urban wastes, agricultural residues, wood, grasses and straws	Fe	Water	Hot plate, not boiling, 16 h, soaked	<60 mesh	0-30% Fe	[29]
SRC Willow	Na, K, Ca, Mg, P, S, Cl	Water	Room temp, 20h stirred	2-4 cm chip	30% Na, 46% K, 14% Mg, 3% Ca, 56% PO ₄ ³⁻ , 10% SO ₄ ²⁻ , up to 100% Cl	[30]
Eucalyptus	Na, K, Ca, Mg, P, S, Cl	Water	Room temp, 20h stirred	2-4 cm chip	60% Na, 45% K, 18% Mg, 4% Ca, 27% PO ₄ ³⁻ , 8% SO ₄ ²⁻ , up to 100% Cl	[30]
Miscanthus	Na, K, Ca, Mg, P, S, Cl	Water	Room temp, 20h stirred	1-3 cm chopped	53% Na, 62% K, 56% Mg, 19% Ca, 49% PO ₄ ³⁻ , 33% SO ₄ ²⁻ , 84% Cl	[30]
Wheat straw	Na, K, Ca, Mg, P, S, Cl	Water	Room temp, 20h stirred	1-3 cm chopped	92% Na, 54% K, 32% Mg, 12% Ca, 0.2% PO ₄ ³⁻ , 21% SO ₄ ²⁻ , 100% Cl	[30]
Peach Stones	K, Na, Cl, Mg, Fe	Water	20°C, 8 h, soaked	?	70% Cl, 30% K, 40% Na, 50% Ca, 70% Mg, 30% Fe	[41]
Wood, forest residue, bark, waste wood	Si, Al, Fe, Ca, Mg, Na, K, P, S	Water	Room temp, soaked	< 5 mm	<10% Si, 4-15% Al, ~5% Fe, 5-15% Ca, 15-20% Mg, 35-45% Na, 50-65% K, 25-50% P, 10-30% S.	[17]
Straw	Si, Al, Fe, Ca, Mg, Na, K, P,	Water	Room temp, soaked	< 5 mm	~5% Si, ~5% Al, ~5% Fe, ~25%Ca, ~40% Mg, ~60%Na, ~80%K, ~65%P,~60% S	[17]

	S					
Spruce, Pine, Birch, Aspen (stem, bark, twigs, branch woods)	K, Na, Mg, Mn, Ca, Al, Fe, Cl, P, S, Si	Water	Room temp. 24 h stirred	< 1 mm	75% K, 65% Na, 40% Mg, 25% Mn (bark, twigs, foliage all species), 25% Ca (stem wood), 10% Al (spruce, birch, aspen), 5% Fe, 90% Cl, 65% P, 15% S, 5% Si	[31]
Wheat straw	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	30, 60, 90°C, 3h	280-450µm	Ash removal increases with temperature of the water (from 55-75% reduction). SiO ₂ removal efficiency increases with water temperature (25-65%). A small benefit for K removal with T, but >90% removed at all temps. S 85-95% removed, Cl 70-85% removed	[32]
Rice straw	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	30, 60, 90°C 3h	280-450µm	Ash removal increases with temperature of the water (from 20-40% reduction). SiO ₂ removal efficiency increases with water temperature (2-30%). A small benefit for K removal with T, but >86% removed at all temps. S 90-95% removed, Cl >90% removed at all temps.	[32]
Corn stalk	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	30, 60, 90°C 3h	280-450µm	Ash removal increases with temperature of the water (from 60-70% reduction). SiO ₂ removal efficiency increases with water temperature (65-75%). A benefit is seen for K removal with T, but >85% removed at all temps. Small benefit of water T for S: >90% removed, Cl 35-58% removed and a negative effect of T seen.	[32]
Cotton stalk	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	30, 60, 90°C 3h	280-450µm	Ash removal increases with temperature of the water (from 20-40% reduction). SiO ₂ removal efficiency increases with water temperature (2-30%). A small benefit for K removal with T, but >86% removed at all temps. S 90-95% removed, Cl also showed a benefit for hot water 85-95% removed.	[32]
Candlenut wood	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	30, 60, 90°C 3h	280-450µm	Ash removal increases with temperature of the water (from 10-30% reduction). SiO ₂ removal efficiency increases with water temperature (10-30%). A large benefit for K removal with T from 70-85% removal. S 75% removed at all temps. Small benefit from hot water for Cl 50-55% removed.	[32]

Rice Hull	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	30, 60, 90°C 3h	280-450µm	Ash removal slightly increases with temperature of the water (from 5-10% reduction). SiO ₂ removal efficiency slightly increases with water temperature (5-10%). A benefit is seen for K removal with T, from 85% to >90%. S 60-80% removed, Cl 68-85% removed, 60°C was best.	[32]
Rice straw,	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	20-25°C spray, pouring, soaking 24h	< 90 mm	Spraying: All species except Si, Ti, Ca, Mg decreased significantly: Cl 50% reduction, Na 20% reduction, K and P 40% reductions, S 10% reduction. Soaking: All species except Si, Ti, Ca decreased significantly: Cl 90%, Mg 55%, Na 90%, K 80%, P 80%, S 70% Rain washed: All species decrease except Si, Ti, Ca. Similar results to soaking observed.	[27]
wheat straw	Al, Si, Ti, Fe, Ca, Mg, Na, K., S, P, Cl	Water	20-25°C spray, pouring, soaking 24h	< 90 mm	Soaking results reported. Greater than 80% removal of Cl, Na, K and S. 37% and 53% removal of Ca and Mg respectively,	[27]
Eucalyptus Loxophleba (mallee)	Na, K, Mg, Ca, Cl	Water	Room Temp. Sampled with time	150-250 µm	Na, K, 80-95% removal; Cl 100% removal; Mg, Ca 10-30% removal. Differences seen between batch and semi-continuous operation.	[33]
Type C Red Pine	As, Cr, Cu	0.19N H ₂ SO ₄	75°C, soaked	<12 mm	1 st leaching step: 71±19% As, 69±21% Cr, 77±15% Cu 2 nd leaching step: 92±+6% As, 87±9% Cr, 94±5% Cu 3 rd leaching step: 98±+1% As, 94±4% Cr, 99±1% Cu	[40]
Empty Fruit Bunch (EFB)	K, Ca, Mg, Fe, Al and Na	Water	25, 40 and 55°C for 1, 3, 5, 10, 30,	0.31 mm	50% ash removal at 5 minutes at 25°C. No effect on ash removal of different temperatures. 71%, 52% and 23% removal of K, Ca and Mg	[42]

			60 and 120 mins, stirred		respectively at 25°C 85%, 71% and 41% removal of K, Ca and Mg respectively at 25°C Al, Fe and Na present in negligible amounts	
Palm Kernel Shell (PKS)	K, Ca, Mg, Fe, Al and Na	Water	25, 40 and 55°C for 1, 3, 5, 10, 30, 60 and 120 mins, stirred	0.72 mm	25% ash removal at 1 minute at 25°C.No further removal of ash with time. Similar trends for metals' leaching as those for EFB	[42]
Sorghum	Total halogens (Cl, Br and I), Cl,	Water	7.6L (single) 15.2L (double) and 22.8L (triple) wash, 7.6L soak	< 8mm	14% ash removal with single pour and 20% ash removal with triple wash. 73% removal of total halogens 57-73% removal of soluble chlorine.	[43]
Sorghum	K. Ca and Mg	Water	7.6L (single) 15.2L (double) and 22.8L (triple) washing, 7.6L soak	< 8mm	Single wash: 42% K, 15% Mg and 14% Ca Double wash: 56% K, 24% Mg and 19% Ca Triple wash: 62% K, 27% Mg and 20% Ca Soak52% K, 25% Mg and 25% Ca	[43]

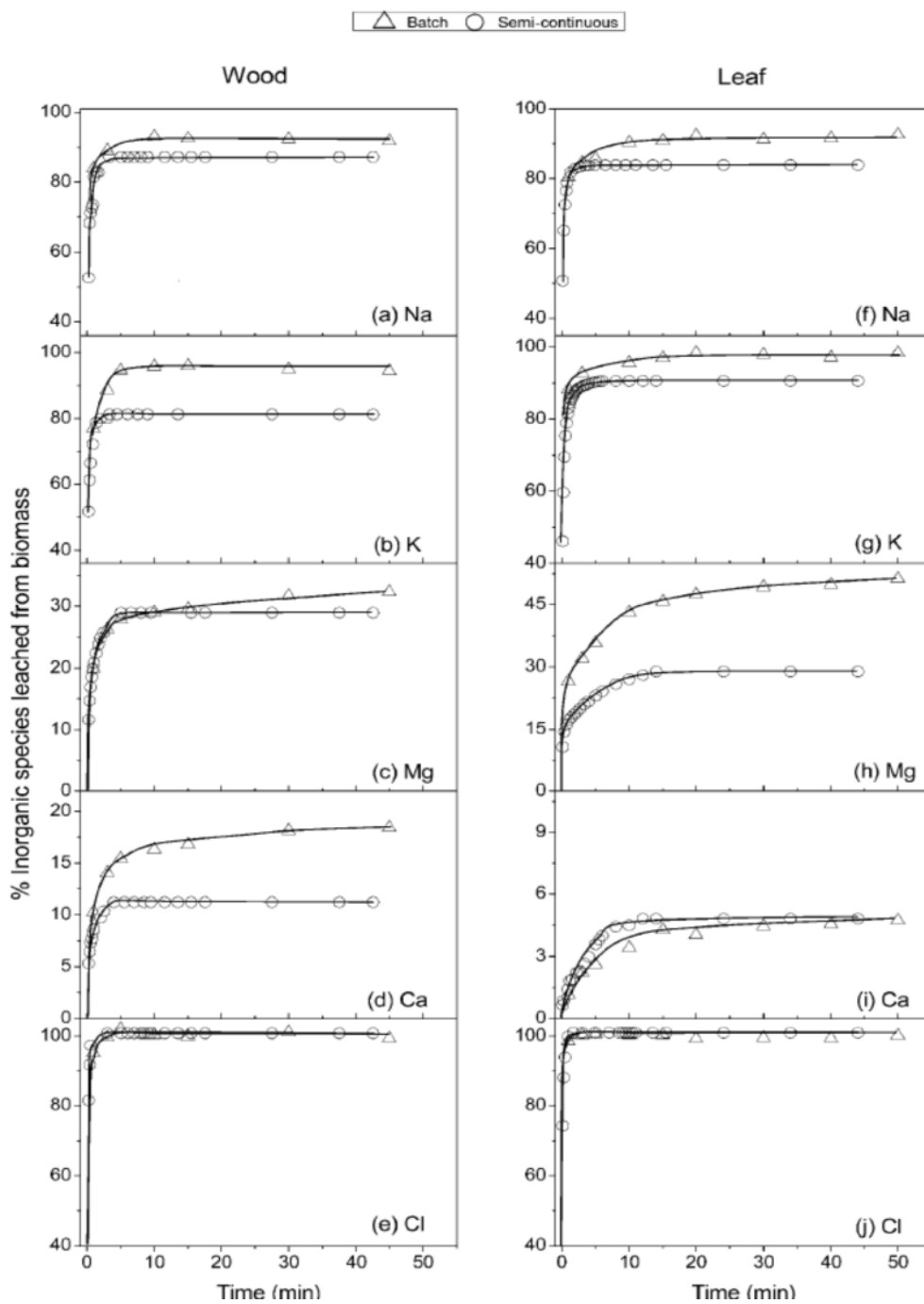


Fig 4 Percentage of various inorganic species leached from the water washing of mallee wood and leaf as a function of leaching time in batch and semi-continuous systems. (Reprinted with permission from Liaw, S.B. and Wu, H., Leaching Characteristics of Organic and Inorganic Matter from Biomass by Water: Differences between Batch and Semi-continuous Operations. *Industrial & Engineering Chemistry Research*, 2013. 52(11): p. 4280-4289. Copyright 2013. American Chemical Society

Washing of biomass also results in extraction of organic material, particularly organic acids (acetic, formic), oxalate [33] and some sugars, lipids, tannins and essential oils [44]. Second order kinetics have been successfully applied to the leaching of organics from *Tilia* sapwood (as measured by mass of dry matter):

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \quad (6)$$

Where: $k = 65.5e^{-21.9/RT}$ (7)

Unpublished work from our laboratory has also suggested that elevated temperature enhances extraction of organics. Extraction of organics can have a small effect on the heating value, especially from high lipid biomass [30]. The impact of emissions of Volatile Organic Compounds (VOC) or other organics and soot during combustion as a result of washing has not been investigated.

3.3 Potential impact on ash behaviour and emissions.

As described earlier, the alkali metals, potassium in particular, are very volatile and during combustion enter the vapour phase as alkali chlorides or hydroxides. These undergo transformation into sulphates and lead to fouling in convective boiler regions because it reduces the ash fusion temperature. During combustion, potassium is released both during volatile and char combustion stages. Jones et al [45] used thermogravimetric analysis to investigate the char combustion peak temperatures for a number of treated willow samples. They increased with decreasing potassium contents indicating that potassium acts as a catalyst during combustion.

Davidsson et al. [46] also studied the release of K from two wheat straws and a wood waste (mainly pine and birch) after various pre-treatments. They washed with water at 20-25°C, as well as acid washing at room temperature. After pre-treatment, samples were heated in N₂ to 1000°C and evolution of K from detected via a surface ionisation detector. Water washing reduced the alkali emission in the 200-500°C region (pyrolysis) by 5-30%, and for emission from the region above 600°C (vapourisation of alkali salts) by 90%. Similar results were observed for both wheat straw and waste woods. Thus decreasing the concentration of alkali metal in the biomass fuels decreases in its fouling propensity. From the results reported by Jenkins et al [27] it is possible to calculate the expected fouling behaviour of rice and wheat straw after exposure to the different washing approaches. For the “65mm rain washed sample”, the sample was exposed to a total of 65mm of rain over 3 days before it was collected from the field. This data is shown in Figure 5 (a). Fouling behaviour is also calculated from data reported by Miles et al and concerning washing of rice straw, wheat straw, alfalfa stems and rice hulls and is reported in Fig 5 (b). Soaking approaches result in fuels which are no longer certain to cause fouling.

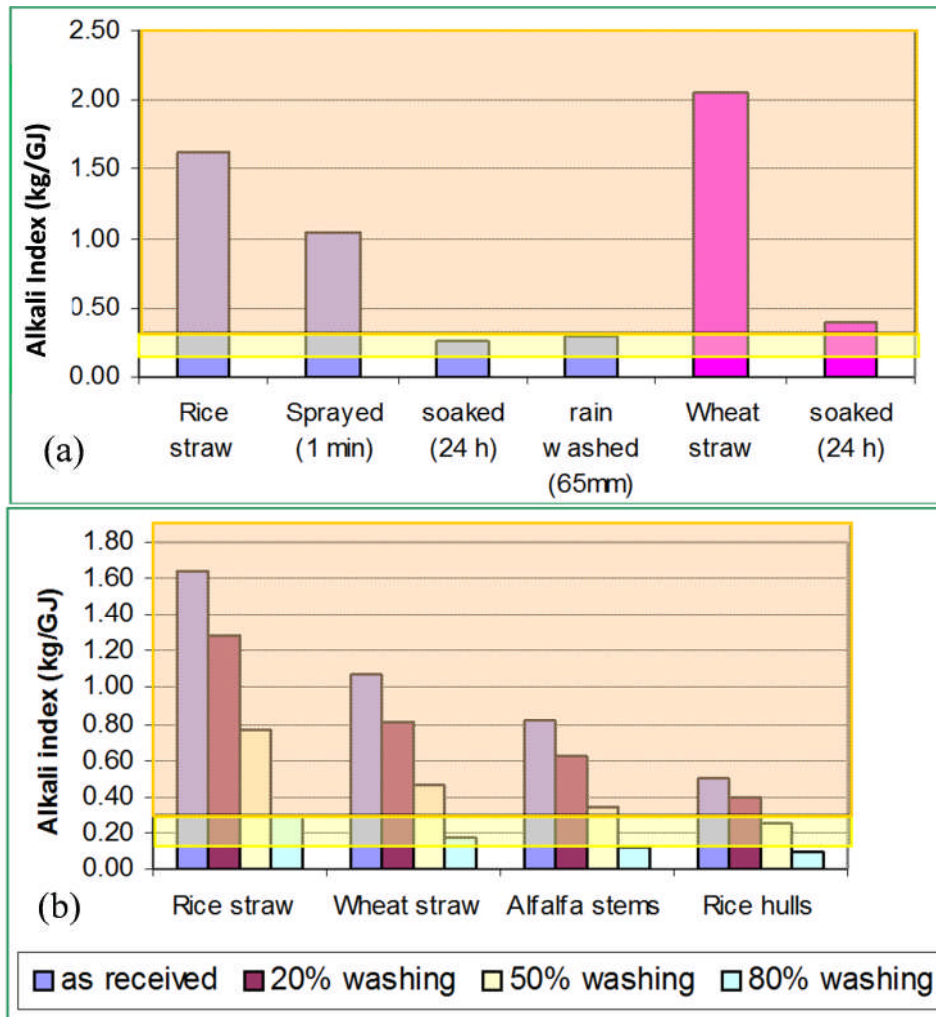


Fig 5 Influence of washing pre-treatment on the alkali index of rice straw and wheat straw. Pink shaded area indicates fouling almost certain, yellow shaded area indicates fouling probable to occur [27, 29].

Data from [27] can be used to examine the influence of pre-treatment on both the base/acid ratio and the Fouling Index as given in Equations (1) and (5) respectively. Results are given in Figure 6 (a) and 6 (b). Based on the $R_{b/a}$, washing is predicted to improve (decrease) the slagging behaviour of both fuels, but particularly wheat straw, as shown in Fig 6 (a). A rule of thumb is severe slagging for $R_{b/a}$ 0.4-0.6 as shown by the red shaded band. Similar benefits are predicted based on the fouling index for rice straw (Fig 6 (b)). Washing of both fuels results in fuels which are predicted to have very much improved ash behaviour.

Several workers have also examined the impact of different washing pre-treatments on ash fusion temperatures. Our own data [30] showed a significant increase in characteristic ash fusion temperatures after water washing. For example, the hemisphere temperature increased by 400 and 290°C for wheat straw and Miscanthus respectively.

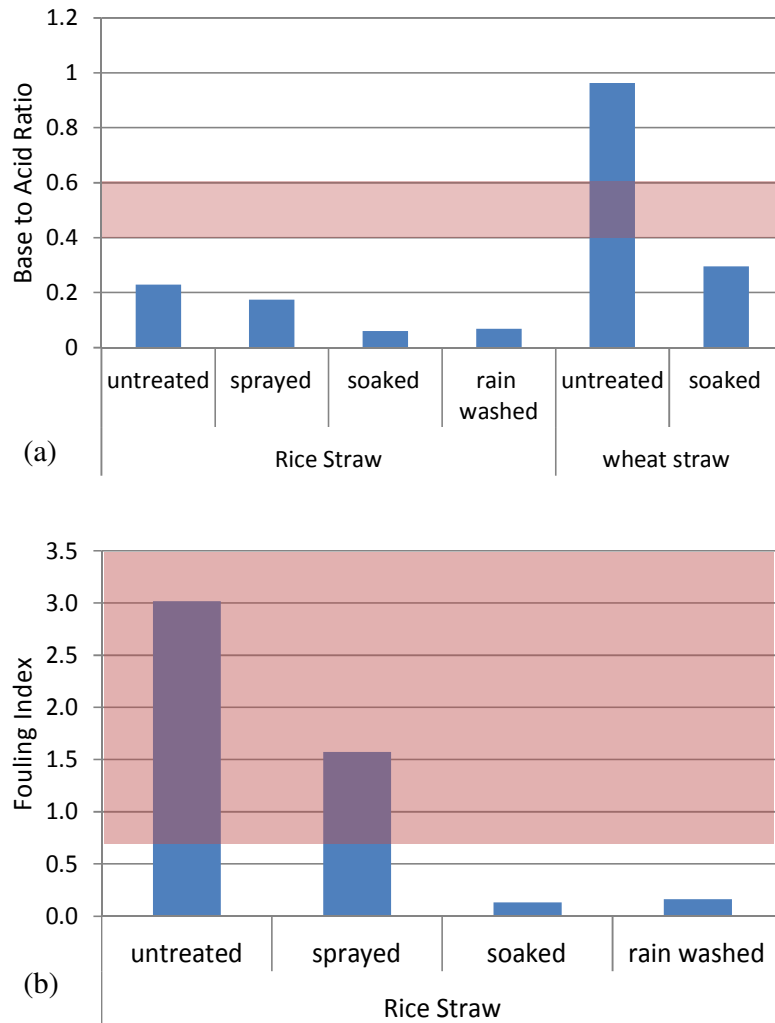


Fig 6 (a) Base to acid ratio of untreated and pre-treated rice straw and wheat straw. Red shaded region shows typical $R_{b/a}$ for low melting ashes. (b) Fouling index of untreated and pre-treated rice straw. Red shaded regions show high fouling risk [27]

EPRI (Electric Power Research Institute) in the States has published recent information concerning their programme in pre-treatment technologies. Fig 7 shows ash melting temperatures of a variety of fuels after pre-treatment. Note that this study includes waste woods, and the ash melting temperature increased from $\sim 850^{\circ}\text{C}$ to 1400°C after pre-treatment. Similar increases are observed for all fuels.

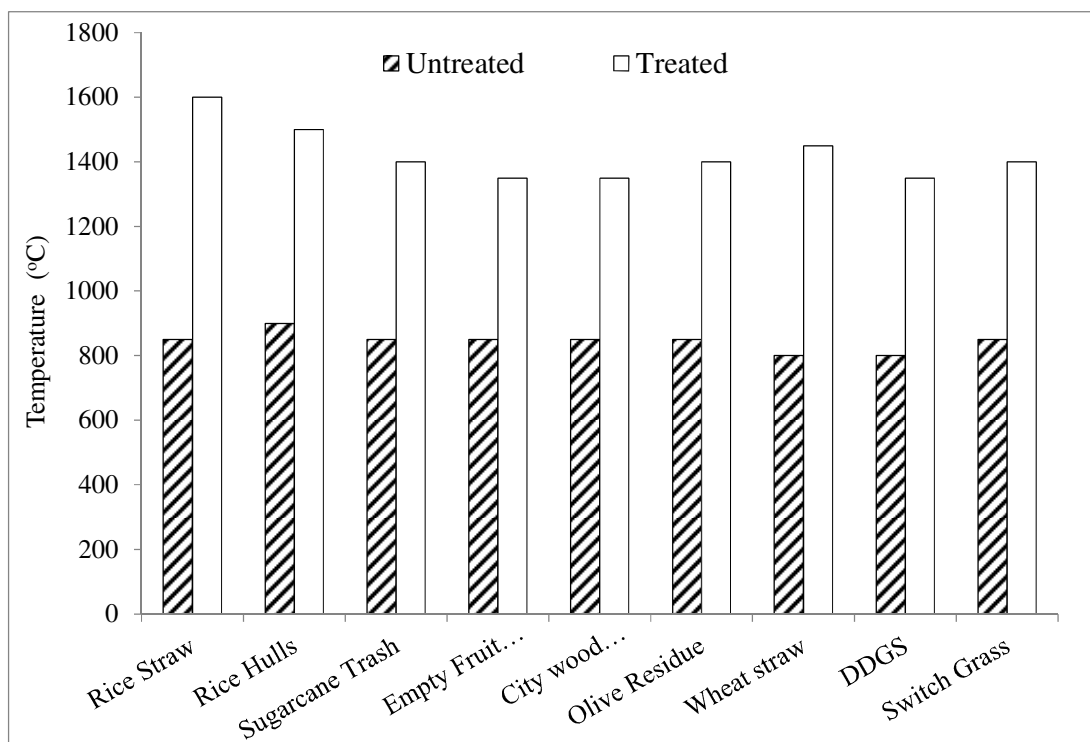


Fig 7 Influence of pre-treatments on the ash melting temperatures of various biomass [47]

In general, large quantities of water are required for washing biomass in order to improve the fuel quality but the disposal of the contaminated water is a problem since it needs to be treated before it can be disposed off into streams or rivers. This increases costs. Hot water washing is a better option since the high temperatures aid in the removal of the impurities from the biomass hence reducing the amount of water required for washing. Potentially in power stations, the effluent from the process can be used to wash the biomass since it is already at high temperatures.

The issues relating to category B and C of waste woods have not been reviewed. Significant leaching of CCA is expected and water remediation would need to be considered in this case. Warm water washing is also expected to enhance extraction of organic components, affecting the COD, BOD and pH of the leachate

4 Conclusions

A literature review based on laboratory scale studies has been undertaken and the following conclusions were made:

1. Washing with water at ambient temperature reduces the ash content of the fuel.
2. The efficiencies of removal decreases as particle size increases, and increases as the temperature of the washing water increases.
3. Hot washing of waste wood has been shown to increase ash melting temperatures from around 820°C at worst through to ca. 1400°C at best.
4. Hot washing of waste wood has been shown to reduce concentrations of chlorine (Cl) by 30-100%, potassium (K) by 50-90%, sodium (Na) by 10-90% (typically

- 40% min), calcium (Ca) by 5-35%, magnesium (Mg) by 5-60%, sulphur (S) by 0-95% {lower end in wood}, phosphorous (P) by 10-80%, and iron (Fe) by 0-30%.
5. Silicon (Si), titanium (Ti), and aluminium (Al) are far less soluble; some small reductions have been observed using cold water washing for these elements however (up to 15%). Studies on SiO₂ suggest improved solubility with hot water. However, this technique will have limited use to mitigate the impacts of these elements in feedstock.
 6. The impact of washing is minimal on High Heating Value (HHV). However ash content tends to reduce significantly, hence reducing the tendency of fouling and slagging to occur in boilers and furnaces.
 7. Reduction in Cl and S contents significantly affects formation of acid gases and consequently acid corrosion on boiler components and associated environmental impacts.

5. Acknowledgements

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