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1 **Meeting EU ELV targets: Pilot-scale pyrolysis automotive shredder residue**
2 **investigation of PAHs, PCBs and environmental contaminants in the solid residue**
3 **products**

4
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11
12

13 **Abstract**

14 The EU's publication of the 2017 End-of-Life Vehicle Recycling and Recovery results
15 reported that the UK failed to meet its targets. The Commission's data showed that the UK
16 only achieved a rate of 94.1% falling short of the 95% target. The treatment of automotive
17 shredder residue (ASR) using pyrolysis technologies offers a potential solution to this
18 shortfall. The pyrolysis products could contribute to the target as well as supporting the
19 circular economy package. However, there are questions about their hazardous nature and
20 whether they qualify as secondary products. ASR, from a commercial plant, was processed
21 through a pilot-scale pyrolysis unit, which separated the char into two fractions: coarse ≥ 0.1
22 mm and fine ≤ 0.1 mm. These were chosen as potential commercial products. Chars were
23 produced from two processing temperatures of 800 and 1000°C. These temperatures
24 maximise gas production and produce the best "quality" char in terms of limiting organic
25 contamination. It was found that the toxicity of the chars changed with both processing
26 temperature and size fraction; with the maximum total PAHs concentration in the fine
27 fraction at 800°C. The coarse fractions were shown to be non-hazardous. It is suggested that
28 some form of post-separation may be required to remove the hazardous component. The
29 implication was that non-separated char could be classified as hazardous even if its overall
30 characteristics were not, due to the role of dilution. If there were any questions about the
31 status of the char this could prevent the use of ASR to meet the higher ELV target.
32

33

34 **Keywords:** Automotive shredder residue; Pyrolysis; Char; PAHs analysis; PCBs analysis;
35 waste acceptance criteria

36

37 **1. Introduction**

38 Once the End-of-Life Vehicle (ELV) has been depolluted and dismantled it is shredded for
39 metals recovery. The unrecoverable material is designated automotive shredder residue
40 (ASR) and is destined for landfilling. The ASR consists of a complex mixture of organic
41 materials such as foams, plastics, rubber, fibres, textiles as well as inorganic materials like
42 glasses, metals and inerts (Cossu and Lai, 2015). The ASR fraction may be up to 25% of the
43 initial ELV's mass. In order to meet the ELV Directive of 95% post-shredder processing is
44 required. The final composition of ASR may vary depending on the post-shredder
45 technologies employed at different shredder sites. Typical differences are based on the use of
46 eddy current separators to remove non-ferrous metal (wires) or trommels and sink float
47 separation for the recovery of polymers (Vermeulen et al., 2011). It is anticipated that in the
48 future, the amount of ASR will increase due to car manufacturing changes to light weighting
49 and new material usage (polymer substitution), (Davies, 2012; Alonso et al., 2007). Other
50 changes to vehicles are the increase in electronic components units and change from
51 combustion fuel to electric batteries or fuel cells. This will result in the presence of high
52 value resources like gold and rare earth metals (Cucchiella et al., 2016; Restrepo et al., 2017)
53 but also brings its own challenges to attempts to meet the ELV directive target.

54 The European ELV Directive (EC, 2000) and the recently adopted Circular Economy
55 Action Plan (EC, 2019) are forcing the shredding operators to recover 95% wt of a vehicle
56 and achieve zero waste to landfill. Already in 2017, the UK failed to meet the higher target
57 by only achieving 94.1% (Eurostat ELV 2019). In order to meet these challenges, it will be
58 necessary to consider thermal treatment of ASR through either gasification or pyrolysis

59 (Cossu and Lai, 2015; Ruffino, 2014). Currently, there are no commercial plants that offer a
60 feasible method for the thermal recovery of ASR (Khodier et al., 2018). For example, at
61 present the Ebara plant in Japan (Cossu et al., 2014) mixes sewage sludge in a 70/30 ratio
62 (Selinger et al., 2003) but this falls short of the Circular Economy Action Plan.

63 Pyrolysis is defined as the thermal degradation of materials in the absence of oxygen
64 at operating temperatures above 300°C. The products of this process are a char (solid
65 residue), condensable organic vapours (condense to a dark brown viscous liquid known as
66 pyrolytic liquids) and gases (non-condensable organics). Depending on the final temperature,
67 pyrolysis will yield mainly char at low temperature ($\leq 450^{\circ}\text{C}$), mainly liquids/oil at moderate
68 temperature (450-700°C) and mainly gases at high temperature ($\geq 800^{\circ}\text{C}$). Char is primarily
69 composed of carbon (carbon content varies as the pyrolysis temperature changes (Williams,
70 2005; Tchobanoglous et al., 1993), low nitrogen and hydrogen contents, metals and other
71 inert materials, which is why it has been seen as a fuel or as an inert additive (Fortuna et al.,
72 1997). Char has a high nutrient retention capacity, high surface area and high water retention
73 capacity and therefore may be applied as a strong soil modifier. The use of the char in this
74 way would assist in meeting the ELV Directive target. However, further studies are necessary
75 to identify whether the char produced from a specific feedstock/material is environmentally
76 inert to be deposited on land or landfilled. There are legislative restrictions to protect the flora
77 and fauna from pollutant up-take to unacceptable levels. For example, polycyclic aromatic
78 hydrocarbons (PAHs) are included in the European Union (EC, 2004) and US Environmental
79 Protection Agency (USDHHS, 1995) list as priority pollutants. PAHs represent the largest
80 group of compounds that are mutagenic, carcinogenic and teratogenic (GFEA, 2012). Other
81 examples which are considered environmental pollutants are polychlorinated biphenyls
82 (PCBs) which are mixtures of up to 209 individual chlorinated compounds, of which 113 are
83 known to be present in the environment and are classified as persistent organic pollutants and
84 may have mutagenic properties (GFEA, 2012; Pascal, 2005).

85 There have been numerous studies over the years on ASR pyrolysis (;Santini et al.,
86 2012; Haydary et al., 2016; Mayyas et al., 2016; Notarnicola et al., 2017; Anzano et al.,
87 2017) which have focused on the product yields based on lab-scale trials (mg-g hr^{-1}). In
88 contrast the characterisation and the use of pyrolysis products, (the char), have received less
89 attention. Also, Vermeulen et al. (2011), Harder and Forton (2007) and Cossu et al. (2014) in
90 their comprehensive review concluded that there was very limited use of ASR pilot-scale
91 pyrolysis experiments. This means that sampling errors from lab-scale experiments
92 potentially play a significant role in the outcome analysis of the ASR products. A notable
93 attempt at addressing the shortfall of lab-based testing was carried out by Day et al. (1996)
94 who used a commercial screw kiln unit. This had a continuous feed of 200 kg hr^{-1} of ASR
95 and corresponded to a residence time of 15 min at 500°C . The chemical composition of the
96 gas, liquid and solid fractions were all determined. The residual char was discharged from the
97 reactor into a catch pot fitted with a screen separator to produce two size fractions: a fine
98 portion ($<0.12 \text{ mm}$) and a coarse portion ($>0.12 \text{ mm}$). Day et al (1996) only carried out heavy
99 metal concentrations and leachability tests on both char portions. Elemental analysis was
100 performed and although heavy metals concentrations were relatively high (zinc, lead and
101 copper in both fine and coarse char fractions), these were not detected in the leachability
102 tests. As they did not investigate the amounts of organic pollutants in the fractions, they could
103 not determine the hazardous or non-hazardous nature of the fractions. Galvagno et al. (2001)
104 used a pilot-scale rotary kiln ($5\text{-}7 \text{ kg hr}^{-1}$), with a residence time up to 40 min. They used
105 varying process temperatures ($550, 600, 680^\circ\text{C}$). Galvagno et al. (2001) carried out similar
106 analysis to Day et al. (1996) with comparable results. Khodier et al. (2017) used a continuous
107 feed of 10 kg hr^{-1} of ASR with a residence time of 15 min at two temperatures of 800 and
108 1000°C . They investigated the characteristics of the char produced from a separator to two
109 size fractions (fine $<0.10 \text{ mm}$ and coarse $>0.10 \text{ mm}$). The results revealed that the higher
110 calorific value was in the fine fractions and therefore had a high economic value. The coarse

111 fraction had a high ash content, iron, silica, aluminium, calcium and nickel. They concluded
112 that the segregation of char would assist in optimisation of energy and resource recovery.
113 However, they recommended that the levels of organic pollutant, such as PAHs, in the char
114 would potentially determine its processing and secondary use. Anzano et al. (2017) claim to
115 be one of the first to investigate the distribution of PAHs in the char produced from ASR
116 pyrolysis. They used lab-scale pyrolysis and did not detect any PAHs in the char produced at
117 500°C, however, at 700°C the maximum total concentration of 19.41 ng g⁻¹ was observed.
118 These results support further investigation of PAHs in the solid residue from larger-scale
119 ASR pyrolysis.

120 This study investigates the organic content of the solid residue from ASR pyrolysed in
121 a pilot-scale rotary kiln test rig at 10 kg hr⁻¹. Solid residue products were characterised for
122 PAHs concentration. Furthermore, unlike other studies in the literature, the concentrations of
123 PCBs, BTEX (benzene, toluene, ethylbenzene, xylenes), TOCs (total organic carbon) were
124 determined. In addition, the study measured all the parameters necessary for the waste
125 acceptance criteria (WAC) in the solid residue and thereby determined their potential
126 environmental impact.

127

128 **2. Experimental methods**

129 **2.1 The ASR feed material**

130 The ASR materials production, sample preparation and size reductions used in this series of
131 tests were reported previously (Khodier et al., 2018; Khodier et al., 2017). A total of 208 t of
132 ASR was collected from a processing plant over four day period. This was cone and
133 quartered to produce a total sample of 800 kg. This was processed through a 50 mm screen to
134 produce the final feedstock. Material compositions, physical and chemical characterisation
135 are presented in Table 1.

136

137 **Table 1.** Characteristics of the ASR feed material used in the study.

| Parameter | Unit | Results | Components | | | |
|--|-------|---------|---------------|------------------|---------------------|-------|
| | | | mg/kg | %wt | | |
| Gross Calorific value | kJ/kg | 16300 | <i>Metals</i> | <i>Materials</i> | | |
| <i>Proximate analysis</i> ^a | | | Cu | 7 | Plastic | 47.88 |
| Moisture | % wt | 22 | Hg | < 1 | Foam | 2.94 |
| Ash | % wt | 20 | Cd | < 1 | Rubber | 15.88 |
| Volatile matter | % wt | 53 | Tl | < 1 | Textile/fabric | 10.35 |
| Fixed carbon | % wt | 5 | Sb | 12 | Cork | 11.05 |
| Total | % wt | 100 | As | < 1 | Wood | 1.17 |
| <i>Ultimate analysis</i> | | | Cr | 16 | Wiring/electrical | 1.76 |
| C | % wt | 38.46 | Co | < 1 | Glass | 0.82 |
| H | % wt | 3 | Pb | 56 | Paper | 0.47 |
| N | % wt | 2 | Mn | 24 | Cardboard | 0.23 |
| O | % wt | 14 | Ni | 7 | Dirt | 0.35 |
| S | % wt | 0.2 | Sn | < 1 | Fines (e.g. soil) | 6.57 |
| Cl | % wt | 0.3 | V | < 1 | Metals ^b | 0.47 |
| | | | | | Others | 0.06 |

138 ^a ASR = as-received (AR) after shredding.

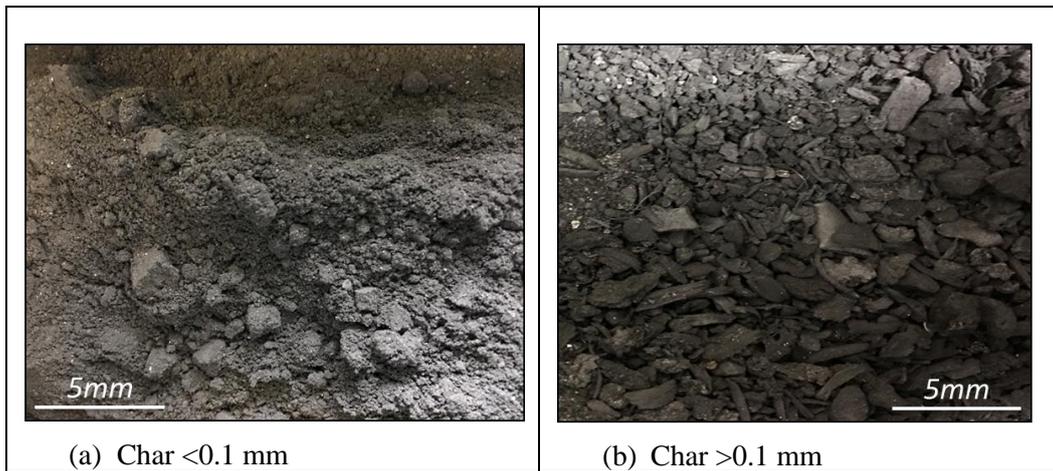
139 ^b fine metals caught into the soil/dirt, (hard to separate).

140

141 2.2 The pyrolysis process – char sample preparation

142 Pyrolysis experiments were performed in a pilot-scale rotary kiln at two temperatures of 800
 143 and 1000°C with a constant ASR feed rate of 10 kg hr⁻¹ which corresponded to a residence
 144 time of about 15 min. The rotary kiln unit description, feeding system and heating procedure
 145 has been explained previously (Khodier et al., 2017). The two temperatures were chosen to
 146 maximise the production of gas and produce char with lowest amounts of residue organics.
 147 By operating at the higher temperatures it would present char with a lower range of
 148 contaminants than those from lower operating temperatures typically in the 500-700°C. Two
 149 char fractions were produced >0.1 mm and <0.1 mm. The proximate split was 80:20% wt
 150 ratio coarse to fine fractions by weight. Fig. 1 shows the two fractions of residue, illustrating
 151 the different physical nature of each one. Samples were collected after each test run, weighed
 152 and stored prior to analysis.

153



154 **Fig. 1.** Optical images of the pyrolysis char products.

155

156 **2.3 Pollutant/Environmental analysis of ASR and the solids residue**

157 *2.3.1 PAHs, PCB, TPH, BTX analysis*

158 The experimental methods used were statistically controlled using both process and
 159 instrument quality control samples. These were sourced independently from the solutions
 160 used to calibrate the analysis methodology. Instrument and process blank solutions were also
 161 run at regular intervals (with each batch) to monitor potential sources of contamination.

162 All samples for the analysis were extracted from cone and quartered samples of the
 163 ASR and pyrolysis solid residues. Ultrasonic-enhanced solvent extraction, based on the EPA
 164 3550 method (USEPA, 2007), was used to prepare samples. Anhydrous sodium sulphate was
 165 added to a 5 g sample and extracted using ultrasonic extraction with a 50:50 mixture of
 166 hexane/acetone. Agilent 7890 and 6890 gas chromatographs, in various configurations, were
 167 used to detect PAH, PCB, TPH and BTX as shown in Table 2.

168

169 **Table 2.** Organic analysis operating conditions.

| Pollutants | Agilent Instrument | Injection volume μ l | Detector | Column | Temperature Programme | Carrier Gas |
|------------|--------------------|--------------------------|----------|--------|-----------------------|-------------|
|------------|--------------------|--------------------------|----------|--------|-----------------------|-------------|

| | | | | | | |
|------|------|-----|---------------------|--------|---|----------------|
| PAH | 7890 | 2.0 | GC/MS ^a | DB-5ms | 40°C for 1 min to 120°C at 25°C min ⁻¹ , then 160°C at 10°C min ⁻¹ and finally to 300°C at 5°C min ⁻¹ , final hold time of 15 min. | He |
| PCB | 7890 | 2.0 | GC/ECD ^b | HP-5ms | 75°C for 3 min, to 150°C at 15°C min ⁻¹ , then to 260°C at 6°C min ⁻¹ , finally to 300°C at 20°C min ⁻¹ rate held for 5 min | N ₂ |
| TPH | 6890 | 1.0 | GC/FID ^c | DB-5ms | 40°C for 1 min to 320°C at 10°C min ⁻¹ , final hold of 40 min. | He |
| BTEX | 6890 | 1.0 | GC/FID | DB-642 | 30°C for 1 min, to 100°C at 5°C min ⁻¹ to 220°C at 8°C min ⁻¹ , final hold of 5 min. | He |

170 ^a GC/MS: gas chromatography equipped with high resolution mass spectrometry

171 ^b GC/ECD: gas chromatography equipped with electron capture detector

172 ^c GC/FID: gas chromatography equipped with flame ionisation detector

173
174

175 2.3.2 TOCs and LOI analysis

176 Samples for both TOC and LOI were prepared from air-dried and ground samples (5
177 g) that had been ground nominally to 212 µm. The ground samples were weighed and heated
178 in a furnace (Lenton Furnaces & Ovens, Hope Valley, UK) to the required temperature. Total
179 organic carbon was analysed for both ASR and char based on the methods used by Heron et
180 al., (1997) and Schumacher, (2002). Samples were mixed with 10 ml of concentrated
181 sulphuric acid. Total organic carbon content was determined using an ELTRA induction
182 furnace fitted with a nondispersive infrared (NDIR) cell (CS-800, ELTRA GmbH, Germany).

183 Loss on ignition was determined from samples in a furnace at 550°C for 2 hr. It was
184 then placed in a desiccator to cool for at least 60 min. Loss on ignition was calculated from
185 the loss in mass of the sample.

186 2.3.3 pH analysis

187 Sample using BS 6068 standard (1986). A Jenway Model 3510 pH meter was used to
188 determine pH of original ASR and char samples.

189 **3. Results and discussion**

190 **3.1 Organic contaminates/Environmental toxicity of ASR**

191 The results obtained from the organic analysis conducted on the ASR are presented in Table
192 3. The criteria used by landfill operators to distinguish inert waste, stable non-reactive waste
193 and non-hazardous waste (transposed from Council Decision annex 2003/33/EC (EC, 2002))
194 are shown in Table 4. It can be seen that the amount of oils and organic contaminants
195 detected in the ASR sample (Table 3) were within the limit values which apply to non-
196 hazardous waste acceptance criteria. Mancini et al. (2010) and Morselli et al. (2010) reported
197 higher amounts of mineral oils contents in the ASR obtained from the Italian shredder
198 industry of 22.3 g kg⁻¹ and 26.8 g kg⁻¹, respectively. This may be in part be explained by the
199 depollution and dismantling technologies applied to the ELVs prior to shredding and be
200 specific to national standards at shredder facilities. The concentrations of the PCB in our
201 study were similar to those reported by Santini et al. (2012) of 0.008 mg kg⁻¹ value. Whereas,
202 Viotti et al. (2010), Morselli et al. (2010), Mancini et al. (2010) and Cossu, (2014) detected
203 higher PCBs concentrations of 2.97, 5.3, 7.9 and 44.45 mg kg⁻¹, respectively. The outcome
204 from TOC, BTEX, LOI and PAHs analysis in the ASR were not reported in the literature for
205 comparison to this study's results.

206 **Table 3.** Organic analysis of the feed material (ASR).

| Parameter | Result |
|---|---------------|
| TOC (% w/w) | 0.26 |
| LOI (% w/w) | 1.39 |
| BTEX (mg kg ⁻¹) | < 0.01 |
| PCBs (7 Congeners) (mg kg ⁻¹) | < 0.01 |
| Mineral oil (C10-C40) (mg kg ⁻¹) | 7.7 |
| PAHs (Total Speciated) (mg kg ⁻¹) | 6.1 |
| pH | 7.20 |

207

208 **Table 4.** Criteria for granular waste acceptable at landfills (Transposed from Council

209 Decision annex 2003/33/EC (EC, 2002)).

| Parameter | Inert waste landfill | Stable non-reactive / non-hazardous | Hazardous waste landfill |
|---|----------------------|-------------------------------------|--------------------------|
| TOC (%w/w) | 3 | 5 | 6* |
| LOI (%w/w) | <10 | <10 | 10* |
| BTEX (mg kg ⁻¹) | 6 | | |
| PCBs (7 Congeners) (mg kg ⁻¹) | 1 | | |
| Mineral oil (C10-C40) (mg kg ⁻¹) | 500 | | |
| PAHs (Total Speciated) (mg kg ⁻¹) | 100 | | |
| pH | | > 6 | |

210 *Keys: * Either TOC or LOI must be used for hazardous wastes*

211

212 3.2 Organic contaminates of char residue

213 The analysis of the residual char was performed on both the coarse and fine fractions. The
 214 coarse materials showed undetectable levels of PAHs, PCBs, BTEXs and TPHs. This
 215 supported previous findings of the inert nature of coarse char (>0.1 mm) (Khodier et al.,
 216 2017). The PAHs' content in the fine chars samples are shown in Table 5. The maximum
 217 total concentration of PAHs was detected in the char produced at 800°C, with naphthalene
 218 and phenanthrene being the most abundant compounds. Similar results for these compounds
 219 were reported by Day et al. (1999) for ASR pyrolysis char produced at 750°C. In contrast at
 220 1000°C, fluoranthene and pyrene were the most abundant compounds with concentration of
 221 879 and 1250 mg kg⁻¹ respectively. The concentration of the total PAHs detected in our study
 222 were higher than the values reported previously in the literature with typical values being:
 223 1.2-100 mg kg⁻¹ (Buss et al., 2016); 1-19.41 ng kg⁻¹ (Anzano et al., 2017). This may be a
 224 reflection that these studies were conducted in small lab-scale experiments. Sampling errors
 225 on the feedstock, due to the limited amount of material processed, would have had a
 226 significant influence. From our ASR feedstock, it was concluded that a significant source of
 227 PAHs was from the plastic and rubber fractions (Table 1).

228 **Table 5.** Concentrations of PAHs in fine char fraction (at 800 and 1000°C).

| Target Compounds | CAS* | R.T. # (min) | Char 800°C (mg kg ⁻¹) | Fit (%) | Char 1000°C (mg kg ⁻¹) | Fit (%) |
|------------------|------|--------------|-----------------------------------|---------|------------------------------------|---------|
|------------------|------|--------------|-----------------------------------|---------|------------------------------------|---------|

| | | | | | | |
|------------------------|----------|-------|----------|----|-----------|----|
| Naphthalene | 91-20-3 | 3.23 | 5010.00 | 99 | 46.60 | 99 |
| Acenaphthylene | 208-96-8 | 4.36 | 2040.00 | 99 | 91.00 | 99 |
| Acenaphthene | 83-32-9 | 4.48 | 56.80 | 73 | < 8.00 | - |
| Fluorene | 86-73-7 | 4.87 | 192.00 | 99 | 9.63 | 97 |
| Phenanthrene | 85-01-8 | 5.72 | 3980.00 | 99 | 429.00 | 99 |
| Anthracene | 120-12-7 | 5.77 | 724.00 | 97 | 101.00 | 98 |
| Fluoranthene | 206-44-0 | 7.07 | 2470.00 | 89 | 879.00 | 90 |
| Pyrene | 129-00-0 | 7.36 | 2870.00 | 87 | 1250.00 | 88 |
| Benzo[a]anthracene | 56-55-3 | 9.05 | 401.00 | 96 | 93.70 | 94 |
| Chrysene | 218-01-9 | 9.11 | 504.00 | 99 | 124.00 | 97 |
| Benzo[b]fluoranthene | 205-99-2 | 10.58 | 583.00 | 97 | 268.00 | 90 |
| Benzo[k]fluoranthene | 207-08-9 | 10.62 | 211.00 | 98 | 70.30 | 90 |
| Benzo[a]pyrene | 50-32-8 | 11.01 | 609.00 | 97 | 336.00 | 96 |
| Indo[1,2,3-cd]pyrene | 193-39-5 | 12.38 | 496.00 | 89 | 451.00 | 91 |
| Dibenzo[a,h]anthracene | 53-70-3 | 12.41 | 42.10 | 85 | 13.10 | 72 |
| Benzo[g,h,i]perylene | 191-24-2 | 12.68 | 524.00 | 93 | 627.00 | 95 |
| Coronene | 191-07-1 | 14.88 | 136.00 | 52 | 285.00 | 68 |
| Total (USEPA16) PAHs | | | 20712.90 | | < 4797.33 | |

229 *Keys: * Chemical abstracts service registry number; # Retention time*
230

231 The occurrence of PCBs and BTEX in the fine fraction produced at various pyrolysis
232 temperatures are presented in Table 6. The concentrations of PCBs in the char at 800°C were
233 lower compared to the 1000°C. This was consistent with the observation by (Conesa et al.,
234 2009) that the dioxin and dioxin-like PCBs concentrations increased in pyrolysis products
235 with increasing chlorinated degree and process temperature. The total concentrations of PCBs
236 in char residues produced at 800°C and 1000°C were < 175.0 µg kg⁻¹ and < 508.7 µg kg⁻¹,
237 respectively. These concentrations were higher than the value reported by Joung et al. (2007)
238 of 0.869 µg kg⁻¹. However, their pyrolysis experiments were carried out using a bench-scale
239 reactor at 600°C with no size separations. Therefore, dilution may have occurred from the
240 more inert coarser fraction. This would have similar limitations to those of Buss et al. (2016)
241 and Anzano et al. (2017). The TPHs concentrations of the fine fraction pyrolysed at 1000°C
242 was significantly lower (a decrease of 67.6%) compared to 800°C material, with its maximum
243 value of 36200 mg kg⁻¹. It was noted that the quantities of BTEX dropped dramatically at
244 pyrolysis temperature of 1000°C. In descending order, the BTEX with the highest
245 concentrations (in the char from 800°C pyrolysis) were benzene, toluene, xylenes, *m/p*-

246 xylenes, *o*-xylene and ethylbenzene. It is interesting to note that thermal treatment of ASR
247 resulted in an increase of organic pollutant emissions (PCBs and BTEX) within the fine
248 fraction, see Table 3. Comparing the values against the waste accepted criteria (Table 4), the
249 coarse chars are non-hazardous and may be safe to be disposed of and/or recycled unlike the
250 fine fraction. This is clearly illustrated in Fig 2 and shows that the fine char does not meet the
251 WAC thresholds. The observed difference between the fine and coarse fractions can be
252 attributed to the residence time within the pyrolyser. The fine fraction had a shorter residence
253 time and therefore a decrease in cracking reactions. This resulted in organic material residing
254 with the char. Similar observation were made by Conesa et al. (2009). Results obtained for
255 TOC (fine fraction) highlighted no significant differences between solid residues of < 25% wt
256 concentrations at various temperatures, whereas values obtained for LOI revealed a slight
257 increase in concentration in 1000°C char residue. Post char treatment may therefore be
258 necessary to meet WAC requirements. However, a potential solution to avoid this would be
259 pretreating the ASR instead. Cossu and Lai, (2013) found that washing of ASR achieved the
260 removal of more than 60% of the dissolved organic carbon and chemical oxygen demand.

261 It was found that the fine material from 1000°C had a similar pH to that of the original
262 ASR material of 7.2 (Table 4). This implies that there will not be any significant leaching of
263 acidic or basic components of the char residues. This is in contrast to the char from 800°C
264 which had a higher pH value of 9.3, which means that it may lead to potential leaching of
265 basic components from the chars.

266 The difference in properties of the two char fractions may require post screening for
267 acceptance by potential end users as well as to minimise any environmental impacts from
268 final disposal into landfill.

269 Char production from the pyrolysis of ASR in this study was between 30-32% wt which is
270 similar to that reported in the literature of 33-68% wt (Harder and Forton, 2007). These
271 quantities may increase with the change of ELV composition to higher proportion of plastics

272 (Vermeulen et al., 2011). Further investigation of the impact of pre-treatment of the ASR on
 273 the fractions would be beneficial as the recycling industry moves towards more post-shredder
 274 treatment activity such as sink-float segregation.

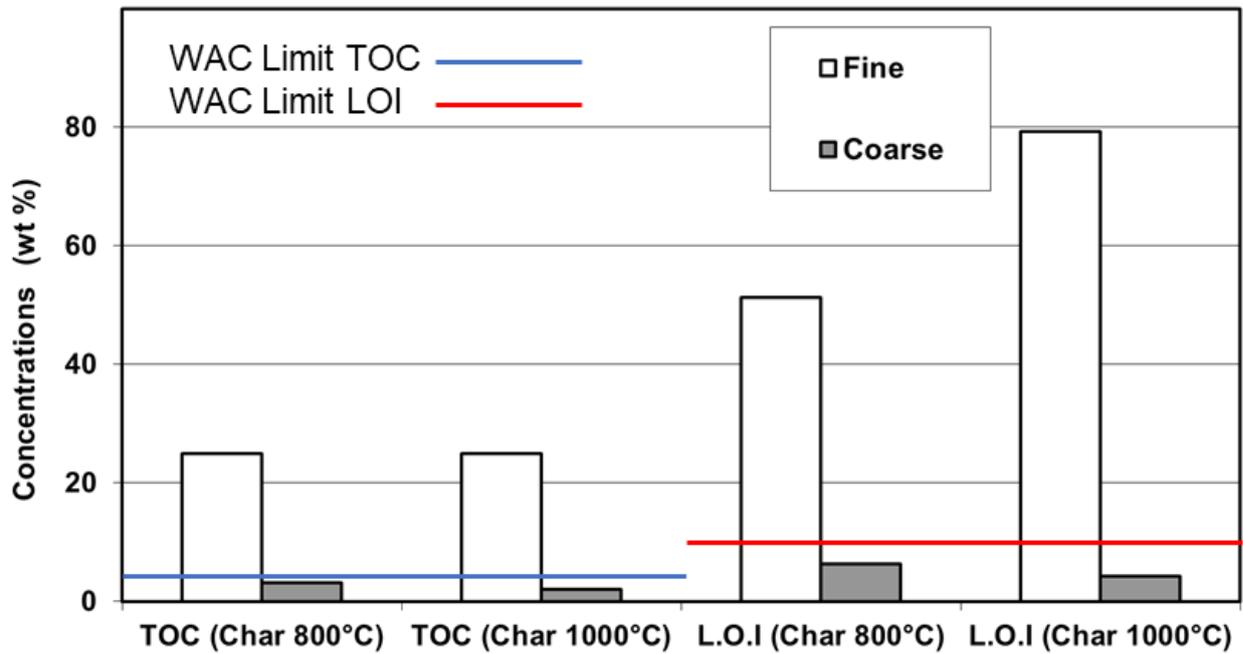
275

276 **Table 6.** Concentrations of PCBs (7 congeners) and BTEX in produced fine char fraction (at
 277 800 and 1000°C).

| Compounds | Char 800°C ($\mu\text{g kg}^{-1}$) | Char 1000°C ($\mu\text{g kg}^{-1}$) |
|---------------------|---|--|
| PCB28 | < 25.0 | 59.1 |
| PCB52 | < 25.0 | 87.2 |
| PCB101 | < 25.0 | 53.9 |
| PCB118 | < 25.0 | < 25.0 |
| PCB153 | < 25.0 | < 25.0 |
| PCB138 | < 25.0 | 210.9 |
| PCB180 | < 25.0 | 47.6 |
| Benzene | 13100 | 420 |
| Toluene | 1220 | < 25 |
| Ethylbenzene | 167 | < 25 |
| Xylenes | 855 | < 75 |
| <i>m/p</i> -xylenes | 679 | < 50 |
| <i>o</i> -xylene | 176 | < 25 |
| MTBE | < 50 | < 50 |

278

279



280

281 **Fig 2.** Concentration of TOC & LOI in char samples (at 800 and 1000°C).

282 4. Conclusions

283 The potential future utilisation of ASR as an energy source in advanced pyrolysis processes is
 284 currently an attractive option for the shredder industry. The increasing legislative pressures
 285 and worsening public perception of plastic materials could prevent the future utilisation of
 286 ASR and its by-products. This study has shown some of the potential challenges of thermally
 287 treating ASR as a recovery route to meet the ELV directive target.

288 A pilot-scale rotary kiln pyrolyser was used to determine and characterise the organic
 289 pollutants from pyrolysis of ASR and untreated ASR. The results revealed that the ASR
 290 (obtained from UK shredder plant) can be classified as a non-hazardous waste due to its low
 291 contents of hazardous organic substances such as PCBs, PAHs, BTEX and mineral oil.
 292 Furthermore, TOC and LOI analysis confirmed that it was an inert waste and complied with
 293 the criteria for granular waste acceptance at UK landfills. However, this may not be the case
 294 once it has undergone pyrolysis. The char was separated into two fractions fine <0.1mm,

295 which comprised 20%wt and >0.1 mm coarse which was 80%wt. Low levels of PAHs,
296 BTEX and TPHs were found in the fine char produced from two pyrolysis temperatures
297 1000°C and 800°C compared to none in the coarse char. The TOC and LOI analysis of the
298 chars showed that the fines did not meet the WAC criteria unlike the coarse char. This meant
299 that the fine char would have to be dealt with at a specialised landfill site. Whereas the coarse
300 char was classified as an inert material and could be used for secondary uses.

301 The choice of appropriate pyrolysis conditions could be an important factor in obtaining
302 saleable products from the char material. Segregation might be required to make it suitable
303 for further resource recovery processes. The results from the analysis indicated that post-
304 pyrolysis segregation could be required. Therefore, allowing it to be used for secondary
305 markets and contribute towards the ELV 95% target. Further studies would be required in
306 order to optimise the segregation of char in order to assist in energy and resource recovery.
307 This would ensure that commercially exploitable products were obtained at a reasonable
308 economic cost.

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