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VIABILITY STUDY OF AUTOMOBILE SHREDDER RESIDUE AS FUEL

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Abstract

Car Fluff samples collected from a shredding plant in Italy were classified based on particle size, and three different size fractions were obtained in this way. A comparison between these size fractions and the original Light Fluff was made from two different points of view: i) the properties of each size fraction as a fuel were evaluated; and ii) the pollutants evolved when each size fraction was subjected to combustion were studied. The aim was to establish which size fraction would be the most suitable for the purposes of energy recovery. The Light Fluff analyzed contained up to 50 wt.% fines (particle size < 20 mm). However, its low calorific value and high emissions of polychlorinated dioxins and furans (PCDD/Fs), generated during combustion, make the fines fraction inappropriate for energy recovery, and therefore, landfilling would be the best option. The 50-100 mm fraction exhibited a high calorific value and low PCDD/F emissions were generated when the sample was combusted, making it the most suitable fraction for use as refuse-derived fuel (RDF). Results obtained suggest that removing fines from the original ASR sample would lead to a material product that is more suitable for use as RDF.

Keywords

ASR; Light Fluff; PCDD/Fs; Energy Recovery; RDF.

1. INTRODUCTION

Once vehicles are no longer useful, they are deregistered and become End-of-life vehicles (ELVs). Only in Europe, more than 9 million tons per year of ELV waste are produced. The volume of ELV waste continues to increase every year, and it is expected to rise to about 10-14 million tons by 2015 [1]. If ELV residues are not properly managed, they can have a negative impact on the environment. In addition, ELVs are

rich in valuable materials, such as metals, and possess a high calorific potential due to their high content in combustibles such as plastics.

ELVs are subjected to depolluting and dismantling; afterwards, hulks are baled and sent to a shredder plant. The main objective at a shredder plant is to recover as many metals as possible (ferrous and non-ferrous). Two material fractions are generated as by-products of the process: Light and Heavy Fluff, which constitute *automobile shredder residue* (ASR). The light fraction, *also called car fluff*, is the fraction lifted up by a zig-zag sorter after shredding the bales, while the heavy fluff is the fraction remaining after ferrous metal separation by means of magnetic drums. The light fraction accounts approximately for 75 wt. % of the total ASR [2], heavily depending on the shredder mill input material. In Europe, light fluff residue is mainly landfilled. ASR has a very heterogeneous composition, which has been pointed out by a great number of studies [3, 4]: it is a complex mixture of plastics (19-35%), rubber (20%), textile (10-40%), wood (2-5%), metals (8%), oils (5%) and others unidentifiable materials (10%) [4, 5]. Polymers such as polyvinyl chloride (PVC), polyethylene (PE) or polypropylene (PP) [6] constitute some of the most valuable components of ASR; they provide it with a high heating value (about 21 MJ/kg [5, 7]), which makes ASR suitable for energy recovery as a refuse derived fuel.

The European Directive 2000/53/CE states that by 2015, a minimum of 95% (in average weight per vehicle and year) of ELVs must be reused or recovered (including energy recovery), and that at least 85% must be reused or recycled, so as to reduce the disposal of this waste in landfills. In 2009, Spain and Italy achieved yields of 86.0 % and 84.2 % in reuse and recovery, and 82.6 % and 81.8 % in reuse and recycling, respectively[1].

The high costs associated with waste disposal in landfills, attached to meeting the required rates stipulated by the European Directive, have led to the development of new

technologies focused on energy recovery from combustible fractions of ASR as well as new recovery and recycling techniques. Similarly, the European Waste Incineration Directive 2000/76/EC establishes that waste containing more than 1% of halogenated organic substances, expressed as chlorine, should comply with specific operational conditions that result in the destruction of as many organic pollutants as possible. The use of ASR as a fuel in a thermal process is a controversial issue since the combustible fraction contains chlorine. On one hand, gases evolved from the combustion process can be corrosive, which can damage the facilities. On the other hand, toxic pollutants such as polychlorinated dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) can be generated as by-products during the incineration if operational conditions and gas cleaning systems are not carefully controlled.

The classification of Light Fluff based on its particle size consists of an easy and cheap physical separation that can be carried out at shredding plants. The aim of this work is to discuss which one of these size fractions would be more suitable for use in an energy recovery treatment than the original Light Fluff; this would allow shredding plants to achieve the ELV targets in a suitable way, since some recent studies have concluded that the option of energy recovery combined with recycling is the most sustainable alternative for this kind of waste [8]. Each size fraction was analyzed from two perspectives: as a solid fuel and as a source of pollutants when subjected to a combustion process.

2. MATERIALS AND METHODS

2.1. Raw Material

A sample of about 50 kg was collected from the Light Fluff output flow of a shredder plant located in the North of Italy. This plant produces about 175 tons per day of ASR,

95 so the light fluff production is about 131 tons per day. Hereinafter, this material will be
96 referred to as *raw material* or RM. The RM sample was stored in suitable containers to
97 avoid humidity loss and contamination. Because of the heterogeneity of the ASR, a
98 quartering procedure following the Italian standardized methodology [9] was performed
99 to ensure that the sample was representative. An extensive characterization of the
100 sample was carried out, and the results are interpreted in terms of the composition of the
101 sample; this is useful when the composition of the residue obtained varies.
102 Particle sizes were classified according to three different-sized sieves: 20 mm, 50 mm
103 and 100 mm. The fraction with particulate size lower than 20 mm was called *fines*
104 although, some authors refer to samples of particulate size smaller than 2 mm as *fines*
105 *fraction* in the literature [10].
106 Afterwards, each size fraction was separately ground using a Pulverisette 19 (Fristch)
107 laboratory mill and passed through a 1 mm sieve, thereby obtaining homogeneous
108 samples. Finally, samples were stored until they were needed for analysis. Four
109 different size fractions were studied: the RM and the other three obtained after sieving.

110

111 2.2. Chemical Analyses

112 Humidity and ash content were measured and calculated according to Italian standard
113 UNI 9903-7:2004 [11]. The humidity was determined by drying homogeneous samples
114 of about 1 g at 105 °C for two hours and measuring the weight loss. Ash content was
115 calculated from the weight loss of 1 g dried and homogenized sample after combustion
116 in a muffle for 4 h at 550°C.

117 Elemental Analysis was conducted in a TruSpec Microanalyzer (LECO), and 3-5 mg
118 samples were combusted at 1000°C during each run. Sulphur was determined by means

119 of a TruSpec Analyzer (LECO), which required samples of about 100 mg each per
120 analysis.

121 For the heating value determination, the combustion of 0.5-1 g samples was performed
122 in a LECO AC-350 bomb calorimeter.

123 Finally, IR analysis was carried out in a Bruker IFS 66/S spectrometer in ATR mode.

124

125 **2.3. Thermal Analyses**

126 Each size fraction sample underwent thermal decomposition in an oxidative

127 atmosphere. Thermogravimetric (TG) runs were carried out in a STA 6000 Perkin-

128 Elmer thermobalance. The total gas flow was 100 mL/min air, and a two-step

129 temperature program was used: 1- Heating from 25 °C to 800 °C at 10°C/min; 2-

130 Constant heating for 5 min at 800°C. A sample of about 5 mg was used for each run.

131 A blank experiment was performed and used to correct for the buoyancy effect caused

132 by the gas flow in the sample runs; the reproducibility of the runs was also tested. Apart

133 from this, an experiment suggested by the literature [12] was carried out with Avicel

134 cellulose to test that the equipment worked properly. Results were in agreement with

135 those in the literature [12].

136

137 **2.4. Total Chlorine Analyses**

138 Sample preparation was carried out following the US EPA Method 5050 [13].

139 Hydrogen chloride evolved from chlorine in complete combustion was collected over a

140 NaHCO₃/Na₂CO₃ solution which was later analyzed by ion chromatography. The

141 instrument used was a Dionex DX-500 with an AS9HC (Dionex) column. Operational

142 conditions were 9 mM Na₂CO₃, 1 mL/min flow rate and ASRS 300 suppressor

143 (Dionex).

144

145 **2.5. Heavy Metal Analyses**

146 Samples were subjected to complete decomposition by microwave digestion with HNO_3
147 and H_2O_2 prior to the determination of the heavy metal content. Two different analytical
148 techniques were used depending on the targeted metal: Inductively Coupled Plasma
149 Optical Emission Spectrometry (ICP-OES) was employed to determine Al, Mn, Fe, Ni,
150 Cu, Zn, Pb and total Cr content – a 7300DV dual vision (Perkin Elmer) was the
151 instrument used for this. On the other hand, volatile metals such as As, Cd and Hg were
152 analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a 7700x
153 (Agilent) instrument.

154 All analyses reported so far were performed at least in duplicate; the results presented
155 are averages. Minimal variations in results were obtained, and therefore, no statistical
156 information is supplied.

157

158 **2.6. Combustion experiments and PCDD/Fs Analyses**

159 Combustion of samples was carried out at 850 °C, considered as the minimum
160 temperature conditions required by the Directive 2000/76/CE for materials with less
161 than 1% of halogenated organic substances [14]. Substoichiometric oxygen conditions
162 were chosen as a way of simulating those areas inside a furnace with lack of oxygen,
163 which can denote unfavorable combustion conditions that lead to incomplete
164 combustion and formation of undesired compounds. The oxygen/stoichiometric oxygen
165 ratios (λ) were estimated on the basis of an elemental analysis of all runs ($\lambda = 0.65$ -
166 0.70). . The equipment used to carry out the experiments consisted of a tubular reactor
167 with the sample carefully distributed lengthwise along a holder. The sample was then
168 introduced at a very precisely controlled speed into a furnace with a constant flow of

169 gas passing through it. This particular reactor setup has already been described
170 previously [15]. A resin trap containing Amberlite® XAD-2 resin was placed at the
171 outlet of the reactor to retain pollutants. Following the US EPA Method 1613 [16],
172 PCDD/Fs were determined by HRGC-HRMS in a Micromass Autospec-Ultima NT
173 with a capillary Restex column RTx Diox2 (60 m; 0.25 mm; 0.25 μ m).
174 Before each experiment, a blank run to detect possible interferences was carried out
175 following the same analytical procedure as the sample run.

176

177 **3. RESULTS AND DISCUSSION**

178 **3.1. Particle Size Distribution**

179 The results of the particle size distribution are presented in Figure 1. It is important to
180 mention that material containing particles bigger than 100 mm was not found in the RM
181 collected at the shredder plant. As reported by other authors [2, 4], this fraction usually
182 corresponds to 2% of the total weight, and consists of big pieces of foam, rubber or
183 plastics. The presence or absence of this size fraction in a Light Fluff fraction can be
184 related to the effectiveness of the hammer mill used during the shredding process.
185 Therefore, three size fractions were obtained: fines, 20-50 mm and 50-100 mm. These
186 fractions were analyzed, and the RM as well.
187 It can be observed that about 55 wt. % of the Light Fluff material had a particle size
188 bigger than 20 mm: most of this was a 20-50 mm size fraction that made up 45.9 % of
189 the total weight, while the 50-100 mm fraction accounted for the smallest percentage,
190 9.4 %.

191 The raw material (RM) contained a high percentage of fines (about 44.7 wt. %). The
192 fines fraction is a mixture of a great variety of small particles, which makes it
193 heterogeneous.

194 Although it is possible to distinguish sand, small glass pieces or metals, it is impossible
195 to carry out more accurate composition analyses [2, 4]. Some information can be
196 derived from IR analysis for the raw material (RM) and the three fractions (fines, 20-50
197 mm and 50-100 mm). The results are shown in Figure 2. According to the IR spectra, in
198 every fraction the main signal, around $2900\text{--}3000\text{ cm}^{-1}$, can be ascribed to the presence
199 of C-H groups and indicates the presence of polymers. The other signals are coherent
200 with the presence of polymers such as PU, PVC, PP and PE, which are car fluff
201 constituents, as reported in the literature.

202

203 **3.2. Light Fluff: Properties as Fuel**

204 Table 1 shows the results for the four particle size fractions in terms of parameters that
205 are useful for the characterization of a fuel.

206 Lower heating values varied from $15000\text{ kJ/kg}_{\text{dry sample}}$ to $24600\text{ kJ/kg}_{\text{dry sample}}$, similar to
207 those of wet wood and town gas respectively, which are in line with values reported in
208 the literature. The calorific values are consistent with ash and carbon content. Morselli
209 et al. [4] stated that 20-50 mm and 50-100 mm fractions are the richest in polymers, and
210 this is in agreement with the observation that these two fractions have the highest
211 heating values.

212 The fines fraction presented the highest ash content (50 wt. %) and, as a consequence,
213 the lowest calorific value. The 20-50 mm and 50-100 mm fractions exhibited very
214 similar properties. Lastly, RM sample results were in agreement with those in the
215 literature reviewed [17]. None of the fractions presented a high sulphur content (0.4-0.8
216 wt. %).

Figure 3 shows the experimental variation of mass loss with temperature obtained for the four samples under the same atmosphere and at the same heating rate. In the figure, w is defined as:

$$w = (m - m_{\infty}) / (m_o - m_{\infty}) \quad (1)$$

where m is the mass at any time; m_{∞} the final mass of the solid residue and m_o the initial solid mass.

Three of the four samples (RM, 20-50 mm and fines) exhibited similar behaviour during thermal degradation. The RM sample is mainly composed of the fines and 20-50 mm fraction, which explains the very similar curves obtained. Fines decomposed slower than the RM and 20-50 mm fractions. The 50-100 mm fraction underwent the slowest decomposition. This fact did not affect the RM curve because the 50-100 mm fraction is only 9.5 wt. % of the total.

All the samples presented a slight loss in mass at temperatures below 150 °C, which can be explained by water volatilization of the sample. The first important mass loss to be observed in any sample only started at a temperature of 250 °C. RM presented only one decomposition step from 250 °C to 500 °C, which coincides with Guo et al.'s results [18].

3.3. Heavy Metals

The results for the metal content of the four material fractions are shown in Table 2. The fines material contained the highest metal concentration compared to RM, 20-50 mm and 50-100 mm respectively. As the data show, Al, Cr, Mn, Fe, Ni and Zn exhibited the same trend. It can be clearly observed that copper and iron were the most abundant metals in all samples. These two metals can act as catalysts for PCDD/Fs formation during or after combustion processes [19-21]. The 50-100 mm fraction had the lowest

iron and copper content compared to the other three material fractions. Copper values reached up to 55600 mg/kg_{dry sample} in the 20-50 mm material fraction. A high content in copper can be ascribed to the wiring and electrical components of a vehicle and Light Fluff can contain around 3 wt. % of these components [22]. Wire copper fragments can be easily recovered by means of suitable equipment, reducing copper content in the residue. The content of iron reached up to 117000 mg/kg_{dry sample} in the fines fraction, and can be put down to the fact that wheel rims and chassis are made of this metal. Zinc, which is used as anti-corrosion agent for the chassis, was among the three top metals found in the ASR samples analyzed. Zinc concentrations varied from 1700 to 11210 mg/kg_{dry sample} in 50-100 mm and fines, respectively. Aluminium is also an abundant metal in car fluff since it is used in the manufacturing of many car components: frame, engine or rims. It is important to pay attention to Pb, Cd, As and Hg because of their high volatility and toxicity. The mercury content of all samples analyzed was around 0.30 mg/kg_{dry sample}, which can be considered as low; cadmium and arsenic concentrations were higher than that of mercury. It may be assumed that all samples had the same lead concentration (630-705 mg/kg_{dry sample}) except for the 50-100 mm sample, whose concentration was lower, 130 mg/kg_{dry sample}. The results obtained are in agreement with those in the scientific literature [4, 5, 23, 24].

3.4. Chlorine and chlorinated organic pollutants

The chlorine present in car fluff can come from polymeric components of the vehicle [6], as well as from inorganic loads. If car fluff is to be used as RDF, chlorine content could be an indicator of the possible formation of chlorinated pollutants, such as PCDD/Fs, during combustion processes. Total chlorine was determined in all particle size fraction samples, and results are shown in Table 3: the 50-100 mm fraction had the

lowest chlorine concentration; all samples contained less than 1% of chlorine in compliance with Directive 2000/76/CE [14].

Several scientific papers have been published reporting information about measurements of chlorinated organic pollutants such as PCDD/Fs in both original Light Fluff samples and emissions from industrial processes. According to Santini et al. [24], Light Fluff contains about 3-4 pg i-TEQ/g of PCDD/Fs, in agreement with Mancini et al.'s results [5]. Van Canenghem et al. [25] obtained a total PCDD/Fs concentration of 9 pg/kg_{DW} in a raw ASR sample – approximately ten times higher than in sludge from waste water treatment (WWT); high chlorinated congeners were the most abundant.

On the other hand, there has been research done into the measurement of PCDD/Fs emissions from industrial combustion of ASR mixed with other fuels. According to the literature [25], adding ASR to the RDF and WWT sludge in the usual waste feed to a real-scale fluidized bed combustor increased the concentration of PCDD/Fs in the flue gas.

To determine PCDD/Fs levels in the gases evolved under a substoichiometric oxygen atmosphere, combustion experiments were carried out for each particle size fraction in the laboratory reactor described previously in section 2.6. The aim of these runs was to study the performance of the different ASR size fractions under critical operating conditions. All congeners, from MoCDD/Fs to OCDD/Fs were analyzed for ASR samples.

Figure 4 shows the total dioxins and furans concentration (from TeCDD/Fs to OCDD/Fs) emitted during the combustion of the different-sized material fractions analyzed. According to the results, if each of the different size fractions were incinerated without proper control of operating parameters, the fines fraction would be the most toxic (800 pg i-TEQ/g), followed by 20-50 mm (298 pg i-TEQ/g), RM (212 pg

292 i-TEQ/g) and 50-100 mm (11 pg i-TEQ/g). PCDD/Fs emissions for fines are of the
 293 same order of magnitude as the results obtained by Font et al. [26] for mobile phone
 294 case combustion. High levels of copper and iron present in the fines fraction could be
 295 responsible for the high PCDD/Fs concentration in the outlet gases. It is important to
 296 mention that the 50-100 mm fraction contained the least amount of copper (7490
 297 mg/kg_{dry sample}) and chlorine (2120 mg/kg_{dry sample}); so this might explain why its
 298 PCDD/Fs concentration was the lowest. Total furans content was higher than total
 299 dioxins in all samples studied, except for the 20-50 mm material.
 300 2,3,7,8-Cl substituted PCDD/F congener patterns emitted from the different ASR size
 301 fractions are shown in Figure 5. It can be clearly observed that there is no similarity
 302 between the profiles obtained. This fact suggests that a complicated network of
 303 reactions take place during the combustion process. RM and fines patterns are
 304 dominated by higher chlorinated PCDFs congeners. 1,2,3,7,8-PeCDD was the isomer
 305 that most contributed to the total toxicity in 20-50 mm material, while 1,2,3,4,7,8-
 306 HxCDF was the most abundant isomer in the 50-100 mm sample.
 307 The total PCDD/Fs emissions produced by each fraction during the combustion runs
 308 were as follows: 29000 pg/g_{dry sample} in fines, 14000 pg/g_{dry sample} in 20-50 mm fraction,
 309 6850 pg/g_{dry sample} in RM and 4700 pg/g_{dry sample} in 50-100 mm fraction. PCDD/Fs were
 310 generated in greatest quantities in the smallest size fraction.
 311 It must be emphasized that the laboratory combustion runs carried out under fuel rich
 312 conditions are useful for analyzing and comparing the potential of the residue to form
 313 PCDD/Fs. In a combustion furnace with oxygen excess, PCDD/Fs emissions will
 314 probably be much lower. In fact, the gas cleaning system used to clean/ treat the
 315 combustion gases will reduce the amount of these pollutants emitted into the
 316 atmosphere. Once formed, PCDD/F emissions can be controlled in the post-combustion

zone with activated carbon [27] or with the presence of a dechlorination catalyst [28-29]. Moreover, the addition of CaO/ Ca(OH)₂ or similar compounds can be effective to minimize the release of hydrogen chloride during the thermal treatment [30-32]. On the other hand, the addition of nitrogenated or sulphur compounds in the combustion chamber has been stated to be an effective way to prevent specifically the formation of chlorinated micropollutants such as PCDD/Fs [33-34].

323

324 **4. CONCLUSIONS**

Based on the heating value and metal content of the samples, as well as pollutants concentration in the gases evolved when samples are subjected to combustion, the 50-100 mm size fraction would be the most suitable for use as RDF.

The fines fraction presented a low heating value (LHV: 15000 kJ/kg_{dry sample}); the high amount of PCDD/Fs formed during the combustion experiments (800 pg-iTEQ/g_{dry sample}) are probably related to the high content in metals seen in the results of analyses for metals. All these results suggest that the fines fraction would be the least suitable to be used as RDF – both from an energetic and an environmental point of view.

Therefore, landfilling disposal is proposed as the best option for this ASR size fraction.

From the point of view of toxic pollutants emissions, the RM and 20-50 mm material behaved similarly, although the latter had a higher low-heating value (18700 vs 23700 kJ/ kg_{dry sample}) making it more suitable to be used as RDF.

Thus, based on the above considerations, the material obtained after removal of the fines fraction from the RM would be suitable for use as RDF. In this case, a high heating value, low metal content and low concentration of toxic pollutants resulted from incineration, would be expected. Further research will be carried out on the matter.

341

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445

446 **Table caption**

447

448 **Table 1.** Chemical analyses results

449 **Table 2.** Metal Content (mg/kg_{dry sample}) of ASR fractions

450 **Table 3.** Total chlorine content of ASR samples

451

452 **Figure caption**

453

454 **Figure1.** Particle size distribution corresponding to raw material (RM)

455 **Figure 2.** IR emission spectrum of all each different size fractions

456 **Figure 3.** Thermogravimetric analyses results

457 **Figure 4.** Comparison of total PCDDS and PCDFs in different ASR size fractions after
458 combustion at 850°C (in pg-iTEQ/g).

459 **Figure 5.** 2,3,7,8-Cl Substituted PCDD/F congener pattern for emissions from different
460 ASR size fractions after combustion at 850 °C (in pg i-TEQ/g)

461

461

462 Table1. Chemical analyses results

463

		RM	FINES	20-50 mm	50-100 mm
Humidity	wt. %	1.2	1.3	1.2	1.1
Ash Content²	wt. %	38.5	50.6	25.5	29.0
C³	wt. % ¹	41.2	35.0	59.9	49.1
H³	wt. % ¹	5.0	4.8	8.6	6.7
N³	wt. % ¹	1.3	0.6	1.8	1.3
S³	wt. % ¹	0.5	0.4	0.5	0.8
UHV	kJ/kg ¹	19900	16100	25700	26200
LHV	kJ/kg ¹	18700	15000	23700	24600

¹ Calculated on dry basis² Experiment carried out at 550°C³ Experiment carried out at 1000°C

HHV/LHV: Higher and Lower Heating Value

463

464 Table2. Metal content (mg/kg_{dry sample}) of ASR fractions

465

mg /kg¹	RM	FINES	20-50 mm	50-100 mm
Al	4690	7870	2310	1130
Cr	150	280	60	20
Mn	340	530	200	90
Fe	63110	117000	22390	5690
Ni	130	200	80	25
Cu	35630	21030	55600	7490
Zn	7280	11210	4590	1700
Pb	630	705	660	130
As	5.2	4.9	5.4	5.9
Cd	4.2	5.2	4.1	0.8
Hg	0.3	0.3	0.3	0.3
¹ Calculated on dry basis				

465

		RM	FINES	20-50 mm	50-100 mm	466 Table 3. Total chlori ne conten t
Chlorine	mg/kg ¹	8013	8440	8800	2120	
¹ Calculated on dry basis						472
(mg/kg _{dry sample}) of ASR sample						

473

474

474 HIGHLIGHTS

- 475 - Four different particle size fractions from a Car Fluff sample were studied
- 476 - Chlorine and metal content was analyzed in all samples
- 477 - PCDD/Fs from combustion of the samples in lab scale were measured and discussed
- 478 - The combustion of fraction smaller than 20 mm produced the highest PCDD/F
- 479 emissions

480

481

482

483

Figure 1. Particle size distribution corresponding to raw material (RM)

Figure 2. . IR emission spectrum of all each different size fractions

Figure 3. Thermogravimetric analyses results

Figure 4. Comparison of total PCDDs and PCDFs in different ASR size fractions after combustion at 850^oC

**Light Fluff
Quartering Procedure**