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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**

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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

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

1. Introduction

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

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

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

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

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

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

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

2. Experimental methods

2.1 The ASR feed material

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

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

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

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

2.2 The pyrolysis process – char sample preparation

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

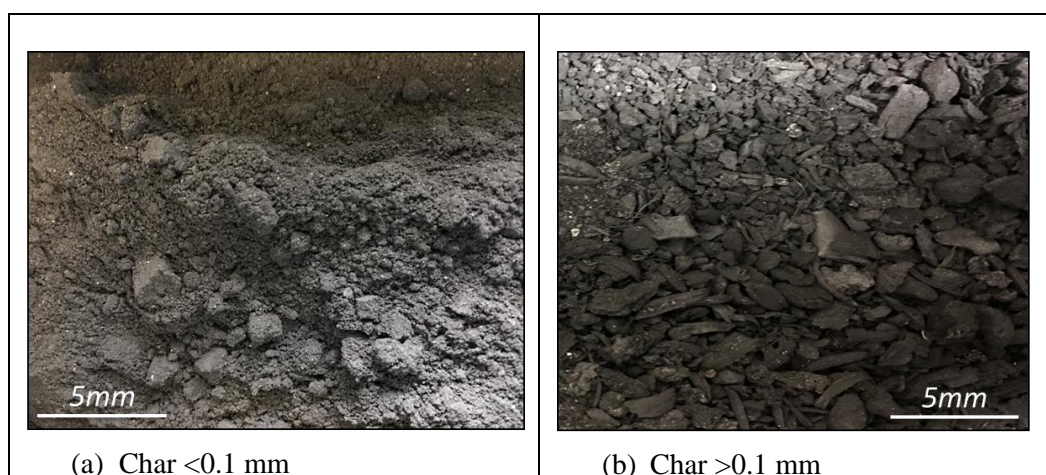


Fig. 1. Optical images of the pyrolysis char products.

2.3 Pollutant/Environmental analysis of ASR and the solids residue

2.3.1 PAHs, PCB, TPH, BTX analysis

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

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

Table 2. Organic analysis operating conditions.

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

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

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

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

2.3.2 TOCs and LOI analysis

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

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

2.3.3 pH analysis

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

3. Results and discussion

3.1 Organic contaminates/Environmental toxicity of ASR

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

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

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 (%)
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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	

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

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

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

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

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

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

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

Table 6. Concentrations of PCBs (7 congeners) and BTEX in produced fine char fraction (at 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

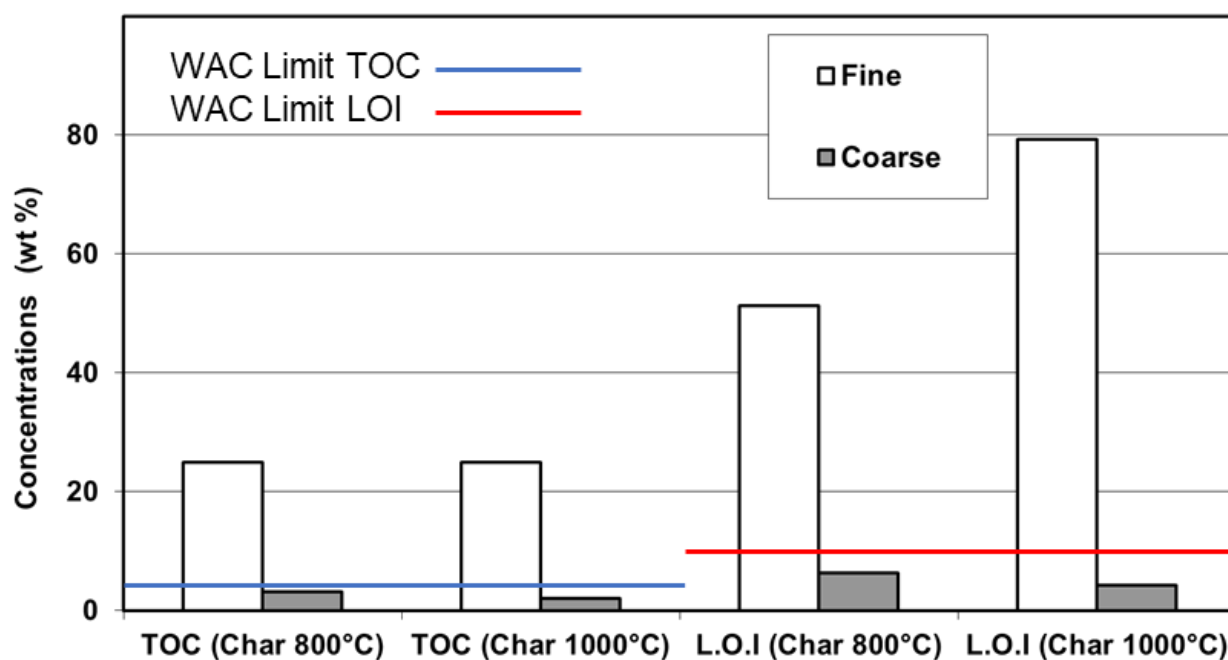


Fig 2. Concentration of TOC & LOI in char samples (at 800 and 1000°C).

4. Conclusions

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

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

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

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

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References

- Alonso, J.C., Doce J., Fleischer, G., Geraghty, K., Greif, A., Rodrigo, J., Schmidt, W.P., 2007. Electrical and electronic components in the automotive sector: economic and environmental assessment. *Int. J. Life Cycle Assess.* 12 (5), 328-335.
- Anzano, M., Collina, E., Piccinelli, E., Lasagni, M., 2017. Lab-scale pyrolysis of the automotive shredder residue light fraction and characterisation of tar and solid products. *Waste Manag.* 64, 263-271.

- BS, British Standards, 1986. BS 6068: Water quality, physical, chemical and biochemical methods – Determination of dissolved oxygen: electrochemical probe method. British Standard Institute.
- Buss, W., Graham, M.C., Mackinnon, G., Mašek, O., 2016. Strategies for producing biochars with minimum PAH contamination. *J. Anal. Appl. Pyrolysis* 119, 24–30.
- Conesa, J.A., Font, R., Fullana, A., Martín-Gullón, I., Aracil, I., Gálvez, A., Moltó, J., Gómez-Rico, M.F., 2009. Comparison between emissions from the pyrolysis and combustion of different wastes. *J. Anal. Appl. Pyrolysis* 84, 95–102.
- Cossu, R., Fiore, S., Lai, T., Luciano, A., Mancini, G., Ruffino, B., Viotti, P., Zanetti, M.C., 2014. Review of Italian experience on automotive shredder residue characterisation and management. *Waste Manage.* 34, 1752–1762.
- Cossu, R., Lai, T. 2013. Washing treatment of automotive shredder residue (ASR). *Waste Manage.* 33, 1770–1775.
- Cossu, R., Lai, T., 2015. Automotive shredded residue (ASR) management: an overview. *Waste Manag.* 45, 143–151.
- Cucchiella, F., Adamo, I. D', Rosa, P., Terzi, S., 2016. Automotive printed circuit boards recycling: an economic analysis. *J. Clean. Prod.* 121, 130–141.
- Davies, G., 2012. *Materials for Automobile Bodies*, second ed. Elsevier Applied Science Publisher, Amsterdam, pp. 11–13.
- Day, M., Cooney, J.D., Shen, Z., 1996. Pyrolysis of automobile shredder residue: an analysis of the products of a commercial screw kiln process. *J. Anal. Appl. Pyrolysis* 37, 49–67.
- Day, M., Shen, Z., Cooney, J.D., 1999. Pyrolysis of auto shredder residues: experiments with a laboratory screw kiln reactor. *J. Anal. Appl. Pyrolysis* 51, 181–200.
- EC, 2000. Directive 2000/53/EC of the European Parliament and the European Council of 18 September 2000 on end-of-life vehicles – commission statements. Off. J. Eur. Comm. L269, 0034-0043, Brussels.
- EC, 2002. Directive 2003/33/EC: Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Off. J. Eur. Comm. L11/27-L11/49, Brussels.
- EC, 2004. No. 850/2004 of the European Parliament and the European Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC. Off. J. Eur. Un. L158/7-49, EN.
- EC, 2019. Report from the commission to the European, the council, the European economic and social committee and the committee of the regions on the implementation of the circular economy action plan. COM/2019/190 final, Brussels, available at http://ec.europa.eu/environment/circular-economy/pdf/report_implementation_circular_economy_action_plan.pdf Accessed 14th November 2019.

- Eurostat ELV, 2019. Statistics Explained End-of-life, available at https://ec.europa.eu/eurostat/statistics-explained/index.php?title=End-of-life_vehicle_statistics&oldid=461386 Accessed 8th January 2020.
- Fortuna, F., Cornacchia, G., Mincarini, M., Sharma, V.K., 1997. Pilot-scale experimental pyrolysis plant: mechanical and operational aspects. *J. Anal. Appl. Pyrolysis* 40-41, 403–417.
- Galvagno, S., Fortuna, F., Cornacchia, G., Casu, S., Coppola, T., Sharma, V.K., 2001. Pyrolysis process for treatment of automobile shredder residue: preliminary experimental results. *Energ. Convers. Manage.* 42, 573–586.
- GFEA, German Federal Environment Agency, 2012. Polycyclic aromatic hydrocarbons – Harmful to the environment, Toxic, Inevitable. November 2012, Press Office, Germany. Available at <https://www.bsnc.nl/wp-content/uploads/2015/10/Polycyclic-Aromatic-Hydrocarbons-why-the-ban.pdf> Accessed 14th November 2019.
- Harder, M.K., Forton, O.T., 2007. A critical review of developments in the pyrolysis of automotive shredder residues. *J. Anal. Appl. Pyrol.* 79 (1), 387-394.
- Haydary, J., Susa, D., Gelinger, V., Cacho, F., 2016. Pyrolysis of automobile shredder residue in a laboratory scale screw type reactor. *J. Environ. Chem. Eng.* 4, 995–972.
- Heron, G., Barcelona, M.J., Andersen, M.L., Christensen, T.H., 1997. Determination of nonvolatile organic carbon in aquifer solids after carbonate removal by sulfurous acid. *Ground Water* 35(1), 6-11.
- Joung, H.T., Seo, Y.C., Kim, K.-H., 2007. Distribution of dioxins, furans and dioxin-like PCBs in solid products and generated by pyrolysis and melting of automobile shredder residues. *Chemosphere* 68, 1636–1641.
- Khodier, A., Williams, K.S., Dallison, N., 2017. Pilot-scale thermal treatment of automotive shredder residue: pyrolysis char is a resource or waste, *WIT Transaction on Ecology & the Environment*. WIT Press, Energy & Sustainability 224, 439-450. www.witpress.com,ISSN 1746-448X.
- Khodier, A., Williams, K.S., Dallison, N., 2018. Challenges around automotive shredder residue production and disposal. *Waste Manag.* 73, 566-573.
- Mancini, G., Tamma, R., Viotti, P., 2010. Thermal process of fluff: preliminary tests on a full-scale treatment plant. *Waste Manag.* 30 (8-9), 1670–1682.
- Mayyas, M., Pahlevani, F., Handoko, W., Sahajwalla, V., 2016. Preliminary investigation on the thermal conversion of automotive shredder residue into value-added products: graphitic carbon and nano-ceramics. *Waste Manage.* 50, 173-183.
- Morselli, L., Santini, A., Passarini, F., Vassura, I., 2010. Automotive shredder residue (ASR) characterisation for a valuable management. *Waste Manag.* 30, 2228–2234.

- Notarnicola, M., Cornacchia, G., De Gisi, S., Di Canio, F., Freda, C., Garzone, P., Martino, M., Valerio, V., Villone, A., 2017. Pyrolysis of automotive shredder residue in a bench scale rotary kiln. *Waste Manag.* 65, 92-103.
- Pascal, M.A., Zabik, M.E., Zabik, M.J., Hernandez, R.J., 2005. Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. *J. Agric. Food Chem.* 53, 164–169.
- Restrepo, E., Løvik, A.N., Wäger, P., Widmer, R., Lonka, R., Müller, D.B., 2017. Stocks, flows and distribution of critical metals in embedded electronics in passenger vehicles. *Environ. Sci. Technol.* 51(3), 1129–1139.
- Ruffino, B., Fiore, S., Zanetti, M.C., 2014. Strategies for the enhancement of automobile shredder residues (ASRs) recycling: results and cost assessment. *Waste Manag.* 34(1) 148–155.
- Santini, A., Passarini, F., Vassura, I., Serrano, D., Dufour, J., Morselli, L., 2012, Auto shredder residue recycling: mechanical separation and pyrolysis. *Waste Manag.* 32, 852–858.
- Schumacher, B.A., 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments. USEPA, Washington, DC, EPA/600/R-02/069 (NTIS PB2003-100822).
- Selinger, A., Steiner, C., Shin, K., 2003. TwinRec – bridging the gap of car recycling in Europe. Proceedings of the International Automotive Recycling Congress, Geneva, Switzerland, 2003 March 12-14.
- Tchobanoglous, G., Theisen, H., Vigil, S., 1993. Integrated Solid Waste Management. McGraw Hill, London, pp. 978.
- USDHHS, 1995. US Department of Health and Human Services, Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). ATSDR (Agency for Toxic Substances and Disease Registry), Public Health Service, Atlanta, GA.
- USEPA, 2007. EPA 3550C, Ultrasonic Extraction, Office of research and development. Available at: www.epa.gov/sites/production/files/2015-12/documents/3550c.pdf Accessed 14th November 2019
- Vermeulen, I., Van Caneghem, J., Block, C., Baeyens, J., Vandecasteele, C., 2011. Automotive shredder residue (ASR): reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals valorisation. *J. Hazard. Mater.* 190 (1), 8-27.
- Viotti, P., Tamma, R., Lombardi, L., Mancini, G., 2010. Thermal process of fluff: results from a full-scale treatment plant experimental campaign, proceeding of Venice 2010, Third International Symposium on Energy from Biomass and Waste, Venice 8-11/11/2010, pp.11.
- Williams, P.T., 2005. Waste Treatment and Disposal, second ed. John Wiley & Sons Ltd, Chichester, pp. 326–336.