



## Article

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

Williams, Karl S and Khodier, Ala

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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  
5 Karl S. Williams <sup>a, \*</sup>, Ala Khodier <sup>a, b</sup>

6  
7 <sup>a</sup> Centre for Waste Management, University of Central Lancashire, Preston, PR1 2HE, UK

8 e-mail: [kswilliams@uclan.ac.uk](mailto:kswilliams@uclan.ac.uk), [akhodier2@uclan.ac.uk](mailto:akhodier2@uclan.ac.uk)

9 <sup>b</sup> Recycling Lives Recycling Park, Preston, Lancashire, PR2 5BX, UK

10 e-mail: [ala.khodier@recyclinglives.com](mailto:ala.khodier@recyclinglives.com)  
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  $\geq 0.1$   
22 mm and fine  $\leq 0.1$  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 ( $\text{mg-g hr}^{-1}$ ). 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  $200 \text{ kg hr}^{-1}$  of ASR  
95   and corresponded to a residence time of 15 min at  $500^\circ\text{C}$ . 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  $10 \text{ kg hr}^{-1}$  of ASR with a residence time of 15 min at two temperatures of 800 and  
108    $1000^\circ\text{C}$ . 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<sup>-1</sup> 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<sup>-1</sup>. 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> <sup>a</sup>			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 <sup>b</sup>	0.47
					Others	0.06

138 <sup>a</sup> ASR = as-received (AR) after shredding.

139 <sup>b</sup> 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<sup>-1</sup> 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

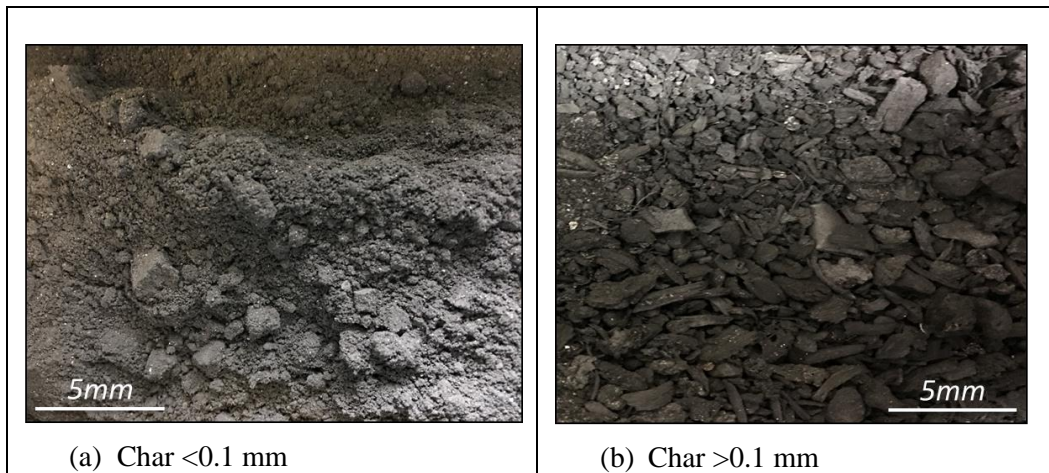
149 char fractions were produced >0.1 mm and <0.1 mm. The proximate split was 80:20% wt

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 $\mu$ l	Detector	Column	Temperature Programme	Carrier Gas
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PAH	7890	2.0	GC/MS <sup>a</sup>	DB-5ms	40°C for 1 min to 120°C at 25°C min <sup>-1</sup> , then 160°C at 10°C min <sup>-1</sup> and finally to 300°C at 5°C min <sup>-1</sup> , final hold time of 15 min.	He
PCB	7890	2.0	GC/ECD <sup>b</sup>	HP-5ms	75°C for 3 min, to 150°C at 15°C min <sup>-1</sup> , then to 260°C at 6°C min <sup>-1</sup> , finally to 300°C at 20°C min <sup>-1</sup> rate held for 5 min	N <sub>2</sub>
TPH	6890	1.0	GC/FID <sup>c</sup>	DB-5ms	40°C for 1 min to 320°C at 10°C min <sup>-1</sup> , 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 <sup>-1</sup> to 220°C at 8°C min <sup>-1</sup> , final hold of 5 min.	He

170 <sup>a</sup> GC/MS: gas chromatography equipped with high resolution mass spectrometry

171 <sup>b</sup> GC/ECD: gas chromatography equipped with electron capture detector

172 <sup>c</sup> 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<sup>-1</sup> and 26.8 g kg<sup>-1</sup>, 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<sup>-1</sup> 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<sup>-1</sup>, 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).

<b>Parameter</b>	<b>Result</b>
TOC (% w/w)	0.26
LOI (% w/w)	1.39
BTEX (mg kg <sup>-1</sup> )	< 0.01
PCBs (7 Congeners) (mg kg <sup>-1</sup> )	< 0.01
Mineral oil (C10-C40) (mg kg <sup>-1</sup> )	7.7
PAHs (Total Speciated) (mg kg <sup>-1</sup> )	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 <sup>-1</sup> )	6		
PCBs (7 Congeners) (mg kg <sup>-1</sup> )	1		
Mineral oil (C10-C40) (mg kg <sup>-1</sup> )	500		
PAHs (Total Speciated) (mg kg <sup>-1</sup> )	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<sup>-1</sup> 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<sup>-1</sup> (Buss et al., 2016); 1-19.41 ng kg<sup>-1</sup> (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 <sup>-1</sup> )	Fit (%)	Char 1000°C (mg kg <sup>-1</sup> )	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<sup>-1</sup> and < 508.7 µg kg<sup>-1</sup>,  
237        respectively. These concentrations were higher than the value reported by Joung et al. (2007)  
238        of 0.869 µg kg<sup>-1</sup>. 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<sup>-1</sup>. 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.

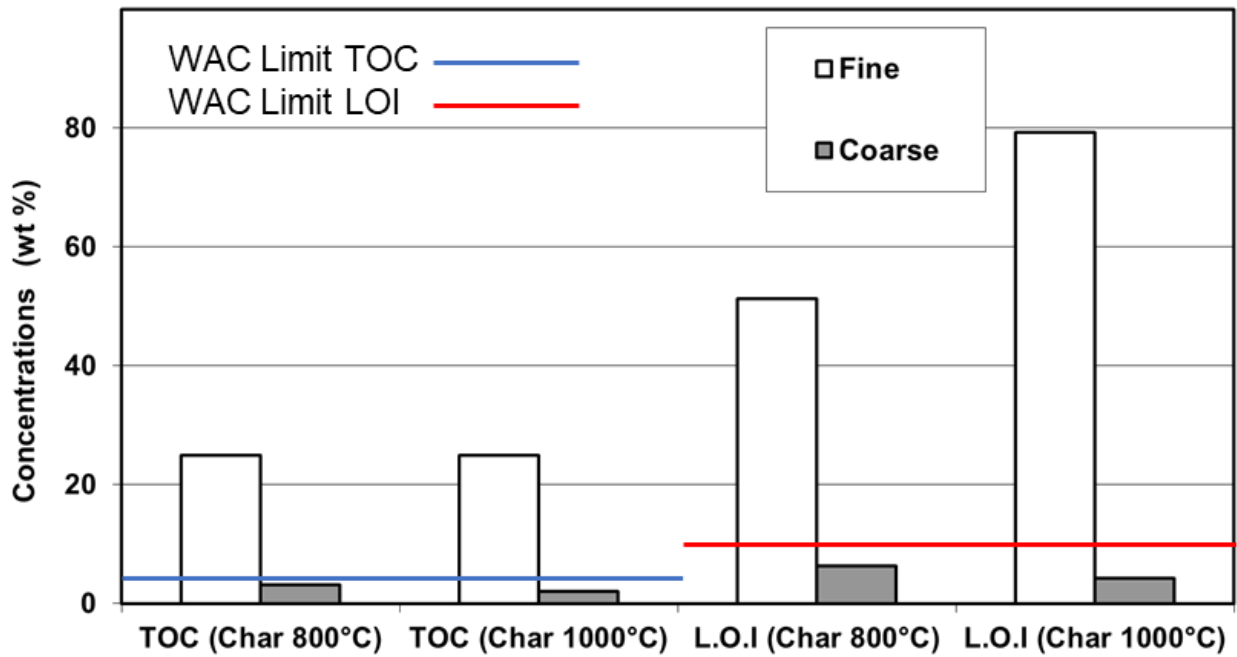
275

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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