Emulation of field storage conditions for assessment of energy properties of torrefied sugarcane bagasses

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ABSTRACT

Sugarcane Bagasse (SCB) has some characteristics that hinder its direct use as fuel. Torrefaction pre-treatment could be considered to improve the SCB properties for an energy use and to reduce the impact of storage on the reduction of these energy properties.

SCB were torrefied at 290°C in a screw reactor, during 5, 7.5 and 10 min. Then, raw and torrefied SCB samples were exposed successively to water-leaching and to white and brown rot fungi, to emulate storage conditions. Mass loss after water-leaching process, moisture content and weight loss due to fungal deterioration after 2, 4, 8, 12, 16 weeks were recorded on each SCB samples. Finally, chemical composition and High Heating Value of the torrefied samples were measured to determine the alterations compared to raw SCB during their storage mimic.

Increasing torrefaction duration improves the SCB decay resistance. According to the fungal exposure duration, loss of carbon was recorded, however, HHV remain higher for torrefied SCB than those of raw SCB. Carbon contents and HHV values of raw and torrefied SCB during *Trametes versicolor* exposure [55.20 % > C > 44.55 % and 21.260 MJ.kg^{-1} > HHV >17.307 MJ.kg^{-1}, results from all tests combined.], and during exposure to *Coniophora puteana* [55.20 % > C > 46.25 % and 21.260 MJ.kg^{-1} > HHV > 17.699 MJ.kg^{-1}] tend to decrease.

Severe torrefaction is therefore a good way to improve SCB energy properties while limiting loss of their energy properties during storage.

KEYWORDS

38   Energy, Fungal decay, Leaching, Storage emulation, Bagasse, Torrefaction.

INDEX SUMMARY

SCB: Sugarcane bagasse (*Saccharum* spp.) residues sample

SCB-HT-5: Sugarcane bagasse – Heat-treated at 290 °C - during 5 min (given for example, the same indexing is used for the different biomass and torrefaction residence time).

SCB-Ref: Sugarcane bagasse reference (raw biomass) sample

TV: *Trametes versicolor* fungi (white rot)

CP: *Coniophora puteana* fungi (brown rot)

SCB-HT-5 (TV): Sugarcane bagasse – Heat-treated at 290 °C - during 5 min and exposed to *Trametes versicolor* fungi (given for example, the same indexing is used for the different biomass, torrefaction residence time and fungi exposures).

ML_{tt}: Mass loss of the sample due to torrefaction process (in %, oven dry basis)

Ext.: Extractives content of the sample (in %, oven dry basis)

ML_{leach}: Mass loss of the sample due to leaching process (in %, oven dry basis)

MC: Moisture content of the sample due to fungal exposure (in %, oven dry basis)

WL: Weight Loss of the sample due to fungal degradation (in %, oven dry basis)

C: Carbon content of the sample (in %, oven dry basis)

H: Hydrogen content of the sample (in %, oven dry basis)

N: Nitrogen content of the sample (in %, oven dry basis)

H/C: Hydrogen / Carbon molar ratio

HHV_0: Higher Heating Value at constant volume of the dry (moisture-free) sample (in $MJ.kg^{-1}$, oven dry basis)

1. INTRODUCTION

Brazil is strongly dependent to the agricultural and forestry production sectors. Brazil is still among the top-countries using the most biomass for energy production with Total Primary Energy Supply (TPES) from solid biomass of 15 GJ/capita [1]. The Brazilian energy production from solid biomass is outranked by those of Finland (62 GJ/capita), Sweden (39 GJ/capita), Estonia (GJ/capita), Austria (24 GJ/capita) and Denmark (20 GJ/capita). However, in term of global production, Brazil is the first country in the world using the most solid biomass for energy production followed by the United States [1]. Lignocellulosic biomasses mainly come from plantations dedicated to energy valorization, or as residues from some agricultural production chain. Due to the huge sugarcane planting area in Brazil with 10 millions hectares [2], sugarcane ranks first among Brazilian crop wastes (including paddy straw, bean straw, soya straw, maize straw and wheat straw) and agro-industrial residues (including rice husk, coffee husk, sugarcane and fruits bagasse, soybean husk and wood wastes) used for energy conversion [3]. Sugarcane bagasse has been widely used for energy generation. Amongst the domestic energy alternatives in Brazil, biomass from sugarcane bagasse accounts for 16.1% [4]. A large resource of bagasse is available at low cost [5], providing raw material for energy production [6]. Each ton of sugarcane is estimated to produce 140 kg of dry bagasse, giving a world supply of 200 million tons per year with energy values range from 17 to 20 MJ.kg^{-1} [7].

Even if sugarcane bagasse (SCB) can be burnt directly to produce heat and electricity, the solid residue after pressing, has some characteristics that hinder its direct use as fuel, compared to fossil fuel, such as high fibrous (43-52%, on a bagasse dry weight basis) and low bulk density (80-120 kg.m^{-3}), high moisture content (46-52%, on a wet basis), inconsistent particle size, heterogeneous chemical composition, hydrophilic nature, and relatively low

86   calorific value [8, 9]. Sugarcane bagasse is composed by approximately 32–34% (on SCB dry

87   weight basis) cellulose, 19–24% (on SCB dry weight basis) hemicelluloses, 25–32% (on SCB

88   dry weight basis lignin, 6–12% (on SCB dry weight basis) extractives, and 2–6% (on SCB dry

89   weight basis) ash [10]. In addition, the storage of the bagasse in humid conditions can cause

90   several damages due to moisture absorption and biological degradation [11]. For example, it

91   has been previously shown that fungal degradation (*Trametes versicolor*) of eucalyptus, pine

92   and coffee husks samples lead to decreases in their HHV values from 17.429 to 17.069 MJ.kg^{-}

93   ^{1}, 18.801 to 17.377 MJ.kg^{-1} and 18.823 to 17.194 MJ.kg^{-1}, respectively [12]. Indeed SCB is

94   usually stored in outdoor piles [13] occurring moisture adsorption by wood and the resultant

95   chemical oxidation and/or microbiological activity lead to hydrolysation [14]. This

96   phenomenon increases the internal temperature of the stored biomass stack thereby

97   accelerating the biomass decay degradation [15, 16]. Such degradations reduce the biomass

98   potential to be processing and consequently decrease its market value.

99

100   Some pre-treatment are then necessary like torrefaction, which is a thermal treatment who

101   improves the biomass energetic, physical and mechanical properties in order to make the

102   biofuel more homogenous and stable to biological degradation [17]. The market potential of

103   torrefied biomass is expected to be huge in Central Europe and the Nordic countries, and

104   also around the world, considering the substitution of coal in large-scale power and heat

105   product [18]. Torrefaction means a thermos-chemical treatment of biomass at 200 to 320°C

106   and the process takes place in oxygen free circumstances [19]. Although the torrefaction

107   allows reducing the hydrophilic behavior, it is possible that the torrefied wood nevertheless

108   reaches, during its storage, a sufficient moisture content level so that the rots can develop

109   [20]. Previous studies showed that such a process can be used in order to improve and

110   preserve the energetic properties of torrefied biomasses (eucalyptus, pine and coffee husks

residues) during water and fungal exposure [12]. Other past studies highlighted that the improvement the quality of bagasse as feedstock can be also done with torrefaction pre-treatment [21]. The utilization of torrefied bagasse in existing handling and storage facilities and associated issues has been reported recently [22-24] and could be one of the solution to preserve its energetic properties during storage depending on the torrefaction treatment intensity [25]. Despite recent advances over the world, torrefaction technology is still under development and only a few techno-economic assessments regarding the entire logistic chain, including storage, have been made [20].

The aim of the study was to determine how the various raw and torrefied SCB materials tolerate moisture and fungal decay exposure, simulating by various storage conditions. SCB was torrefied at 290°C with 5, 7.5 and 10 min residence time then leached and exposed to different fungal decay (brown and white rots) during five different exposure durations (from 2, 4, 6, 8, 12 and 16 weeks). Both effects of the torrefaction duration and the storage conditions of SCB were investigated. The impact of water-leaching (without decay exposure) and the fungal degradation impact on the chemical (elemental composition) and energy properties (High Heating Values) of raw and torrefied SCB for an energy conversion were thus evaluated. Finally, importance of the torrefaction intensity, depending on the process duration, on these different mechanisms was highlighted. The results obtained through this study could be a great additional data potentially enhancing the models used to predict the energy properties and the degradation level of torrefied biomass during storage.

2. MATERIALS AND METHODS

2.1. Biomass samples

Sugarcane bagasse residues (*Saccharum* spp. hybrids) (SCB) were obtained from Jatiboca Sugar and Ethanol industry (Ponte nova, Minas Gerais, Brazil). SCB was first dried outdoors in a drying yard during 30 days, until they reached hygroscopic equilibrium moisture (about 20%, on wet basis). Afterwards, milling was done in a knife mill and a classification in screen sieves between 6 and 2 mm, collecting the fraction retained on the 2 mm sieves to diminish the presence of fine particles, which might compromise subsequent analysis. SCB particles, with long size ranged from 10 to 20 mm (and 2-6 mm diameter), were oven-dried at 103 ± 2 °C for 48 hours with constant air circulation to reach a moisture content near to 0% and avoiding the influence of water on treatments.

2.2. Torrefaction process

SCB was then torrefied at 290° C using 5 kg of biomass for each sample. The three following residence times were evaluated: 5, 7.5, 10 minutes. Two torrefaction replicates were performed for each modality. Torrefaction processes were carried out in an endless screw type reactor, developed in the Panels and Energy Laboratory of the Federal University of Viçosa (Fig. 1). The heating section (with length of 1.375 m) was built in carbon steel main structure with an indirect heating exchange system with a combustion gas followed by an indirect water cooling system.

Two timers controlling the gear motor were used to control the residence time of the biomass sample within the reactor. The first of one was used to activate the gear motor for approximately 4 seconds (time required for one complete revolution of the worm screw), and the second timer was used to stop the gear motor for a predetermined time. The sum of these two durations recorded but the both timers, multiplied by the number of revolutions of the

158 worm screw (without end with the roasting section) then defined the residence time of the

159 biomass samples it torrefaction process. A Gulton Gulterm 700-10S digital thermometer,

160 using eight type J thermocouples (Figure 1) was used to continuously record and control the

161 temperature of the torrefaction chamber. More information of the biomasses torrefaction

162 process and reactor can be found in Magalhães et al. 2018 [26].

163   Figure 1

164

165 **2.3. Mass loss due to thermal degradation**

166 The Mass Loss (ML%) due to the thermal degradation was determined according to the

167 Equation 1 (Eq. 1):

168 $$ML_{tt} \ (in \ \%, oven \ dry \ basis) = \frac{(m_0 - m_1)}{m_0} \times 100 \qquad (1)$$

169   Where :

170   ML_{tt} = mass loss of the sample due to torrefaction process (in %, dry basis)

171   m_0 = initial oven-dried mass before torrefaction

172   m_1 = final oven-dried mass after torrefaction

173

174 **2.4. Chemical composition of raw and torrefied SCB samples**

175 The Chemical Composition was obtained for the determination of the Extractive, total Lignin

176 (insoluble and soluble), and Holocellulose contents. The samples were ground and sieved

177 with mesh of 40 (420 µm) and 60 (250 µm).

178 The total extractive content was determined according to TAPPI 204 cm-97 (TAPPI

179 1996).After a drying step performed at 103 °C until mass stabilization, the sawdust (10 g) was

180 extracted in a Soxhlet with a solution of 1/3 ethanol and 2/3 benzene [from Carlo Erba

181 Reagents Group (France)] during 6 h, and then dried at 103 °C for 48 h to obtain the oven-

182   dried mass of the free extractives sample. Extractive contents were determined by the oven-

183   dried mass difference.

184   The soluble lignin, insoluble lignin and holocellulose contents were determined on free-

185   extractives SCB samples, with some adjustments, according to the guidelines from the

186   methodology used by Pereira et al. [27].

187   Soluble and insoluble lignin contents were determined as following: 500 mg of the three

188   native and torrefied biomasses sawdust, previously extracted (by the 1/3 ethanol: 2/3 benzene

189   solvent extraction process), were separately mixed with 72% H_2SO_4 (10 mL) for 4 h at 30 °C.

190   The mixture was then diluted with distilled water until a H2SO4 concentration of 3%,

191   submitted to another hydrolysis at 2 atm pressure and 121 °C for 1 h. The insoluble lignin

192   content was determined by filtration and the soluble lignin content by UV spectrometry. Total

193   lignin was obtained by the sum of insoluble and soluble lignin fractions.

194   Holocellulose content was determined as following: 500 mg of the three native and torrefied

195   biomasses sawdust, previously extracted (by the 1/3 ethanol: 2/3 benzene solvent extraction

196   process), were separately placed in a 100 mL flask containing 30 mL of distilled water and

197   heated at 75 °C. Acetic acid (0.1 mL) and 15% aqueous sodium chlorite (2 mL) were then

198   added each hour for 7 h. The mixture was filtered on a Büchner funnel and the residue washed

199   with water, soxhlet extracted for 2 h with ethanol and dried at 103 °C to a constant mass.

200

201   **2.5. Fungal decay exposure**

202   All samples (raw and torrefied) were firstly submitted to leaching process according to the

203   NFX 41-568 [28] standard. This standardized procedure for accelerated ageing is commonly

204   used for natural durability wood testing. Samples were immersed in distilled water (1 volume

205   of biomass for 5 volumes of water) and subjected for six leaching periods of increasing

206   duration under continuous shaking at 20°C. Water was replaced by fresh water after each

207   leaching period. A first cycle of 3 leaching periods of 1, 2 and 4 hours was performed.

208   Samples were then kept air drying for 16 hours. Leaching was pursued for 3 additional

209   periods of 8, 16 and 48 hours, with change of water between each period. The leached

210   samples were then oven-dried at 103°C and weighed (m_2). Percentage of leaching was

211   calculated following the Equation 2 (Eq.2):

212    $$ML_{leach} \ (in \ \%, oven \ dry \ basis) = \frac{(m_1 - m_2)}{m_1} \times 100 \qquad (2)$$

213   Where :

214   ML_{leach} = Mass loss of the sample due to leaching process (in %, dry basis)

215   m_1 = initial oven-dried mass of sample before leaching

216   m_2 = final oven-dried mass of leached sample

217
218   Then, raw and treated biomasses were place into plastic grid bags (dimensions of 10 x 3 x 1.5

219   cm) in order to expose themselves to basidiomycete attacks. Before starting the fungal

220   exposure experiment, the bags were oven dried 103 °C for 24 h and the initial dry mass (m_3)

221   was measured for further determination of the weight loss of the sample due to the fungal

222   degradation. Each sample was crafted to have an initial dried mass of sample around 3 grams.

223   All samples were then placed in conditioned room (22°C, 70% Relative Humidity) in order to

224   keep humidity prior to the decay exposure tests. After that, all samples were sterilized by x-

225   ray process with a dose of 25.0 (± 5.6%) kGy, as recommended by the NFX 41-568 [28]

226   standard, by Ionisos Compagny (France). Contrary to autoclave sterilization, such a Gamma-

227   radiation does not cause significant changes in wood properties and not affect the wood

228   natural durability. In addition x-ray process is more efficient than oven drying to sterilized

229   wood samples.

230   Decay resistance of raw (leached and not leached) and torrefied biomasses after leaching was

231   tested according to an adaptation of XP CEN/TS 15083-1 [29] standard criteria, on both fungi

232   species required by the standard: *Trametes versicolor* (white rot) and *Coniophora puteana*

233   (brown rot). The following fungal exposure duration were tested: 2, 4, 8, 12 and 16 weeks.

234   During these fungal exposures, all test devices were place in dark conditioned chamber (at

235   22°C, 70% Relative Humidity). After the different decay exposure duration, mycelia were

236   removed and each sample was weight (m_4) and then was dried at 103 °C for 24 h and the final

237   dried mass was determined (m_5).

238   The final moisture content (MC) after fungal exposure of the sample was determined

239   according to the following formula (Eq. 3):

240             $$\text{MC } (in \text{ } \%, oven \text{ } dry \text{ } basis) = \frac{(m_4 - m_5)}{m_5} \times 100 \qquad (3)$$

241   Where :

242   MC = Moisture content of the sample due to fungal exposure (in %, dry basis)

243   m_4 = wet mass of fungal decayed sample sample

244   m_5 = oven-dried mass of fungal decayed sample

245

246   The Weight Loss was determined according to the following formula (Eq. 4):

247             $$WL \text{ } (in \text{ } \%, oven \text{ } dry \text{ } basis) = \frac{(m_3 - m_5)}{m_3} \times 100 \qquad (4)$$

248   Where :

249   WL = Weight Loss of the sample due to fungal degradation (in %, dry basis)

250   m_3 = initial oven-dried mass of sample before fungal exposure

251   m_5 = final oven-dried mass of fungal decayed sample

252

253   The decay exposure tests were conducted as follows:

254   - The three torrefaction intensities for sugarcane bagasse, after leaching, were tested in order

255   to evaluate the impact of the heat treatment intensity on the biomasses durability;

256   - For both each fungus and fungal exposure duration, 4 replicates of raw biomasses (after

257   leaching) and for each torrefied biomasses (after leaching) were done.

258   - Beech (*Fagus sylvatica*) and Pine (*Pinus sylvestris*) sapwood samples of the dimensions

259   50x25x15mm^3 (L, R, T) were used as controls for the virulence of the strains (8 tested blocks

260   for each fungus and for each fungal exposure duration).

261

262   **2.6. Sample characterization**

263   The impacts of leaching and fungal degradation, according to the duration of fungal exposure

264   were evaluated on the following raw and treated biomass properties according to 3

265   characterizations: (i) the Weight Losses (WL) caused by fungal degradation, the Elemental

266   Compositions (EC); and (iii) the High Heating Values (HHV). For each tested modality, the

267   four replicated used for decay test were mixed, ground using a cutting mill Retsch SM 100

268   and sieved. Particle sizes fraction of 0.1 to 0.2 mm was retained. Sawdust was then

269   conditioned at 103 °C for 24 h and stored in air-tight bottle before analysis.

270   *2.6.1. Elemental composition*

271   Elemental analyses were carried out with an ElementarVario Macro tube CHN analyzer

272   according to the BS EN 15104 [30]. Prior to analysis, the samples were packed in a tin foil

273   and two tests were performed for each sample. Atomic H/C (Eq. 4) ratios of samples were

274   determined following Patch et al. [31] and Ascough et al. [32]:

$$\text{Atomic} \frac{\text{H}}{\text{C}} \text{ratio } = \frac{\text{Number of H atoms}}{\text{Number of C atoms}} = \frac{\% \, H/1}{\% \, C/12} \qquad (4)$$

276   *2.6.2. High Heating Values*

277   The calorific value was measured using an Automated Isoperibol Fixed Bomb Parr 6200

278   bomb calorimeter, following the CEN/TS 14918 [33].

12

279   1 g of oven-dried biomass, with a particle size < 0.2 mm, were required to perform the

280   calorific test. 2 replicates have been done for each sample and all the results are given with an

281   accuracy of ± 5.00%.

282

283   **2.7. Statistical analysis**

284   ANOVA (one-way analysis of variance) and Duncan's comparison test, carried out by the

285   JMP 10.0.2 program (SAS Institute Inc., Cary, NC, USA) by applying the Fisher test, were

286   used to evaluate:

287   - The impact of torrefaction duration and leaching process on elemental composition and

288   HHv values of SCB samples. Results were then ranked into several categories from "A" to

289   "D" to evaluate the influence torrefaction duration and from "a" to b" to compare unleached

290   and leached SCB samples (Tab.1).

291   - The impact of torrefaction duration on the chemical composition of SCB samples . Results

292   were then ranked into several categories from "A" to "D" (Figure 5).

293   - The impact of torrefaction duration on ML_{tt} (in %, dry basis) and ML_{leach} (in %, dry basis)

294   of SCB samples . Results were then ranked into several categories from "A" to "D" (Fig. 4).

295   - The impact of torrefaction duration on the chemical composition of SCB samples. Results

296   were then ranked into several categories from "A" to "D" (Fig. 5).

297   - The impact of fungal exposure duration on MC (in %, dry basis) (Fig. 6a) and WL (in %,

298   dry basis) (Fig. 7a) of pine and beech control samples. Results were then ranked into several

299   categories from "A" to "E", "A'" to "E'", "a" to "e" and "a'" to "e'" for beech control (CP),

300   pine control (CP) , beech control (TV) and pine control (TV), respectively.

301   - The impact of torrefaction duration on MC (in %, dry basis) (Fig. 6b) and WL (in %, dry

302   basis) (Fig. 7b), according to the fungal exposure duration of SCB samples. Results were then

303   ranked into several categories from "A" to "D", "a" to "d", for CP and TV, respectively.

304

305 The assumption of homogeneity of variance and normal distribution of the sample required

306 for the use of parametric statistics are satisfied. The impact of a parameter on a system not

307 connected by the same letter was considered as no significant at the 5% level.

308

309 For a better comprehension of the study approach, a scheme of the different analysis protocols

310 are presented in Fig. 2. In addition, the sampling and analytical devices used in this study are

311 illustrated in Fig. 3.

312   Figure 2

313   Figure 3

314
315 **3. RESULTS AND DSICUSSION**

316 **3.1. Mass loss determination (ML$_{tt}$ %)**

317 According to the exponential kinetic of wood thermal degradation, the treatment duration has

318 an impact on treatment intensity as well as on mass loss kinetic [25]. The results presented in

319 Fig. 4, are in accordance with this statement. For heat treatments performed at 290 °C, ML$_{tt}$

320 (%) of SCB samples increased with the increasing of the process duration, from 12 ± 0.20 %

321 (t=5 min.) to $23,5 \pm 0.21$ % (t=10 min.). This phenomenon is due to the fact of for a given

322 temperature, the quantity of each degradation product increases progressively as the treatment

323 duration increases [34].

324   [Figure 4]

325
326 **3.2. Chemical composition changes after torrefaction processes**

327 According to the Fig. 5, raw sugarcane bagasse sample (SCB-Ref) was composed of 69.15 %

328 holocellulose, 25.49 % lignin (including 24.47 % insoluble lignin and 1.02% soluble lignin)

329 and 5.36 % extractive compounds. Fig. 5 indicated that extractives content of SCB increased at

14

290 °C – 5 and 7.5 minutes and seemed to decrease at 290°C – 10 minutes. These results are consistent with other past studies [35, 36], highlighting that the major increase at low intensity was due to water and ethanol extractives because of polysaccharide degradation. Almost all of the original extractives released and new compounds were generated by hemicelluloses and lignin thermal degradation. These mainly included monosaccharides and their dehydratation products, as well as syringaldehyde, syringic acid and sinapaldehyde, as the most prominent lignin derived compounds [36, 37].

The proportion of lignin increases considerably after thermal treatment, mainly due to the increase of insoluble lignin content, whereas soluble lignin content decreases according to the heat treatment duration. The ether linkages of lignins are cleaved and new free phenolic hydroxyl groups and a- and b-carbonyl groups arise, which are responsible for crosslinking via formation of methylene bridges [38-40]. The methoxyl content decreases and the new reactive sites on the aromatic ring can lead to further condensation reactions [39]. The decomposition of the holocellulose, mainly due to hemicellulose degradation [41] is statistically significant as the residence time is increasing. The holocellulose is decomposed greatly and the proportion of lignin in the material increases, leaving a highly lignified material [42-44].

Figure 5

FT-IR spectra analyses, performed on raw and torrefied sugarcane bagasse by Manatura (2020) [45] indicated the changes in the chemical structures of the hemicellulose, cellulose and lignin, which were associated with the functional groups such as C-O, C=O, O-H, C=C, and C-C-O. Even if the thermal degradation kinetics are different than those of other wood

15

354 species, the undergone chemicals changes are similar for the sugarcane than those of woods,

355 in despite of their difference in chemical compositions and anatomical structures.

356

357 **3.3. Elemental Composition and High Heating Values of raw and heat-treated SCB**

358 **samples before and after leaching**

359 The objectives of this section are to (i) evaluate the influence of leaching step on the

360 elemental composition and energy properties (HHV) of sugarcane bagasse changes, and then

361 to (ii) determine if torrefaction process, according to the curing temperature and residence

362 time, improves the SCB energy properties and limit the impact of leaching for an energy use

363 (mainly for combustion conversion).

364 As shown in Tab. 1, torrefaction duration affects the element compositions of SCB materials.

365 The carbon and nitrogen in the material increased with residence time, while the hydrogen

366 decreased. Hydrogen and oxygen are released as water vapor and carbon dioxide emissions

367 [46]. Hemicelluloses mainly generate carbon monoxide and carbon dioxide through

368 decarboxylation reactions of acid groups linked to hemicelluloses [47], while cellulose

369 generates small amounts of carbon dioxide [48]. In addition, small volatile molecules (as

370 acetic acid, furfural, methylfurfural, vanillin, syringaldehyde, etc.) are released during

371 biomass torrefaction [34].

372 <div align="center">Table 1</div>

373 As shown in Tab. 1, HHV increased with the residence time. Overall, Tab. 1 and Fig. 4

374 indicate that the HHV increased with an increase of Mass Loss due to thermal degradation in

375 SCB samples.

376 One of the processes in material usage outdoors is leaching. Leachates of thermally modified

377 wood consist mainly of wood constituents' degradation products (tannic acid, acetic acid,

378 furfural and furfural derivatives), but also extractives [48], that may explain the higher

16

379   ML_{leach}% of SCB-HT-5 than those of the three other samples (Fig. 4). In addition, due to the

380   thermal degradation of SCB biomass components, the content of hydroxyl groups decreases

381   leading to increased hydrophobity and wettability that is more difficult. According to obtained

382   results of wood mass loss during the thermal treatment, degradation process in SCB-HT-10

383   (ML_{leach}= 2.16%) occurs at greater degree than in SCB-Ref (ML_{leach}= 3.54%), SCB-HT-5

384   (ML_{leach}= 4.88%) and SCB-HT-7.5 (ML_{leach}= 2.78%), thereby reducing the amount of

385   substances accessible to leach (Fig. 5). These results are in accordance with other past studies

386   showing that thermally modified pine and eucalyptus woods (temperature 190, 200 and

387   210°C; durations: 2, 6 and 12 hours are less sensitive to water depending on the treatment

388   intensity, than their respective native woods [49, 50]. Finally, thermally modified SCB treated

389   during 10 minutes (SCB-HT-10) is more environmentally friendly, than the other treatment,

390   due to less water leachable substances (Fig. 4).

391   Tab. 1 also highlights that the HHV of raw and heat-treated SCB samples was decreased by

392   leaching process. In view of the fact that the elemental composition is not significantly

393   modified for all SCB samples following leaching, the decreases of HHV values could be

394   explained by the removal of some extractives compounds during this leaching process. In

395   fact, previous studies shown that extractives content and composition are strongly correlated

396   to the HHV of woody biomass [51, 52].

397

398   **3.4. Decay degradation of raw and heat-treated SCB samples according to the fungus**

399   **exposure duration**

400   The objectives of this section is to simulate the storage of raw and torrefied SCB in order to

401   (i) evaluate the impact of SCB decay degradation on its energy properties and then to (ii)

402   determine if torrefaction process, according to the curing temperature and residence time,

403   allows to limit the impact of decay degradation on the energy properties.

3.4.1. Moisture content

Fig. 6 shows the final moisture content in % of control beech and pine samples, raw and torrefied SCB samples, after *Trametes versicolor* and *Coniophora puteana* fungi exposures and according to the duration of these decay expositions.

Whatever the fungi exposed to the SCB samples, the final moisture content of SCB sample was directly proportional to its hemicellulose content. By comparing Fig. 6 and Tab. 1, it clearly appears that the amount of water absorbed by sugarcane bagasse during fungi test increased when its hemicellulose content increased. The hydrophilic nature of bagasse is mainly due to the high content of hemicellulose. Hemicellulose polymers have many hydroxyl groups (–OH) which drive sugarcane bagasse to be polar and to make easily hydrogen bonds with water molecules [53]. Hemicellulose degradation during torrefaction causes the loss of hydroxyl groups in sugarcane bagasse [51]. Thus, torrefied sugarcane bagasse loses its hydrophilic nature, since there are no hydroxyl groups, which tend to be polar and easily make hydrogen bonds with water molecules. In addition, the changes of lignocellulosic polymers during torrefaction lead to the formation of unsaturated non-polar structures in sugarcane bagasse.

The degradation of hemicellulose, cellulose, and lignin in sugarcane bagasse during torrefaction causes shortening of polymer chains. The changes of sugarcane bagasse properties into less fibrous, soft, and brittle is mainly caused by the degradation of hemicellulose and cellulose [54].

Figure 6

The hydrophobic behavior of raw SCB is very similar than those of beech and pine control samples. Their moisture content levels increase highly during the first four fungi exposition weeks, and then continue to increase more slowly for longer tests durations (Fig. 6).

18

428 The moisture content of torrefied SCB samples, after decay exposure, is lower than those of

429 beech and pine control samples and raw SCB samples, whatever the decay test duration and

430 the fungi type. In addition, we can observe a significant moisture content decrease for SCB-

431 HT-7.5 and SCB-HT-10 samples compared to raw and SCB-HT-5 samples. The moisture

432 content of SCB-HT-7.5 and SCB-HT-10 seems to be increased highly during the four first

433 weeks and tend to stabilize for longer fungal exposure duration.

434 ***3.4.2. Decay degradation***

435 The overall Weight Loss (WL %) due to *Trametes versicolor* and *Coniophora puteana*

436 exposure of beech and pine control samples, raw and torrefied SCB samples, is shown in Fig.

437 7a.

438 According to the weight loss values obtained concerning the fungal degradation of beech and

439 pine wood control sample after 16 weeks, the decay resistance test performed through this

440 study has been validated. Indeed, the following minimal degradation levels (according to XP

441 CEN/TS 15083-1 [29]) of control samples were reached:

442 - *Coniophora puteana* (Brown rot) on Pine: WL = 57.12 % > 30%

443 - *Coniophora puteana* (Brown rot) on Beech: WL = 48.18 % > 30 %;

444 - *Trametes versicolor* (White rot) on Pine: WL = 24.18 % – no requirement;

445 - *Trametes versicolor* (White rot) on beech: WL = 44.24 % > 20 %.

446 For the both tested rots, a similar tendency concerning the decay resistance improvement of

447 SCB was observed after torrefaction. In addition, as for the results observed previously with

448 respect to the moisture content levels, conferred durability to SCB by thermal modification

449 depends on the heat treatment duration.

450 Average values of weight loss due to fungal degradation showed raw and torrefied SCB

451 samples are generally similar to *Coniophora puteana* (Brown rot) than *Trametes versicolor*

452 (White rot). In addition, it clearly appears that SCB-HT-7.5 and SCB-HT-10 samples are

significantly more resistant to the tow fungal degradations than SCB-Ref and SCB-HT-5. According to the torrefaction duration, the torrefied SCB samples suffered a destruction of their cell wall [55], a largely hemicelluloses degradation than the other macromolecular components [56], occurring moisture exclusion [57-59] and a limited feed stock, then resulting in a high capacity to limit the colonization and the damages caused by the both fungi.

According to the Fig. 7a, the both fungal degradation of beech and pine control samples appears to begin as early as the fourth week of rot exposure. The fungal degradation (TV and CP) of SCB-HT-5 starts as early as the second week of rot exposure, while those of SCB-HT-7.5 and SCB-HT-10 samples is delayed and begins only from the eighth week of fungal contact and then increase very slowly. Finally, SCB-HT-7.5 (WL < 5 %) and SCB-HT-10 (WL < 2%) seem to be very promising treatment ways to preserve SCB properties during the biomass storage (Fig. 7b).

<p style="text-align:center">Figure 7</p>

3.5. Impact of fungal exposure on the energy properties of raw and heat-treated SCB samples

3.5.1. Degradation by Trametes versicolor (TV) – White rot

Loss of carbon was recorded in all samples with white rotter *Trametes versicolor* (TV) (Fig. 8a). According to the literature, white rot mainly degrades the lignin polymer, causing loss of carbon [50]. Indeed, fungal activity was expected to reduce the carbon content as carbon compounds serve as nutrients and are respired as CO_2 by fungi [60, 61].

The Nitrogen content increased according to the fungal exposure duration, in all tested materials (Fig. 8c), whereas Hydrogen content decreased for SCB-HT and SCB-HT-5 and increased for SCB-HT-7.5 and SCB-HT-10 (Fig. 8b). Previous study highlighted that fungi

478 have the capacity to scavenge and import nitrogen to decaying wood via a translocating

479 network of mycelium [62]. It results that, for all tested samples, H/C ratio increases according

480 to the *Trametes versicolor* (TV) exposure duration, where the most significant evolution

481 occurs in the first four weeks of fungal exposure (Fig. 8d).

482 As observed in Figures 8e and 8f, the decreases of HHV values, for each SCB samples (raw

483 and heat-treated), according the fungal exposure duration are in agreement with the litterature.

484 Depletion of carbon will lower the calorific value and here, statistically significant changes

485 were detected in carbon content. The heat content is related to the oxidation state of the

486 natural fuels in which carbon atoms generally dominate and overshadow small variations of

487 hydrogen and nitrogen content [63]. Susott et al. [63] and Tillman [64] found a linear

488 relationship between the higher heating value and the carbon content of the natural fuels,

489 chars, and volatiles. Huang et al. [65] and Protàsio et al. [66] have also put highlight that

490 Carbon and Hydrogen are the elements that contribute most to the Heating Values of

491 charcoal. Therefore, low O/C ratio is good to have high HHV values and low H/C ratio is not

492 really desired for the use of wood and charcoals for energy, by combustion process. However

493 high H/C ratios could be suitable for gasification conversion, making more reactive the

494 torrefied biomass.

495 <div align="center">Figure 8</div>

496 *3.5.2. Degradation by Coniophora puteana (CP) – Brown rot*

497 Concerning the changes in Hydrogen (Fig. 9b) and Nitrogen (Fig. 9c) contents during fungal

498 exposure, similar results were observed for *Coniophora puteana* (CP) and *Trametes*

499 *versicolor* (TV). Regarding the Carbon content, different behavior were observed during

500 *Coniophora puteana* (CP) exposure, according to the heat treatment intensity. It results that

501 Carbon content decreases for SCB-HT-7.5 and SCB-HT-10 samples relating to the

502 *Coniophora puteana* (CP) exposition duration, whereas Carbon content increases for SCB-

503   Ref and SCB-HT-5 samples (Fig. 9a). These results could be explained by the remaining

504   cellulose and the hemicelluloses after torrefaction at low temperature (SCB-Ref and SCB-HT-

505   5) are degraded by *Coniophora puteana* (CP), increasing the relative carbon content. In fact,

506   brown-rot fungus (*C. puteana*) causes more weight loss than the white-rot (*T. versicolor*),

507   because it removes the cellulosic fraction and leaves lignin structurally modified. Brown

508   rotter *Coniophora puteana* (CP) prefers coniferous wood species, but seems to cause also

509   carbon loss in SCB. It uses endoglucanases to degrade cellulose and hemicelluloses, but has

510   also been reported to produce cellobiohydrolases that erode crystalline cellulose and could

511   therefore also utilize quite severely torrefied wood [67]. We observe a decrease of H/C ratio

512   and an increase HHV value for SCB-Ref and SCB-HT-5 samples according to the *T.*

513   *versicolor* exposure duration, whereas an increase of H/C ratio and a decrease HHV value for

514   SCB-7.5 and SCB-HT-10 samples were observed in the same conditions (Fig. 9d and Fig. 9e).

515   The increase of HHV in that case (SCB-Ref and SCB-HT-5), may be associated with the

516   degradation of the low-energy content components (e.g., leaf materials or agro-food residues)

517   that were easily accessible to the enzymatic community during storage condition [68].

518   Krigstin and Wetzel [69] explained in their review that changes to the proportion of

519   components in the biomass will affect energy content. For example, the preferential

520   decomposition of hemicellulose will result in increased heating values, but the loss of

521   extractives or the preferential fungal decomposition of lignin would tend to reduce heating

522   values.

523   Figure 9

524   *3.5.3 Balance sheet*

525   The High Heating Value of SCB was significantly increased according to the torrefaction

526   duration. However, HHVs of raw and torrefied SCB were affected by the decay exposure

527   duration. There was a relationship between the HHV and decay exposure time across all the

528   thermal treatments and fungi, but the change over time was small (Fig. 8e and Fig. 9e).

529   *Trametes versicolor* is a white rot fungus, degrading mainly the lignin polymer, therefore

530   occurred to all SCB samples a decrease in HHV according to the fungal exposure duration. At

531   the opposite, *Coniophora puteana*, a brown rot fungi degrading mainly the hemicelluloses and

532   cellulose fractions, brings an increase in HHV of SCB-Ref and SCB-HT-5 samples and only a

533   small decrease in HHV of SCB-HT-7.5 and SCB-HT-10 samples. Numerous studies on wood

534   storage have recently reported no significant change or a decrease of the higher heating value

535   [70-72], while others have reported a slight increase of heating value [73-75] at the end of the

536   storage.

537   From our laboratory experiment, it was clear that fungi are able to settle on seemingly

538   unfavorable material, which is said to be hydrophobic and suitable for outside storage. The

539   more mildly treated samples experienced more carbon loss, but took in less moisture in

540   outside storage, contrary to the more severely treated samples [20]. The loss of dry matter

541   (WL%) and carbon (C%) as well as the increasing moisture content decrease the calorific

542   value of the fuel and thus increase associated costs [20]. Therefore, torrefaction could be a

543   viable method to eliminate some of the disadvantages of raw biomass as it significantly

544   improves energy content and prevents absorption of moisture during storage [76]. Even if

545   HHV values decrease during fungal exposure, HHV values are still higher for high-intensity

546   treated SCB samples (SCB-HT-7.5 and SCB-HT-10) than those in the raw and or slightly

547   thermally modified (SCB-Ref and SCB-HT-5) (Fig. 8f and Fig. 9f).

548

549   **4. CONCLUSION**

550   The torrefaction residence time has an important impact on sugarcane bagasse (SCB) mass

551   loss kinetic during torrefaction process, undergoing chemical and elemental composition

552   modifications, High Heating Values and decay resistance improvements of torrefied SCB.

23

553 The storage emulation tests developed in laboratory show that raw and torrefied SCB are still

554 subjected to biological degradation and dry matter losses. It can be stated that in the most

555 cases, the two tested fungi use mainly the carbon fraction of native and torrefied SCB, which

556 leads to a decrease in calorific value. However, the recorded carbon loss due to fungal decay

557 decreased towards the torrefaction performed with a long residence time (290°C during 7.5 or

558 10 min).Torrefaction pre-treatment performed at severe intensity is therefore a good way to

559 improve SCB's energy properties while limiting lose torrefied biomass quality during storage.

560 Future studies will be needed to simulate the exact fungal degradation dynamics and evaluate

561 the properties changes of different torrefied biomasses during real-life storage.

562
563 **5. AKNOWLEDGMENT**

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568 **6. REFERENCE**

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Torrefaction Reactor Components

- ▨ Refractory Concrete
- ▨ Insulation Blanket
- ▨ Heat Exchanger
- ◕ Thermocouple
- ▨ Heating
- ▨ Cooling
- ▨ Transport
- ⇨ Water Vapors
- ⇒ Volatile
- ⚡ Biomass
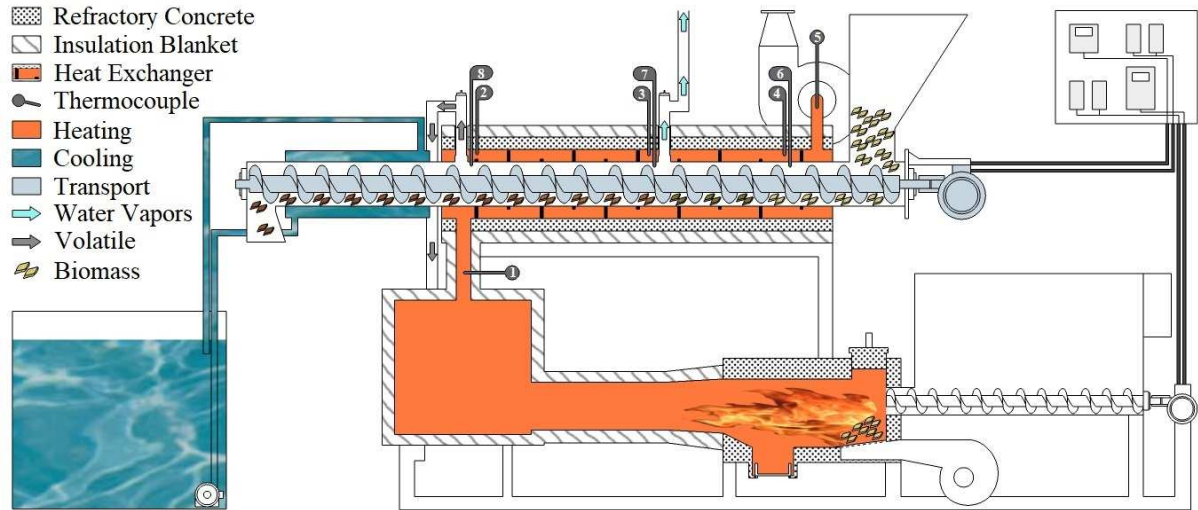
① to ⑧ : *Thermocouples used in order to control the homogeneity of the temperature in the entire torrefaction chamber*

**Fig. 1 :** Layout in side view of the reactor for biomass torrefaction in semi-continuous flow [18].
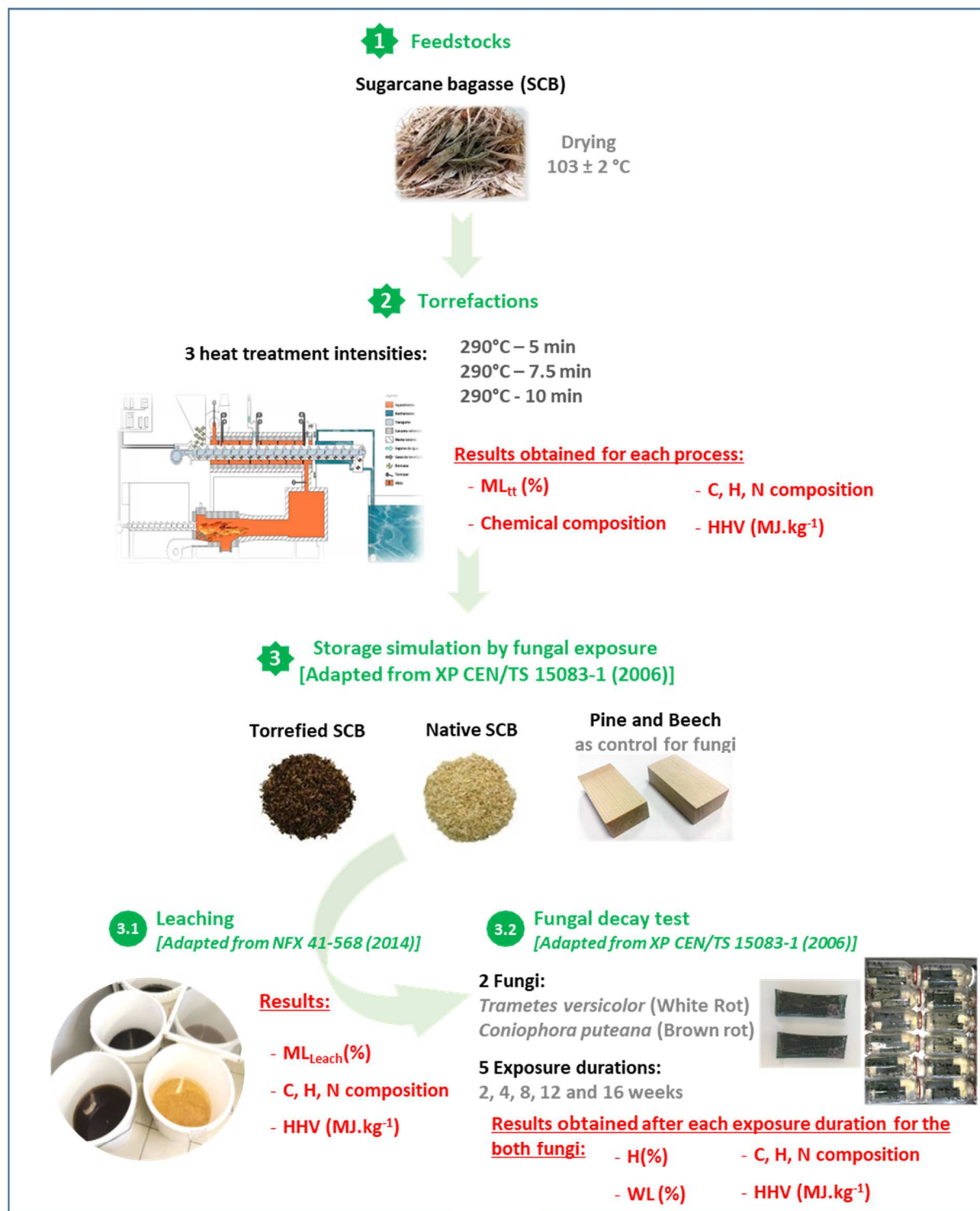
Fig. 2: Synthesis of the overall approach and the different analysis protocols used for this study.

Fig. 3: The various sampling and analysis apparatus used in this study: (a) cutting mill Retsch SM 100, (b) ElementarVario Macro tube CHN analyzer, (c) an Automated Isoperibol Fixed Bomb Parr 6200 bomb calorimeter.
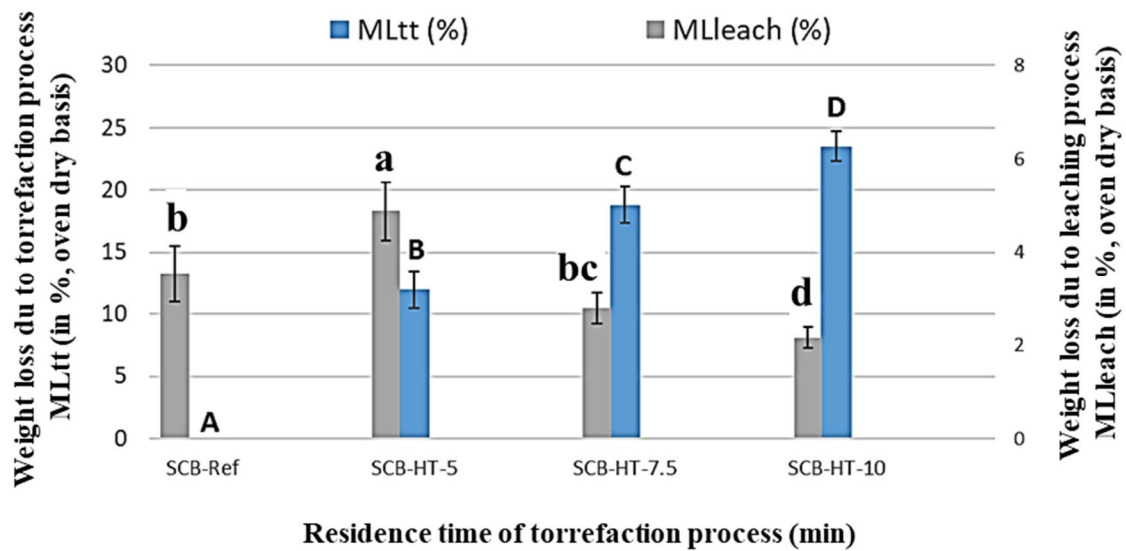
Letters: bar followed by the same letter are not significantly different. Here, the letters from A to D and from a to d indicate the influence of torrefaction duration on the Mass Losses (MLtt %) due to thermal degradation and Mass Losses (MLleach %) due to leaching process of SCB samples, respectively.

Fig. 4: Average values of raw and torrefied SCB Mass Losses (ML_{tt} %) due to thermal degradation and Mass Losses (ML_{leach} %) due to leaching process.
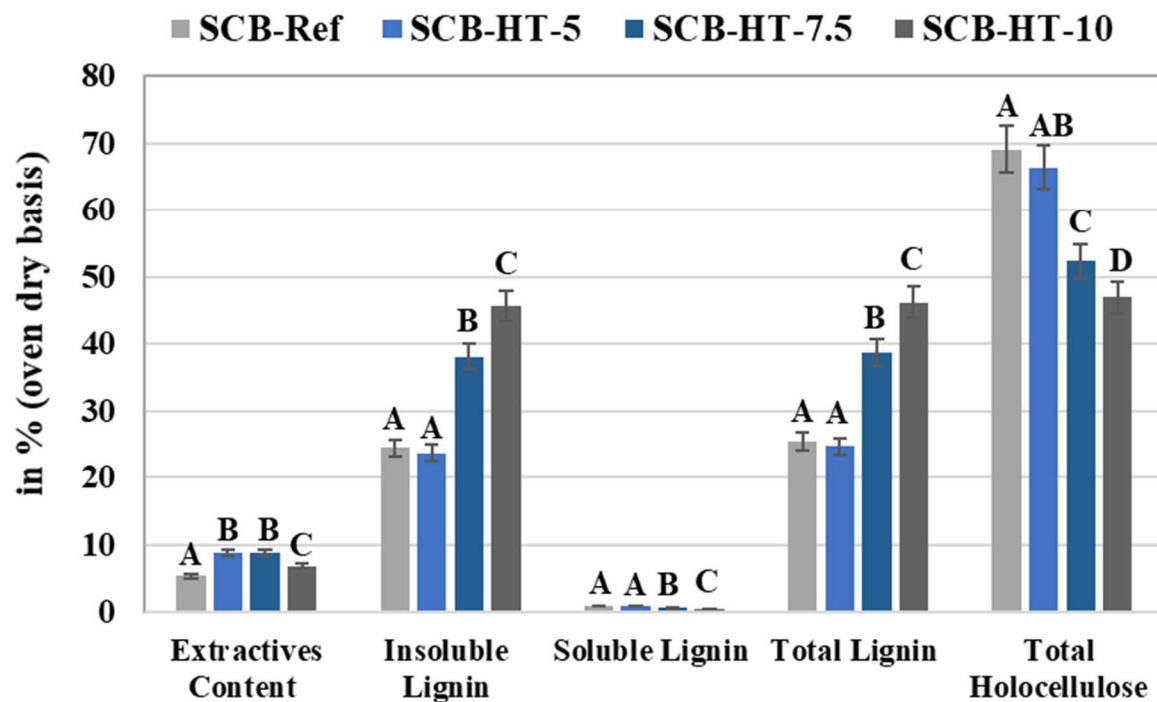
Letters: bar followed by the same letter are not significantly different. Here, the letters indicate the influence of torrefaction duration on the chemical composition of SCB samples.

Fig. 5: Chemical composition of raw and torrefied sugarcane bagasse (SCB). For each group, the means with the same letter were not significantly different at 5% (a = 0.05).
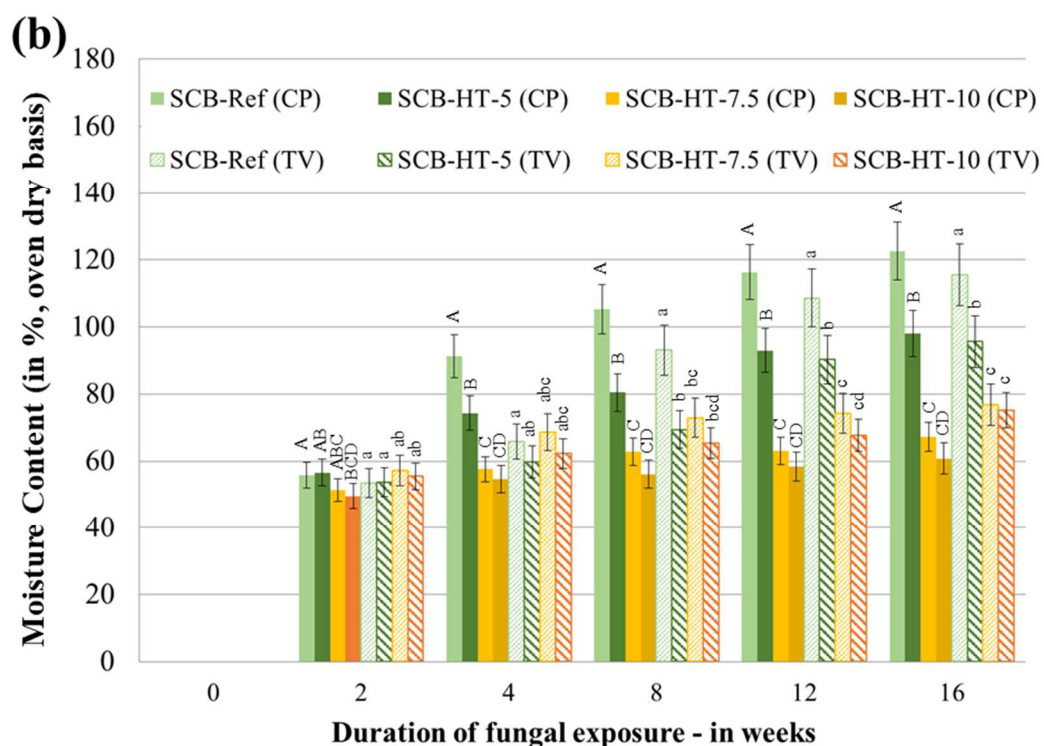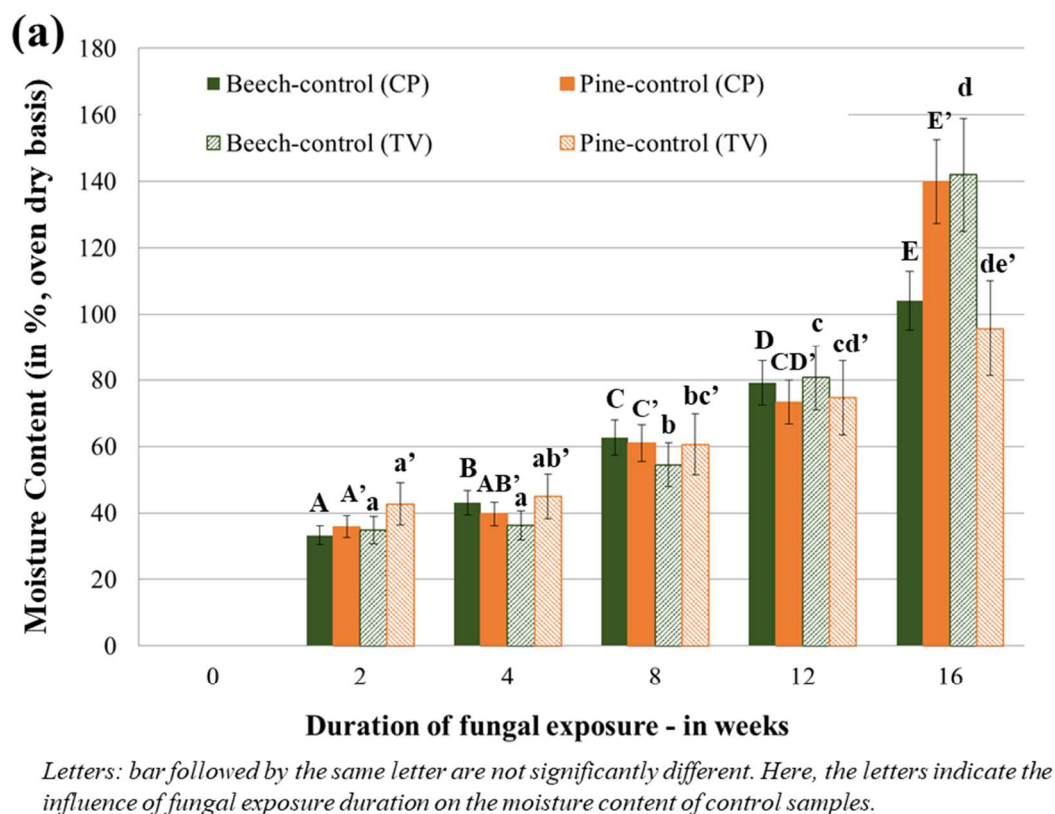
Fig. 6: Final moisture content (%) after *Coniophora puteana* (CP) and *Trametes versicolor* (TV) exposure of pine and beech control samples (a) and native and torrefied sugarcane bagasse (SCB) (b), according to the fungal exposure duration.

(a)

Letters: bar followed by the same letter are not significantly different. Here, the letters indicate the influence of fungal exposure duration on the weight loss of control samples.

(b)

Letters: bar followed by the same letter are not significantly different. Here, the letters indicate the influence of torrefaction duration on the weight loss of SCB samples for each fungal exposure duration.
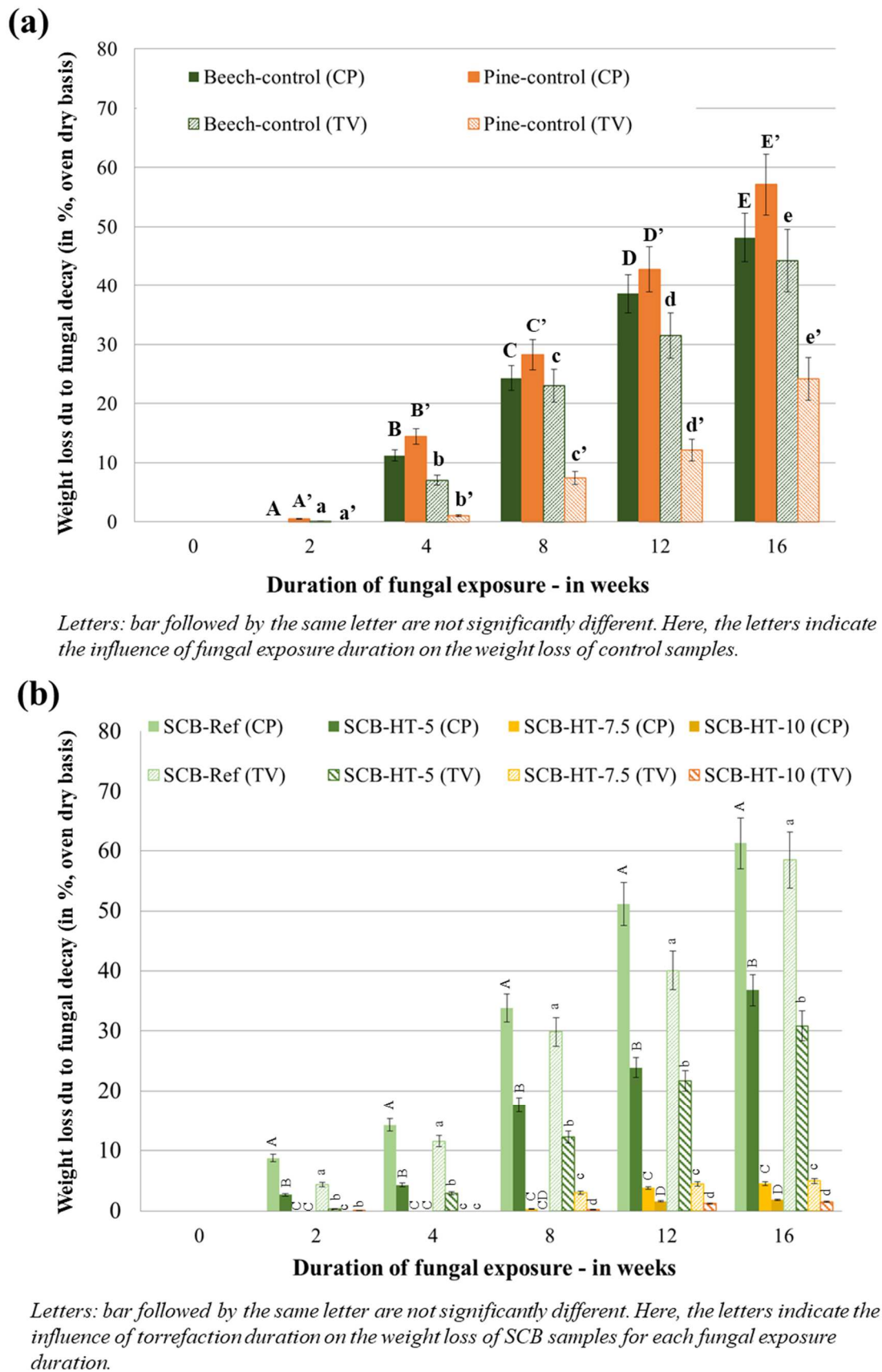
Fig. 7 : Weight losses (WL%) due to *Coniophora puteana* (CP) and *Trametes versicolor* (TV) degradation of pine and beech control samples (a) and raw and torrefied sugarcane bagasse (SCB) (b), according to the fungal exposure duration.
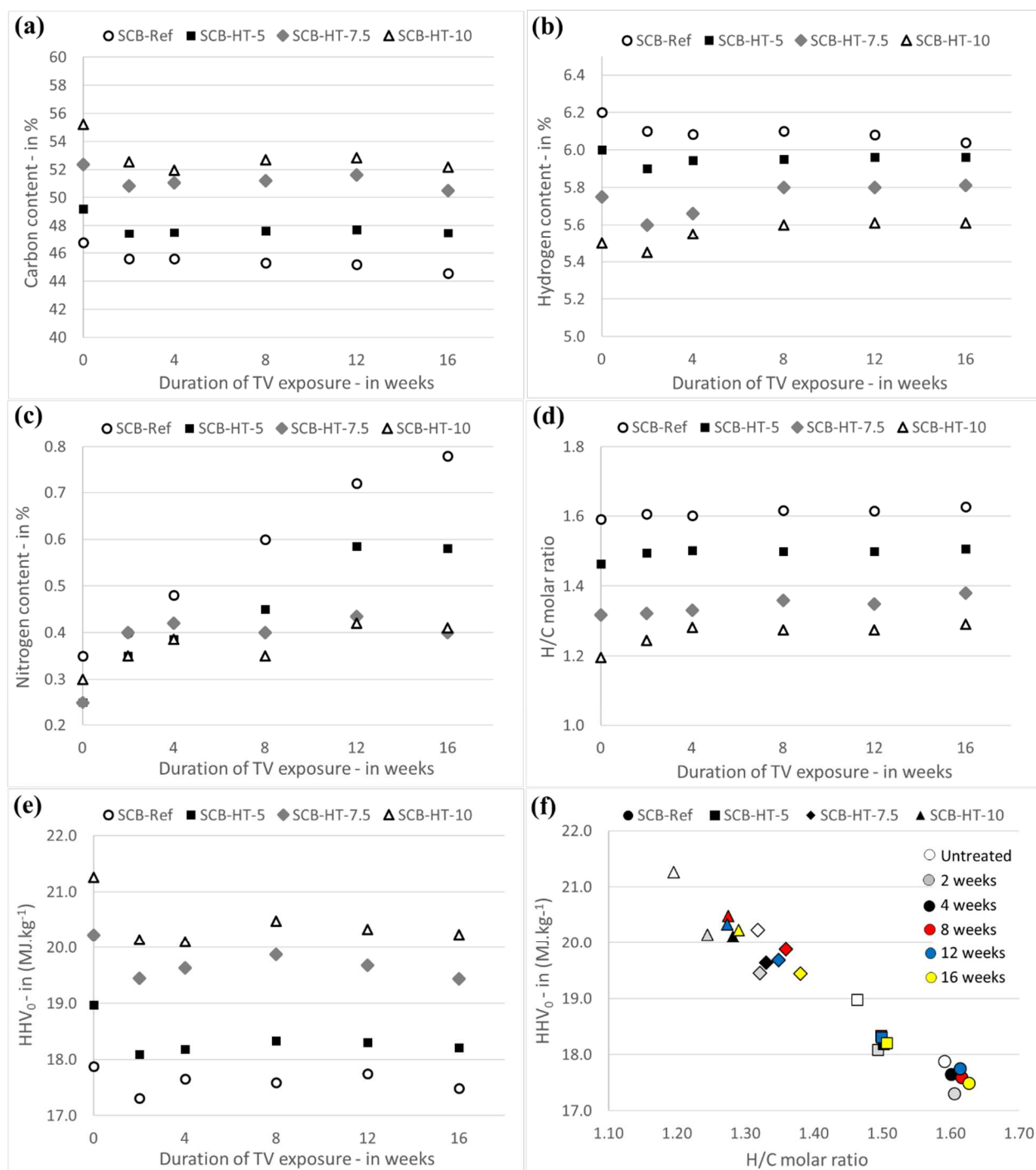
Fig. 8 : (a) Carbon, (b) Hydrogen and (c) Nitrogen contents (%), (d) H/C molar ratio and (e) HHV$_0$ (MJ.kg^{-1}) of raw and torrefied sugarcane bagasse (SCB), according to *Trametes versicolor* exposure duration; (f) Correlation between HHV$_0$ (MJ.kg^{-1}) and atomic H/C ratio of the different sugarcane bagasse (SCB) samples.
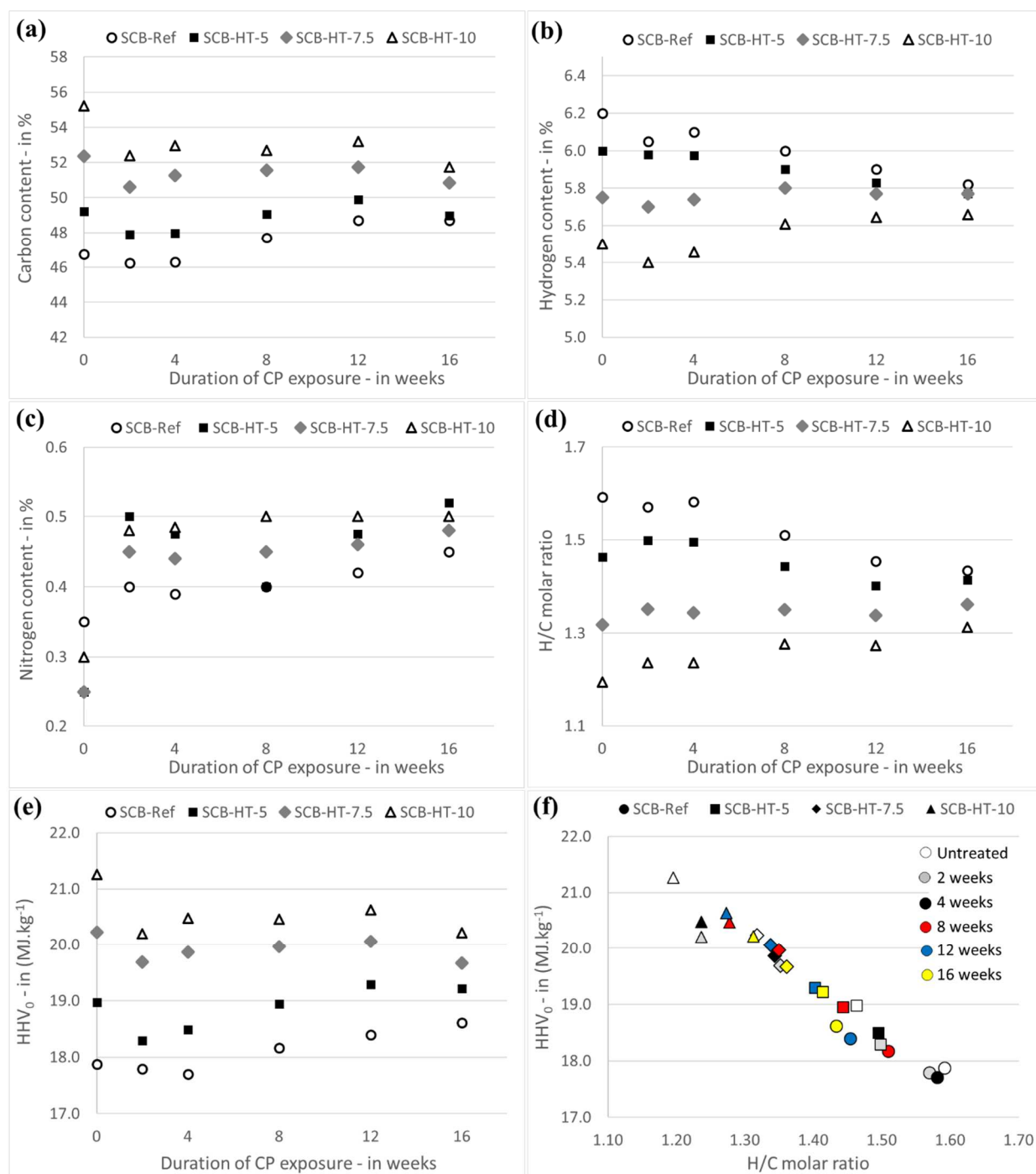
Fig. 9: (a) Carbon, (b) Hydrogen and (c) Nitrogen contents (%), (d) H/C molar ratio and (e) HHV_0 (MJ.kg^{-1}) of raw and torrefied sugarcane bagasse (SCB), according to *Coniophora puteana* exposure duration; (f) Correlation between HHV_0 (MJ.kg^{-1}) and atomic H/C ratio of the different sugarcane bagasse (SCB) samples.

Tab. 1: Elemental Compositions and High Heating Values (HHV), before and after leaching of raw and torrefied SCB samples. For each group, the means with the same letter were not significantly different at 5% (α= 0.05)

Reference	Before Leaching process*					After Leaching process*				
	C (%)	H (%)	H/C	N (%)	HHV$_0$** (MJ.kg^{-1})	C (%)	H (%)	H/C	N (%)	HHV$_0$** (MJ.kg^{-1})
SCB-Ref	47.05 **(A) (a)**	6.00 **(A) (a)**	1.53 **(A) (a)**	0.30 **(A) (a)**	18.479 **(A) (a)**	46.75 **(A) (b)**	6.20 **(A) (b)**	1.59 **(A) (a)**	0.35 **(A) (b)**	17.874 **(A) (a)**
SCB-HT-5	49.60 **(B) (a)**	5.80 **(B) (a)**	1.40 **(B) (a)**	0.35 **(B) (a)**	19.241 **(AB) (a)**	49.20 **(B) (b)**	6.00 **(AB) (b)**	1.46 **(AB) (a)**	0.25 **(C) (b)**	18.975 **(AB) (a)**
SCB-HT-7.5	53.15 **(C) (a)**	5.60 **(C) (a)**	1.26 **(C) (a)**	0.40 **(C) (a)**	20.732 **(BC) (a)**	52.35 **(C) (b)**	5.75 **(ABC) (b)**	1.32 **(BC) (a)**	0.25 **(C) (b)**	20.228 **(BC) (a)**
SCB-HT-10	55.10 **(D) (a)**	5.40 **(D) (a)**	1.18 **(D) (a)**	0.40 **(C) (a)**	21.491 **(CD) (a)**	55.20 **(D) (a)**	5.50 **(BCD) (b)**	1.20 **(CD) (a)**	0.30 **(B) (b)**	21.260 **(CD) (a)**

* Each analysis has been duplicate and all the results are given with an accuracy of ± 0.20 %.

** Each analysis has been duplicate and all the results are given with an accuracy of ± 5.00 %.

Letters: bar followed by the same letter are not significantly different.
Here, the letters from "A" to "D" indicate the influence of the influence torrefaction duration on the elemental composition and HHV values (comparing rows). The letters from "a" to "b" indicate the influence of the water leaching process on the elemental composition and HHV values (comparing columns).

Emulation of field storage conditions for assessment of energy properties of torrefied sugarcane bagasses

GRAPHICAL ABSTRACT