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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 H_2S 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 fractions17 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

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

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

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 H_2, CO, CO_2, CH_4 and N_2 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 SO_2 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 H_2S, CS_2, COS, SO_2, S_2 as well as traces of

53   C_4H_4S (thiophene), CH_3-C_4H_3S (methylthiophene), C_2H_2HS (acetylmercaptan), CH_3SH (methanethiol

54   or methylmercaptan) et CH_3-S-CH_3 (dimethylsulfide) [12–14]. Some nitrogen compounds, commonly

55   found in biomass air gasification effluents, are NH_3, HCN for the gaseous compounds and pyridine

56   and its derivatives, quinoleine and isoquinoleine 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 H_2S is the main sulfur produced during SRF air gasification. Although

72 the initial sulfur in the fuel are close (from 2 to 5 $g.kg^{-1}$), H_2S concentrations in the gas widely vary from

73 0.1 to 500 $\mu mol.mol^{-1}$, 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 $\mu mol.mol^{-1}$).

76   Concerning nitrogen, NH_3 is the main compound reported in SRF air gasification. As observed for

77 H_2S, the initial fuel nitrogen contents are similar (from 6.8 to 8 $g.kg^{-1}$), but NH_3 concentrations in the

78 gas are varying from 3.6 to 5 000 $\mu mol.mol^{-1}$ [19–21]. Berrueco et al. [19] also highlighted the

79 presence of HCN in non-negligible amounts (129 to 352 $\mu mol.mol^{-1}$).This suggests the need for

80 greater focus on HCN concentrations, considering its higher toxicity potential than NH_3.

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 H_2 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 H_2S and NH_3 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

5

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 301and 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

6

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 μGC-TCD equipped with two columns: MolSieve 5A and PoraPlotQ. The in-line

175 measurements allowed the quantification of H_2S and NH_3. 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 H_2S standard gas bottles. Therefore, the sulfur compounds concentrations are

190 expressed in this work in $H_2S_{equivalent}$.

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 scrapper 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 (H_2, CO, CH_4, CO_2). 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 H_2 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: CH_4 reached 2.7-3.5%,

232   C_2H_4 increased to 0.87-0.98% and C_2H_6 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, H_2S is the main compound found in the product gas. Wood and SRF wood

250   produced a gas with low H_2S concentrations (6 to 8 $\mu mol.mol^{-1}$) 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 H_2S concentrations from 44 to 96 $\mu mol.mol^{-1}$, similarly to Berrueco et al.

253   [19]. In combustion processes, one mole of H_2S leads to the formation of one mole of SO_2. According

254   to the European Waste Incineration Directive [11], the SO_2 limit is set to 50 mg. m^{-3} which is equivalent

255   to a concentration of 17 $\mu mol.mol^{-1}$. 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 SO_2 limit.

257

258   TABLE 4

259

260   However, H_2S 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 SO_2 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 H_2S one, while it represents about 50% of the

266   H_2S concentration for SRF mixes. Moreover, H_2S 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 CS_2 and thiophene,

269 especially with mix A. The removal of H_2S (and SO_2) 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, NH_3 was the main nitrogen compound identified in product gas. Wood

277 produced a gas with NH_3 concentration of 619 $\mu mol.mol^{-1}$, while NH_3 increased from 2,107 to 7,518

278 $\mu mol.mol^{-1}$ 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. Leppälahti and Koljonen [15] explained that for

280 biomasses, small amino acids are almost completely converted to gaseous species, among them NH_3.

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 $\mu mol.mol^{-1}$. As the oxidation of one

285 mole of NH_3 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 NH_3 combustion in the

287 flue gas would reach about the half of the NH_3 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 NH_3.

290

291 TABLE 6

292

293   In practice, measurements of NH_3 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 NH_3 concentration.

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

299   indicator of NH_3 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.

14

386   The sulfur in form of H_2S 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 H_2S 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 N_2 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, NH_3 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 Leppälahti 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 "N_2" but

418 without any analysis to confirm this point. Leppälahti and Koljonen [15] reported "N_2" values from 25 to

419 85 % of the initial nitrogen in the fuels. A possible way to distinguish the N_2 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 N_2 from the air and

423 the N_2 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:

- Firstly, the cyclone performances to remove particles are lower than industrially designed cyclones. As a consequence, metallic droplets or fine agglomerates could bypass the cyclone. However, the cyclone is the most widely used treatment to remove particles, even if finer particles can be dragged in the gas. A specific dimensioning should be considered.

- Secondly, the pipes downstream the reactor are heated to 350°C to prevent any tar and water condensation. At this temperature, metals such as cadmium shows significant vapor pressure [33]. Considering the low concentrations of these metals in the solids, this could suggest that they remained in the gas state at 350°C and do not condense on fine particles, resulting in low recovery rates.

- Finally, these metals are present in very low concentrations, which justifies the name of "trace elements". As a result, the quantification of these metals is highly sensitive to measurements uncertainties. This work has been performed at pilot scale, which drives relatively low amount of samples (about 500 g for chars and 10-30 g for fine particles). Better balance closures could be reached with studies at higher scale and/or for longer test durations.

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

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

TABLE 8

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

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 concentratons 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

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

685   6. **Declaration of Interest :** none

686

687   7. **ACKNOWLEDGMENTS**

688

702

703

TABLES

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	SRF from MSW	2	6.8	H_2S : 0.1 - 26	NH_3 : 3.6 - 177
[19]	Air - Lab-scale fluidized bed		2	8	ER = 0.31 H_2S : 20-85	ER = 0.31 NH_3 : < 5 HCN : 129 - 352
[21]			5	8	H_2S : 500	NH_3 : 600 – 5 000
[22]	Air - lab and industrial scale Downdraft fixed bed	Waste Wood	n.d.	n.d.	Lab scale H_2S : 100 COS : 10 Industrial Scale H_2S : 200-400 COS : 6-17	n.d.

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

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_2H_4 - %	0.57	0.56	0.98	0.88	0.87
Volume fraction of C_2H_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

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716

717   *Table 4: In-line H_2S measurement in GC-TCD for each fuel – concentrations in $\mu mol.mol^{-1}$*

Fuel	Wood	SRF wood	Mix A	Mix B	Mix C
Mean H_2S content	8	6	96	44	87

718

719

720 *Table 5: Off-line product gas GC-FPD measurements for each fuel – concentrations in μmol.mol⁻¹,*
721 *expressed in $H_2S_{equivalent}$*

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 NH$_3$ 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 µmol.mol^{-1},*
728 *expressed in H$_2$S$_{equivalent}$*

Compound	Retention time - min	Wood	SRF Wood	Mix A	Mix B	Mix C
Thiophene	32.9	-	-	2		< 1
2 Me-Thiophene	37.3	-	-	2		-
n.id.	37.7	-	-	1	Tar Sampling disruptions	-
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

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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

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748

FIGURES CAPTIONS

Figure 1 : Photos of the fuels

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

a: Poplar wood chips.

b: SRF Wood chips.

c: SRF Tire chunks.

d: SRF Plastic fluff.

e: SRF Sewage Sludge powder.

Figure 2 : Scheme of the reactor

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

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

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

Figure 4 : NH_3 concentrations versus CH_4 concentrations in the producer gas

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

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

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

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

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

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

This figure shows the mass balances of sulfur after gasification, classified as char, fine particles, H_2S and non-quantified.

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

This figure shows the mass balances of nitrogen after gasification, classified as char, fine particles, N-tars, NH_3, and non-quantified.

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

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

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

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

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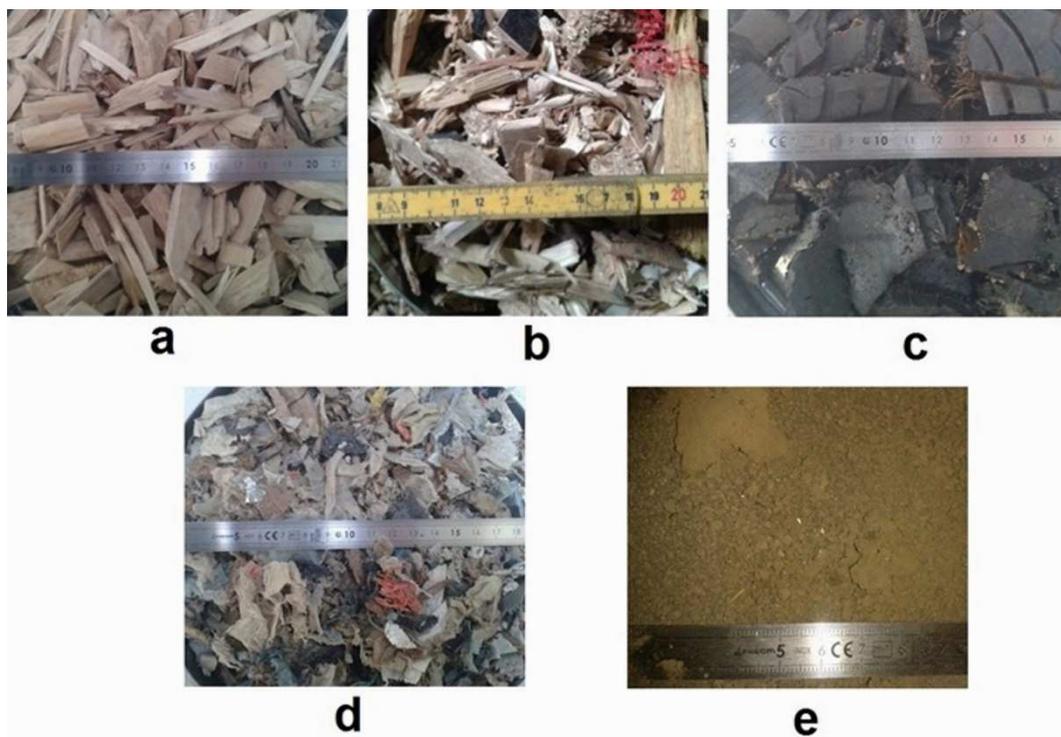
FIGURES

Figure 1: Photos of the fuels - scale unit in cm. a) Poplar wood chips, b) SRF wood chips, c) SRF Tire chunks, d) SRF Plastic fluff, e) SRF Sewage sludge powder.
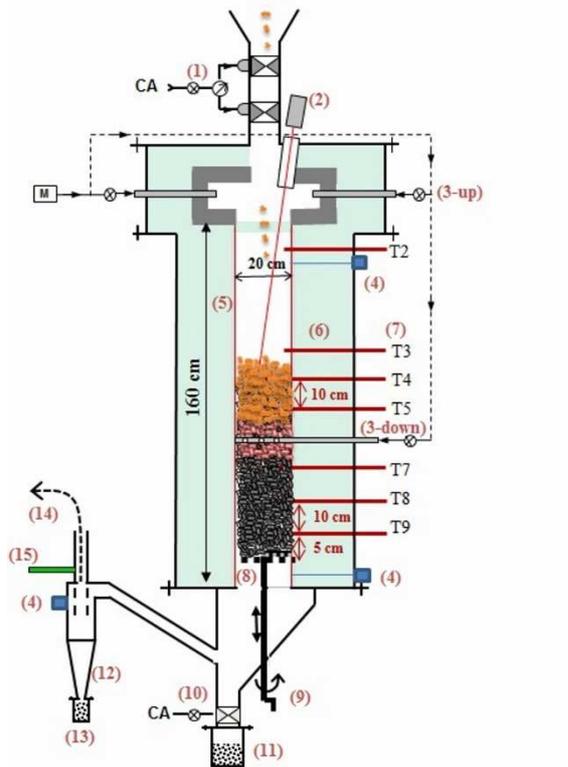
1- Pneumatic valves
2- Laser sensor
3-up – Upper air inlet
3-down - Main air inlet
4- Transducers
5- Reactor tube
6- Insulation
7- Thermocouples
8- Grate

9- Char extraction system
10- Guillotine Valve
11- Char bucket
12- Cyclone
13- Fines Bucket
14- Toward Post-combustion system
15- Gas sampling point
M- Mass Air Flowmeter
CA- Compressed air

Figure 2: Schematic representation of the fixed bed downdraft reactor
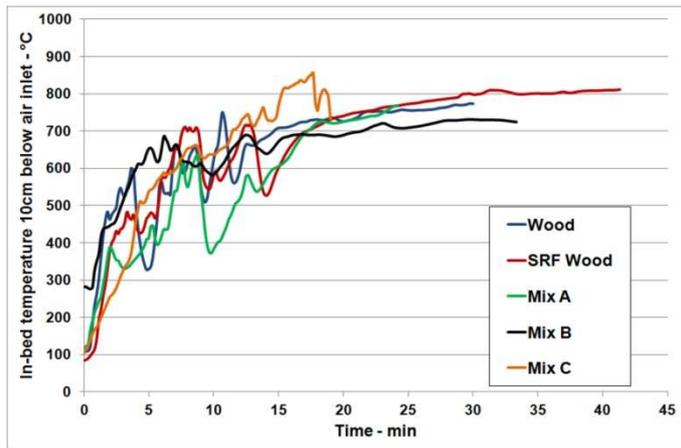
805

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

808
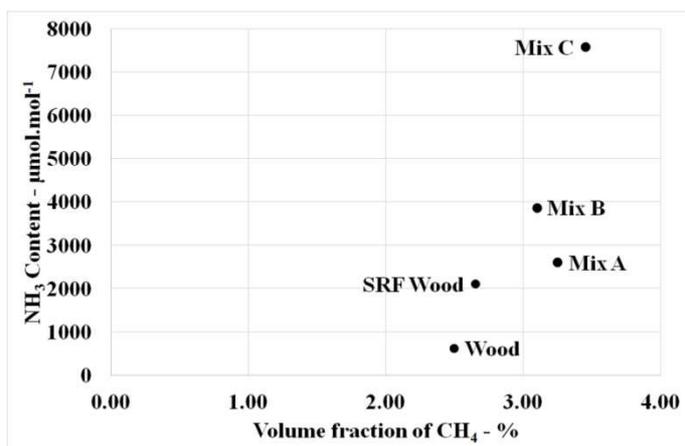
809
810 *Figure 4: NH₃ concentrations versus CH₄ concentrations in the producer gas*
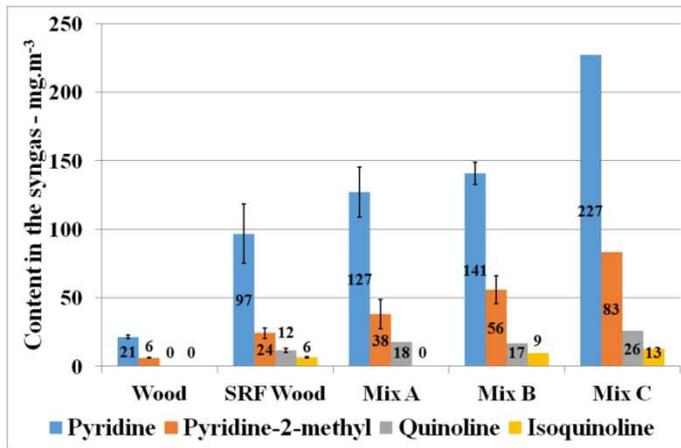
811
812   *Figure 5: Nitrogen-containing tars concentrations in the producer gas for each fuel*
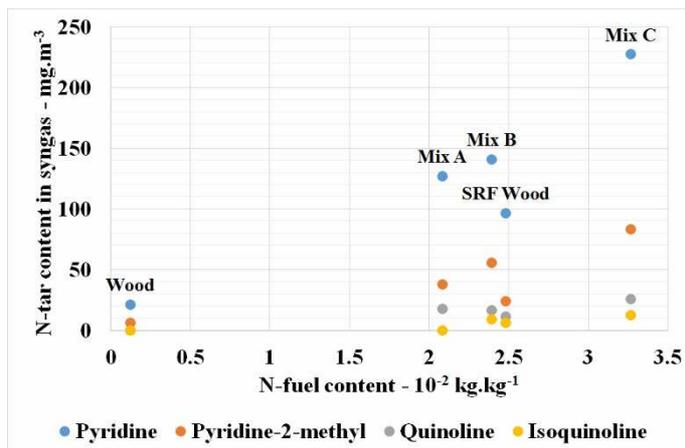
*Figure 6: N-tar concentration in the producer gas versus N-fuel concentrations in the fuels*
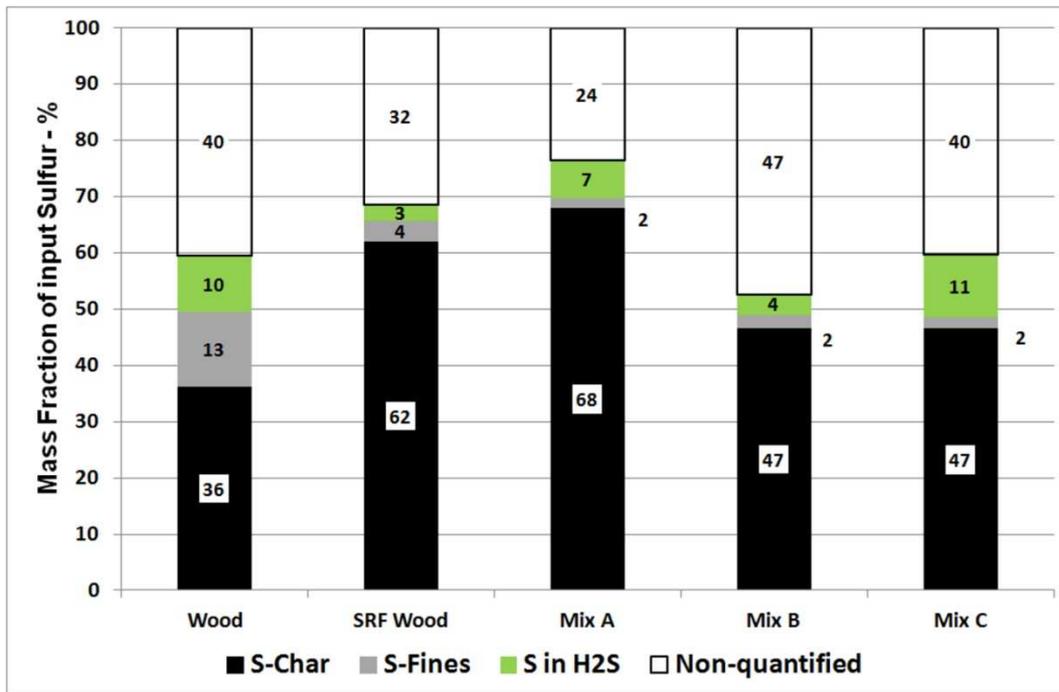
816

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

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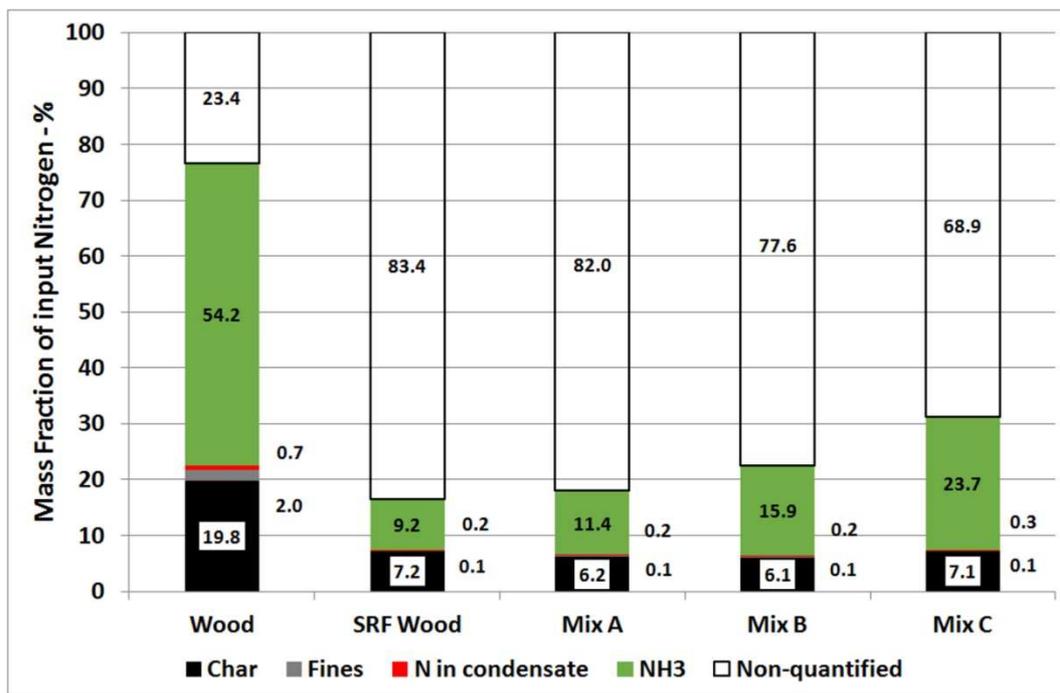
819

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

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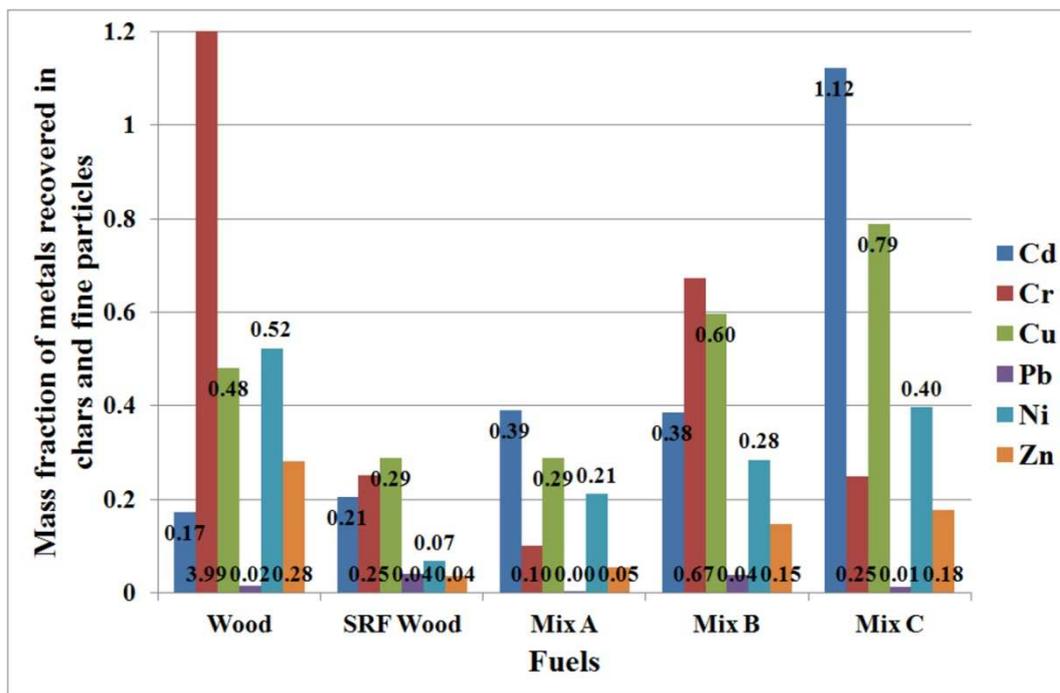
Figure 9: Mass fraction of metals recovered for each fuel in char+fine particles

825
826   *Figure 10: Metallic particles found in the char from Mix C – scale unit in cm*

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