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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 $\mu mol.mol^{-1}$), when SRF mixes led to higher concentrations (44-96 $\mu mol.mol^{-1}$) 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 $\mu mol.mol^{-1}$), 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

downdraft fixed bed reactors. The aim of gasification is to convert a solid fuel into a combustible gas (also called producer gas), mainly composed of H_2, CO, CO_2, CH_4 and N_2 which can be used in internal combustion engines or gas turbines for the production of electricity and heat [5,6]. Fixed bed reactors are typically used at small to medium scales (< 5 MW) offering a simple process handling and producing a gas with relative low tar concentrations compared to other reactor designs at the considered scale, but with higher fuel quality requirements (moisture, particle size, ash content) [5].

However, the use of waste as a fuel - which contains additives leading to pollutants - may impact product gas quality, process performances and environmental emissions. The major pollutants found in gasification are condensable species called tars, which are extensively studied especially in biomass gasification [7], and are considered as the “Achilles heel of biomass gasification” [8]. However, minor pollutant precursors such as sulfur, nitrogen or heavy metals are less considered despite their potential high environmental impact as well as their influence on the process i.e. corrosion or fouling and slagging due to the melting and volatilization of inorganic species. Compared to raw wood, SRF can present higher sulfur content (from 0.1-0.5 $g.kg^{-1}$ for raw wood [9] to 13 $g.kg^{-1}$ for tire [10]) , higher nitrogen content (from 1 $g.kg^{-1}$ for wood [9] to 220 $g.kg^{-1}$ for waste wood [9]), and higher heavy metals content (coatings, paints, metal accumulation in sludge…). Sulfur and nitrogen containing compounds are a matter of concern, notably in combustion processes since they lead to the formation of SO_2 and NO_x, considered as pollutants by emissions standards [11]. Moreover, these two compounds can damage process pipes and engine or turbine parts as they are corrosive. Heavy metal emissions have to be controlled as well [11], as they are toxic for living organisms. Gasification mainly converts a solid fuel into gas, but also into a small amount of liquid (condensable) and solid (char). Therefore pollutants are distributed within these three phases. Sulfur compounds typically found during the gasification of wood or fossil coals are H_2S, CS_2, COS, SO_2, S_2 as well as traces of C_4H_4S (thiophene), CH_3-C_4H_3S (methylthiophene), C_2H_2HS (acetylmercaptan), CH_3SH (methanethiol or methylmercaptan) et CH_3-S-CH_3 (dimethylsulfide) [12–14]. Some nitrogen compounds, commonly found in biomass air gasification effluents, are NH_3, HCN for the gaseous compounds and pyridine and its derivatives, quinoleine and isoquinoleine for condensable compounds [15–17]. During air gasification, the distribution of heavy metals highly depends on their volatility at a given reaction zone temperature. Highly volatile metals such as cadmium (Cd) are entrained with the gaseous species, which results in an important lost fraction of the considered metal when a balance is to be performed.

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

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

An overview of the works that focused on sulfur and nitrogen pollutant precursors found in the producer gas obtained from SRF gasification is presented in the Table 1. As reported by Berrueco et al. [19] this table highlights that H_2S is the main sulfur produced during SRF air gasification. Although the initial sulfur in the fuel are close (from 2 to 5 $g.kg^{-1}$), H_2S concentrations in the gas widely vary from 0.1 to 500 $\mu mol.mol^{-1}$, along with the considered fuel and process conditions [19–22]. Le et al. [22] highlighted the presence of COS using waste wood during air gasification in downdraft fixed bed gasifiers, with non-negligible contents (6 - 17 $\mu mol.mol^{-1}$).

Concerning nitrogen, NH_3 is the main compound reported in SRF air gasification. As observed for H_2S, the initial fuel nitrogen contents are similar (from 6.8 to 8 $g.kg^{-1}$), but NH_3 concentrations in the gas are varying from 3.6 to 5 000 $\mu mol.mol^{-1}$ [19–21]. Berrueco et al. [19] also highlighted the presence of HCN in non-negligible amounts (129 to 352 $\mu mol.mol^{-1}$).This suggests the need for greater focus on HCN concentrations, considering its higher toxicity potential than NH_3.

However, Broer et al. [23] showed impacts of the syngas conditioning methods on HCN measurements, resulting in low accuracy. Their work highlights the difficulties to perform analyses of HCN, but interrogate on the impact at larger scale for all of these low concentration compounds (compared to major product gas compounds as H_2 or CO). These difficulties result in low accuracy and low precision during analyses and also explain why studies focusing on these minor compounds in concentrations are still limited.

TABLE 1

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

In this context, this work focuses on precursors released during air gasification of waste based fuels using a downdraft fixed bed reactor. As waste gasification is developing, the knowledge of the types and emission levels of produced pollutants is the object of a growing concern of the scientific community. The study of the gasification performances of these fuels is briefly discussed in this paper and detailed in our recent work [24]. This work was realized performing SRF gasification tests with in-line analysis of H_2S and NH_3 in the product gas, in parallel to major product gas compounds, as well as off-line measurements of sulfur and nitrogen tars, and heavy metal contents in remaining solids (char and fine particles). The present work aims to contribute to a better understanding of air gasification of waste at small to medium scales, especially regarding pollutant precursors releases and product gas quality.

2. MATERIAL AND METHODS

2.1. Fuels

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

Wood (poplar) was provided by the company “Ets Houée” (Brittany, France), which produces wood packaging out of poplar (Figure 1a). SRF wood was provided by “KERVAL Centre Armor”, a waste treatment syndicate in Brittany, France. In this facility, SRF wood is separately collected and therefore composed of waste furniture, waste pallets… which are brought by citizens to waste collection sites (Figure 1b). SRF tires, in the form of chips (Figure 1c), were provided by “Aliapur”, a French company 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 448$g.kg^{-1}$, while it was
145 lower for SRF Wood down to 394$g.kg^{-1}$. 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 354$g.kg^{-1}$.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 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

product gas. The isopropanol was analyzed afterwards in the BioWooEB research unit using a GC-MS (chromatograph Agilent 6890, column Agilent DB1701, mass spectrometer Agilent 5975) in order to identify and quantify the tar compounds [24]. In this study, we focused on nitrogen-containing tars ("N-tar"). In addition, for sulfur compounds, gas bags and isopropanol samples were analyzed afterwards in the research unit "Institut Charles Gerhardt Montpellier" (ICGM 5253) using a GC-FPD (chromatograph Shimatzu 2014, column ZB-50) equipped with a FPD (Flame Photometric Detector) in order to provide qualitative analyses of sulfur compounds (gaseous compounds and sulfur-containing tars or "S-tar"). Sulfur compound standards have been used to perform identification of unknown compounds by determination of matching retention time. As FPD response mainly depends on the number of sulfur elements in a given molecule [31], the calibration of the equipment has been performed using H_2S standard gas bottles. Therefore, the sulfur compounds concentrations are expressed in this work in $H_2S_{equivalent}$.

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

3. **RESULTS AND DISCUSSION**

3.1. Product gas fuel properties

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

TABLE 3

In-bed temperature measurements 10 cm below air injection for each fuel are reported in Figure 3. As showed in a previous study [24], the temperature measurements (as well as gas concentrations) showed two distinct phases during each test : first a transient phase following ignition, characterized by erratic temperature and gas composition profiles, which were observed until the reaction zone reached the air-inlet position. At this point, a “steady-state” was reached, with a stable char bed temperature comprised between 690 and 850°C, along with stable concentrations for major product gas components (H_2, CO, CH_4, CO_2). In the “steady-state” phase (after 17min in Figure 3), Wood, SRF Wood and Mix A showed similar in-bed char temperatures evolutions, increasing from 710°C to 760°C 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 temperature showed smoother increase from 690°C to 730°C. As reported in the literature [8], this lower char temperature might lead to higher tar concentrations, including sulfur and nitrogen containing tars.

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

FIGURE 3

Syngas compositions from Wood and SRF Wood were similar, and close to the typical values of syngas from biomass gasification [6]. The addition of a mass fraction of 20% of non-woody fuel to SRF Wood led to a decrease of H_2 down to 9.8-13.9% and a decrease of CO down to 13-15%. However, these shifts are balanced by the increases of light hydrocarbon concentrations: CH_4 reached 2.7-3.5%, 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 for each fuel, and ranged between 4.9 and 5.4 $MJ.Nm^{-3}$. This implies that comparing pollutants on volume-based (thus, on molar basis $mol.mol^{-1}$) or energy-based ($mg.MJ^{-1}$) concentrations is acceptable, as the energy output is proportional to the volume of product gas. Moreover, as reported in Table 3, the stoichiometric combustion of the product gas is performed with an air/product gas molar ratio close to 1.1 $mol.mol^{-1}$, which is typically the value found with product gas from downdraft fixed bed gasifier [6]. This implies that using a SRF product gas in an engine would dilute by a factor 2 the

pollutant concentrations in the exhaust gas.

3.2. Pollutants produced in gasification

3.2.1. Gaseous pollutant precursors

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

3.2.1.1. Sulfur gaseous pollutants

Regarding sulfur, H_2S is the main compound found in the product gas. Wood and SRF wood produced a gas with low H_2S concentrations (6 to 8 µmol.mol^{-1}) due to low sulfur mass fractions in the fuels (185 and 505 mg.kg^{-1}, respectively). SRF mixes, with increased initial sulfur mass fractions up to 3 g.kg^{-1}, produced a gas with H_2S concentrations from 44 to 96 µmol.mol^{-1}, similarly to Berrueco et al. [19]. In combustion processes, one mole of H_2S leads to the formation of one mole of SO_2. According to the European Waste Incineration Directive [11], the SO_2 limit is set to 50 mg. m^{-3} which is equivalent to a concentration of 17 µmol.mol^{-1}. Even considering a dilution after air/product gas combustion in an engine, only Wood and SRF wood produce a gas which complies with the SO_2 limit.

TABLE 4

However, H_2S is not the only sulfur compound found in the product gas. Off-line product gas measurements in GC-FPD highlighted the presence of non-negligible concentration of another sulfur compound at a residence time of 11 min (Table 5). Considering that SO_2 and methylmercaptan can be excluded (their standard compounds presented different residence times, i.e. 15.7 and 19.2 min, respectively) and based on the study of Gai et al. [13], this compound is believed to be COS. For Wood and SRF wood, its concentration is similar to the H_2S one, while it represents about 50% of the H_2S concentration for SRF mixes. Moreover, H_2S concentration in off-line analyses are lower than in-line results due to gas sampling bag leaks, which suggest higher contents in reality. In addition, others sulfur compounds have been found in product gas from SRF mixes, among them CS_2 and thiophene,

especially with mix A. The removal of H_2S (and SO_2) appears to be well developed [32], however the removal of the other sulfur compounds identified in this study is not well established, which appears as a critical issue for the SRF gasification development.

TABLE 5

3.2.1.2. Nitrogen gaseous pollutants

Regarding nitrogen, NH_3 was the main nitrogen compound identified in product gas. Wood produced a gas with NH_3 concentration of 619 µmol.mol^{-1}, while NH_3 increased from 2,107 to 7,518 µmol.mol^{-1} when using the SRF (Table 6). These values are similar to results reported by Pinto et al. [21], although the reactor design is different. Leppälahti and Koljonen [15] explained that for biomasses, small amino acids are almost completely converted to gaseous species, among them NH_3. Because of the presence of additional groups able to form hydrogen bonding, thermal degradation of bigger amino acids leads to the formation of smaller amount of gases but higher quantities of heavier compounds such as pyrrole or pyridine [15]. According to the European Waste Incineration Directive [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 mole of NH_3 leads to the formation of one mole of NO_x, and considering the typical air/product gas molar ratio equal to 1 in internal combustion engines, NO_x concentration from NH_3 combustion in the flue gas would reach about the half of the NH_3 concentration in the product gas. This implies that none of the fuels (even poplar wood) complies with this regulation, and therefore a specific gas cleaning operation has to be performed for NH_3.

TABLE 6

In practice, measurements of NH_3 appeared difficult, as a result of being highly sensitive to water concentration in the product gas. Indeed, ammonia and water show very close molar masses (17 vs 18 g.mol-1, respectively) and dipole moment (1.42 vs 1.85 D, respectively) [33,34]. Combined with high affinity of ammonia and water, it is believed that these two molecules are subject to co-elute in the column PoraPlotQ, misleading the evaluation of the NH_3 concentration.

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

TABLE 7

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

3.2.2.2. Nitrogen-containing tars

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

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

FIGURE 5

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

3.4.1.Char

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

TABLE 9

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

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

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

TABLE 10

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

FIGURE 10

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

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

TABLE 11

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

3.4.2.Fine particles

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

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.

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

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

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

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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 $\mu mol.mol^{-1}$	Nitrogen pollutants $\mu mol.mol^{-1}$
[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

715

716

717 *Table 4: In-line H_2S measurement in GC-TCD for each fuel – concentrations in µmol.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 $H_2S_{equivalent}$*

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

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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.
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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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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

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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

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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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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.

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 .

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

FIGURES

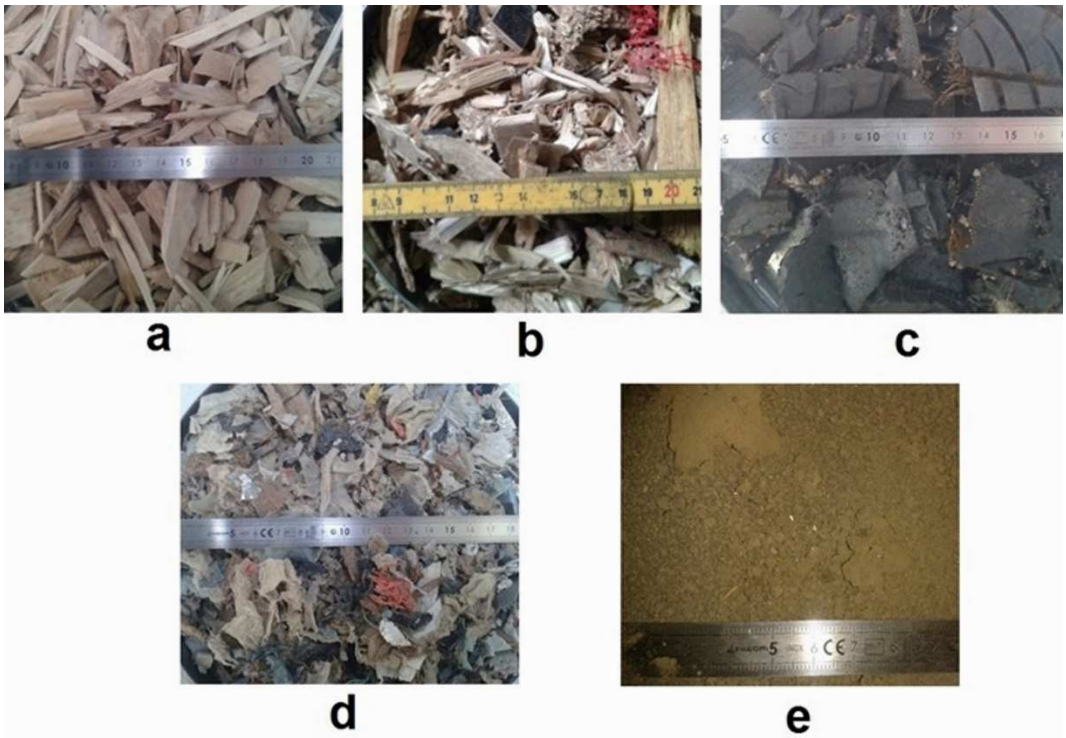
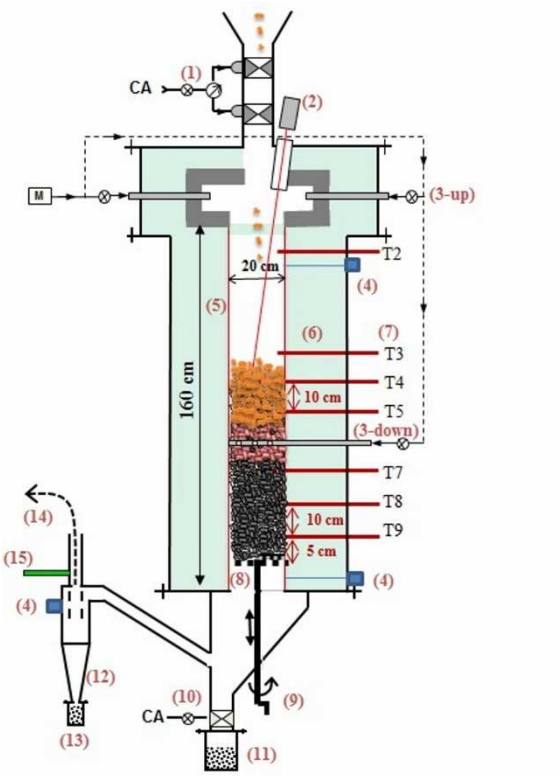


Figure 1: Photos of the fuels - scale unit in cm. a) Poplar wood chips, b) SRF wood chips, c) SRF Tire chunks, d) SRF Plastic fluff, e) SRF Sewage sludge powder.



1- Pneumatic valves	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

Figure 2: Schematic representation of the fixed bed downdraft reactor

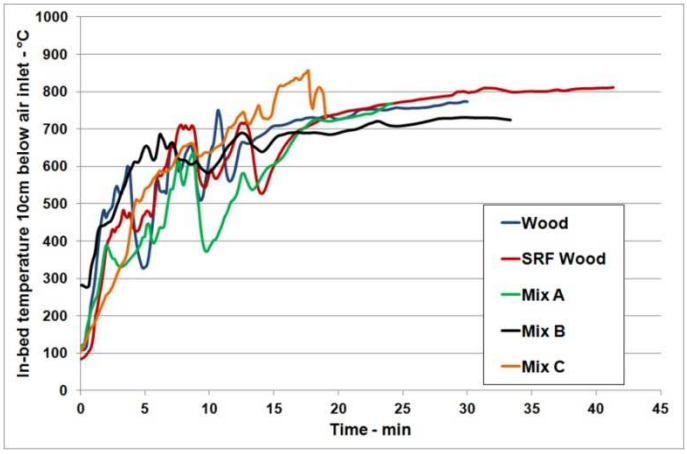


Figure 3: In-bed temperature measurement located 10cm below air inlet during gasification test for each fuel

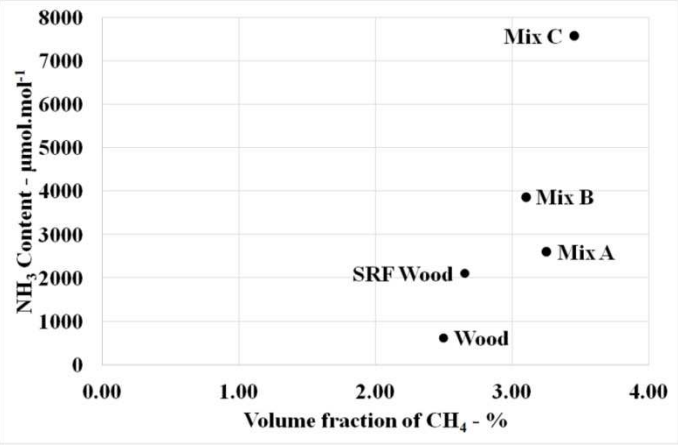


Figure 4: NH_3 concentrations versus CH_4 concentrations in the producer gas

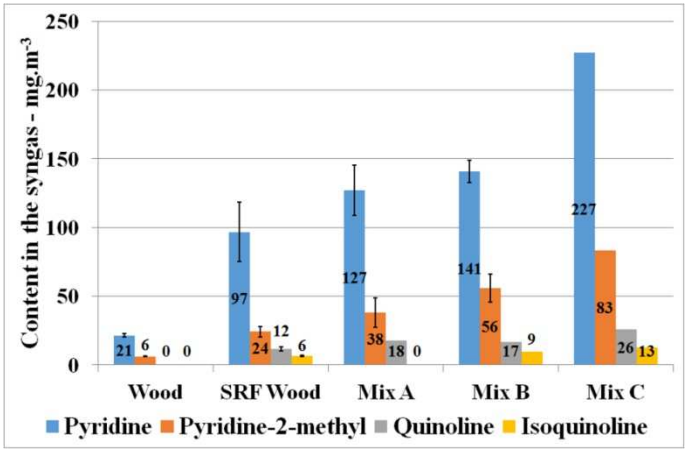


Figure 5: Nitrogen-containing tars concentrations in the producer gas for each fuel

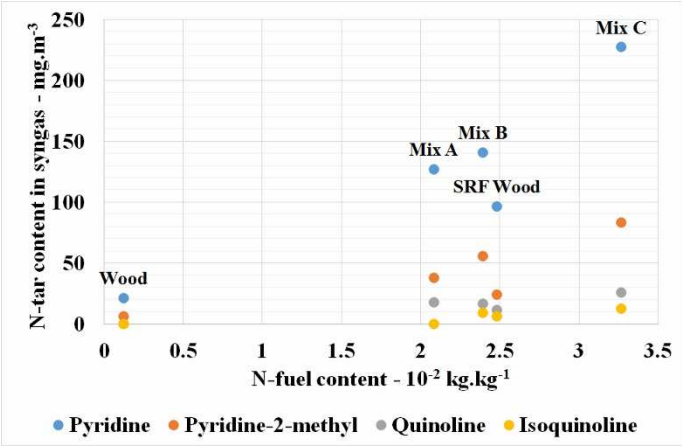
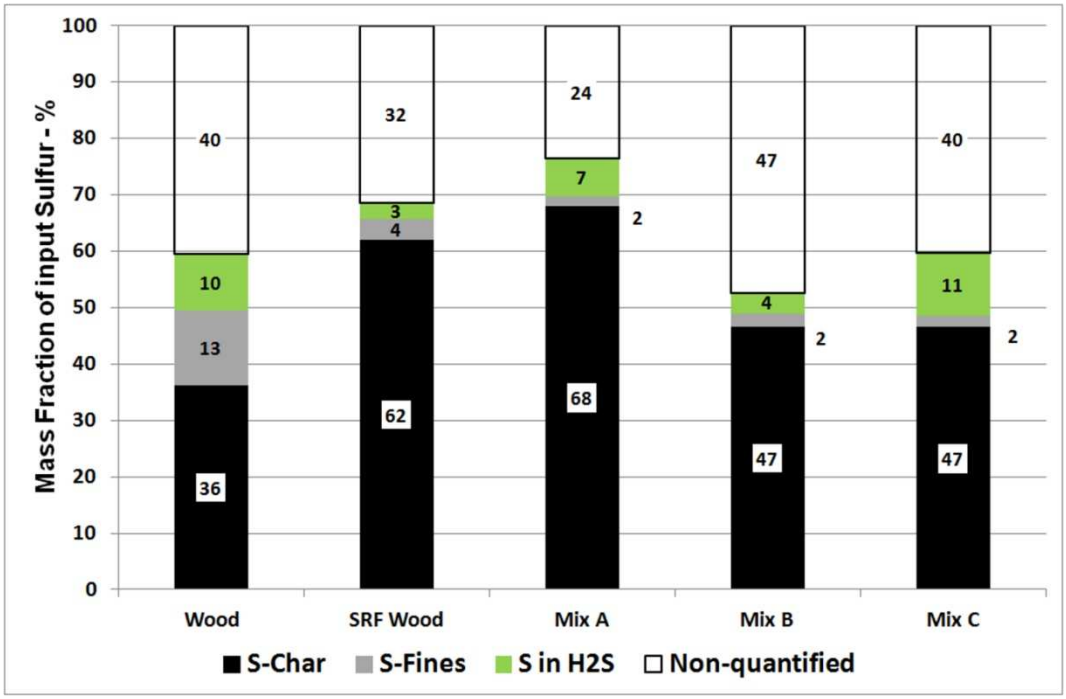


Figure 6: N-tar concentration in the producer gas versus N-fuel concentrations in the fuels



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

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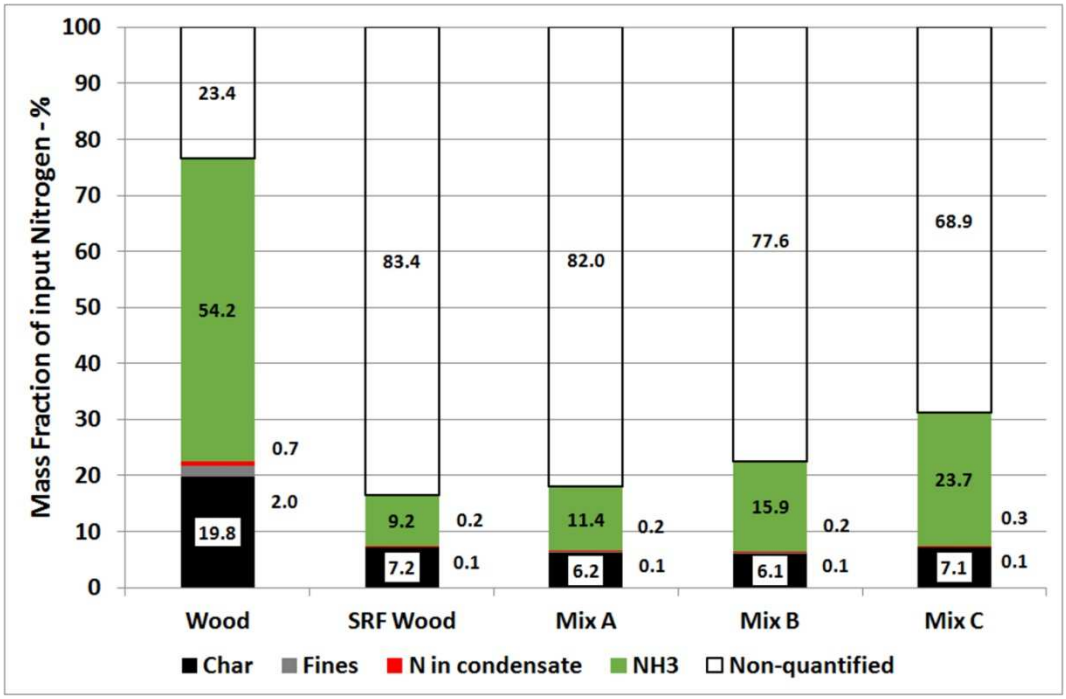

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820 *Figure 8 : Mass balance of nitrogen after gasification for each fuel*

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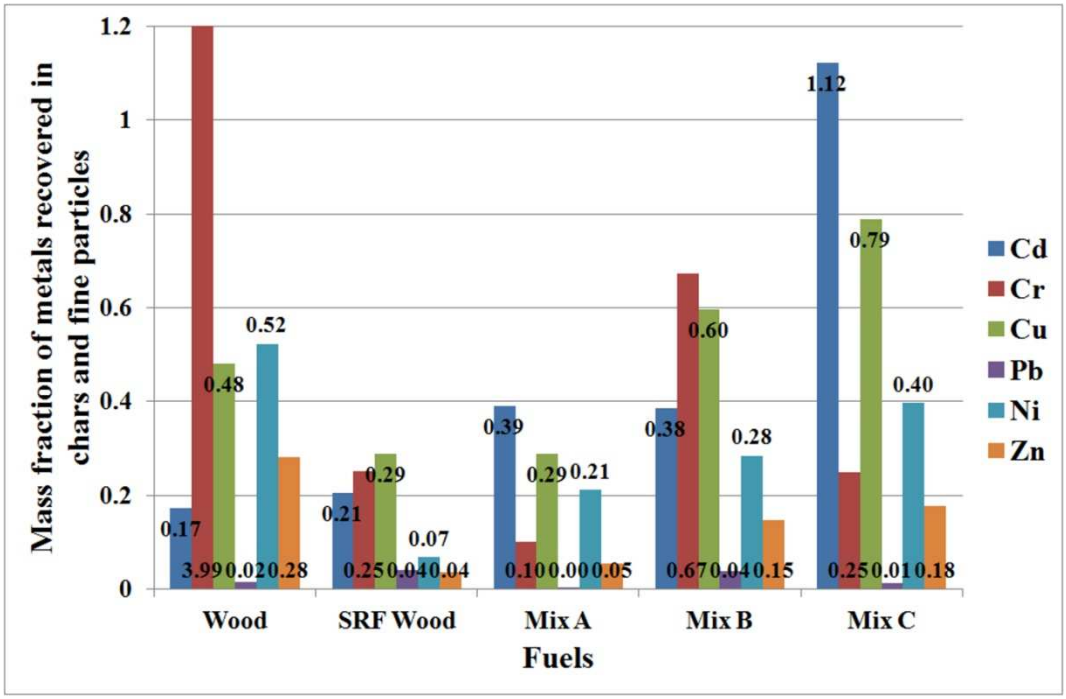

Figure 9: Mass fraction of metals recovered for each fuel in char+fine particles

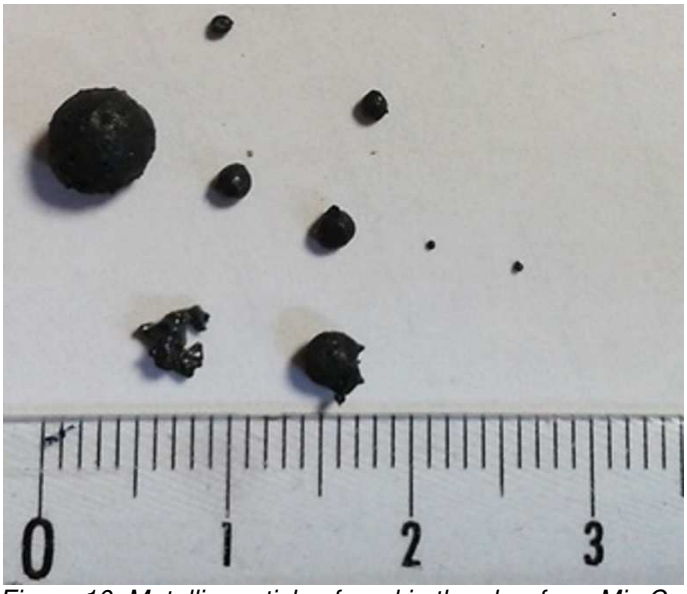

Figure 10: Metallic particles found in the char from Mix C – scale unit in cm