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

water alone giving the highest energy yield of 93%. Hence, coupling the water-washing ash reduction
process with fast pyrolysis appears to be a suitable technology for valorising feedstocks with high ash
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 determined (HMRC, 2014; Watts, 2016). This increase in landfill disposal costs means that alternative 40 methods are required. Based on the direct link between the organic content and LOI, it becomes 41 42 sensible to reduce or eliminate the organic fraction of trommel fines through energy recovery. Apart from incineration, pyrolysis appears to be a possible energy recovery technology to be applied to 43 trommel fines. Pyrolysis offers more versatility in products (gas, liquid and solid) compared to heat 44 45 energy from incineration. However, the large presence of inorganic materials (including ash) in trommel fines sample (stones, aggregates, glass and soil), represent a significant technical problem 46 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 system. Operationally, the inorganics in feedstock for fast pyrolysis can remain in the fluidized bed 50 reactor, leading to increase in volume and weight of bed material, which can have significant 51 52 influence on the pyrolysis process. In addition, the chemical properties such as thermal decomposition and catalytic activity of the inorganic materials can influence the yield and selectivity of fast pyrolysis 53 54 reaction products. For example, the presence of certain types of ash have been reported to promote the formation of solids and gas at the expense of pyrolysis liquid yield (Xue, Braden and Bai, 2017; 55 Banks, 2014; Oasmaa et al., 2010; Teng et al., 1998). In some cases, through attrition, the inorganics 56 57 can become fine particles capable of being entrained in the fluidising gas, giving rise to the contamination of the liquid and char products (Bernardo et al., 2010). These problems highlight the 58 59 need to reduce the inorganic contents of high-ash feedstocks such as trommel fines prior to fast pyrolysis. In addition, the reduction of inorganic material through physical pre-treatment will lead to 60 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.

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

2

with agitation (Jenkins et al., 1996; Baxter et al., 1998; Fahmi et al., 2007; Renkonen, 2016). 69 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 sedimentation process leading to improved ash content removal (Banks, Nowakowski, Bridgwater, 72 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).

The aim of this present work was to investigate the possibility of applying fast pyrolysis technology to 78 79 recover energy from a high-ash feedstock as a solution to preventing the diversion of trommel fines from landfills. Thus, saving costs on trommel fines disposal due to the recently increased landfill gate 80 fees for this type of solid waste. In this work, reduction of the ash/inorganic contents of a prepared 81 82 (0.5 - 2 mm particle size range) trommel fines feedstock was carried by an agitated washing and sedimentation procedure prior to applying the feedstock for fast pyrolysis using a bubbling fluidized 83 bed (BFB) reactor. The particle size range was selected to meet the requirements of the feeding 84 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 the yields of fast pyrolysis products was investigated at an optimum temperature 500 °C, as 90 determined from preliminary work. 91

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 particle size range of 0.5 - 2 mm. This size range, labelled as dry physically pre-treated (DPT), 98 represented over 70 wt% of the original feedstock as well as more than 80% of its energy content. The 99 100 detailed procedure for obtaining DPT feedstock has been reported earlier (Eke, Onwudili and Bridgwater, 2017). 101

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



117

Figure 1: Block flow diagram for agitated washing and sedimentation of prepared trommel finessample.

120

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

with 100% distilled water) and WPT2 (for the agitated washing with 1 vol% surfactant solution). The
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 (washing) procedure, the quantities of remaining solids (sediment and dissolved solids) were 131 determined gravimetrically according to USEPA Method 160.3 (APHA, 1992). For the dissolved 132 solids, the filtered wastewater was sampled into clean pre-weighed porcelain crucibles and evaporated 133 to dryness on a water bath. Thereafter, the evaporated porcelain crucibles were dried to constant 134 weight in an oven at 105 °C. The weight of dissolved solids was determined by difference. Five 135 replicate determinations were carried out on each waste water with standard deviations of <1%. The 136 sediments were likewise quantitatively transferred into pre-weighed large porcelain boat with water, 137 evaporated to dryness, oven-dried at 105 °C and weighed. 138

In addition, the elemental compositions of the ash contents of all three samples were analysed by a simple scan using a Bruker S8 Tiger X-ray Fluorescence (XRF) spectrometer, capable of quantifying elements from sodium to uranium. Firstly, the samples were separately pulverised with mortar and pestle to make fine powders and weighed into a sample cup with Mylar window. The volume of each sample was approximately 1 cm³. The results of the elements with concentrations ≥ 0.02 wt% are reported in this work.

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

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

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

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



174 175

176 177 Figure 2. Bench scale 300 g h⁻¹ fluidized bed fast pyrolysis rig set-up

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

182

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 ₂ , CO, N ₂ and O ₂) and CP-PortaPLOT held
189	isothermally at 90 °C (for CO_2 and C_1 - C_4 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 $HHV (MJ kg^{-1}) = \sum_{i=1}^{n} (x_i. HVV_i)$Eq. 1.

197 where;

i \dots = 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⁻
- 201

202 2.4.2. Characterization of liquid products

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

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

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

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

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

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

236 HHV (dry) = 0.3491C + 1.1738H + 0.1005S - 0.103400 - 0.0151N..... Eq. 2

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

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

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

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

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

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

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

282

283 3.0 Results and Discussions

284 **3.1.** Characterization of pre-treated feedstocks

From visual observations, there was no difference between the two sets of washed trommel fines 286 feedstocks. Photographs of the different fractions of DPT obtained after the washing process (with 287 288 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 influence on the feeding of the washed feedstock into the pyrolysis reactor (see Table 3 below). The 295 296 stone/glass and dissolved solids were classified as rejects, being composed mainly of inorganics.

297

285

Table 1: Mass balance results from the agitation-sedimentation pre-treatment of DPT trommel finesfeedstock

	Washing procedure		
Fractions (wt%)	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	
Total	99.8 ± 0.3	99.4 ± 0.5	

300

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

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

2011; Deng et al., 2013; Gudka et al., 2016). For instance, using the same washing procedure Deng et
al. (2013) found that ash removal efficiencies were lower for high-ash biomass samples such as rice
straw and rice hull, which also contained very high silica (SiO₂) contents of over 80%.

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

	Pre-treated trommel fines feedstock					
Parameters	DPT	WPT1	WPT2			
Proximate compositions (wt%)						
Ash content ^a	35.1 ± 6.85	22.3 ± 4.46	21.9 ± 4.69			
Volatile Matter ^a	54.7 ± 1.50	67.2 ± 1.92	68.1 ± 0.44			
Fixed Carbon ^{a, b}	7.52	7.28	6.40			
Moisture content (wt.%)	2.69 ± 0.06	3.22 ± 0.50	3.63 ± 0.32			
HHV (Bomb Calorimeter, MJ kg ⁻¹)	13.8 ± 0.33	17.5 ± 0.41	18.1 ± 0.32			
Ultimate compositions (wt%) ^a	Y					
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 ^b	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

326 **3.2. Fast pyrolysis results**

327 **3.2.1. Product yields and distribution**

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

³²⁵

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

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

Table 3: Mass balance results from the fast pyrolysis of the pre-treated trommel fines feedstock at 500 °C
 for 1 hour

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

^a dry basis

350

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

- Table 3 also shows that solid residues were the dominant product from the fast pyrolysis of DPT at 52.1 wt%, whereas the WPT1 and WPT2, resulted in much lower solid residues, decreasing by at least 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
- sol agraced washing and sedimentation, which can be attributed to their increased proportions of
- 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 small quantities of C_1 – C_4 hydrocarbon gases. Apart from propylene and CO_2 , the washing procedure 366 did not affect the yields of gas components significantly. Only a slight increase in CO₂ yield was 367 368 obtained while propylene increased nearly two-fold from the washed feedstock. The formation of propylene during catalytic fast pyrolysis of MSW has been well reported in literature to be due 369 370 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 enriched as they floated in water and then scooped with the organic materials during feedstock 373 washing. More interestingly, the increased yield of propylene obtained from the washed feedstocks, 374 375 led to 3% (WPT1) and 15% (WPT2) increases in the higher heating values of gas products compared to DPT. 376

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
HHV (MJ kg ⁻¹) ^a	14.8	15.3	17.1

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

378 ^a 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

their physical and chemical compositions. Fast pyrolysis oils from biogenic feedstock are known to

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

Table 5 shows the results of semi-quantitative XRF analysis of the three feedstocks, which indicates much higher silicon (possibly, as silica) to aluminium (possibly, as alumina) ratio, which may indicate a reduction in acidity. This may have resulted in reduced potential for dehydration reactions, which 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

	C	oncentration w	t%
Element	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
Total	19.03	11.28	9.76

398

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

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

The solids contents entrained in the liquid products from all three feedstocks were within similar 411 412 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 presented in Table 6. The elemental composition results show that water washing led to slight 415 increases in the carbon and hydrogen contents of the liquid products, while the oxygen contents 416 reduced. The increase in the carbon and hydrogen contents as well as the calorific values in secondary 417 condensates of WPT1 and WTP2 were considerably higher than in the primary condensates. These 418 results are consistent with the enrichment of organics (including biogenics, plastics and textiles) in the 419 feedstocks after washing. With regards to nitrogen contents, the washing procedures proved to be 420 effective in dramatically reducing the presence of nitrogen compounds in the liquids (both primary 421 and secondary condensates), thereby reducing the potential for NOx emissions during combustion of 422 pyrolysis oils. 423

	Pre-treated trommel fines feedstocks			
Characteristics	DPT	WPT1	WPT2	
Primary Condensate (wt%) ^a				
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	
Elemental Analysis (wt%) ^b				
С	62.9	64.0	66.5	
Н	8.75	11.2	10.7	
N	2.95	1.20	1.17	
S	0.10	0.12	0.13	

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

ACCE	EPTED MANUS	CRIPT	
O ^b	25.3	23.5	21.5
HHV (Bomb Calorimeter, MJ kg ⁻¹) ^a	32.4 ± 0.09	32.5 ± 0.23	33.8 ± 0.41
HHV dry (MJ kg ⁻¹) ^{a, d}	31.2	31.8	32.3
Secondary Condensate (wt%) ^a			
Water content	67.9 ± 2.78	28.7 ± 0.72	31.41 ± 0.36
Elemental Analysis (wt%) ^b			
С	44.7	58.5	57.1
Н	6.63	11.2	10.8
S	1.47	0.42	0.50
Ν	6.36	0.21	0.20
O ^b	40.9	29.7	31.4
HHV dry (MJ kg ⁻¹) ^{a, d}	17.4	25.9	26.4

^a dry basis; ^b dry-ash-free basis; ^c calculated by difference; ^d Eq. 2

426

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

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

The fast pyrolysis process led to the degradation of the feedstocks to produce a number of organic 440 compounds with carbon chain lengths from $C_3 - C_{16}$ as identified from GC/MS analysis. Examples of 441 442 GC/MS chromatograms of the organic portions of the primary and secondary condensates from the fast pyrolysis experiments are given in the Supplementary Information (SI3). 443

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

			% Peak Area		ea
Retention	SI%	Compound	DPT	WPT1	WPT2
time					
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	α-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

The condensation system used in the work, clearly aided in separating the organic liquids into heavy 447 448 and light fractions in the primary and secondary condensates, respectively. Essentially, the primary condensates from all three feedstocks were dominated by phenols, while the secondary condensates 449 450 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 primary and secondary condensates are shown in Table 7 and Table 8, respectively. Along with their 453 retention times, the indicative concentrations of the various compounds are represented by the 454 455 asterisks symbols shown, based on peak area percentages.

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

			% Peak Area		
Retention time	SI%	Compound	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-β-D-glucopyranose (levoglucosan)	*	***	***
31.86	90	Ethyl citrate	**		

459 SI: Similarity index

460

In general, the liquid products showed the presence of compounds commonly derived from biomass 461 (e.g. furans and phenols) and plastics (e.g. 1,2-diphenylpropane) (Hall et al., 2009). The liquid 462 products from the washed feedstocks appeared to contain higher yields of the different classes of than 463 464 those obtained from DPT, which can be attributed to the enrichment of volatile matter. The presence of a few nitrogen-containing compounds in the secondary condensate from DPT corroborated the high 465 466 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

The catalytic influence of ash on the yields of fast pyrolysis products have been well described in 474 475 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 watercooled condenser after the fast pyrolysis experiment as presented in Figure 3. 483



485 Figure 3: Ash/inorganics balance/distribution after fast pyrolysis of pre-treated trommel fine486 feedstocks

484

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.

To support the reduction in ash accumulation in the bed material, photographs of the reactor bed after 496 pyrolysis of the three feedstocks, after burning-off the char can be found in the Supplementary 497 498 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

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

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

Table 9 also shows the elemental composition of the solid residues on a dry-ash-free (daf) basis, which corroborate the influence of ash reduction in the washed feedstocks. Clearly, ash reduction led to significant increase in the carbon contents of the solid residues. Consequently, the calorific values of the solid residues from the washed feedstocks increased by nearly three times compared to DPT. Hence, energy recovery of the solid residues e.g. via incineration in cement kilns could be possible application of solid residues from the washed feedstocks. The quality of the ash could also possibly be 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.%) ^a	13.7 ± 0.52	36.3 ± 0.63	31.9 ± 1.43
Ash/inorganics (wt.%) ^a	86.3 ± 1.60	63.7 ± 1.32	68.1 ± 2.11
Elemental Analysis (wt.%) ^b			
C	66.0	85.7	82.7
н	4.17	6.25	6.08
Ν	2.42	3.55	3.39
s	1.68	1.18	1.35
O ^c	25.7	3.30	6.49
HHV (Bomb Calorimeter, MJ kg ⁻¹) ^a	4.12 ± 0.71	13.5 ± 1.27	11.7 ± 0.93

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 Energy yield % =
$$\frac{(m \ x \ HHV) solids + (m \ x \ HHV) liquids + (m \ x \ HHV) gas}{(m \ x \ HHV) feeds tock} \ x \ 100 \ \dots$$
 Eq. 6

535 where, m = mass (g) and HHV = higher heating values (KJ g⁻¹)

The results of the energy yield calculations are presented in Figure 4, which shows that the washing
procedures increased the amount of energy recovered from the trommel fines feedstock by at least
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 was slightly lower for WPT2 compared to WPT1, possibly due to the presence of unidentified gas 541 542 components detected during GC analysis, which did not form part of the energy yield calculation. Hence, using agitated washing with water gave a better feedstock for fast pyrolysis in terms of energy 543 544 yield and would simplify the treatment of the wastewater from the washing process, compared to using a surfactant. It can be seen from Figure 4 that the liquid products dominated the energy yields 545 for all three feedstock and was a least two times higher than the energy contents of the gas products 546 547 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.





- 551 Figure 4: Energy yields and distribution from fast pyrolysis of pre-treated trommel fines
- 552

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

560

561 **4. Conclusions**

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

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.

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579

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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