

# Accepted Manuscript

Effects of ash removal by agitated aqueous washing and sedimentation on the physico-chemical characteristics and fast pyrolysis of trommel fines

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PII: S1743-9671(18)30976-0

DOI: <https://doi.org/10.1016/j.joei.2019.02.008>

Reference: JOEI 571

To appear in: *Journal of the Energy Institute*

Received Date: 11 October 2018

Revised Date: 22 February 2019

Accepted Date: 26 February 2019

Please cite this article as: J.A. Onwudili, J.E. Eke, Effects of ash removal by agitated aqueous washing and sedimentation on the physico-chemical characteristics and fast pyrolysis of trommel fines, *Journal of the Energy Institute*, <https://doi.org/10.1016/j.joei.2019.02.008>.

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1 **Effects of ash removal by agitated aqueous washing and sedimentation on the physico-chemical**  
2 **characteristics and fast pyrolysis of trommel fines**

3  
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7  
8 **Abstract**

9 A pre-treated trommel fines feedstock (DPT) with 35.1 wt% ash content and particle size range of 0.5  
10 -2 mm was processed through two (100% distilled water and 1% surfactant in distilled water) aqueous  
11 agitated washing and sedimentation procedures for ash reduction prior to fast pyrolysis in a bubbling  
12 fluidized bed reactor. The washing process led to more than 36% reduction in the ash/inorganic  
13 contents of the DPT feedstock and yielded about 78 wt% of organic-rich feedstocks denoted as WPT1  
14 and WPT2. Characterization and fast pyrolysis of all three feedstocks were carried out to evaluate the  
15 effect of the washing process on their physico-chemical characteristics and yields of fast pyrolysis  
16 products. Results show that the ash reduction led to increase in the volatile matter contents of the  
17 washed feedstocks by 20%, while reducing nitrogen contents. In addition, fast pyrolysis of the  
18 feedstocks show improved yield of liquid and gas products, with a dramatic reduction of reaction  
19 water, indicating that the ash removal reduced the catalytic effect of the ash on water formation  
20 during the fast pyrolysis process. The major organic compounds in the liquids included phenols and  
21 furans from biogenic fraction of the feedstock as well as aromatic hydrocarbons such as those  
22 obtained from pyrolysis of plastics. More importantly, the overall energy yields from the fast  
23 pyrolysis process increased by over 35% after washing the feedstock, with washing with only distilled  
24 water alone giving the highest energy yield of 93%. Hence, coupling the water-washing ash reduction  
25 process with fast pyrolysis appears to be a suitable technology for valorising feedstocks with high ash  
26 contents such as trommel fines for energy and chemicals.

27 **KEYWORDS:** *pre-treated trommel fines; agitated washing; ash removal; fast pyrolysis; energy*  
28 *recovery*

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## 34 1.0. Introduction

35 Trommel fines, obtained from the mechanical recycling of municipal solid wastes (MSW), is a special  
36 kind of waste; it is a complex admixture of organic and inorganic materials. The organic content of  
37 this waste is considered too high, so that landfilling is no longer an acceptable disposal method,  
38 without incurring recently increased landfill gate fees. A recent development is the assessment of the  
39 organic content by a 'loss-on-ignition' (LOI) test, through which gate fee classifications are  
40 determined (HMRC, 2014; Watts, 2016). This increase in landfill disposal costs means that alternative  
41 methods are required. Based on the direct link between the organic content and LOI, it becomes  
42 sensible to reduce or eliminate the organic fraction of trommel fines through energy recovery. Apart  
43 from incineration, pyrolysis appears to be a possible energy recovery technology to be applied to  
44 trommel fines. Pyrolysis offers more versatility in products (gas, liquid and solid) compared to heat  
45 energy from incineration. However, the large presence of inorganic materials (including ash) in  
46 trommel fines sample (stones, aggregates, glass and soil), represent a significant technical problem  
47 during fast pyrolysis.

48 Depending on their physical characteristics (e.g. particle size, density and hardness), these inorganic  
49 materials can cause blockages to parts of process equipment such as grinding mill and reactor feeding  
50 system. Operationally, the inorganics in feedstock for fast pyrolysis can remain in the fluidized bed  
51 reactor, leading to increase in volume and weight of bed material, which can have significant  
52 influence on the pyrolysis process. In addition, the chemical properties such as thermal decomposition  
53 and catalytic activity of the inorganic materials can influence the yield and selectivity of fast pyrolysis  
54 reaction products. For example, the presence of certain types of ash have been reported to promote the  
55 formation of solids and gas at the expense of pyrolysis liquid yield (Xue, Braden and Bai, 2017;  
56 Banks, 2014; Oasmaa et al., 2010; Teng et al., 1998). In some cases, through attrition, the inorganics  
57 can become fine particles capable of being entrained in the fluidising gas, giving rise to the  
58 contamination of the liquid and char products (Bernardo et al., 2010). These problems highlight the  
59 need to reduce the inorganic contents of high-ash feedstocks such as trommel fines prior to fast  
60 pyrolysis. In addition, the reduction of inorganic material through physical pre-treatment will lead to  
61 an apparent increase in the volatile content of the feedstock. As such, the proportions of volatile  
62 fractions delivered for pyrolysis at any set feeding rate will increase, leading to better fast pyrolysis  
63 process and indeed better yields as well as qualities of pyrolysis products. In particular, the presence  
64 of alkali metal has been reported to favour gas formation (Pradhan, 2015; Renkonen, 2016) over oil,  
65 which is the desired product of fast pyrolysis.

66 One of the methods recommended for the separation of inorganics from high-ash waste materials is to  
67 wash them with aqueous solutions. For example, some researchers have reported substantial removal  
68 of majority of soluble alkali metals following their dissolution in water, which became more effective

69 with agitation (Jenkins et al., 1996; Baxter et al., 1998; Fahmi et al., 2007; Renkonen, 2016).  
70 However, ash due to soil contamination tend to have low solubility in water (Fahmi et al., 2007) but  
71 could be removed by sedimentation. In addition, the application of surfactants can further aid the  
72 sedimentation process leading to improved ash content removal (Banks, Nowakowski, Bridgwater,  
73 2014). While significant amount of research has been reported on aqueous washing of biomass for ash  
74 removal, the extension of this practice to waste streams with much higher ash contents is novel.  
75 Indeed, reports of ash removal from high-ash wastes have centred mostly on flyash and bottom ash  
76 from the post-incineration of municipal solid waste (Sani et al., 2010; Chen et al., 2016; Quek et al.,  
77 2016), mostly to remove soluble chloride and sulphate salts prior to application (e.g. in construction).

78 The aim of this present work was to investigate the possibility of applying fast pyrolysis technology to  
79 recover energy from a high-ash feedstock as a solution to preventing the diversion of trommel fines  
80 from landfills. Thus, saving costs on trommel fines disposal due to the recently increased landfill gate  
81 fees for this type of solid waste. In this work, reduction of the ash/inorganic contents of a prepared  
82 (0.5 – 2 mm particle size range) trommel fines feedstock was carried by an agitated washing and  
83 sedimentation procedure prior to applying the feedstock for fast pyrolysis using a bubbling fluidized  
84 bed (BFB) reactor. The particle size range was selected to meet the requirements of the feeding  
85 system of BFB reactor (Eke, Onwudili and Bridgwater, 2017). The agitated washing involved the use  
86 of aqueous media to partition the organic and inorganic materials in the trommel fines sample into  
87 separate fractions based on density differences. Using this procedure, the expectation was that the  
88 organic components would remain afloat in the water, while the heavier inorganics settled at the  
89 bottom; thus, allowing separation and removal of the inorganics. The influence of washing process on  
90 the yields of fast pyrolysis products was investigated at an optimum temperature 500 °C, as  
91 determined from preliminary work.

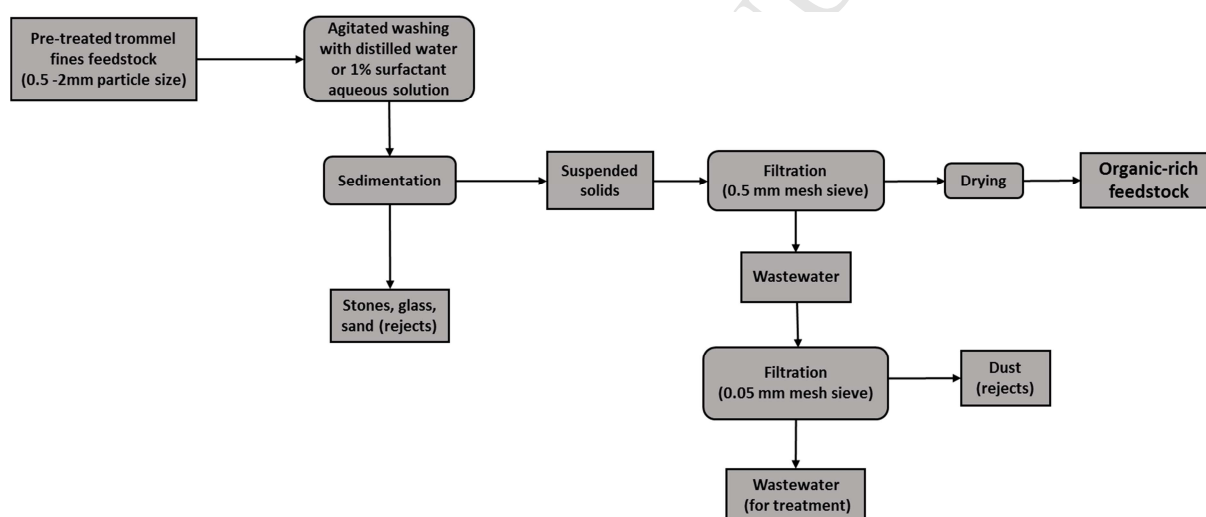
## 92 **2.0 Materials and methods**

### 93 **2.1 Trommel fines feedstock**

94 Trommel fines feedstock (<10 mm particle size) was supplied by Biffa Limited, a UK commercial  
95 waste management company, based in Leicester. Due to the high heterogeneity of the feedstock,  
96 manual separation was initially used to remove large particles of stones, concrete and textiles before  
97 subjecting it to mechanical processing (including size reduction by grinding and sieving) to obtain a  
98 particle size range of 0.5 – 2 mm. This size range, labelled as dry physically pre-treated (DPT),  
99 represented over 70 wt% of the original feedstock as well as more than 80% of its energy content. The  
100 detailed procedure for obtaining DPT feedstock has been reported earlier (Eke, Onwudili and  
101 Bridgwater, 2017).

### 102 **2.2. Agitation - sedimentation procedure**

103 Figure 1 shows the schematic of the process designed to reduce the inorganic/ash contents of the DPT  
 104 feedstock prior to fast pyrolysis. Two different aqueous washing agents were used in this present  
 105 study; namely 100% distilled water and distilled water containing 1 vol% of a surfactant (Decon  
 106 Neutracon). The surfactant is a commercial formulation of anionic and non-anionic surfactants in a  
 107 polyhydric alcohol base, with a neutral (pH 7) It is biodegradable, non-toxic, non-flammable and  
 108 highly water soluble (totally rinsable), which means it is safe to use and does not leave any residues  
 109 when washed off with water. Distilled water was used to prevent any contamination of the feedstock.  
 110 In the procedure, batches of 300 g (dry basis) of the DPT feedstock were separately washed with 3  
 111 litres each of distilled water or distilled water containing the surfactant, respectively. The washing  
 112 was carried out by adding the DPT feedstock into a large laboratory plastic bucket containing each  
 113 liquid. The mixture was stirred for 30 min at room temperature with a metal bar and left to settle for 1  
 114 hour, allowing for sedimentation of the denser components, notably the inorganics (stones, glass, sand  
 115 etc.). To accumulate sufficient pre-treated feedstock material for a fast pyrolysis experiments,  
 116 duplicate washings were carried for both methods and the recovered feedstock materials combined.



117

118 Figure 1: Block flow diagram for agitated washing and sedimentation of prepared trommel fines  
 119 sample.

120

121 To recover the washed feedstocks, a plastic bowl was initially used to scoop the suspended/floating  
 122 solids and passed through a 0.5 mm sieve tray. This procedure helped to recover a large proportion of  
 123 the washed solid feedstocks. However, it was found that some floating solids remained in the water  
 124 and these were recovered by careful decantation of the liquid through the 0.5 mm sieve tray, while the  
 125 sediment remained at the bottom of the bucket. The recovered washed feedstocks were each air-dried  
 126 for 24 hours in the laboratory and then dried in a Swallow oven at  $60\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  for 48 h. The dried  
 127 washed feedstocks obtained for fast pyrolysis were designated as WPT1 (for the agitated washing

128 with 100% distilled water) and WPT2 (for the agitated washing with 1 vol% surfactant solution). The  
129 wastewater was subsequently passed through a 0.05 mm sieve to remove suspended dusts and fines.

130 To account for the distribution of the original DPT feedstock used for the washing-sedimentation  
131 (washing) procedure, the quantities of remaining solids (sediment and dissolved solids) were  
132 determined gravimetrically according to USEPA Method 160.3 (APHA, 1992). For the dissolved  
133 solids, the filtered wastewater was sampled into clean pre-weighed porcelain crucibles and evaporated  
134 to dryness on a water bath. Thereafter, the evaporated porcelain crucibles were dried to constant  
135 weight in an oven at 105 °C. The weight of dissolved solids was determined by difference. Five  
136 replicate determinations were carried out on each waste water with standard deviations of <1%. The  
137 sediments were likewise quantitatively transferred into pre-weighed large porcelain boat with water,  
138 evaporated to dryness, oven-dried at 105 °C and weighed.

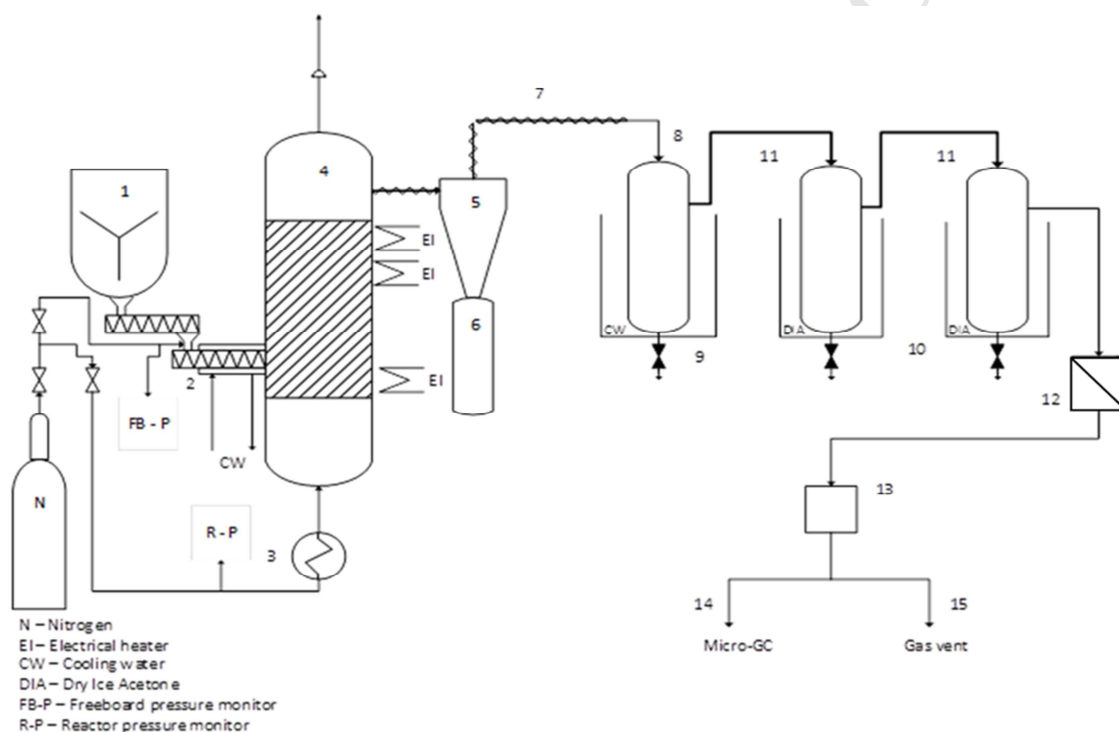
139 In addition, the elemental compositions of the ash contents of all three samples were analysed by a  
140 simple scan using a Bruker S8 Tiger X-ray Fluorescence (XRF) spectrometer, capable of quantifying  
141 elements from sodium to uranium. Firstly, the samples were separately pulverised with mortar and  
142 pestle to make fine powders and weighed into a sample cup with Mylar window. The volume of each  
143 sample was approximately 1 cm<sup>3</sup>. The results of the elements with concentrations  $\geq 0.02$  wt% are  
144 reported in this work.

### 145 **2.3. Process description for fast pyrolysis of pre-treated trommel fines feedstock**

146 Fast pyrolysis of the pre-treated feedstocks (DPT, WPT1 and WPT2) was carried out using an  
147 existing bubbling fluidized bed (BFB) system (Figure 2), which has been fully described previously  
148 (Banks, Nowakowski and Bridgwater, 2014). Briefly, the system consisted of a 300 g h<sup>-1</sup> bench-scale  
149 bubbling fluidized bed reactor unit, linked to a dome-bottomed cylindrical hopper-feeder system and a  
150 product collection system. The feeder uses a dual screw gravimetric feeding system with variable  
151 speed motor for feeding, attached to a fast screw. The pyrolysis chamber is a tubular steel reactor  
152 having 41 mm internal diameter and a height of 320 mm. About 150 g of calcined sand of particle size  
153 range of 500 – 600  $\mu\text{m}$  was used as bed material, fluidized by a stream of nitrogen gas at a flow rate  
154 of 6 L min<sup>-1</sup> to create the bubbling effect for enhanced heat transfer (Kalgo, 2011; Banks,  
155 Nowakowski and Bridgwater, 2014). The product collection system consisted of a water-cooled  
156 condenser and two dry ice/acetone-cooled condensers, followed by a cotton wool filter.

157 Each fast pyrolysis experiment was initiated by deaerating the system with nitrogen flow for 10 min,  
158 after which the reactor was preheated using an electrical furnace to a temperature maintained at 500  
159 °C (to within + 5% accuracy) throughout the duration of each run. Once the temperatures stabilised,  
160 the prepared trommel fines feedstock was continuously fed into the reactor at the middle of the  
161 fluidised bed by nitrogen entrained flow via an air-cooled feeding tube. The feeding rate was  
162 nominally set at 170 g h<sup>-1</sup> and each experiment lasted for 1 h. After pyrolysis in the reactor, the

163 pyrolysis vapours including aerosols, water and non-condensable gases, were carried by the nitrogen  
 164 gas stream through a cyclone to remove entrained solids, which were collected in the char pot. The  
 165 ensuing vapour stream then passed through the system of two sets of condensers, where the  
 166 condensable components were collected as liquids. In this work, the primary condensate referred to  
 167 the liquid recovered from the water-cooled condenser, while any liquid recovered downstream of the  
 168 water-cooled condenser was regarded as secondary condensate. A cotton wool filter was installed  
 169 after the last condenser to trap uncondensed vapours before the stream of non-condensable  
 170 (permanent) gases was directed into a gas meter, where the volume of the exit gas was recorded. A  
 171 portion of the exit gases was taken by an automatic sampling system into an online gas  
 172 chromatograph (GC) for gas composition analysis at 3 min intervals. The remainder of the gas was  
 173 vented through an installed ventilation system.



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Figure 2. Bench scale 300 g h<sup>-1</sup> fluidized bed fast pyrolysis rig set-up

**Key:** 1 - feed hopper with twin screw feeder, 2 – fast screw, 3 – nitrogen preheater, 4 – fluidised bed reactor, 5 – cyclone, 6 – charpot, 7 – metal transition pipe, 8 – glass transition pipe, 9 – water cooled condenser, 10 – dry ice acetone condenser, 11 – rubber transition pipe, 12 – cotton wool filter, 13 – gas meter, 14 – micro-gc, 15 – gas vent

## 183 2.4. Characterization of fast pyrolysis products

### 184 2.4.1. Analysis of gas products



185 During a fast pyrolysis experiment, the non-condensable gases were sampled every 3 min into a  
 186 Varian micro gas chromatograph (Micro-GC) with a thermal conductivity detector (TCD) (Banks,  
 187 Nowakowski and Bridgwater, 2014). The gas components were separated on two columns; namely  
 188 Varian CP-5A Molsieve held isothermally at 80 °C (for H<sub>2</sub>, CO, N<sub>2</sub> and O<sub>2</sub>) and CP-PortaPLOT held  
 189 isothermally at 90 °C (for CO<sub>2</sub> and C<sub>1</sub>-C<sub>4</sub> hydrocarbon gases prior to detection. Quantitation was  
 190 achieved by external standard method by calibrating the detector response using a standard gas mix  
 191 containing these gases at 3 vol% concentrations in nitrogen. The mass yields of the gas components  
 192 were calculated using the general gas equation, based on the gas volume composition obtained from  
 193 GC analysis, total gas volume and the exit gas temperature and recorded pressure. The calorific values  
 194 (as higher heating values, HHV) of gas product were estimated from the volume percentage of each  
 195 gas component and their higher heating values, according to Eq.1.

$$196 \quad HHV \text{ (MJ kg}^{-1}\text{)} = \sum_{i=1}^n (x_i \cdot HHV_i) \dots\dots\dots \text{Eq. 1.}$$

197 where;

198  $i \dots n$  = each combustible component in the gas product

199  $x$  = mass fraction of combustible components in gas product

200  $HHV_i$  = higher heating value of each component in MJ kg<sup>-1</sup>

201

#### 202 2.4.2. Characterization of liquid products

203 Each liquid product composed of both aqueous and organic fractions. The liquid products were  
 204 characterized for their water and solids contents as well as GC-MS analysis of the organic fractions to  
 205 determine the main compounds present. Elemental analysis and heating values of the liquid products  
 206 were also determined.

207 Volumetric Karl-Fischer (KF) titration was used to determine the water content of all the fast  
 208 pyrolysis primary and secondary condensates. The primary and secondary condensates were dissolved  
 209 in a known amount of acetone (1:6) prior to analyses. All analyses were performed in triplicate with  
 210 the water content obtained automatically from the KF titrator. A blank determination using the same  
 211 amount of acetone was used to correct the final water contents (Banks, Nowakowski and Bridgwater,  
 212 2014).

213 Solids content in the primary condensates were determined using the vacuum filtration technique  
 214 suggested by Oasmaa and Peacocke (2001). The sample was filtered through a pre-dried and pre-  
 215 weighed Whatman No. 2 qualitative filter paper with mean pore size of 8 µm. The filter paper with  
 216 the retentate was then washed with excess amount of acetone until the filtrate became clear. The filter



217 paper with the residue was air-dried for approximately 15 min, placed in an oven at 105 °C for 1 h and  
218 cooled in a desiccator before weighing to a constant weight.

219 Elemental analyses of the primary and secondary condensates were carried out using a CE-440 and  
220 Carlo Erba elemental analysers with  $\pm 0.3\%$  absolute accuracy (Banks, Nowakowski and Bridgwater,  
221 2014). In the procedure, the liquid samples were mixed with a known amount of acetone (1:6) to  
222 obtain the carbon, hydrogen and nitrogen (CHNS) contents. The CHNS composition of the organic  
223 fraction of the liquid product was calculated by subtracting the carbon, hydrogen and oxygen contents  
224 of the product water and the added acetone. Hence, the CHNS data were obtained on dry, solvent-free  
225 basis. Oxygen content was determined by difference, using the percentage composition of CHNS.

226 Bomb calorimetric determination of the energy content of the liquid products was carried out only on  
227 the primary condensates, which had more organic product and less water content than the secondary  
228 condensates (please see Figure 4 later). In the procedure, approximately 1 g of the solvent-free  
229 primary condensate was burnt completely in an excess oxygen environment in a steel bomb  
230 calorimeter (Parr 6100 calorimeter) at constant volume. Each experiment was repeated three times  
231 and averages reported (standard deviations  $< 5\%$ ). Results from the experimental determination were  
232 compared with those calculated from the elemental composition of the liquid products, using the HHV  
233 correlation formula (Equation 2) developed and reported by Channiwala and Parikh (2002). The two  
234 sets of results were found to be similar (see Table 4 later), and hence, the correlation was used to  
235 calculate the HHV of all the secondary condensates.

$$236 \text{ HHV (dry)} = 0.3491C + 1.1738H + 0.1005S - 0.1034O - 0.0151N \dots \dots \dots \text{Eq. 2}$$

237 where C, H, S, O, N and A represent mass percentages on dry basis of carbon, hydrogen, sulphur,  
238 oxygen, nitrogen and ash contents of liquid products, respectively.

239 Compositional analyses of organic fractions of the liquid products were performed using a  
240 PerkinElmer Clarus 680 GC-MS system (Banks, Nowakowski and Bridgwater, 2014). Samples for  
241 GC-MS analysis were prepared by mixing the one volume of the pyrolysis liquids with six volumes of  
242 GC grade acetone, followed by filtration using a 0.2  $\mu\text{m}$  pore size Sartorius filter. A sample volume of  
243 1  $\mu\text{L}$  was injected into the GC column via an injection port maintained at 300 °C, with 1:50 split ratio.  
244 The GC oven programme was initially held at 50 °C for 2 min, then ramped at 5 °C  $\text{min}^{-1}$  to 275 °C,  
245 and finally held at 275 °C for 3 min, giving a 50-min analysis time. Helium was used as carrier gas at  
246 a constant flow rate of 15  $\text{ml min}^{-1}$ . Compounds separated on the column were detected by the mass  
247 selective (MS) detector held at 250 °C. Mass spectra were obtained using 70 eV ionisation energy in  
248 the molecular mass range of  $m/z = 35 - 300$ , with a scan time of 0.35 seconds. (Banks, Nowakowski  
249 and Bridgwater, 2014). Assignments of the main peaks were made from mass spectral detection  
250 (NIST05 MS library), with similarity indexes  $> 85\%$ .

251

## 252 2.4.3. Characterization of solid residues

253 Solid products obtained from these experiments were distributed into the bed material, char pot and  
 254 liquid product obtained from the water-cooled condenser. However, in this work, the solid residue in  
 255 the char pot represented over 90 wt% of the total solid products and was therefore considered of  
 256 interest for detailed characterization (*see section 3.3.4.2*). The ash content of this solid residues was  
 257 determined according to the ASTM D1762-84 method (ASTM, 2013). Approximately 4 - 5 g of solid  
 258 residue was weighed into each pre-calcined and pre-weighed crucible set (crucible and lid) and placed  
 259 in a furnace. The samples were ashed at 750 °C for 6 h, followed by cooling in a desiccator to room  
 260 temperature. After weighing to a constant weight, the ash content was obtained by the difference in  
 261 mass between the crucible + ash and the empty crucible. The average of five replicate analysis was  
 262 carried out to account for the heterogeneity of the samples, with standard deviations of <5%.  
 263 Furthermore, the solid residues were analysed for their ultimate compositions and calorific values  
 264 using the same techniques used for the liquid products as described in section 2.4.2.

265

266 **2.5. Fast pyrolysis mass balance calculation**

267 Mass balances (wt. % on dry feed basis) were calculated by comparing the mass yields of final fast  
 268 pyrolysis products (liquids, solid residues and non-condensable gases) with the mass of feedstock  
 269 fines feedstock processed. All post-reactor removable parts of pyrolysis (including pipes and  
 270 condensers) were weighed before and after each run, to determine any weight increase arising from  
 271 the pyrolysis products. By difference in weight of trommel fines added to hopper before and feedstock  
 272 left in hopper after each experiment, the amount of feedstock fed can be calculated. The quantity of  
 273 solid residues included those collected from the char pot, reactor and metal transition pipe, and the  
 274 solid fines found in the liquid products. The liquid products were collected as two portions; primary  
 275 condensate and secondary condensate. The yields of products were calculated using the following  
 276 equations;

$$277 \text{ Gas yield (wt \%)} = \frac{\sum \text{mass of gas components produced} \times 100}{\text{mass of pre-treated trommel fines feedstock used}} \dots\dots\dots \text{Eq. 3.}$$

278

$$279 \text{ Oil yield (wt \%)} = \frac{\text{mass of oil produced} \times 100}{\text{mass of pre-treated trommel fines feedstock used}} \dots\dots\dots \text{Eq. 4.}$$

280

$$281 \text{ Solid Residue/Char yield (wt \%)} = \frac{\text{mass of solid residue or char produced} \times 100}{\text{mass of pre-treated trommel fines feedstock used}} \dots\dots \text{Eq. 5.}$$

282

283 **3.0 Results and Discussions**284 **3.1. Characterization of pre-treated feedstocks**

285

286 From visual observations, there was no difference between the two sets of washed trommel fines  
 287 feedstocks. Photographs of the different fractions of DPT obtained after the washing process (with  
 288 water only) have been provided in the *Supplementary Information (SII)*. The quantitative distribution  
 289 of the feedstock after the wet pre-treatment procedures are given in Table 1. Nearly 100% of the DPT  
 290 feedstock was accounted for after the washing procedure. Table 1 shows that overall, the two  
 291 washing methods gave very similar results, within the margin of errors. Interestingly, both washing  
 292 methods helped to recover about 78 wt% of organic-rich fractions which were used for fast pyrolysis.  
 293 These fractions comprised of water-insoluble components of DPT, which were less dense than water.  
 294 Hence, WPT1 and WPT2 were more fibrous in nature than DPT, which seemed to have some  
 295 influence on the feeding of the washed feedstock into the pyrolysis reactor (see Table 3 below). The  
 296 stone/glass and dissolved solids were classified as rejects, being composed mainly of inorganics.

297

298 Table 1: Mass balance results from the agitation-sedimentation pre-treatment of DPT trommel fines  
 299 feedstock

Fractions (wt%)	Washing procedure	
	Water	Water + 1 vol% Surfactant
Recovered organic-rich feedstock (suspended solids)	78.3 ± 0.9	77.8 ± 0.8
Sediment (stone, glass)	17.7 ± 0.6	17.4 ± 0.7
Dissolved solids	3.8 ± 0.9	4.2 ± 0.7
<b>Total</b>	<b>99.8 ± 0.3</b>	<b>99.4 ± 0.5</b>

300

301 Table 2 presents the proximate and ultimate compositions of the three pre-treated feedstocks. The  
 302 results however, show that not all the inorganics or ash in the DPT fines feedstock could be removed  
 303 or separated out by the washing procedure. For instance, lighter inorganic items in the feedstock, such  
 304 as aluminium sheets and very fine solids were suspended in water along with the organic fraction  
 305 during the washing-sedimentation process. These were recovered together with the organic solids  
 306 during the scooping and decantation of floating materials. Hence, they remained as ash in the washed  
 307 feedstocks.

308 As shown in Table 2, the ash content of the wet pre-treated feedstocks decreased by 36 - 37%  
 309 compared to DPT. Consequently, the removal of ash led to an increase in the volatile contents of  
 310 WPT1 and WPT2. Evidently, the volatile matter contents of the feedstock, which could undergo  
 311 degradation during fast pyrolysis to give useful products, increased by about 20%. Literature shows  
 312 that ash removal by water washing or leaching has been reported to be influence by the amount and  
 313 composition of ash as well as washing conditions, especially temperature and additives (Liu et al.,

314 2011; Deng et al., 2013; Gudka et al., 2016). For instance, using the same washing procedure Deng et  
 315 al. (2013) found that ash removal efficiencies were lower for high-ash biomass samples such as rice  
 316 straw and rice hull, which also contained very high silica (SiO<sub>2</sub>) contents of over 80%.

317 While DPT and WPT1 showed similar fixed carbon content (7.52% and 7.28%, respectively), it was  
 318 lower in WPT2 (6.4%), giving nearly 15% reduction after washing with the surfactant, possibly due to  
 319 increased floatability of substances with lower fixed carbon contents. The elemental compositions  
 320 (dry basis) of the feedstocks showed that there were slight improvements in the carbon and hydrogen  
 321 contents after the washing procedure, due to enrichment of the organic fraction. There were also  
 322 considerable increases in the calorific values of the washed feedstocks from about 14 MJ kg<sup>-1</sup> (DPT)  
 323 to 18 MJ kg<sup>-1</sup> (WPT2).

Parameters	Pre-treated trommel fines feedstock		
	DPT	WPT1	WPT2
<b>Proximate compositions (wt%)</b>			
Ash content <sup>a</sup>	35.1 ± 6.85	22.3 ± 4.46	21.9 ± 4.69
Volatile Matter <sup>a</sup>	54.7 ± 1.50	67.2 ± 1.92	68.1 ± 0.44
Fixed Carbon <sup>a, b</sup>	7.52	7.28	6.40
Moisture content (wt.%)	2.69 ± 0.06	3.22 ± 0.50	3.63 ± 0.32
<b>HHV (Bomb Calorimeter, MJ kg<sup>-1</sup>)</b>	13.8 ± 0.33	<b>17.5 ± 0.41</b>	18.1 ± 0.32
<b>Ultimate compositions (wt%) <sup>a</sup></b>			
Nitrogen	2.75 ± 3.16	1.54 ± 0.92	1.89 ± 0.52
Carbon	33.7 ± 6.93	36.4 ± 3.03	39.4 ± 3.56
Hydrogen	4.62 ± 0.92	6.08 ± 0.75	6.22 ± 0.84
Sulphur	0.26 ± 0.20	0.58 ± 0.24	0.54 ± 0.18
Oxygen <sup>b</sup>	23.5	33.1	30.1

a = dry basis; b = calculated by difference

324 Table 2: Proximate and ultimate compositions of the pre-treated trommel fines feedstocks

325

## 326 3.2. Fast pyrolysis results

### 327 3.2.1. Product yields and distribution

328 Table 3 shows the product yields, product distributions and mass balance closures obtained from the  
 329 fast pyrolysis of pre-treated trommel fines feedstocks (DPT, WPT1 and WPT2). The product yields  
 330 were determined on a dry basis, therefore, the water yields presented here were the water (reaction  
 331 water) generated by the fast pyrolysis reaction excluding the water in the feed. Each experiment was  
 332 conducted three times and mass balances gave standard deviations within a 5% range. It is worth  
 333 pointing out that, the more fibrous nature of WPT1 and WPT2 compared to DPT, affected the feeding

334 of the feedstocks into the pyrolyzer. Stones, glasses and sand are much denser and more crystalline  
 335 than biomass or any floating organic material. Hence the removal of the denser materials as ash by  
 336 sedimentation led to a reduction of the density of the recovered feedstock. Hence, the reduced density  
 337 meant that using the same volume of feeding system, less mass of WPT1 and WPT2 were delivered to  
 338 the reactor compared to DPT at the fixed time of one hour. As shown in Table 3, less quantities of  
 339 WPT1 and WPT2 were delivered into the reactor after 1 hour compared to DPT, even though a  
 340 nominal feed rate of  $170 \text{ g h}^{-1}$  was maintained throughout this work.

341 The overall mass balance closures for the pre-treated trommel fines feedstock from the fast pyrolysis  
 342 were between 93 and 98 wt% (dry basis). The pyrolysis process mass balance closures were slightly  
 343 lower after washing, possibly due to the increased volatile matter contents, leading to increase in the  
 344 production of unidentified and undetected gases. In contrast, the reaction water product decreased  
 345 after washing, this might indicate that the presence of certain ash components promoted pyrolysis  
 346 reactions leading to water formation (e.g. dehydration) in DPT. Hence, removal of such ash  
 347 components during washing minimized water formation.

348 Table 3: Mass balance results from the fast pyrolysis of the pre-treated trommel fines feedstock at  $500 \text{ }^{\circ}\text{C}$   
 349 for 1 hour

Parameter measured <sup>a</sup>	DPT	WPT1	WPT2
<b>Quantity of Feed delivered (g)</b>	158.9	109.9	107.7
<b>Liquid Product: Primary condensate (wt%)</b>	$12.5 \pm 0.40$	$8.81 \pm 0.44$	$9.02 \pm 0.07$
<b>Liquid Product: Secondary condensate (wt%)</b>	$7.07 \pm 0.72$	$27.6 \pm 0.40$	$25.8 \pm 0.39$
<b>Liquid Product: Reaction water (wt%)</b>	$13.0 \pm 0.56$	$8.30 \pm 0.85$	$8.69 \pm 0.60$
<b>Total Liquid product (wt%)</b>	<b><math>32.6 \pm 0.58</math></b>	<b><math>44.8 \pm 0.90</math></b>	<b><math>43.5 \pm 1.06</math></b>
<b>Solid Residue: Char port (wt%)</b>	$45.5 \pm 1.23$	$30.4 \pm 0.34$	$31.7 \pm 0.09$
<b>Solid Residue: Reactor bed (wt%)</b>	$6.15 \pm 0.85$	$1.09 \pm 0.56$	$1.58 \pm 0.34$
<b>Solid Residue: Liquid product (wt%)</b>	$0.495 \pm 0.16$	$0.225 \pm 0.42$	$0.265 \pm 0.23$
<b>Total solid residue</b>	<b><math>52.1 \pm 1.23</math></b>	<b><math>31.7 \pm 0.34</math></b>	<b><math>33.5 \pm 0.09</math></b>
<b>Gas (wt%)</b>	<b><math>12.9 \pm 0.02</math></b>	<b><math>16.7 \pm 0.56</math></b>	<b><math>15.8 \pm 0.36</math></b>
<b>Closure (wt%)</b>	<b><math>97.6 \pm 0.69</math></b>	<b><math>93.1 \pm 0.81</math></b>	<b><math>92.9 \pm 0.61</math></b>

<sup>a</sup> dry basis

350

351 The total liquid produced from fast pyrolysis of pre-treated trommel fines feedstocks increased after  
 352 the washing procedure by about 33%, with similar yields from both washed feedstocks (Stefanidis et  
 353 al., 2015). In particular, WPT1 and WPT2 produce dramatic increases in yields of secondary  
 354 condensates compared to DPT. In comparison, the liquid yield from DPT was lower than those  
 355 reported in literature for pyrolysis of RDF and MSW, whereas the washed feedstocks gave  
 356 comparable yields to MSW (Miskolczi, Ates, Borsodi, 2013; Buah et al., 2007; Chen et al., 2015).

357 Table 3 also shows that solid residues were the dominant product from the fast pyrolysis of DPT at  
 358 52.1 wt%, whereas the WPT1 and WPT2, resulted in much lower solid residues, decreasing by at least  
 359 36% compared to DPT. These results were consistent with the reduced ash content in the two washed  
 360 feedstocks (WPT1, 23.1 wt% and WPT2, 22.8 wt%; dry basis). The gas yield increased slightly after  
 361 agitated washing and sedimentation, which can be attributed to their increased proportions of volatile  
 362 matter as shown in Table 2.

### 363 3.3. Detailed characterization results of fast pyrolysis products

#### 364 3.3.1. Effect of pre-treatment methods on gas products

365 Results in Table 4 show that the gas products contain mainly of carbon dioxide and propylene with  
 366 small quantities of C<sub>1</sub>–C<sub>4</sub> hydrocarbon gases. Apart from propylene and CO<sub>2</sub>, the washing procedure  
 367 did not affect the yields of gas components significantly. Only a slight increase in CO<sub>2</sub> yield was  
 368 obtained while propylene increased nearly two-fold from the washed feedstock. The formation of  
 369 propylene during catalytic fast pyrolysis of MSW has been well reported in literature to be due  
 370 dehydration of biomass-derived sugars or the cracking of polypropylene plastics in the presence of  
 371 aluminosilicates or zeolite-type catalysts (Fivga, 2011; Sebestyén et al., 2017). Such catalytic  
 372 materials could be present in the fine ash particles (dust) in the feedstocks, and their presence could be  
 373 enriched as they floated in water and then scooped with the organic materials during feedstock  
 374 washing. More interestingly, the increased yield of propylene obtained from the washed feedstocks,  
 375 led to 3% (WPT1) and 15% (WPT2) increases in the higher heating values of gas products compared  
 376 to DPT.

377 Table 4: Yields of gas components during fast pyrolysis of pre-treated trommel fines

Gas component (wt%)	DPT	WPT1	WPT2
Hydrogen	0.01	0.01	0.01
Carbon monoxide	0.08	0.03	0.04
Methane	0.52	0.18	0.20
Carbon dioxide	8.82	11.4	10.4
Ethylene	0.25	0.16	0.22
Ethane	0.24	0.10	0.12
Propylene	2.45	4.55	4.69
Propane	0.41	0.23	0.33
n-Butane	0.16	0.08	0.11
<b>HHV (MJ kg<sup>-1</sup>)<sup>a</sup></b>	<b>14.8</b>	<b>15.3</b>	<b>17.1</b>

378 <sup>a</sup> Equation 1

#### 379 3.3.2. Effect of feedstock pre-treatment method on liquid product characteristics

380 The liquid products obtained from the fast pyrolysis experiments were characterized to determine  
 381 their physical and chemical compositions. Fast pyrolysis oils from biogenic feedstock are known to

382 contain water as part of the product (Czernik and Bridgwater, 2004; Oasmaa et al., 2010). Moreover,  
 383 due to fluidization, fine solids can become entrained in the gas/vapour stream and may contaminate  
 384 the condensed liquid products; this is particularly so for feedstocks with high ash contents.  
 385 Photographs of the primary and secondary condensates produced from fast pyrolysis of the three  
 386 trommel fines feedstocks are given in the *Supplementary Information (SI2)*. The liquids produced  
 387 exhibited some physical differences between them; for instance, the primary condensate from DPT  
 388 appeared much more viscous than those from WPT1 and WPT2. In addition, DPT produced a  
 389 secondary condensate that appeared to be much more watery and lighter than those obtained from the  
 390 washed feedstocks. The physical appearance of the liquid products may indicate the influence of ash  
 391 during the fast pyrolysis process, with the high ash content of DPT causing dehydration (Pradhan,  
 392 2015) of the feedstocks to give a tarry primary condensate and a watery secondary condensate.

393 Table 5 shows the results of semi-quantitative XRF analysis of the three feedstocks, which indicates  
 394 much higher silicon (possibly, as silica) to aluminium (possibly, as alumina) ratio, which may indicate  
 395 a reduction in acidity. This may have resulted in reduced potential for dehydration reactions, which  
 396 consequently reduced the formation of tarry products in WPT1 and WPT2 compared to DPT.

397 Table 5: Results of XRF analysis of DPT, WPT1 and WPT2 trommel fines feedstocks

Element	Concentration wt%		
	DPT	WPT1	WPT2
Calcium	4.23	3.28	3.22
Silicon	3.89	3.48	3.21
Lead	3.51	0.84	0.98
Iron	2.56	1.91	0.49
Potassium	0.79	0.23	0.21
Aluminium	0.75	0.15	0.12
Chlorine	0.7	0.05	0.06
Copper	0.65	nd	0.08
Sulphur	0.42	0.34	0.39
Manganese	0.32	0.19	0.28
Niobium	0.28	0.18	0.18
Phosphorus	0.22	0.27	0.21
Zinc	0.22	0.11	0.08
Magnesium	0.2	0.25	0.24
Titanium	0.16	0.02	0.02
Strontium	0.09	nd	nd
Nickel	0.02	nd	nd
Zirconium	0.02	nd	nd
<b>Total</b>	<b>19.03</b>	<b>11.28</b>	<b>9.76</b>

398



399 Table 6 shows the physical and elemental compositions of the liquid products in both the primary and  
 400 secondary condensates. The results show that in total, the liquid products contained between 34 and  
 401 74 wt% of water. While the primary condensates from the three feedstocks contained similar amounts  
 402 of water (around 5.4 - 6.5 wt%), the secondary condensates were largely different.

403 The water contents of the secondary condensate obtained from DPT was more than twice those  
 404 obtained from WPT1 and WPT2, which may be attributed to the influence of the ash during pyrolysis.  
 405 For instance, water production from DPT could be from decomposition of hydrated salts in the ash  
 406 and/or from ash-catalysed dehydration of biogenic components in the feedstock. Depending on their  
 407 ratios, silica and alumina have been reported to cause biomass dehydration during pyrolysis, leading  
 408 to increased water contents of bio-oils (Pradhan, 2015). Indeed, the washing procedure appeared to  
 409 have reduced the water contents to levels within the range reported in literature for pyrolysis oils of  
 410 different biogenic feedstocks, which is typically from 15 – 35 wt% (Elliott 1994; Bridgwater 2012).

411 The solids contents entrained in the liquid products from all three feedstocks were within similar  
 412 values, which indicated that majority of the entrained solids was made up of very fine particles which  
 413 could not be separated by washing and sedimentation. The elemental compositions and heating values  
 414 of both the primary and secondary condensate liquids produced from all three feedstocks are also  
 415 presented in Table 6. The elemental composition results show that water washing led to slight  
 416 increases in the carbon and hydrogen contents of the liquid products, while the oxygen contents  
 417 reduced. The increase in the carbon and hydrogen contents as well as the calorific values in secondary  
 418 condensates of WPT1 and WTP2 were considerably higher than in the primary condensates. These  
 419 results are consistent with the enrichment of organics (including biogenics, plastics and textiles) in the  
 420 feedstocks after washing. With regards to nitrogen contents, the washing procedures proved to be  
 421 effective in dramatically reducing the presence of nitrogen compounds in the liquids (both primary  
 422 and secondary condensates), thereby reducing the potential for NO<sub>x</sub> emissions during combustion of  
 423 pyrolysis oils.

424 Table 6. Physical and chemical characteristics of liquid products obtained from fast pyrolysis of pre-  
 425 treated trommel fines feedstocks

<b>Pre-treated trommel fines feedstocks</b>			
<b>Characteristics</b>	<b>DPT</b>	<b>WPT1</b>	<b>WPT2</b>
<b>Primary Condensate (wt%)<sup>a</sup></b>			
Water content	5.8 ± 0.56	5.39 ± 0.60	6.52 ± 0.74
Solid content	3.58 ± 0.85	2.34 ± 0.74	2.68 ± 0.62
<b>Elemental Analysis (wt%)<sup>b</sup></b>			
C	62.9	64.0	66.5
H	8.75	11.2	10.7
N	2.95	1.20	1.17
S	0.10	0.12	0.13

O <sup>b</sup>	25.3	23.5	21.5
HHV (Bomb Calorimeter, MJ kg <sup>-1</sup> ) <sup>a</sup>	32.4 ± 0.09	32.5 ± 0.23	33.8 ± 0.41
HHV dry (MJ kg <sup>-1</sup> ) <sup>a, d</sup>	31.2	31.8	32.3
<b>Secondary Condensate (wt%)<sup>a</sup></b>			
Water content	67.9 ± 2.78	28.7 ± 0.72	31.41 ± 0.36
<b>Elemental Analysis (wt%)<sup>b</sup></b>			
C	44.7	58.5	57.1
H	6.63	11.2	10.8
S	1.47	0.42	0.50
N	6.36	0.21	0.20
O <sup>b</sup>	40.9	29.7	31.4
HHV dry (MJ kg <sup>-1</sup> ) <sup>a, d</sup>	17.4	25.9	26.4

<sup>a</sup> dry basis; <sup>b</sup> dry-ash-free basis; <sup>c</sup> calculated by difference; <sup>d</sup> Eq. 2

426

427 The HHV of the primary condensates were fairly the same (32.4 – 33.8 MJ kg<sup>-1</sup>) for all three  
 428 feedstocks as shown in Table 6. The total HHV of the pyrolysis oils were close to the value of 35.5  
 429 MJ kg<sup>-1</sup> reported by Buah and Williams (2016) for dewatered oils obtained from the pyrolysis of  
 430 RDF. The heating values of the primary condensate obtained from these feedstocks were higher than  
 431 those reported for bio-oil, due to the presence of plastics and textile materials, which carry higher  
 432 energy contents than biomass (Velghe et al., 2011; Miskolczi, Ates and Borsodi, 2013). For the  
 433 secondary condensates, there was an increase in HHV after the feedstock washing procedures from  
 434 17.4 MJ kg<sup>-1</sup> (DPT) to 25.9 MJ kg<sup>-1</sup> (WPT1) and 26.4 MJ kg<sup>-1</sup> (WPT2). The HHV of the secondary  
 435 condensates from washed feedstocks were similar to an average of 27 MJ kg<sup>-1</sup> reported for pyrolysis  
 436 oils derived from MSW (Velghe et al., 2011). Therefore, the energy contents of the condensates,  
 437 particularly from the washed feedstocks, show considerable potential for energy recovery of trommel  
 438 fines using fast pyrolysis.

### 439 3.3.3 Indicative yields of major organic compounds in the liquid products

440 The fast pyrolysis process led to the degradation of the feedstocks to produce a number of organic  
 441 compounds with carbon chain lengths from C<sub>3</sub> - C<sub>16</sub> as identified from GC/MS analysis. Examples of  
 442 GC/MS chromatograms of the organic portions of the primary and secondary condensates from the  
 443 fast pyrolysis experiments are given in the *Supplementary Information (SI3)*.

444 Table 7: Peak area % of major organic compounds identified in the primary condensates obtained  
 445 from fast pyrolysis of pre-treated trommel fines feedstocks

Retention time	SI%	Compound	% Peak Area		
			DPT	WPT1	WPT2
3.327	95	Glycerol	*	*	*
6.37	90	3-Penten-2-one, 4-methyl-	*		

9.24	93	2-Pentanone, 4-hydroxy-4-methyl-	*		
13.61	95	$\alpha$ -Methylstyrene		*	*
14.81	94	Phenol	**	*	**
17.63	96	Phenol, 2-methyl-	**	**	**
18.64	97	Phenol, 4-methyl-	**		
18.71	98	Phenol, 3-methyl-	**	**	**
19.92	93	Phenol, 3,4-dimethyl-	*	***	***
20.25	92	Naphthalene		***	***
25.06	88	Phenol, 2-methoxy-4-(1-propenyl)-		*	
28.21	93	1,3-Diphenyl propane		*	
29.74	95	1,1-Diphenylbutene	*	****	*****
31.24	99	1,3-Diphenyl-3-methylpropene	***	****	****
35.64	96	n-Hexadecanoic acid		****	***
43.49	96	2,4-Diphenyl-4-methyl-1-pentene	****		
43.66	97	Bisphenol-A		**	
45	85	1-phenyl-1(3-phenyl-3butenyl)cyclopropane	****	*****	*****

446 SI: Similarity Index

447 The condensation system used in the work, clearly aided in separating the organic liquids into heavy  
 448 and light fractions in the primary and secondary condensates, respectively. Essentially, the primary  
 449 condensates from all three feedstocks were dominated by phenols, while the secondary condensates  
 450 contained mostly sugar-derived and furan-type compounds. This kind of staged-condensation system  
 451 can be useful for separate processing of liquid products into chemicals and fuels (Imran et al., 2016;  
 452 Johansson et al., 2017). The major organic compounds identified (with similarity index > 85%) in the  
 453 primary and secondary condensates are shown in Table 7 and Table 8, respectively. Along with their  
 454 retention times, the indicative concentrations of the various compounds are represented by the  
 455 asterisks symbols shown, based on peak area percentages.

456 Table 8: Peak area % of major organic compounds identified in the secondary condensates obtained  
 457 from fast pyrolysis of pre-treated trommel fines feedstocks  
 458

Retention time	SI%	Compound	% Peak Area		
			DPT	WPT1	WPT2
2.413	96	Pentanone	*	*	*
3.399	94	Acetic acid, 1-methylethyl ester		***	***
4.043	95	1,2-Propanediol, 2-acetate	***	***	***
5.85	94	2,4-Dimethyl-2-oxazoline-4-methanol	*		
6.61	93	Cyclopropane-1,1-dicarboxylic acid	*		
6.82	90	Cyclopentanone	*		
7.606	91	Furan, 3-methyl-	**	**	**
7.652	96	Furfural	***	***	***
8.817	93	1,3-Dioxolane, 2,2,4-trimethyl-	**	**	**

9.207	97	Furan, 2,5-dimethyl-	**	**	*
10.45	96	2-Cyclopenten-1-one, 2-methyl-	**		
11.597	95	2-Furancarboxaldehyde, 5-methyl-		**	**
11.62	86	1,4-Pentanediamine	**		
13.665	93	1,2-Cyclopentanedione, 3-methyl-	**	**	**
15.24	89	Oxazole, 2-ethyl-4,5-dihydro-	**		
24.3	88	(Z),(Z)-2,5-Dimethyl-2,4-hexadienedioic acid	**	*	*
30.832	96	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	*	***	***
31.86	90	Ethyl citrate	**		

459 SI: Similarity index

460

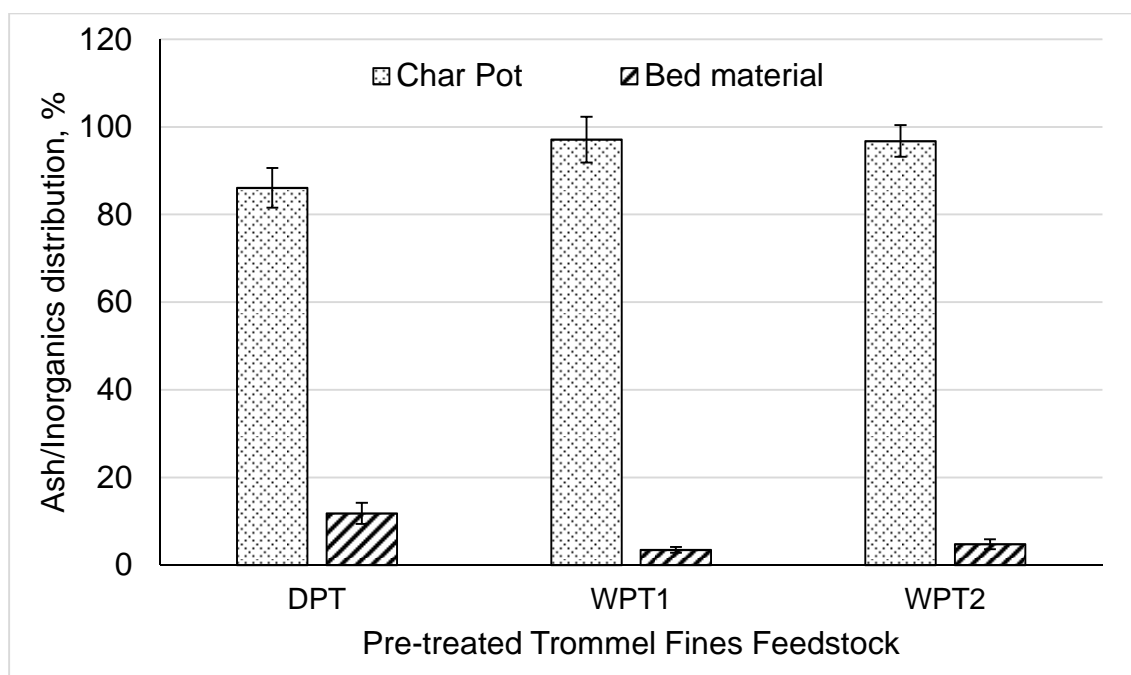
461 In general, the liquid products showed the presence of compounds commonly derived from biomass  
 462 (e.g. furans and phenols) and plastics (e.g. 1,2-diphenylpropane) (Hall et al., 2009). The liquid  
 463 products from the washed feedstocks appeared to contain higher yields of the different classes of than  
 464 those obtained from DPT, which can be attributed to the enrichment of volatile matter. The presence  
 465 of a few nitrogen-containing compounds in the secondary condensate from DPT corroborated the high  
 466 elemental nitrogen content earlier reported in Table 6. These compounds were in the form of amines  
 467 and their derivatives, which were lower in the liquid products from washed feedstocks. The reduction  
 468 of the nitrogen-containing compounds would indicate that the original nitrogen-bearing materials in  
 469 DPT were either water-soluble, too dense to float on water or became dense by absorbing water.

470

### 471 3.3.4 Effect of feedstock pre-treatment method on characteristics of char pot solid residues

#### 472 3.3.4.1 Distribution of the inorganic/ash contents of the pre-treated feedstocks after fast 473 pyrolysis

474 The catalytic influence of ash on the yields of fast pyrolysis products have been well described in  
 475 literature; mainly on the extensive cracking of pyrolysis vapour to give higher yields of gas and  
 476 reaction water (Pradhan, 2015; Mohan et. al 2006; Buah et al., 2007; Zhou et al., 2013; Chen et al.,  
 477 2014). However, the physical impacts of the solid residues on the pyrolysis system and products also  
 478 require attention and could provide information on system design for handling high-ash feedstocks.  
 479 Due to the high contents of inorganic materials in the trommel fines feedstocks (even after washing),  
 480 it was important to account for their distributions within the fast pyrolysis equipment units. In this  
 481 work, the inorganic constituents (mostly stones, glass, concrete and ash) present in the feedstocks  
 482 were distributed between the reactor bed, the char pot and the primary condensates in the water-  
 483 cooled condenser after the fast pyrolysis experiment as presented in Figure 3.



484

485 Figure 3: Ash/inorganics balance/distribution after fast pyrolysis of pre-treated trommel fine  
 486 feedstocks

487 For all feedstocks, majority of the ash was found in the char pot due to their fine nature, considering  
 488 that DPT was obtained after initial size reduction and sieving of the raw trommel fines to a particle  
 489 size range of 0.5 – 2 mm. The ash in the char pot could cause operational concerns due to rapid filling  
 490 of the char pot, which could lead to large pressure drops. However, more problematic would be the  
 491 ash deposited in the bed material, which could increase the weight of bed, decreasing bed fluidization,  
 492 increase the attrition of bed material and even lead to increased vapour residence time due to  
 493 restriction of gas and vapour flow. Figure 3 thus show that the accumulation of ash in the reactor  
 494 reduced by at least 60% due to the washing procedure, thereby minimizing any of the negative effects  
 495 mention above.

496 To support the reduction in ash accumulation in the bed material, photographs of the reactor bed after  
 497 pyrolysis of the three feedstocks, after burning-off the char can be found in the *Supplementary*  
 498 *Information (SI4)*. There were obvious differences in the size and heterogeneity of inorganic materials  
 499 left on the bed from DPT compared to the washed feedstocks (WPT1 and WPT2). Hence, the  
 500 influence of reducing the proportion of inorganics in the feedstock via washing and sedimentation  
 501 indicated that the reactor bed could be used for extended periods without considerable change in its  
 502 physical characteristics. Therefore, the reactor system could be designed to periodically draw-off bed  
 503 materials using the bed weight as control parameter. Whereas for DPT, the observed accumulation  
 504 and physical characteristics to the accumulated bed material, would require complete changing after  
 505 short periods of operation. Hence, the ash removal process would also be important in ensuring less  
 506 disruption in the operation of the pyrolysis operation.

507

### 508 3.3.4.2: Effect of pre-treatment methods on quality of char pot solid residues from pre-treated 509 trommel fines feedstocks

510 Among the solid residues collected after fast pyrolysis, only those obtained from the char pots could  
511 be quantitatively sampled for any further commercial application (e.g. energy recovery via  
512 combustion). Hence, only these samples were characterised for their ash contents, elemental  
513 composition, and calorific values. Table 9 shows that for all feedstocks, ash dominated the solid  
514 residues but with dramatic decreased values from the washed feedstocks. The decrease in the ash  
515 contents following the washing procedure, led to increase in char contents by over 230% compared to  
516 DPT.

517 Table 9 also shows the elemental composition of the solid residues on a dry-ash-free (daf) basis,  
518 which corroborate the influence of ash reduction in the washed feedstocks. Clearly, ash reduction led  
519 to significant increase in the carbon contents of the solid residues. Consequently, the calorific values  
520 of the solid residues from the washed feedstocks increased by nearly three times compared to DPT.  
521 Hence, energy recovery of the solid residues e.g. via incineration in cement kilns could be possible  
522 application of solid residues from the washed feedstocks. The quality of the ash could also possibly be  
523 right for use in cement production.

524

525 Table 9: Physico-chemical characteristics of the solid residues obtained from char pot after fast  
526 pyrolysis of pre-treated trommel fines

Characteristics	DPT	WPT1	WPT2
Char (wt.%) <sup>a</sup>	13.7 ± 0.52	36.3 ± 0.63	31.9 ± 1.43
Ash/inorganics (wt.%) <sup>a</sup>	86.3 ± 1.60	63.7 ± 1.32	68.1 ± 2.11
Elemental Analysis (wt.%) <sup>b</sup>			
C	66.0	85.7	82.7
H	4.17	6.25	6.08
N	2.42	3.55	3.39
S	1.68	1.18	1.35
O <sup>c</sup>	25.7	3.30	6.49
HHV (Bomb Calorimeter, MJ kg <sup>-1</sup> ) <sup>a</sup>	4.12 ± 0.71	13.5 ± 1.27	11.7 ± 0.93
<sup>a</sup> dry basis; <sup>b</sup> dry-ash-free basis, <sup>c</sup> calculated by difference			

527

528

### 529 3.4. Energy yields from trommel fines feedstocks

530 Due to the focus of this work being energy recovery from trommel fines, it is useful to demonstrate  
 531 the energy yields from the fast pyrolysis of three feedstocks. The energy yield here refer to the  
 532 amount of energy contained in the pyrolysis products in relation to the energy content of the  
 533 feedstocks as shown in Equation 6.

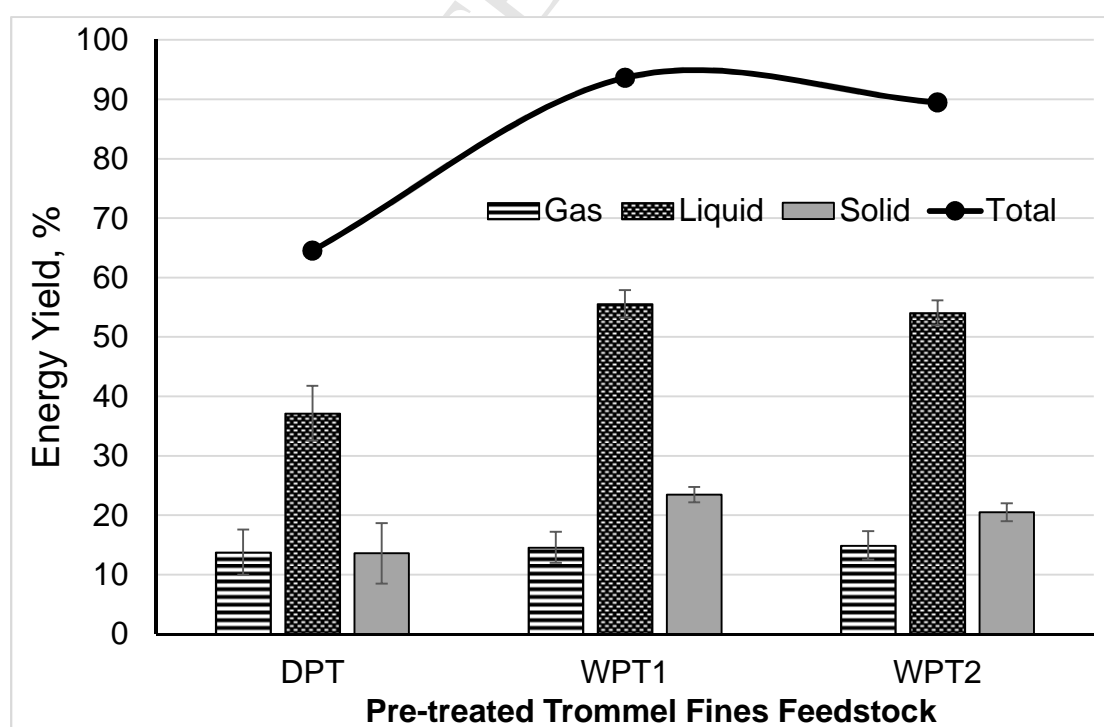
$$534 \text{ Energy yield \%} = \frac{(m \times \text{HHV})_{\text{solids}} + (m \times \text{HHV})_{\text{liquids}} + (m \times \text{HHV})_{\text{gas}}}{(m \times \text{HHV})_{\text{feedstock}}} \times 100 \dots\dots\dots \text{Eq. 6}$$

535 where, m = mass (g) and HHV = higher heating values (KJ g<sup>-1</sup>)

536 The results of the energy yield calculations are presented in Figure 4, which shows that the washing  
 537 procedures increased the amount of energy recovered from the trommel fines feedstock by at least  
 538 35% compare to DPT.

539 More interestingly, WPT1 which was obtained by washing with 100% deionised water, gave the  
 540 highest total energy yield of 93.6%, which is a 45% increment compared to DPT. The energy yield  
 541 was slightly lower for WPT2 compared to WPT1, possibly due to the presence of unidentified gas  
 542 components detected during GC analysis, which did not form part of the energy yield calculation.  
 543 Hence, using agitated washing with water gave a better feedstock for fast pyrolysis in terms of energy  
 544 yield and would simplify the treatment of the wastewater from the washing process, compared to  
 545 using a surfactant. It can be seen from Figure 4 that the liquid products dominated the energy yields  
 546 for all three feedstock and was a least two times higher than the energy contents of the gas products  
 547 and solid residues. This was in line with the goal of fast pyrolysis i.e. to convert carbonaceous  
 548 materials mainly into a liquid product.

549



550



551 Figure 4: Energy yields and distribution from fast pyrolysis of pre-treated trommel fines

552

553 However, the considerable energy contents of the solid residues from WPT1 and WPT2, may make  
554 them suitable for thermal and material recovery in cement kilns. The results of this work showed that  
555 by adopting a wet pre-treatment process, the operational problematic issues relating to the high ash  
556 contents of trommel fines may be resolved. Clearly, the reduction in ash led to considerable increase  
557 in volatile matter content and therefore energy recovery via pyrolysis. This was a big step over the dry  
558 physical pre-treatment earlier reported (Eke, Onwudili and Bridgewater, 2017), which although  
559 improved the feeding characteristics of the feedstock, ash remained a major problem.

560

#### 561 **4. Conclusions**

562 The influence of aqueous washing of a very high ash trommel fines feedstock on the yields of liquid,  
563 solid and gases produced from fast pyrolysis has been experimentally investigated. The total liquid  
564 yields (organic and water) increased after the washing procedures, with an organic yield of 36.5 wt.%  
565 dry basis. Solid residues emerged as the largest proportion of products due to the original ash contents  
566 of the feedstocks but decreased by more than 36% following washing. The addition of a surfactant  
567 during the washing procedure did not clearly influence the physico-chemical characteristics of the  
568 washed feedstocks, neither did it significantly affect the fast pyrolysis product yields. Overall, the  
569 washing procedure, reduced the ash/inorganic contents, increased the proportion of volatile matter in  
570 the feedstocks, thereby increasing the overall energy yields from the fast pyrolysis process.

571 This present work, shows that pre-treatment of high-ash waste can produce an organic-rich feedstock  
572 for thermochemical conversion by fast pyrolysis and by extension, incineration and gasification.  
573 There is a potential issue with the generation of wastewater from the washing process, which will  
574 require treatment. However, a sustainable approach could involve the use of non-heavy metal  
575 contaminated industrial wastewater streams destined for wastewater treatment plants for the washing  
576 process.

577

#### 578 **5. References**

579

580 APHA, 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed. and later  
581 revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-35:  
582 Section 1090 (Safety).

583

584 ASTM, 2013. ASTM D1762 – 84: Standard Test Method for Chemical Analysis of Wood Charcoal.  
585 American Society for Testing of Materials, Pennsylvania, USA.

586

- 587 Banks, S. W., 2014. Ash control methods to limit biomass inorganic content and its effect on fast  
588 pyrolysis bio-oil stability. PhD Thesis. Aston University Library, Aston University, Birmingham, UK.  
589
- 590 Banks, S.W., Nowakowski, D.J., Bridgwater, A.V., 2014. Fast pyrolysis processing of surfactant-  
591 washed Miscanthus. *Fuel Proc. Technol.* 128, 94–103.  
592
- 593 Baxter, L.L., Miles, T.R., Miles Jr., T.R., Jenkins, B.M., Milne, T., Dayton, D., Bryers, R.W. and  
594 Oden, L.L., 1998. The behaviour of inorganic material in biomass-fired power boilers: Field and  
595 laboratory experiences. *Fuel Proc. Technol.* 54(1-3), 47-78.  
596
- 597 Bernardo M., Lapa N., Gonçalves M., Barbosa R., Mendes B., Pinto F., Gulyurtlu, I., 2010. Toxicity  
598 of char residues produced in the co-pyrolysis of different wastes. *Waste Management.* 30:628–35.  
599
- 600 Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass and*  
601 *Bioenergy* 38, 68-94.  
602
- 603 Buah, W.K., Cunliffe, A.M., Williams, P.T., 2007. Characterization of products from the pyrolysis of  
604 municipal solid waste. *Process Safety Environ. Prot.* 85, 450–457.  
605
- 606 Channiwala, S.A., Parikh, J., 2002. A unified correlation for estimating HHV of solid, liquid and  
607 gaseous fuels. *Fuel* 81, 1051–1063.  
608
- 609 Chen, S., Meng, A., Long, Y., Zhou, H., Li, Q. and Zhang, Y., 2015. TGA pyrolysis and gasification  
610 of combustible municipal solid waste. *J. Energy Institute.* 88, (3), 332-343.  
611
- 612 Chen, X., Bi, Y., Zhang, H., Wang, J., 2016. Chlorides removal and control through water-washing  
613 process on MSWI fly ash. *Procedia Environmental Sciences*, 31, 560-566  
614
- 615 Czernik, S., Bridgwater, A.V. 2004. Overview of applications of biomass fast pyrolysis oil. *Energy*  
616 *and Fuels* 18, 590–598.  
617
- 618 Deng, L., Zhang, T., Che, D., 2013. Effect of water washing on fuel properties, pyrolysis and  
619 combustion characteristics, and ash fusibility of biomass. *Fuel Proc. Technol.* 106, 712–720  
620
- 621 Eke, J., Onwudili, J.A., and Bridgwater, A.V., 2017. Physical pre-treatment of biogenic-rich trommel  
622 fines for fast pyrolysis. *Waste Management* 70, 81 – 90.  
623

- 624 Elliott, D. 1994. Water, alkali and char in flash pyrolysis oils. *Biomass and Bioenergy* 7, 179-185.  
625
- 626 Fahmi, R., Bridgwater, A.V., Darvell, L.I., Jones, J.M., Yates, N., Thain, S. and Donnison, I.S., 2007.  
627 The effect of alkali metals on combustion and pyrolysis of *Lolium* and *Festuca* grasses, switchgrass  
628 and willow. *Fuel* 86(10-11), 1560-1569.  
629
- 630 Fivga, A., 2011. Comparison of the effect of pre-treatment and catalysts on liquid quality from fast  
631 pyrolysis of biomass. PhD Thesis, Aston University Library, Aston University, Birmingham, UK.  
632
- 633 Gudka, B.A., Jones, J.M., Lea-Langton, A.R., Williams, A., Saddawi, A., 2016. A review of the  
634 mitigation of deposition and emission problems during biomass combustion through washing pre-  
635 treatment. *J. Energy Institute*, 89 (2), 159-171.  
636
- 637 Hall, W.J., Miskolczi, N., Onwudili, J. and Williams, P.T., 2008. Thermal processing of toxic flame-  
638 retarded polymers using a waste fluidized catalytic cracker (FCC) catalyst. *Energy and Fuels* 22,  
639 1691-1697.  
640
- 641 HMRC, 2014. Landfill Tax – Liability of waste ‘fines’. Her Majesty Revenue & Customs. Available  
642 online:[https://www.gov.uk/government/uploads/system/uploads/attachment\\_data/file/325100/Landfill](https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/325100/Landfill_tax_condoc.pdf)  
643 [\\_tax\\_condoc.pdf](https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/325100/Landfill_tax_condoc.pdf). [Accessed 10 September 2016].  
644
- 645 Imran, A., Bramer, E.A., Seshan, K., Brem, G., 2016. Catalytic flash pyrolysis of biomass using  
646 different types of zeolite and online vapor fractionation. *Energies* 9(3), 187-203.  
647
- 648 Jenkins, B.M., Bakker, R.R. and Wei, J.B. 1996. On the properties of washed straw. *Biomass and*  
649 *Bioenergy* 10(4), 177-200.  
650
- 651 Johansson, A., Lisa, K., Sandström, L., Ben, H., Pilath, H., Deutch, S., Wiinikka, H., and Öhrman,  
652 O.G.W., 2017. Fractional condensation of pyrolysis vapours produced from Nordic feedstocks in  
653 cyclone. *J. Anal. Appl. Pyrolysis* 23, 244-254.  
654
- 655 Kalgo, S.A., 2011. The development and optimisation of a fast pyrolysis process for bio-oil  
656 production. PhD Thesis. Aston University Library, Aston University, Birmingham, UK.  
657
- 658 Liu, X., Bi, X. T., 2011. Removal of inorganic constituents from pine barks and switchgrass. *Fuel*  
659 *Proc. Technol.* 92(7), 1273 – 1279.  
660

- 661 Miskolczi, N., Ates, F., Borsodi, N., 2013. Comparison of real waste (MSW and MPW) pyrolysis in  
662 batch reactor over different catalysts. Part II: contaminants, char and pyrolysis oil properties. *Biores.*  
663 *Technol.* 144, 370–379.  
664
- 665 Mohan, D., Pittman, C.U., Steele, P. H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical  
666 review. *Energy and Fuels* 20, 848–889.  
667
- 668 Oasmaa, A. and Peacocke, G.V.C., 2001. A guide to physical property characterisation of biomass  
669 derived fast pyrolysis liquids. VTT Technical Research Centre of Finland, Espoo, Finland, VTT  
670 Publication 450.  
671
- 672 Oasmaa, A., Solantausta, Y., Arpiainen, V., Kuoppala, E. and Sipilä, K., 2010, Fast pyrolysis bio-oils  
673 from wood and agricultural residues. *Energy and Fuels* 24(2), 1380-1388.  
674
- 675 Pradhan, U., 2015. Physical treatments for reducing biomass ash and effect of ash content on  
676 pyrolysis products. MSc Dissertation, Auburn University, Alabama, USA. Available online:  
677 [https://etd.auburn.edu/bitstream/handle/10415/4726/Master%20thesis\\_Ujjain.pdf?sequence=2&isAllo](https://etd.auburn.edu/bitstream/handle/10415/4726/Master%20thesis_Ujjain.pdf?sequence=2&isAllowed=y)  
678 [wed=y](https://etd.auburn.edu/bitstream/handle/10415/4726/Master%20thesis_Ujjain.pdf?sequence=2&isAllowed=y). [Accessed April 1, 2017].  
679
- 680 Quek, A., Xu, W., Guo, L., Wu, D., 2016. Heavy metal removal from incineration bottom ash through  
681 washing with rainwater and seawater. *Int. J. Waste Resource* 6 (1), 1- 9 (Open Access)  
682
- 683 Renkonen, S., 2016. Removal of alkali metals for the enhancement of fast pyrolysis process. Master's  
684 Thesis. Aalto University, Espoo, Finland. Available online: [https://cris.vtt.fi/en/publications/removal-](https://cris.vtt.fi/en/publications/removal-of-alkali-metals-for-the-enhancement-of-fast-pyrolysis-pr)  
685 [of-alkali-metals-for-the-enhancement-of-fast-pyrolysis-pr](https://cris.vtt.fi/en/publications/removal-of-alkali-metals-for-the-enhancement-of-fast-pyrolysis-pr). [Accessed: 16 May 2018].  
686
- 687 Sani, M.S.H.M., Muftah, F., Muda, Z., 2010. The properties of special concrete using washed bottom  
688 ash (WBA) as partial sand replacement. *Int. J. Sust. Const. Eng. Technol.* 1(2), 65 – 76.  
689
- 690 Sebestyén, Z., Miskolczi, N., Barta-Rajnai, E., Jakaba, E., Czégény, Zs., 2017. Thermocatalytic  
691 studies on municipal solid waste. *Energy Procedia* 105, 706 – 711.  
692
- 693 Stefanidis, S.D., Heracleous, E., Patiaka, D.T., Kalogiannis, K.G., Michailof, C.M. and Lappas, A.A.  
694 2015. Optimization of bio-oil yields by demineralization of low quality biomass. *Biomass and*  
695 *Bioenergy* 83, 105-115.  
696

- 697 Teng, H. and Wei, Y.C., 1998. Thermogravimetric studies on the kinetics of rice hull pyrolysis and  
698 the influence of water pretreatment. *Ind. Eng. Chem. Res.* 37(10), 3806-3811.  
699
- 700 Velghe, I., R. Carleer, J. Yperman, and Schreurs, S., 2011. Study of the pyrolysis of municipal solid  
701 waste for the production of valuable products. *J. Anal. Appl. Pyrolysis* 92(2), 366-375.  
702
- 703 Watts, J., 2016. Trommel Fines: The Journey so far. Proceedings of CIWM North West Centre Open  
704 Meeting, March 2016. Liverpool, UK.  
705
- 706 Xue, Y., Braden, J. and Bai, X., 2017. Effect of Pretreatment on biomass pyrolysis for better quality  
707 of bio-oil. Proceedings of the AIChE Annual Meeting, October 2017. Indianapolis, USA.  
708
- 709 Zhou, C., Yang, W. Blasiak, W., 2013. Characteristics of waste printing paper and cardboard in a  
710 reactor pyrolyzed by preheated agents, *Fuel Process. Technol.* 116, 63–71.

**Highlight**

- Up to 36% ash was removed from a trommel fines (TF) feedstock by agitated washing and sedimentation
- About 78 wt% organic-rich feedstock was obtained for fast pyrolysis using a BFB bed reactor system
- VM content and pyrolysis liquid product yield increased by 20% and 35%, respectively after washing
- More than 90% of the energy content of washed TF feedstock was recovered in fast pyrolysis products.
- Liquid product gave the highest energy yields by more than two-fold for all three TF feedstocks