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ANALYSIS OF POLLUTANTS IN THE PRODUCT GAS OF A PILOT SCALE DOWNDRAFT GASIFIER FED WITH WOOD, OR MIXTURES OF WOOD AND WASTE MATERIALS

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ABSTRACT: Small scale gasification of Solid Recovered Fuels (SRF) in downdraft reactors could be an alternative to large scale waste-to-energy schemes. In this perspective, the assessment of the pollutant emissions at pilot scale is necessary. This work compares pollutant emissions from wood and SRF air gasification in a downdraft fixed bed gasifier. Five fuels have been studied: Poplar wood, SRF wood, and three different mixtures containing mass fractions of 80 % SRF wood with 20 % of either tire, plastic waste or sewage sludge. Air gasification was performed in a pilot scale reactor in fed-batch mode using a fuel mass ranging from 5 to 8 kg and an air inlet flow of 170–180 L.min⁻¹ (at 0°C and 101 325 Pa). Depending on the fuel, Equivalence Ratios (ER) ranged from 0.22 to 0.29 and gasification temperatures from 690 to 850°C. Emissions analyses were performed on product gas, condensable species and remaining chars, with a particular focus on sulfur, nitrogen and heavy metals. Regarding sulfur, wood and SRF wood led to low H₂S contents (6-8 µmol.mol⁻¹), when SRF mixes led to higher concentrations (44-96 µmol.mol⁻¹) in addition to of up to 11 heavier sulfur compounds. Regarding nitrogen, SRF produced higher ammonia concentrations (2.1 – 7.6 mmol.mol⁻¹) than Wood (619 µmol.mol⁻¹), as a result of initial nitrogen mass fractions 17 to 27 times higher in the SRF mixes. Heavy metals analyzed in remaining solids after gasification showed low recovery rates (< 0.4%), and tend to accumulate in fine particles, as a result of their volatility.

Keywords: Downdraft gasification, Solid Recovered Fuel, Pollutants, Sulfur, Nitrogen, Heavy Metals.

1. INTRODUCTION

2

3 Waste, according to the article 2 of the Basel Convention on Hazardous Waste are: *“substances or*
4 *objects which are disposed, intended or required to be disposed of by the provisions of national law”*
5 [1]. Waste generation and collection rates strongly depend on national income. Moreover, the higher
6 the incomes, the higher the amount of waste which are produced and collected [2,3]. Formerly
7 considered as a problem to dispose of, they are more and more considered as a resource [4].
8 Industrial waste sorting has reached good recovery levels, as it results from national regulations.
9 However, Municipal Solid Waste (MSW) are made of various types of materials and are collected as
10 mixes, which drives difficult handling, especially regarding valorization of materials. Either diluted in
11 the overall waste volume or contaminated at the contact of wet food, material recovery appears as an
12 intricate challenge. It must involve preliminary measures such as the reduction of waste matter,
13 combined to the improvement of domestic sorting by a wider employment of specific bins (organic,
14 glass, “packaging”) and voluntary waste drop-off receptacles (used wood and furniture, metals, used
15 electrical and electronic equipment...). However, waste resulting from sorting still require treatments to
16 efficiently recover materials, which from a certain threshold become too expensive compared to the
17 prices of raw materials.

18 From this point, waste should enter in the energy recovery step, which is to date mainly performed
19 in incinerators and almost only in higher income countries (Gross National Income > 10 725 \$/cap) [2].
20 After removal of valuable materials, residuals are sent to incinerators in order to reduce their volume to
21 be landfilled. Therefore, fuel properties of these residuals are relatively unknown as they regroup a
22 wide range of materials (plastics, organic, inerts). Their combustion leads to high pollutant precursors
23 such as sulfur, nitrogen or heavy metals, which have to be eliminated in the flue gas cleaning process.
24 This results in contaminated effluents (bottom ash, fly ash, washing solvent...) along with the cleaned
25 flue gas. A possible way to increase fuel properties of waste is to improve sorting in order to create
26 different types of fuels, with distinctive properties. This leads to the creation of a Solid Recovered Fuel
27 (SRF). SRF is composed of tire, wood, plastics or sewage sludge, with the objective to respond to two
28 worldwide and major concerns, namely energy production and waste treatment.

29 Another possible way to recover energy from waste at local scale is to use air gasification in

30 downdraft fixed bed reactors. The aim of gasification is to convert a solid fuel into a combustible gas
31 (also called producer gas), mainly composed of H₂, CO, CO₂, CH₄ and N₂ which can be used in
32 internal combustion engines or gas turbines for the production of electricity and heat [5,6]. Fixed bed
33 reactors are typically used at small to medium scales (< 5 MW) offering a simple process handling and
34 producing a gas with relative low tar concentrations compared to other reactor designs at the
35 considered scale, but with higher fuel quality requirements (moisture, particle size, ash content) [5].

36 However, the use of waste as a fuel - which contains additives leading to pollutants - may impact
37 product gas quality, process performances and environmental emissions. The major pollutants found
38 in gasification are condensable species called tars, which are extensively studied especially in
39 biomass gasification [7], and are considered as the "Achilles heel of biomass gasification" [8].
40 However, minor pollutant precursors such as sulfur, nitrogen or heavy metals are less considered
41 despite their potential high environmental impact as well as their influence on the process i.e.
42 corrosion or fouling and slagging due to the melting and volatilization of inorganic species. Compared
43 to raw wood, SRF can present higher sulfur content (from 0.1-0.5 g.kg⁻¹ for raw wood [9] to 13 g.kg⁻¹
44 for tire [10]), higher nitrogen content (from 1 g.kg⁻¹ for wood [9] to 220 g.kg⁻¹ for waste wood [9]), and
45 higher heavy metals content (coatings, paints, metal accumulation in sludge...). Sulfur and nitrogen
46 containing compounds are a matter of concern, notably in combustion processes since they lead to
47 the formation of SO₂ and NO_x, considered as pollutants by emissions standards [11]. Moreover, these
48 two compounds can damage process pipes and engine or turbine parts as they are corrosive. Heavy
49 metal emissions have to be controlled as well [11], as they are toxic for living organisms. Gasification
50 mainly converts a solid fuel into gas, but also into a small amount of liquid (condensable) and solid
51 (char). Therefore pollutants are distributed within these three phases. Sulfur compounds typically
52 found during the gasification of wood or fossil coals are H₂S, CS₂, COS, SO₂, S₂ as well as traces of
53 C₄H₄S (thiophene), CH₃-C₄H₃S (methylthiophene), C₂H₂HS (acetylmercaptan), CH₃SH (methanethiol
54 or methylmercaptan) et CH₃-S-CH₃ (dimethylsulfide) [12–14]. Some nitrogen compounds, commonly
55 found in biomass air gasification effluents, are NH₃, HCN for the gaseous compounds and pyridine
56 and its derivatives, quinoline and isoquinoline for condensable compounds [15–17]. During air
57 gasification, the distribution of heavy metals highly depends on their volatility at a given reaction zone
58 temperature. Highly volatile metals such as cadmium (Cd) are entrained with the gaseous species,
59 which results in an important lost fraction of the considered metal when a balance is to be performed.

60 Moderately volatile metals such as copper (Cu) and lead (Pb) are partially lost in the gas stream, and
61 tend to condense preferentially on fine particles collected in the cyclone than in the char and ashes
62 gasification by-product [18].

63 There are several studies on SRF gasification, but most of them focused on fluidized bed reactors,
64 as they can handle a wide range of fuel, as long as the fuel particle size is fine enough. However, the
65 research considering the use of downdraft fixed bed reactors for SRF gasification are few, although it
66 represents a low-cost and efficient process to convert solid fuel into product gas [5,6]. Moreover, since
67 the existing researches primarily aim at gas production and improving product gas quality, the studies
68 of pollutants released during SRF gasification are still rare, especially at pilot scale.

69 An overview of the works that focused on sulfur and nitrogen pollutant precursors found in the
70 producer gas obtained from SRF gasification is presented in the Table 1. As reported by Berrueco et
71 al. [19] this table highlights that H₂S is the main sulfur produced during SRF air gasification. Although
72 the initial sulfur in the fuel are close (from 2 to 5 g.kg⁻¹), H₂S concentrations in the gas widely vary from
73 0.1 to 500 μmol.mol⁻¹, along with the considered fuel and process conditions [19–22]. Le et al. [22]
74 highlighted the presence of COS using waste wood during air gasification in downdraft fixed bed
75 gasifiers, with non-negligible contents (6 - 17 μmol.mol⁻¹).

76 Concerning nitrogen, NH₃ is the main compound reported in SRF air gasification. As observed for
77 H₂S, the initial fuel nitrogen contents are similar (from 6.8 to 8 g.kg⁻¹), but NH₃ concentrations in the
78 gas are varying from 3.6 to 5 000 μmol.mol⁻¹ [19–21]. Berrueco et al. [19] also highlighted the
79 presence of HCN in non-negligible amounts (129 to 352 μmol.mol⁻¹). This suggests the need for
80 greater focus on HCN concentrations, considering its higher toxicity potential than NH₃.

81 However, Broer et al. [23] showed impacts of the syngas conditioning methods on HCN
82 measurements, resulting in low accuracy. Their work highlights the difficulties to perform analyses of
83 HCN, but interrogate on the impact at larger scale for all of these low concentration compounds
84 (compared to major product gas compounds as H₂ or CO). These difficulties result in low accuracy
85 and low precision during analyses and also explain why studies focusing on these minor compounds
86 in concentrations are still limited.

87

88 TABLE 1

89

90 Arena and Di Gregorio [20] are among the few who analyzed heavy metal distribution during air
91 gasification of SRF from MSW in a fluidized bed. They observed an accumulation of chromium, iron,
92 magnesium, manganese, nickel and silica into the particles in the bed, while they detected an
93 accumulation of aluminum, lead, copper and zinc into fine particles collected in a cyclone. Finally, they
94 showed that cobalt, antimony, arsenic, cadmium, mercury and vanadium tend to continue their way in
95 the gas, leading to losses in elemental mass balances.

96 In this context, this work focuses on precursors released during air gasification of waste based
97 fuels using a downdraft fixed bed reactor. As waste gasification is developing, the knowledge of the
98 types and emission levels of produced pollutants is the object of a growing concern of the scientific
99 community. The study of the gasification performances of these fuels is briefly discussed in this paper
100 and detailed in our recent work [24]. This work was realized performing SRF gasification tests with in-
101 line analysis of H₂S and NH₃ in the product gas, in parallel to major product gas compounds, as well
102 as off-line measurements of sulfur and nitrogen tars, and heavy metal contents in remaining solids
103 (char and fine particles). The present work aims to contribute to a better understanding of air
104 gasification of waste at small to medium scales, especially regarding pollutant precursors releases and
105 product gas quality.

106

107 2. MATERIAL AND METHODS

108

109 2.1. Fuels

110 Prior to pollutant precursor analyses, gasification tests were performed in order to produce gas,
111 condensates and char using 5 different fuels: Poplar wood, SRF wood, and three different mixtures
112 composed of a mass fraction of 80% SRF wood and either 20% of SRF tire (mix A), 20% of SRF
113 plastics (mix B) or 20% of SRF sewage sludge (mix C).

114 Wood (poplar) was provided by the company "Ets Houée" (Brittany, France), which produces wood
115 packaging out of poplar (Figure 1a). SRF wood was provided by "KERVAL Centre Armor", a waste
116 treatment syndicate in Brittany, France. In this facility, SRF wood is separately collected and therefore
117 composed of waste furniture, waste pallets... which are brought by citizens to waste collection sites
118 (Figure 1b). SRF tires, in the form of chips (Figure 1c), were provided by "Aliapur", a French company
119 composed by tire producers, in charge of collecting and retreating tire waste, in accordance with the

120 Extended Producer Responsibility (EPR) in force in France. SRF plastic was composed of waste
121 plastics recovered from MSW sorting, and was in the form of fluff (Figure 1d). Sewage sludge was
122 provided by “Lannion Trégor Communauté”, a Public Establishment for Intercommunal Cooperation in
123 charge of wastewater treatment. This sewage sludge, dried in a greenhouse, comes from a
124 wastewater plant located in Louannec, France, and appears as a powdered soil (Figure 1e).
125 These fuels are qualified in this work as SRF as they come from a separate collection (SRF wood,
126 SRF tire and SRF sewage sludge), specific sorting (SRF plastic), and a drying step (SRF Sewage
127 sludge). This results in higher quality fuels compared to municipal solid waste.

128

129 FIGURE 1

130

131 Elemental analyses and fuel ash content of the studied fuels were performed in the BioWooEB
132 research unit (for carbon (C), hydrogen (H), Oxygen (O) and nitrogen (N) and ash content) and in the
133 independent laboratory SOCOR (for sulfur (S), cadmium (Cd), chromium (Cr), copper (Cu), mercury
134 (Hg), lead (Pb), nickel (Ni) and zinc (Zn)) in accordance with European Norms relative to SRF ([25–
135 28]). These characteristics are reported in Table 2, in addition to the fuel ash content. The analytical
136 equipment used for fuel elemental analyses is not able to measure the oxygen content, therefore the
137 provided oxygen values are obtained by difference, considering each element and the ash content.

138

139 TABLE 2

140

141 Carbon and Hydrogen contents in the different fuels were close for each fuel, ranging between 476
142 and 561 g.kg⁻¹ for Carbon and between 55.9 and 58.4 g.kg⁻¹ for Hydrogen.

143 As expected, SRF contained a higher amount of pollutant precursors than Wood. Nitrogen contents
144 were increased by factors of 17 to 27. The Oxygen content for Wood reached 448g.kg⁻¹, while it was
145 lower for SRF Wood down to 394g.kg⁻¹. Due to higher hydrocarbon content (for Mix A and B) and ash
146 content in the mixes of SRF, their oxygen content were lower ranging between 301 and 354g.kg⁻¹. The
147 sulfur content in SRF wood was slightly higher than in Wood, and reached a higher content in the
148 three SRF mixes. For the metal contents, Wood showed the lowest concentrations. SRF contained

149 higher metal concentrations due to the presence of additives such as glue, coatings, and paints.

150

151 **2.2. Reactor**

152 The pilot scale experiments were performed in fed-batch mode in an open-core downdraft gasifier
153 (see Figure 2) developed by and located in the research unit “BioWooEB”, in Montpellier, France.

154 This reactor, previously described in literature [29], is a fixed bed tubular reactor made of stainless
155 steel with dimensions of 160 cm high and 20 cm wide. It is equipped with in-bed temperature
156 measurements (thermocouples T2 to T9, see label 7 in Figure 2). The measurement of the bed height
157 evolution during reaction was performed via a laser located at the top (label 2, Figure 2). For the
158 purpose of the present study, the setup has been modified in order to locate the air inlet 35 cm above
159 the grate (see label 3 in Figure 2).

160

161 **FIGURE 2**

162

163 The test protocol, fully described in a previous study [24] was initialized with the ignition of a small
164 amount of charcoal (10 cm height; about 600 g), followed with the introduction of the full amount of
165 wood/SFR fuel (5 to 8kg). After closure of the top of the reactor, air was introduced at the middle of the
166 bed, and the reaction zone propagated upward in the bed of combustible, producing a bed of charcoal
167 through which the reaction products could react and leave the reactor at the bottom. The inlet air flow,
168 expressed in this work at 0°C and 11 325Pa, was set to 180 L.min⁻¹ for each test, except for mix C
169 where air flow was lowered to 170 L.min⁻¹ in order to keep the Equivalence Ratio close to 0.25,
170 because of the high ash content (320 g.kg⁻¹) in sewage sludge.

171

172 **2.3. Sampling and Analytical equipment**

173 Sampled gas was conditioned using isopropanol according to the “Tar Protocol” [30], and analyzed
174 in-line using a Varian μ GC-TCD equipped with two columns: MoISieve 5A and PoraPlotQ. The in-line
175 measurements allowed the quantification of H₂S and NH₃. The presented results are concentration
176 averages of measurements during the stable phase of the tests, at a gasification temperature of 690-
177 850°C, depending on the fuel. Gas samples were also collected using Supel-Inert Foil Gas Sampling
178 Bags of 0.6L, before and after the “Tar Protocol”, i.e. with raw product gas and condensable-cleaned

179 product gas. The isopropanol was analyzed afterwards in the BioWooEB research unit using a GC-MS
180 (chromatograph Agilent 6890, column Agilent DB1701, mass spectrometer Agilent 5975) in order to
181 identify and quantify the tar compounds [24]. In this study, we focused on nitrogen-containing tars (“N-
182 tar”). In addition, for sulfur compounds, gas bags and isopropanol samples were analyzed afterwards
183 in the research unit “Institut Charles Gerhardt Montpellier” (ICGM 5253) using a GC-FPD
184 (chromatograph Shimatzu 2014, column ZB-50) equipped with a FPD (Flame Photometric Detector) in
185 order to provide qualitative analyses of sulfur compounds (gaseous compounds and sulfur-containing
186 tars or “S-tar”). Sulfur compound standards have been used to perform identification of unknown
187 compounds by determination of matching retention time. As FPD response mainly depends on the
188 number of sulfur elements in a given molecule [31], the calibration of the equipment has been
189 performed using H₂S standard gas bottles. Therefore, the sulfur compounds concentrations are
190 expressed in this work in H₂S_{equivalent}.

191 At the end of the test, fine particles were collected under the cyclone (label 13 in Figure 2), and
192 char was extracted with a scraper and collected in a bucket located below the reactor (label 11 in
193 Figure 2). Solid samples (fines particles, and char) were analyzed according to the European norms
194 relative to SRF [25–27], in the BioWooEB research unit (N) and in the independent laboratory SOCOR
195 (S-Cd-Cr-Cu-Hg-Pb-Ni-Zn).

196

197 3. RESULTS AND DISCUSSION

198

199 3.1. Product gas fuel properties

200 Gasification tests for the five different fuels showed similar gasification performances whether using
201 Wood or SRF. Major gasification results from a previous study [24], including detailed product gas
202 concentrations, product gas LHV and Cold Gas Efficiency (CGE – energy in product gas divided by
203 energy input), are reported in Table 3. During these gasification tests in fed-batch mode and fixed inlet
204 air flow rate, the ER ranged between 0.22 and 0.29, which is typically the range observed in air
205 gasification [6]. Lower ER (0.22 and 0.23) were obtained with Mixes A and B, due to the higher carbon
206 mass fractions in tires and plastics, while higher ER were obtained with Wood, SRF Wood and Mix C.

207

208 TABLE 3

209

210 In-bed temperature measurements 10 cm below air injection for each fuel are reported in Figure 3. As
211 showed in a previous study [24], the temperature measurements (as well as gas concentrations)
212 showed two distinct phases during each test : first a transient phase following ignition, characterized
213 by erratic temperature and gas composition profiles, which were observed until the reaction zone
214 reached the air-inlet position. At this point, a “steady-state” was reached, with a stable char bed
215 temperature comprised between 690 and 850°C, along with stable concentrations for major product
216 gas components (H₂, CO, CH₄, CO₂). In the “steady-state” phase (after 17min in Figure 3), Wood, SRF
217 Wood and Mix A showed similar in-bed char temperatures evolutions, increasing from 710°C to 760°C
218 for Mix A, to 774°C for Wood and up to 810°C for SRF Wood. In the case of Mix B, the in-bed char
219 temperature showed smoother increase from 690°C to 730°C. As reported in the literature [8], this
220 lower char temperature might lead to higher tar concentrations, including sulfur and nitrogen
221 containing tars.

222 In the case of Mix C, char temperature was unstable, increasing from 700°C to 850°C, with noteworthy
223 temperature drops. This behavior could be due to the very fine particles of sewage sludge, which tend
224 to react more rapidly than SRF Wood chips, and then led to non-homogeneous reaction kinetics.

225

226 FIGURE 3

227

228 Syngas compositions from Wood and SRF Wood were similar, and close to the typical values of
229 syngas from biomass gasification [6]. The addition of a mass fraction of 20% of non-woody fuel to SRF
230 Wood led to a decrease of H₂ down to 9.8-13.9% and a decrease of CO down to 13-15%. However,
231 these shifts are balanced by the increases of light hydrocarbon concentrations: CH₄ reached 2.7-3.5%,
232 C₂H₄ increased to 0.87-0.98% and C₂H₆ reached 0.14-0.27%. As a result, product gas LHV were close
233 for each fuel, and ranged between 4.9 and 5.4 MJ.Nm⁻³. This implies that comparing pollutants on
234 volume-based (thus, on molar basis mol.mol⁻¹) or energy-based (mg.MJ⁻¹) concentrations is
235 acceptable, as the energy output is proportional to the volume of product gas. Moreover, as reported
236 in Table 3, the stoichiometric combustion of the product gas is performed with an air/product gas molar
237 ratio close to 1.1 mol.mol⁻¹, which is typically the value found with product gas from downdraft fixed
238 bed gasifier [6]. This implies that using a SRF product gas in an engine would dilute by a factor 2 the

239 pollutant concentrations in the exhaust gas.

240

241 **3.2. Pollutants produced in gasification**

242

243 **3.2.1. Gaseous pollutant precursors**

244 In this section are presented compounds found in the product gas after the “Tar Protocol”, in other
245 words pollutant precursors which are likely to be resistant to existing gas cleaning protocols in use for
246 wood gasification.

247

248 **3.2.1.1. Sulfur gaseous pollutants**

249 Regarding sulfur, H₂S is the main compound found in the product gas. Wood and SRF wood
250 produced a gas with low H₂S concentrations (6 to 8 μmol.mol⁻¹) due to low sulfur mass fractions in the
251 fuels (185 and 505 mg.kg⁻¹, respectively). SRF mixes, with increased initial sulfur mass fractions up to
252 3 g.kg⁻¹, produced a gas with H₂S concentrations from 44 to 96 μmol.mol⁻¹, similarly to Berrueco et al.
253 [19]. In combustion processes, one mole of H₂S leads to the formation of one mole of SO₂. According
254 to the European Waste Incineration Directive [11], the SO₂ limit is set to 50 mg. m⁻³ which is equivalent
255 to a concentration of 17 μmol.mol⁻¹. Even considering a dilution after air/product gas combustion in an
256 engine, only Wood and SRF wood produce a gas which complies with the SO₂ limit.

257

258 TABLE 4

259

260 However, H₂S is not the only sulfur compound found in the product gas. Off-line product gas
261 measurements in GC-FPD highlighted the presence of non-negligible concentration of another sulfur
262 compound at a residence time of 11 min (Table 5). Considering that SO₂ and methylmercaptan can be
263 excluded (their standard compounds presented different residence times, i.e. 15.7 and 19.2 min,
264 respectively) and based on the study of Gai et al. [13], this compound is believed to be COS. For
265 Wood and SRF wood, its concentration is similar to the H₂S one, while it represents about 50% of the
266 H₂S concentration for SRF mixes. Moreover, H₂S concentration in off-line analyses are lower than in-
267 line results due to gas sampling bag leaks, which suggest higher contents in reality. In addition, others
268 sulfur compounds have been found in product gas from SRF mixes, among them CS₂ and thiophene,

269 especially with mix A. The removal of H₂S (and SO₂) appears to be well developed [32], however the
270 removal of the other sulfur compounds identified in this study is not well established, which appears as
271 a critical issue for the SRF gasification development.

272

273 TABLE 5

274

275 **3.2.1.2. Nitrogen gaseous pollutants**

276 Regarding nitrogen, NH₃ was the main nitrogen compound identified in product gas. Wood
277 produced a gas with NH₃ concentration of 619 μmol.mol⁻¹, while NH₃ increased from 2,107 to 7,518
278 μmol.mol⁻¹ when using the SRF (Table 6). These values are similar to results reported by Pinto et al.
279 [21], although the reactor design is different. Leppälähti and Koljonen [15] explained that for
280 biomasses, small amino acids are almost completely converted to gaseous species, among them NH₃.
281 Because of the presence of additional groups able to form hydrogen bonding, thermal degradation of
282 bigger amino acids leads to the formation of smaller amount of gases but higher quantities of heavier
283 compounds such as pyrrole or pyridine [15]. According to the European Waste Incineration Directive
284 [11], the NO_x limit is set to 200 mg. m⁻³, which is equivalent to 97 μmol.mol⁻¹. As the oxidation of one
285 mole of NH₃ leads to the formation of one mole of NO_x, and considering the typical air/product gas
286 molar ratio equal to 1 in internal combustion engines, NO_x concentration from NH₃ combustion in the
287 flue gas would reach about the half of the NH₃ concentration in the product gas. This implies that none
288 of the fuels (even poplar wood) complies with this regulation, and therefore a specific gas cleaning
289 operation has to be performed for NH₃.

290

291 TABLE 6

292

293 In practice, measurements of NH₃ appeared difficult, as a result of being highly sensitive to water
294 concentration in the product gas. Indeed, ammonia and water show very close molar masses (17 vs
295 18 g.mol⁻¹, respectively) and dipole moment (1.42 vs 1.85 D, respectively) [33,34]. Combined with
296 high affinity of ammonia and water, it is believed that these two molecules are subject to co-elute in
297 the column PoraPlotQ, misleading the evaluation of the NH₃ concentration.

298 However, as shown in Figure 4, methane concentration in the product gas seems to be a good

299 indicator of NH₃ concentration in the product gas, as previously highlighted for product gas from
300 biomasses or coals [15]. This could be a useful tool in practice, as methane concentration is
301 commonly monitored in industrial plants.

302

303 FIGURE 3

304 As ammonia is very soluble in water (89.9 g in 100g of cold water [33]), the removal of higher
305 loads in product gas from SRF can be performed in wet scrubbers, commonly used in gas cleaning
306 [32], at the expense of an increase in water renewal frequency.

307

308 **3.2.2. Condensate pollutant precursors – S-tar and N-tar**

309 “Tars” are one of the most problematic and studied pollutants in gasification of biomass, as they
310 are “ *the most cumbersome and problematic parameter in any gasification commercialization effort* ”
311 [8]. They represent a risk for human health and environment, especially if they contain condensed
312 species produced out of SRF gasification. With such increases in sulfur and nitrogen mass fractions in
313 SRF compared to Wood, it is of great interest to focus on sulfur-containing tars and nitrogen-
314 containing tars, as they could be produced in considerable greater quantities.

315

316 **3.2.2.1. Sulfur-containing tars**

317 Isopropanol from the 1st impinger of the “Tar Protocol” setup has been sampled and analyzed in
318 GC-FPD in order to perform a qualitative analysis of heavier sulfur compounds produced in SRF
319 gasification (Table 7). No heavy sulfur tar was found in isopropanol for Wood and SRF wood. The
320 analyses highlighted the presence of 9 sulfur compounds in the isopropanol when adding 20%w of
321 SRF tire, among them thiophene and its derivative as well as thiophenol. The addition of 20%w of
322 SRF Sewage Sludge led to the presence of thiophene only. Tests with mix B faced tar sampling
323 disruptions caused by clogging in the glass frit of the impinger n°3, and no proper tar analysis could be
324 performed. Several molecules could not be identified. Among tested standard molecules, 3 sulfur
325 compounds, namely dimethyl-disulfide, tetrahydrothiophene and 1,3-propanedithiol, can be excluded
326 as their retention times (36.5, 38.5 and 45.0 min, respectively) do not fit with detected compounds.

327

328 TABLE 7

329

330 Identified sulfur compounds present very low to even no solubility in water [33], this implies the use
331 of a specific gas treatment which could handle these high loads of sulfur-containing tars in the product
332 gas from SRF gasification. Also in the case of condensable sulfur species, a specific management of
333 liquid effluents resulting from the SRF product gas cleaning has to be developed.

334

335 3.2.2.2. Nitrogen-containing tars

336 The isopropanol of each impinger was mixed and analyzed in GC-MS in order to quantify nitrogen
337 containing tars. Among 81 quantifiable compounds used in the research unit BioWooEB for wood
338 gasification tars analysis, four nitrogen containing tars could be quantified: pyridine, pyridine-2-methyl,
339 quinoline and isoquinoline. The measured concentrations of nitrogen containing tars in the isopropanol
340 are divided by the total volume of sampled product gas in order to express results of N-tars
341 concentrations on product gas volume basis (mg.m^{-3}). The quantification of their concentrations in the
342 product gas is reported in Figure 5. Pyridine and pyridine-2-methyl were the only quantified
343 compounds in Wood air gasification, with concentrations of 21 and 6 mg.m^{-3} , respectively. SRF Wood
344 and Mixes A and B showed close pyridine concentrations (97, 127 and 141 mg.m^{-3} , respectively) and
345 quinoline concentrations (12, 18 and 17 mg.m^{-3} , respectively).

346 Mix C showed the highest N-tar concentrations with pyridine reaching 227 mg.m^{-3} , pyridine-2-
347 methyl reaching 83 mg.m^{-3} and quinoline reaching 26 mg.m^{-3} and isoquinoline reaching 13 mg.m^{-3} .

348

349 FIGURE 5

350 As observed in previous studies on biomass and coal gasification [15,17], pyridine was the
351 main N-tar, representing a mass fraction of 63 to 77 % of the total identified N-tars. Compared to
352 Wood, pyridine and pyridine-2-methyl using SRF have been multiplied by factors ranging respectively
353 from 4 to 10 and from 4 to 13, whereas N-fuel in SRF increased by a factor ranging from 17 to 27.
354 Moreover as presented in Figure 6, increasing N-fuel led to an increase in N-tar concentrations.
355 However SRF Wood has the 2nd highest N-fuel mass fraction and yet showed the lowest N-tar
356 concentrations among SRF. This can be explained considering that although having a similar N-fuel
357 mass fractions to SRF Wood, part of the nitrogen in mixes A and B (which contain tire and plastics)

358 was included in hydrocarbon chains. Compared to wood, the thermal decomposition of these
359 hydrocarbon polymers led to larger tar formation [35]. As a result, for a similar N-fuel mass fraction,
360 mixes A and B led to the formation of N-tar in higher proportions than SRF Wood. The high loads of N-
361 tars with Mix C are due to the high proteins mass fraction in sewage sludge, which is known to
362 conduct to the formation of ammonia and pyridine in pyrolysis conditions [36].

363

364 FIGURE 6

365 Pyridine and pyridine-2-methyl are soluble in water, while quinoline and isoquinoline are slightly
366 soluble [33], this suggests the possible removal of these higher loads in N-tars concentrations by
367 using wet scrubbers, at the expense of an increased maintenance, such as water renewal. This has
368 for consequence to produce more effluents, which should be properly managed.

369 **3.3. Sulfur and Nitrogen mass balances**

370 In this section the mass balances of sulfur and nitrogen after gasification are presented for each fuel.
371 Mass balances regroup results of quantified sulfur and nitrogen presented above, in addition to
372 analyses of sulfur and nitrogen remaining in fine particles and chars after gasification tests.

373

374 **3.3.1. Sulfur balance**

375 The sulfur mass balances for each fuel are reported in Figure 7. Firstly, the mass fraction of the sulfur
376 held in the remaining chars was found to be higher, ranging from 36 to 68% of the initial sulfur in the
377 fuels. This is due to the batch mode operation of the reactor which conducted to stop the tests before
378 the complete conversion of the char resulting from fuels gasification. In a continuous mode, this sulfur
379 is likely to be released in the product gas as the char is converted into product gas. Therefore sulfur
380 pollutant precursor levels reported in this study are underestimated in comparison to a continuous
381 operation.

382 Sulfur held in fine particles represents a mass fraction ranging from 2 to 13 % of the initial sulfur in the
383 fuels, which is in the same order of the reported mass fraction of 5.6% of sulfur held in the “soot and
384 dust” by Kaupp and Goss [12]. Considering the high ash mass fraction of fine particles (Table 12), the
385 sulfur is likely to be both organic, bound to the char, and inorganic, in form of sulfate for example.

386 The sulfur in form of H₂S represents 3 to 10% of the initial sulfur mass fraction in the fuels, which is
387 low compared to the mass fraction reaching 66% of total sulfur in form of H₂S reported when using
388 fossil coals [12].

389 Finally, the non-quantified fraction represents from 24 to 47 % of the initial sulfur in the fuels. As
390 presented above in the sulfur analyses sections, there are several unknown compounds in the gas
391 and the condensate, and a proper calibration should be made for each compounds. Moreover, as
392 presented in a previous work, the product gas flow is calculated based on N₂ conservation between air
393 and product gas [24], which led to uncertainties in the quantification of the mass of product gas, and
394 therefore in the overall mass balance.

395

396 FIGURE 7

397

398 **3.3.2.Nitrogen balance**

399 The nitrogen mass balances for each fuel are reported in Figure 8. Firstly, the mass fractions of
400 nitrogen held in the remaining chars are ranging between 6 and 20 % of the initial nitrogen in the fuels,
401 which is lower than values with sulfur. Yu et al. [17] reported that after fluidized bed gasification, the
402 nitrogen held in the char represented mass fractions from 0 to 9.4% of the initial nitrogen in the fuels
403 with biomasses, but reached 34% with fossil coal. Gasification tests have been performed in fed-batch
404 mode, which suggest that this nitrogen is likely to be released in the product gas in a continuous
405 mode. Therefore, nitrogen pollutant precursor levels reported in this study are likely to be higher in
406 continuous operation.

407 Nitrogen held in fine particles represents low mass fractions from 0.1 to 2 % of the initial nitrogen in
408 the fuels. The nitrogen in form of N-tars represents 0.2 to 0.7 % of the initial nitrogen in the fuels, in
409 accordance with Yu et al. [17], who reported mass fractions from 0.37 to 1.30 % of nitrogen in form of
410 tars, when gasifying biomasses.

411 For Wood, NH₃ represents 54% of the initial nitrogen in the fuels, but only represents 9 to 24% of the
412 initial nitrogen in the fuels when considering SRF. Ammonia is reported to represent from 7.5 to 34.3

413 % of the initial nitrogen by Yu et al. [17], and Leppälähti and Koljonen [15] measured mass fractions
414 ranging from 10 to 70% depending on the reactor and operating conditions.

415 For Wood, 23.4 % of the nitrogen could not be detected either in solid, liquid phases, but for SRF it
416 reached 68.9 to 83.4 % of the initial nitrogen in the fuels, in accordance with Yu and al. [17] with non-
417 quantified fractions from 58 to 76%. This “non-quantified” nitrogen is often considered to be “N₂” but
418 without any analysis to confirm this point. Leppälähti and Koljonen [15] reported “N₂” values from 25 to
419 85 % of the initial nitrogen in the fuels. A possible way to distinguish the N₂ formed in gasification from
420 the nitrogen contained in the fuel could be to use a gas tracer in the air inlet such as Ar or He. By
421 conservation of this tracer between the input and the output of the reactor, the dilution factor could be
422 determined and therefore, it would be possible to quantify in the product gas the N₂ from the air and
423 the N₂ from the fuel.

424

425 FIGURE 8

426

427 **3.4. Remaining solid after gasification**

428 In this section are presented seven metals (Cd, Cr, Cu, Hg, Pb, Ni and Zn) found in remaining char
429 and fine particles. These metals are subject to environmental emission regulations as they belong to
430 the so-called “heavy metals”. The relative shares of each metal recovered in char and fine particles for
431 each fuel are presented in Figure 9.

432

433 FIGURE 9

434 The first point highlighted by the metal analyses in remaining solids is that metal balance
435 closures reached low recovery rates. Experimentally, after gasification of biomass, Tafur-Marinos et al.
436 [18] obtained metal losses reaching mass fractions of 30 % for copper, 54 % for zinc, 66 % for lead
437 and up to 91 % for the cadmium. Moreover, they observed increases in chromium (107 %) and nickel
438 (83 %), due to contaminations from inox alloys from the reactor. This could explain the good recovery
439 of chromium in the case of Wood (recovered mass fraction reached 3.99%). These low recovery rates
440 could be explained by three factors:

- 441 • Firstly, the cyclone performances to remove particles are lower than industrially designed
442 cyclones. As a consequence, metallic droplets or fine agglomerates could bypass the cyclone.
443 However, the cyclone is the most widely used treatment to remove particles, even if finer
444 particles can be dragged in the gas. A specific dimensioning should be considered.
- 445 • Secondly, the pipes downstream the reactor are heated to 350°C to prevent any tar and water
446 condensation. At this temperature, metals such as cadmium shows significant vapor pressure
447 [33]. Considering the low concentrations of these metals in the solids, this could suggest that
448 they remained in the gas state at 350°C and do not condense on fine particles, resulting in low
449 recovery rates.
- 450 • Finally, these metals are present in very low concentrations, which justifies the name of “trace
451 elements”. As a result, the quantification of these metals is highly sensitive to measurements
452 uncertainties. This work has been performed at pilot scale, which drives relatively low amount
453 of samples (about 500 g for chars and 10-30 g for fine particles). Better balance closures
454 could be reached with studies at higher scale and/or for longer test durations.

455

456 In order to comply with environmental legislations when the gasifier is fed with SRF, the low
457 recovery rates of these selected metals highlight the need for a specific gas cleaning.

458

459 According to the European Union [37], the limits in sludge for soil amendment purposes will be
460 considered as reference of comparison in order to evaluate a possible valorization route for remaining
461 solids in SRF gasification. The limits for cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), lead
462 (Pb) and zinc (Zn) set by the directive are reported in Table 8. This comparison only aims to give a first
463 outlook of the toxicity potentials of the remaining solids in SRF gasification, but further studies
464 regarding experimental toxicities are needed regarding metals, such as leachability [38], but also
465 regarding others type of pollutants such as dioxins and Polycyclic Aromatic Hydrocarbons (PAH).

466

467 TABLE 8

468

469 **3.4.1.Char**

470 Metal analyses of the chars are reported in Table 9. As expected, metal concentrations were higher
471 in chars from SRF than in char from Wood. Char from Wood showed higher metal concentrations than
472 in the original fuel, while chars from SRF showed higher concentrations than raw fuels only for copper
473 and zinc but lower concentrations for mercury and nickel. Lead concentrations were lower in the case
474 of chars from SRF Wood and mix A, but higher in the case of chars from Mixes B and C.

475

476 TABLE 9

477

478 Relative Enrichment Factor (EF) is used to quantify the volatile behavior of metals [20,39], and is
479 defined as:

480

481
$$EF = \frac{\text{metal concentration in the char or fines particles}}{\text{metal concentration in the raw fuel}} * \frac{\%w \text{ ash in the fuel}}{100}$$

482

483 EF calculations for each metal in the chars are reported in Table 10. Most of the metals showed low
484 enrichment factors (below 0.2-0.3), which is consistent with the volatile behavior of these metals [33].
485 In the case of Mix A, the zinc showed an enrichment factor of 0.84, which is relatively high. Zinc, used
486 in tire manufacturing process, is integrated in the rubber matrix. Therefore, during the thermal
487 decomposition, a large quantity of zinc might remain “trapped” in the char matrix.

488

489 TABLE 10

490

491 The case of mix C is interesting as it shows the highest enrichment factors (except for chromium),
492 and moreover enrichment factors higher than 1 for cadmium, copper and zinc, meaning an
493 accumulation of these metals in the char, although their volatile properties.

494

495 FIGURE 10

496 In fact, small metallic spherical particles have been found in the remaining char after Mix C tests,
497 as shown in Figure 10. The chemical analyses of these particles, performed by the laboratory

498 SOCOR, are reported in Table 11. Concentrations of chromium, copper, nickel and lead are higher in
499 the particles than in the char, which shows that metals accumulated in the particles. Compared to
500 demolition wood, sewage sludge has a higher calcium concentration [9]. The addition of calcium leads
501 to the decrease of the slag melting point [40]. Therefore, it is believed that the addition of 20% of
502 sewage sludge might have increased the calcium concentration in Mix C, which led to the formation of
503 these small particles, in which metals have accumulated. Moreover, a higher sludge share in the fuel
504 mix is likely to lead to the formation of slag [41], which implies to carefully choose sewage sludge
505 share.

506

507 TABLE 11

508

509 Finally, each char shows metal concentrations within limit values set by the European Union [37].
510 This suggests a possible way to further valorize the remaining solid for example in soil remediation to
511 remove organic and inorganic pollutants [42], or mixed with manure to improve compost properties
512 [43]. Remaining charcoal is often set aside of the overall gasification process in the case of biomass
513 gasification, and even more so in the case of SRF gasification. However, as SRF are still considered
514 as “waste”, the remaining solids after gasification are also “waste”. Therefore, in order to reduce the
515 amount to be landfilled, it might be better to convert as much as possible the remaining char, which
516 will lead to an increase in metal concentrations by accumulation.

517

518 **3.4.2. Fine particles**

519 Fine particles, collected through a cyclone, showed higher metal concentrations than raw fuels, as
520 shown in Table 12. These trends are consistent with previous studies [18,20,44], and are mainly due
521 to inherent volatile properties of these metals. Each metal (except chromium) belongs to the Group 2
522 of the trace element categorization based on volatility behavior [44], which means that they are partly
523 volatile and are subject to distribution between bottom char and fine particles. However, some of these
524 are more volatile such as cadmium, lead and zinc.

525

526 TABLE 12

527

528 EF calculations for each metal in fine particles are reported in Table 13. The results highlight the
529 volatile properties of these metals as the EF in fine particles are higher than in chars. Only copper
530 showed lower EF in fine particles than in chars, as a result of its lower volatility. However, lead showed
531 high EF, especially for char from Mixes, with EF ranging from 1.62 to 5.27.

532 In the case of Mix C as a result of the accumulation of metal in the char, EF of cadmium and lead
533 were much lower than for other Mixes.

534

535 TABLE 13

536

537 Only fine particles from Wood and SRF Wood are below European limits for sludge in soil
538 amendments. This suggests a possible way to further use fines particles from Wood and SRF Wood.
539 However, this firstly implies to find a proper solution/treatment for fine particles from SRF mixes.

540

541

542 4. CONCLUSION

543

544 In this work, an evaluation of pollutant precursors released by SRF in comparison to Wood during air
545 gasification in a downdraft fixed bed reactor has been performed. A particular attention has been paid
546 to gaseous sulfur and nitrogen compounds, sulfur and nitrogen-containing tars, and seven heavy
547 metals contained in remaining solid. In order to bring useful information to researchers or process
548 managers running downdraft wood gasifiers, our tests were performed at pilot scale in fed-batch
549 mode, with close fuel load and air flow rates. Therefore, the reported bed temperatures and emissions
550 (gas, tars, solids) are resulting from the properties of the selected SRF mixes.

551 Based on pollutant precursors measured in this study, SRF wood seems to be a good substitute to
552 Wood in air gasification. It produces similar sulfur compounds, moreover with concentrations below
553 emission limits. The increase in nitrogen pollutant precursors (ammonia and N-tar) appears to be
554 handled by conventional gas cleaning devices (wet scrubbers). Remaining solids (char and fines
555 particles) present metal levels which are below the acceptable limits given for soil amendment.

556 On the contrary, the addition of a mass fraction of 20% of Tire, Plastics or Sewage Sludge to SRF
557 wood could substitute Wood in air gasification provided that a specific gas treatment for high sulfur
558 pollutant loads is developed. The dimensioning of the gas cleaning equipment (usually wet scrubbers)
559 would be necessary, particularly the frequency of cleaning water renewal. The capture of fine particles
560 would also need to be upgraded.

561 A standard tar protocol procedure, improved by the use of adequate analysis methods, was used to
562 perform this work. For analytical reasons, an important share of the total sulfur, nitrogen and heavy
563 metal could not be quantified, and explains the inaccuracy of the mass balances. This highlights the
564 necessity to develop new protocols for the determination of pollutant precursor species for SFR
565 gasification.

566 Further studies should address the impact of SRF mixes and resulting char bed characteristics
567 (permeability, density) on the products and pollutants distribution. In this objective, mixing and
568 densification (pelletization) of different SRF mixes would be an interesting approach in order to control
569 the process emissions. A more detailed study of temperature and ER in continuous operation will be
570 necessary in the presented experimental setup.

571

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683

684

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686

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688

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702

703

704 **TABLES**

705

706 *Table 1: State-of-the-art of Sulfur and Nitrogen pollutants found in the product gas in SRF gasification*

Source	Gasification agent - Type of reactor	Fuel properties			Pollutants found in the product gas	
		Fuel	S g.kg ⁻¹	N g.kg ⁻¹	Sulfur pollutants μmol.mol ⁻¹	Nitrogen pollutants μmol.mol ⁻¹
[20]	Air - Industrial fluidized bed		2	6.8	H ₂ S : 0.1 - 26	NH ₃ : 3.6 - 177
[19]	Air - Lab-scale fluidized bed	SRF from MSW	2	8	ER = 0.31 H ₂ S : 20-85	ER = 0.31 NH ₃ : < 5 HCN : 129 - 352
[21]			5	8	H ₂ S : 500	NH ₃ : 600 – 5000
[22]	Air - lab and industrial scale Downdraft fixed bed	Waste Wood	n.d.	n.d.	Lab scale H ₂ S : 100 COS : 10 Industrial Scale H ₂ S : 200-400 COS : 6-17	n.d.

707 ER : Equivalence Ratio, defined as the ratio of the experimental oxygen consumed over the
708 stoichiometric oxygen required for complete combustion

709

710

711 *Table 2: Elemental analyses of the 5 raw fuels*

Element – mg.kg⁻¹-dry	Wood	SRF Wood	Mix A (20%Tire)	Mix B (20% Plastics)	Mix C (20% Sew. Slud.)
C (g.kg⁻¹-dry)	479	501	561	482	476
H (g.kg⁻¹-dry)	57.8	57.5	58.4	56	55.9
O* (g.kg⁻¹-dry)	448	394	301	351	354
S	185	505	3 004	2 694	1 823
N	1 200	24 800	20 800	23 900	32 700
Cd	0.4	1	1.8	1.2	1.2
Cr	0.8	70	60	112	61
Cu	2	107	126	344	128
Hg	<0.05	<0.05	1.04	<0.05	0.16
Pb	1	121	100	125	99
Ni	1.5	30	28	31.6	28
Zn	4	308	3,046	n.d.	339
Ash concentration (g.kg⁻¹-dry)	13	21	52.8	81.8	78.4

712 *: by difference

713

714 *Table 3: Summary of gasification tests for the 5 fuels [24]*

	Wood	SRF wood	Mix A	Mix B	Mix C
Fuel - kg	5.9	7.8	7.5	7.5	6.3
Air - kg	7.6	10.5	9.1	7.4	8.7
ER	0.29	0.26	0.22	0.23	0.27
Volume fraction of H ₂ - %	16.9	16.1	13.9	12.6	9.8
Volume fraction of CO - %	18.1	16.6	14.9	13.3	15.0
Volume fraction of CH ₄ - %	2.5	2.7	3.3	2.7	3.5
Volume fraction of CO ₂ - %	13.9	14.7	14.9	14.3	17.4
Volume fraction of C ₂ H ₄ - %	0.57	0.56	0.98	0.88	0.87
Volume fraction of C ₂ H ₆ - %	0.10	0.08	0.18	0.14	0.27
Product gas LHV – MJ.Nm ⁻³	5.4	5.2	5.3	5.1	4.9
Stoichiometric air/product gas molar ratio – mol.mol ⁻¹	1.13	1.13	1.17	1.02	1.09
CGE - %	52	50	39	37	47

715

716

717 *Table 4: In-line H₂S measurement in GC-TCD for each fuel – concentrations in $\mu\text{mol.mol}^{-1}$*

Fuel	Wood	SRF wood	Mix A	Mix B	Mix C
Mean H ₂ S content	8	6	96	44	87

718

719

720 *Table 5: Off-line product gas GC-FPD measurements for each fuel – concentrations in $\mu\text{mol.mol}^{-1}$,*
 721 *expressed in $\text{H}_2\text{S}_{\text{equivalent}}$*

Compound	Retention time - min	Wood	SRF Wood	Mix A	Mix B	Mix C
1. H_2S	10	3	3	40	44	43
2. n.id.	11	2	3	20	18	21
3. n.id.	24.5	-	-	-	< 1	-
4. CS_2	24.9	-	-	2	-	< 1
5. Thiophene	32.9	-	-	2	< 1	< 1

722 n. id.: not identified

723

724 *Table 6: In-line NH₃ measurements in GC-TCD for each fuel – concentrations in μmol.mol⁻¹*

Fuel	Wood	SRF wood	Mix A	Mix B	Mix C
Mean NH ₃ content	619	2 107	2 609	3 870	7 578

725

726

727 *Table 7: Off-line isopropanol measurements in GC-FPD for each fuel – content in $\mu\text{mol}\cdot\text{mol}^{-1}$,*
 728 *expressed in $\text{H}_2\text{S}_{\text{equivalent}}$*

Compound	Retention time - min	Wood	SRF Wood	Mix A	Mix B	Mix C
Thiophene	32.9	-	-	2	Tar Sampling disruptions	< 1
2 Me-Thiophene	37.3	-	-	2		-
n.id.	37.7	-	-	1		-
2-5 diMe-Thiophene	40.7	-	-	1		-
n.id.	41.3	-	-	1		-
n.id.	42.1	-	-	1		-
n.id.	42.6	-	-	1		-
n.id.	43.8	-	-	1		-
Thiophenol	45.4	-	-	1		-

729 n. id.: not identified
 730

731 *Table 8: Cd, Cu, Ni, Pb, Zn and Hg limits for sludge according to European Union [37]*

Element	Limit value – mg.kg⁻¹-dry
Cd	20 - 40
Cu	1 000 - 1 750
Hg	16 - 25
Ni	300 - 400
Pb	750 - 1 200
Zn	2 500 – 4 000

732

733

734 Table 9: Cd, Cr, Cu, Hg, Pb, Ni and Zn contents in char for each fuel – mg.kg⁻¹-dry

Fuel	Wood	SRF wood	Mix A	Mix B	Mix C
Ash content – g.kg ⁻¹	90	130	130	320	420
Cd	1	1	1.76	2	8
Cr	56	94	26	492	90
Cu	17	171	184	1 357	622
Hg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Pb	7	36	75	197	226
Ni	6	4	5	28	29
Zn	90	420	14 267	2 511	1 959

735 *: in addition of a content of 120 g.kg⁻¹ in form of metallic wires, from the original tire chunks.

736

737 *Table 10: Enrichment Factors for metals in chars from each fuel*

Element	Wood	SRF Wood	Mix A	Mix B	Mix C
Cd	0.03	0.02	0.18	0.54	2.05
Cr	0.91	0.03	0.08	1.43	0.45
Cu	0.11	0.03	0.26	1.28	1.49
Pb	0.09	0.01	0.13	0.51	0.70
Ni	0.05	0.00	0.03	0.29	0.31
Zn	0.29	0.03	0.84	n.d.	1.78

738

739

740 *Table 11: Chemical analyses of metallic particles found in char from Mix C*

Element	Content – mg.kg⁻¹-dry
Cr	187
Cu	790
Ni	73
Pb	450
Zn	1 673

741

742

743 *Table 12: Cd, Cr, Cu, Hg, Pb, Ni and Zn contents in fine particles for each fuel – mg.kg⁻¹-dry*

Fuel	Wood	SRF wood	Mix A	Mix B	Mix C
Ash concentration – g.kg ⁻¹	460	430	430	380	560
Cd	6.15	12	118	38	25
Cr	111	438	343	393	317
Cu	31	396	392	665	668
Hg	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	58	707	2 188	1 404	1 190
Ni	41	156	163	104	143
Zn	n.d.	4 429	31 797	14 654	8 592

744

745

746 *Table 13: Enrichment factors (EF) for fine particles from each fuel*

Element	Wood	SRF Wood	Mix A	Mix B	Mix C
Cd	0.08	0.25	12.07	6.18	0.96
Cr	0.03	0.10	2.34	0.26	1.08
Cu	0.02	0.05	0.38	0.16	0.33
Pb	0.11	0.41	5.27	2.32	1.62
Ni	0.09	0.82	5.56	1.21	1.52
Zn	n.d.	0.22	0.40	1.90	1.35

747

748

749 **FIGURES CAPTIONS**

750 **Figure 1 : Photos of the fuels**

751 This figure shows the fuels studied in this work, with a scale in cm to improve reader's visualizing fuel
752 morphologies.

753 a: Poplar wood chips.

754 b: SRF Wood chips.

755 c: SRF Tire chunks.

756 d: SRF Plastic fluff.

757 e: SRF Sewage Sludge powder.

758

759

760 **Figure 2 : Scheme of the reactor**

761 This figure shows a detailed scheme of the pilot fixed bed reactor used in this work with the location
762 and position of the air inlet pipe as well as thermocouple locations.

763

764 **Figure 3 : In-bed temperature measurement located 10 cm below air inlet**

765 This figure shows temperature profile of in-bed measure located 10 cm below air inlet, for each fuel.

766

767 **Figure 4 : NH₃ concentrations versus CH₄ concentrations in the producer gas**

768 This figure represents the concentrations of NH₃ measured in the product gas versus the
769 concentrations of methane in the product gas for each of the 5 fuels.

770

771 **Figure 5 : Nitrogen-containing tars concentrations in the producer gas for each fuel**

772 This figure shows the concentrations of nitrogen containing tars (N-tars) in the product gas for the 5
773 fuels studied.

774

775 **Figure 6 : N-tar concentration in the producer gas versus N-fuel concentrations in the fuels**

776 This figure represents the concentrations of nitrogen containing tars (N-tars) versus the nitrogen
777 content in the fuel.

778

779 **Figure 7: Mass balance of sulfur after gasification for each fuel**

780 This figure shows the mass balances of sulfur after gasification, classified as char, fine particles, H₂S
781 and non-quantified.

782

783 **Figure 8: Mass balance of nitrogen after gasification for each fuel**

784 This figure shows the mass balances of nitrogen after gasification, classified as char, fine particles, N-
785 tars, NH₃, and non-quantified.

786

787 **Figure 9 : Metal balances for each fuel in char+fine particles**

788 This figure shows the mass balances of seven metals found in the char and the fine particles for each
789 fuel .

790

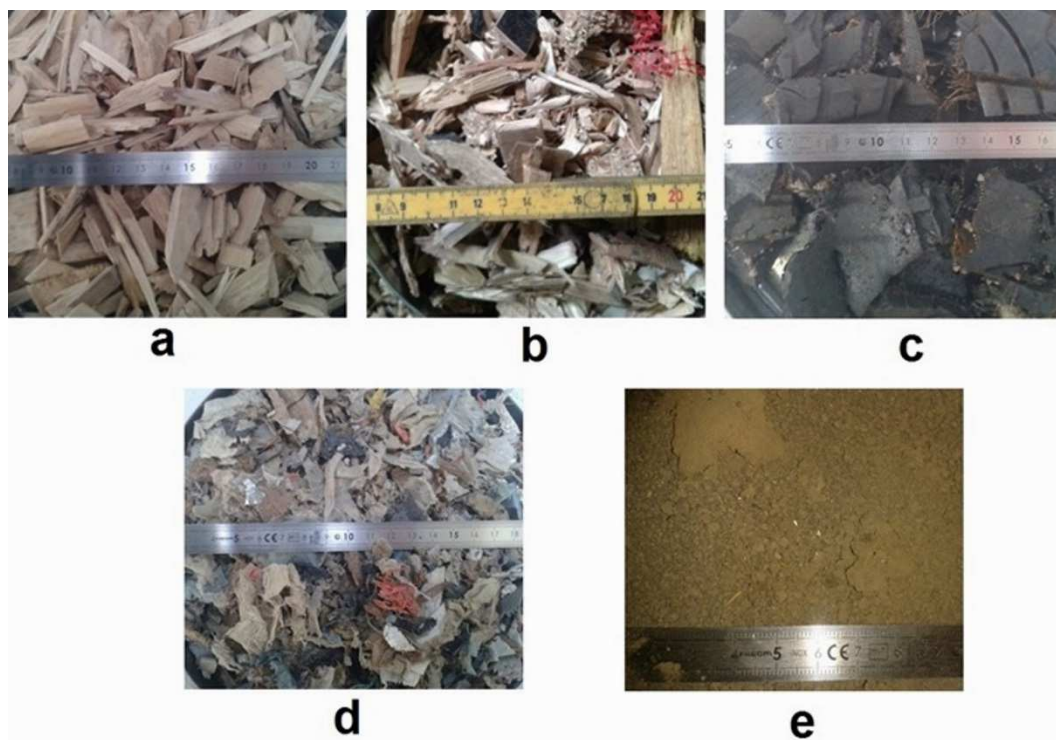
791 **Figure 10 : Metallic particles found in the remaining char in Mix C tests**

792 This figure shows the photo of the metallic particles found in the char after using Mix C. The scale unit
793 is in cm

794

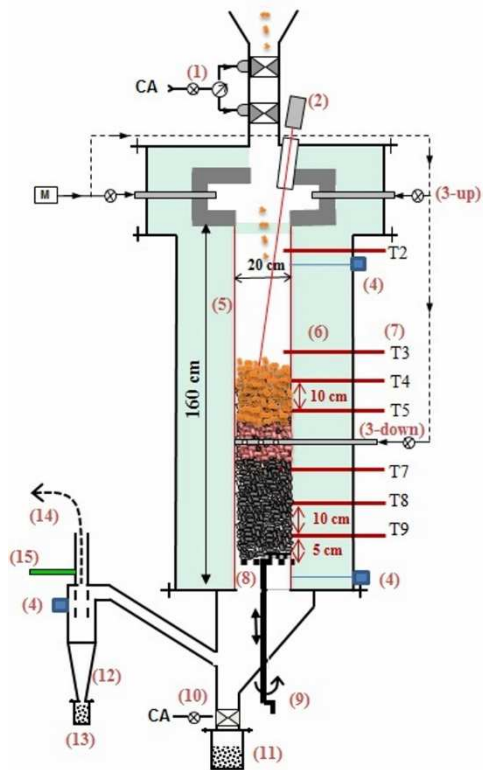
795

796 **FIGURES**



797
798 *Figure 1: Photos of the fuels - scale unit in cm. a) Poplar wood chips, b) SRF wood chips, c) SRF Tire*
799 *chunks, d) SRF Plastic fluff, e) SRF Sewage sludge powder.*

800

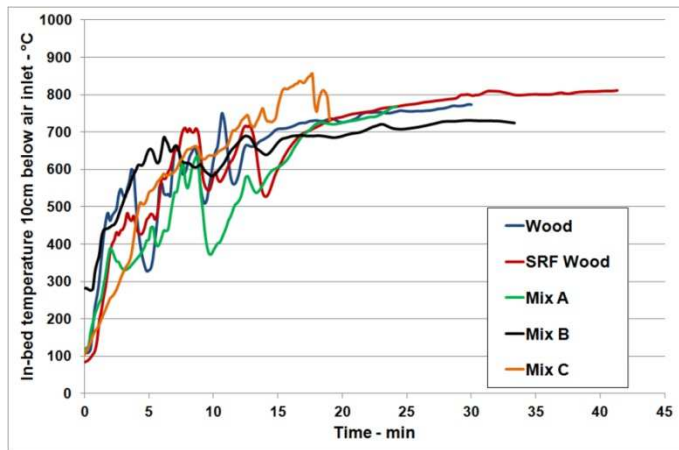


- | | |
|-------------------------|-----------------------------------|
| 1- Pneumatic valves | 9- Char extraction system |
| 2- Laser sensor | 10- Guillotine Valve |
| 3-up - Upper air inlet | 11- Char bucket |
| 3-down - Main air inlet | 12- Cyclone |
| 4- Transducers | 13- Fines Bucket |
| 5- Reactor tube | 14- Toward Post-combustion system |
| 6- Insulation | 15- Gas sampling point |
| 7- Thermocouples | M- Mass Air Flowmeter |
| 8- Grate | CA- Compressed air |

801
802 *Figure 2: Schematic representation of the fixed bed downdraft reactor*

803

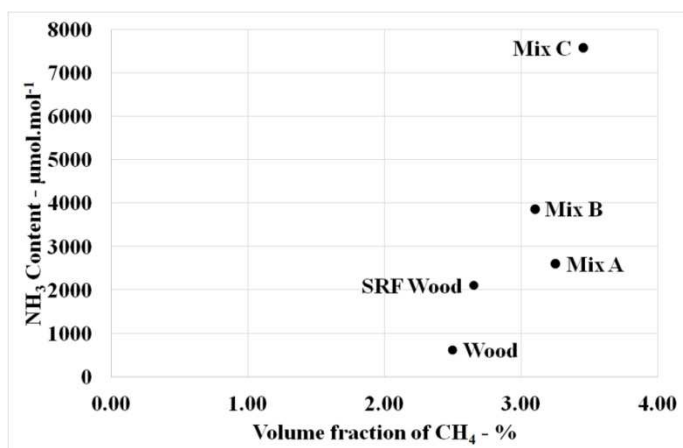
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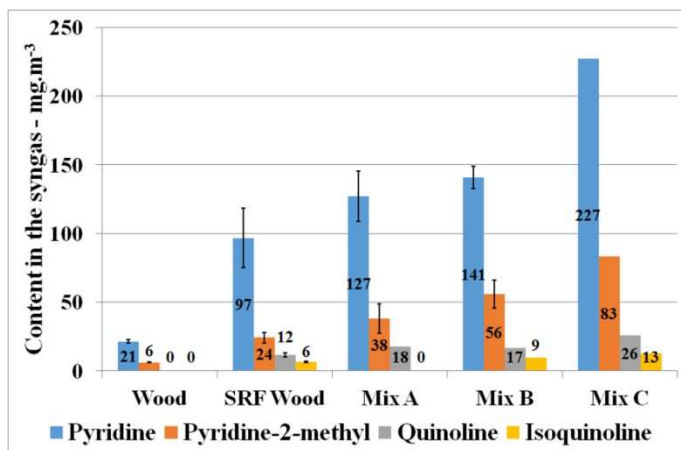
806 *Figure 3: In-bed temperature measurement located 10cm below air inlet during gasification test for*
 807 *each fuel*

808



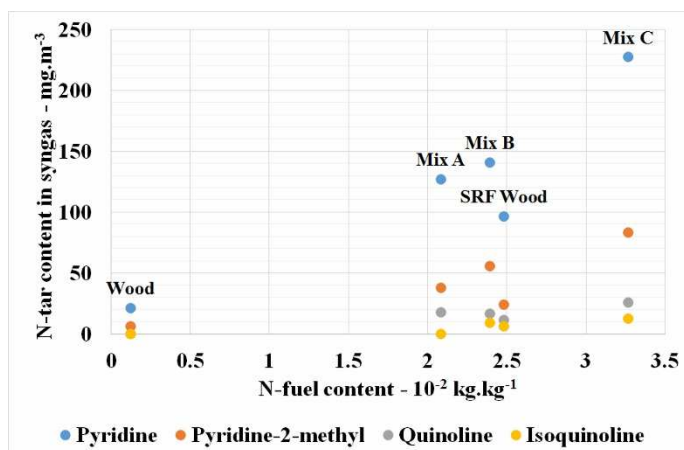
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Figure 4: NH₃ concentrations versus CH₄ concentrations in the producer gas



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Figure 5: Nitrogen-containing tars concentrations in the producer gas for each fuel

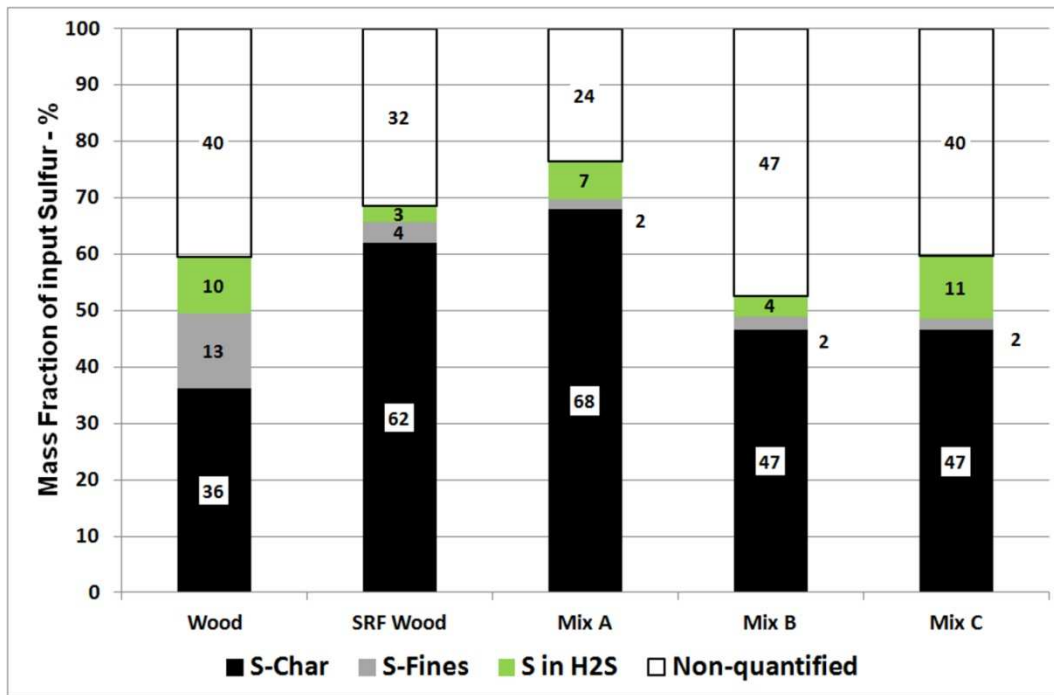


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Figure 6: N-tar concentration in the producer gas versus N-fuel concentrations in the fuels

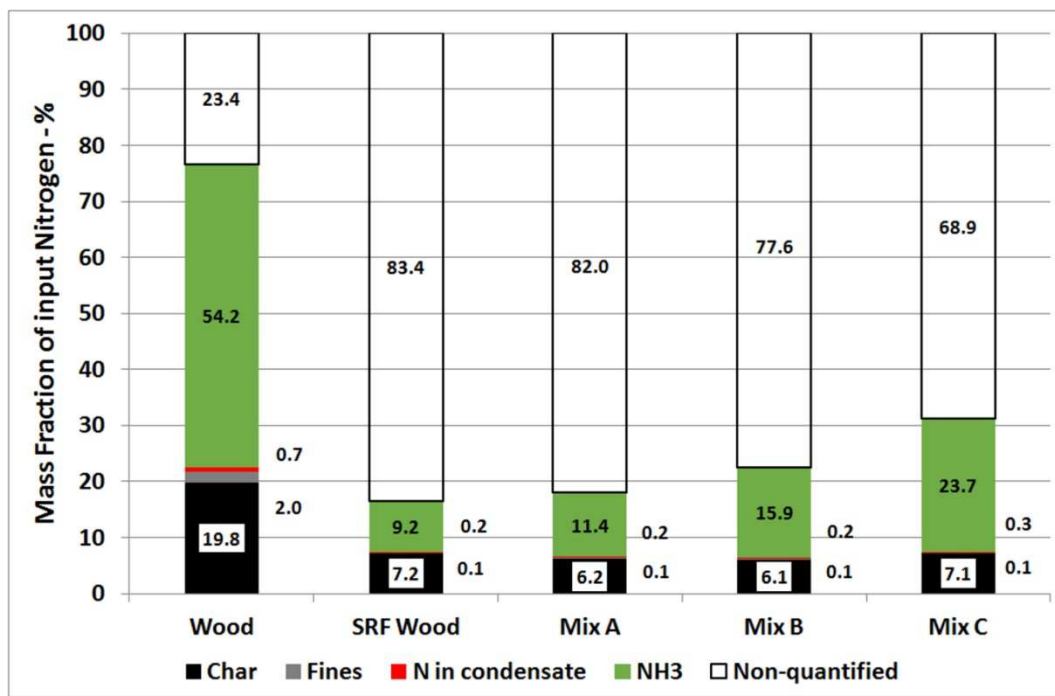
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817 *Figure 7: Mass balance of sulfur after gasification for each fuel*

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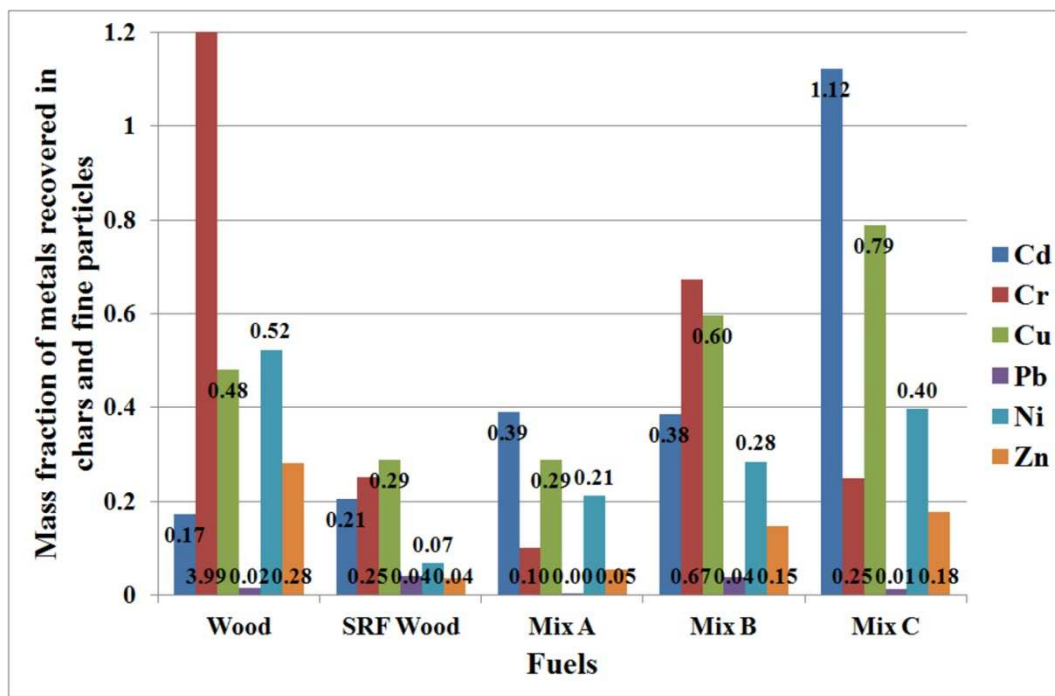


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820 *Figure 8 : Mass balance of nitrogen after gasification for each fuel*

821

822



823
824

Figure 9: Mass fraction of metals recovered for each fuel in char+fine particles



825
826

Figure 10: Metallic particles found in the char from Mix C – scale unit in cm

827