

1 **Comparative environmental Life Cycle Assessment of integral revalorization of vine shoots**  
2 **from a biorefinery perspective**

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12 **Abstract**

13 The use of vine shoots as feedstock in biorefining activities to obtain bioproducts under efficient and  
14 optimized conditions could be crucial to make future high added value compounds and processes  
15 more sustainable. In this study, five different potential valorization scenarios from vine shoots differing  
16 on diverse extraction and delignification steps were assessed from an environmental perspective  
17 using the Life Cycle Assessment methodology to identify the most sustainable biorefining route. The  
18 main findings from this study reported that an increment on the number of valorization steps involved  
19 higher energy and chemical requirements deriving on worse environmental profiles. Scenarios  
20 incorporating fermentation of the glucose liquors or organosolv delignification performed the worst  
21 profiles. Autohydrolysis, concentration and freeze drying and enzymatic hydrolysis were the main  
22 responsible stages of the environmental burdens. Further research should be focused on optimizing  
23 chemicals and electricity requirements to develop greener systems.

24

25 **Keywords:** biopolymers; environmental profile; ethanol; LCA; organosolv

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## 27 **1. Introduction**

28 Nowadays, the society is facing important challenges mainly related with the substitution of petroleum  
29 based materials by renewable ones. In this way not only the the high dependence on finite-fossil fuels  
30 consumption could be reduced but also the unstable production of petroleum based materials and the  
31 derived environmental impacts, as the greenhouse gases (GHGs) emission (Spiridon et al., 2016).

32 Therefore, numerous initiatives are being developed to promote the production and use of  
33 bioresources-based alternatives instead of petrochemical ones (Cherubini and Ulgiati, 2010; Gullón et  
34 al., 2016). In this sense, biomass could be considered as a sustainable alternative raw material to  
35 produce biomaterials and bioproducts because of its abundant availability, diversity and recyclability  
36 (Spiridon et al., 2016).

37 It has been demonstrated that the use of bioresources instead of petrochemicals for the production of  
38 biofuels (González-García et al., 2010) and biofoams (González-García et al., 2016a) causes lower  
39 GHGs emission. Nevertheless, there are concerns regarding their benefits in terms of other  
40 environmental impact categories, as the use of the land could change due to the cultivation activities  
41 related with the biomaterial-feedstock production, mainly in areas with significant social value  
42 (Searchinger et al., 2008). Therefore, a sustainability study should be required so as to identify the  
43 situations in which the use of bioresources could be environmentally feasible over petrochemical  
44 alternatives.

45 The use of lignocellulosic biomass residues and wastes from agro-food-industrial, agricultural and  
46 forestry activities could be considered as a potential alternative for the manufacture of added value  
47 products instead of using dedicated crops. The employment of biomass residues could avoid the  
48 derived negative impact from the cultivation phase of crops and it could give a solution to residual  
49 streams which must be managed in a sustainable manner without entering in confrontation with food  
50 and feed availability. In fact, all these residues, which are generated in billions of tons a year,  
51 represent a renewable source available to be used for further applications (Forster-Carneiro et al.,  
52 2013). The use of residues is probably the lowest cost form of available biomass, but the range of

53 costs can considerably vary depending on the residue as they involved items such as harvest, salaries  
54 and transportation (Gallagher et al., 2003). Furthermore, the removal of biomass residues from  
55 croplands could also derive on negative consequences closely related to the loss of soil organic  
56 carbon content as well as to the reduction of crops yields (Wilhelm et al., 2007).

57 The composition of the lignocellulosic residues changes depending on the feedstock species and  
58 origin. However, in general lines, they are mainly constituted by cellulose, hemicellulose and lignin as  
59 well as by organic extractives and inorganic minerals (Dávila et al., 2016; Thakur et al., 2015) and they  
60 can be considered as attractive biorenewable polymers (from now, biopolymers) which could replace  
61 the traditional synthetic ones (Thakur et al., 2015). For that reason, biorefineries based on these  
62 lignocellulosic materials are drawing special attention (Dávila et al., 2016; González-García et al.,  
63 2017) for different applications from biomedical to automotive (Thakur et al., 2015). Examples of  
64 lignocellulosic biorefineries viable at industrial scale are Borregaard Company and Envergent  
65 Technologies. Borregaard Company, is a Norwegian company which in the 1930s started the  
66 production of bioethanol by the fermentation of the sugar obtained from spruce wood. It is organized  
67 into five production sections, such as: cellulose and bioethanol, lignin-based binding and dispersing  
68 agent, fine chemicals for the pharmaceutical sector, vanillin for the food sector and microfibrillated  
69 cellulose. Envergent Technologies is a corporate between Honeywell's UOP and Ensyn Corporation,  
70 established in 2008 in Des Plaines, Illinois. Ensyn is the proprietary of the Rapid Thermal Processing  
71 (RTP™) technology. Nowadays, there are seven commercial RTP plants in the United States and  
72 Canada. These biorefining industries are converting residual biomass (mainly wood and agricultural  
73 wastes) into more than 30 added value products encompassing green fuels, chemicals, food  
74 flavorings, adhesive resins for construction, etc. (Sillanpää and Ncibi, 2017).

75 Cellulose is the most abundantly available bioresource and its demand is continuously increasing due  
76 to its environmental friendly, biodegradable and biocompatible nature (Watkins et al., 2015).  
77 Nowadays, cellulose finds several applications as building materials, paper, textiles, as well as  
78 clothing (Brichi et al., 2013). Another rising application of cellulose is as reinforcement in composite  
79 materials (Watkins et al., 2015). In the last two decades the employment of cellulose to obtain energy

80 has been extensively exploited, as great efforts have been performed to improve the conversion of  
81 cellulose to ethanol, methane and in the most recent years to hydrogen (Menon et al., 2012).

82 After cellulose, the second most abundant renewable polysaccharide on the earth is the  
83 hemicellulose. (Gullón et al., 2016). Thus, it could offer a sustainable alternative for materials,  
84 chemicals and fuels production (Kemppainen et al., 2014). However, the use of this biopolymer is not  
85 so extended than other natural polysaccharides (e.g. chitosan, cellulose and starch) mainly because  
86 its heterogeneous composition makes its application difficult at industrial scale (Gullón et al., 2016).  
87 Nevertheless, in recent years, numerous research activities have been developed to integrate this  
88 attractive, renewable and cheap polysaccharide in the industry under a biorefinery approach  
89 specifically to produce prebiotic functional food ingredients (Nabais et al., 2010; Dávila et al., 2016;  
90 González-García et al., 2016b). The employment of hemicelluloses for the production of films  
91 (Hartman et al., 2006) and hydrogels (Gullón et al., 2016) as well as their use as food additives  
92 (González-García et al., 2017) are attracting special interest.

93 After cellulose, lignin is the next most abundant natural polymer in the nature. Lignin possesses  
94 chemical and physical properties that make it an excellent candidate to substitute any product  
95 obtained from petrochemical sources; moreover, it is a natural and biorenewable feedstock, obtainable  
96 at an affordable cost. Lignin can be used as emulsifiers, dyes, synthetic floorings, sequestering,  
97 binding, thermosets, dispersal agents, paints and fuels to treatments for roadways (Watkims et al.,  
98 2015).

99 Within the different activities carried out in the agricultural sector, viticulture requires special interest  
100 since it is one of the most spread crops in the world (Nabais et al., 2010) and specifically in countries  
101 such as Spain (Dávila et al., 2016). The wine sector involves the production of a large amount of  
102 residues such as pomace, grape stalks and vine shoots (Benetto et al., 2015; Dávila et al., 2017a), all  
103 of them with multiple applications. Pomace or grape march is primarily used for animal feed and  
104 fertilizer (Gómez et al., 2010; Vaccarino et al., 1992) although studies can be found regarding its use  
105 for compost (Fernández et al., 2008) and even for the production of pellets (Benetto et al., 2015).  
106 Grape stalks can be used as metal sorbent (Miralles et al., 2008; Valderrama et al., 2010). Regarding

107 vine shoots, they are considered novel biomass agricultural residues (Sánchez et al., 2002; Max et al.,  
108 2010; Sánchez-Gómez et al., 2017) and their management under a biorefinery perspective is  
109 attracting notice (Nabais et al., 2010; Dávila et al., 2016). These wastes have been traditionally poorly  
110 exploited. Vine shoots are usually burned in the field to prevent proliferation of phytopathogens  
111 (Sánchez et al., 2002) or even left in the field as organic fertilizer (Jiménez Gómez et al., 1993;  
112 Peralbo-Molina et al., 2013) since their economic value is very small (Peralbo-Molina et al., 2013) .  
113 Thus, one of the main challenges for the wine sector is to identify strategies to increase the added  
114 value of the vast amount of vine shoots produced. Numerous studies are available in the literature  
115 focused on the valorization of vine shoots to obtain high added value products, such as activated  
116 carbon (Nabais et al., 2010), polyphenols (Gullón et al., 2017), ethanol (Jiménez et al., 2007), lactic  
117 acid and/or xylitol (Rivas et al., 2007). However, to the best of our knowledge, the environmental  
118 sustainability of these production schemes has not been assessed yet. Only one environmental study  
119 has been published with special focus on the environmental footprints of different production schemes  
120 of soluble saccharides of polymeric and oligomeric nature from woody residual streams (González-  
121 García et al., 2016b) using the Life Cycle Assessment (LCA) methodology. This methodology is used  
122 to understand and address the environmental impacts throughout a production system (ISO 14040,  
123 2006).

124 In this study, the assessment of the environmental impacts derived from the valorization of vine shoots  
125 from the wine sector into high added value products has been performed considering five different and  
126 alternative valorizing schemes. The evaluation of the schemes would permit the identification of  
127 environmental *hotspots* responsible of the largest environmental impacts. These scenarios differ on the  
128 extraction, delignification and/or hydrolysis routes and are based on experiments and protocols carried  
129 out at semi-pilot scale. The LCA models for each scenario were developed in accordance with the  
130 requirements of ISO 14040 (2006).

## 131 **2. Materials and methods**

132 Life cycle assessment (LCA) is a standardised framework for the systematic evaluation of  
133 environmental aspects of a product or service system through all stages of its life cycle (ISO 14040,

134 2006) by means of the assessment of environmental impacts of a product from its extraction of raw  
135 materials to its disposal.

## 136 **2.1 Goal and scope definition**

137 This study aims to assess the environmental performance of different valorizing routes of vine shoots  
138 to obtain high added value products with potential uses from biopolymers to energy production from  
139 their three major constituents; cellulose, lignin and hemicelluloses. Production batches for each  
140 valorization scenario have been specifically designed and performed to analyse in detail the  
141 conversion routes. Different side-streams are derived from the valorizing systems which could be used  
142 for further applications, such as cellulose, lignin, antioxidants as well as biomass rich on nitrogen. The  
143 description of the different valorization scenarios is included below. Thus, the function of this study is  
144 the valorization of an agro-industrial waste into valuable products with potential industrial and  
145 nutraceutical applications.

146 Taking into consideration the goal and scope of the study, a functional unit based on the amount of  
147 biomass valorized per batch, i.e. 100 kg of oven-dried vine shoots provided by a local farmer at the  
148 semi-pilot plant gate, has been defined and considered for comparison. Vine shoot are characterized  
149 by three main fractions: cellulose (34%  $\pm$ 1.5), hemicellulose (19% $\pm$ 0.5), and lignin (27% $\pm$ 1.3) - raw  
150 material oven dry weigh (Max et al., 2010). The semi-pilot facility is located in the Chemical and  
151 Environmental Engineering Department of the University of the Basque Country (San Sebastián,  
152 Spain). All the scenarios under assessment are multi-outputs systems in which more than one product  
153 are obtained. According to the functional unit chosen, no allocation procedure has been required and  
154 a system expansion approach has been considered (if necessary). The consideration of a reference  
155 unit based on the amount of waste-mass valorized is commonly used in LCA studies involving waste  
156 management systems (González-García et al., 2017). In addition, this functional unit will allow the  
157 comparison of the different schemes in spite of yielding on different high added value products.

158

## 159 2.2 Description of the valorizing scenarios under study

160 The base scenario (Scenario I) consisted of seven main subsystems: autohydrolysis (SS1),  
161 centrifugation (SS2), oligosaccharides extraction (SS3), ethyl acetate recovery (SS4), concentration  
162 and freeze drying (SS5), delignification (SS7) and wastewater treatment (SS6). The subsystems and  
163 stages of the process included within the system boundaries are represented in **Figure 1a** and they  
164 are described below.

165

166 <**Figure 1a** around here>

167

168 Vine shoots are produced as a result of vine pruning activities. The vine pruning is a necessary  
169 process as it equilibrates the growth of the vegetation and the fruit, and it also influences the shape,  
170 size, quantity, and quality of grapes (Sanchez et al., 2012). Vine shoots production related process  
171 (silviculture activities) has been excluded from the system boundaries since the derived environmental  
172 impacts were entirely allocated to the grape harvesting (the principal product by far). Thus, allocation  
173 criteria has not been required in this study.

174 The vine shoots at an optimum size ( $\approx 0.4$ mm) are received at the semi-pilot plant directly supplied by  
175 a local farmer and are treated with water in a stainless steel Parr reactor (SS1) at a liquid-to solid ratio  
176 of 8 kg/kg (oven-dried basis) and under non-isothermal reaction at 200 °C (15.54 bar), conditions  
177 reported as optimal for the hemicellulose solubilisation by Dávila et al. (2016). Once the treatment is  
178 completed, the reaction media is cooled by internal refrigeration for approximately 10 min, and the  
179 solid and liquid fractions are separated and recovered by centrifugation (SS2). The liquid stream  
180 (autohydrolysis liquor) is a mixture of hemicellulosic oligosaccharides and its composition is reported  
181 in **Table 1**. It is important to note that this stage is common to all the valorization sequences proposed  
182 for analysis.

183

184 <**Table 1** around here>

185

186 In order to obtain two different streams of high-added value compounds, one rich in antioxidant and  
187 the other one rich in oligosaccharides with potential nutraceutical and pharmaceutical applications,  
188 these liquors are processed in two stages. First of all, the liquors are extracted with ethyl acetate (1:3

189 (v/v) hydrolysate: solvent ratio) in a single extraction stage under stirring for 15 min at room  
190 temperature (SS3). The organic and aqueous phases are separated by decantation and processed as  
191 follows: a) the organic phase is vacuum-evaporated at 40 °C to recover the solvent and to obtain an  
192 extract rich in antioxidants (SS4) and, b) the aqueous phase is concentrated to obtain a stream rich in  
193 oligomeric compounds using a membrane processing unit (SS5) as described previously by González-  
194 García et al. (2016b). Briefly, the experiments are performed using a regenerated cellulose membrane  
195 of 1 kDa cutoff (Millipore) operating at a pressure of 4 bar. The concentration is performed up to reach  
196 a ratio of overall retentate to feed of 1:4. The processing is carried out at room temperature. At the end  
197 of process, the retentate is freeze-dried and the residual stream (permeate) is sent to wastewater  
198 treatment (SS6). The solid fraction obtained after the hydrothermal processing (SS1), composed  
199 mainly by cellulose (27.7%) and lignin (52%), is subjected to alkaline delignification to obtain both  
200 fractions separately enabling their individual use for applications of added value (SS7). Briefly, the  
201 alkaline delignification stage is carried out using a ratio liquid:solid of 10 kg/kg, NaOH 12% (w/w) at  
202 124 °C (pressure= 2.32 bar) during 105 min in a autoclave (Dávila et al., 2017b). After the  
203 pretreatment, the slurry is vacuum filtered to separate the black liquors (containing the dissolved  
204 lignin) from the delignified solid. The lignin is precipitated from the black liquors using H<sub>2</sub>SO<sub>4</sub> at 96%  
205 until pH 2 and then it is recovered by filtration and washed several times first with acidified water and  
206 then with water. The delignified solid is washed several times with water to remove the alkali until its  
207 pH is about 7 and then it is filtered. Thus, lignin and cellulose are also obtained as co-products from  
208 this valorization scheme.

209

#### 210 *Alternative valorization scenarios*

- 211 • Scenario II: this scenario follows the same scheme as the one depicted in Scenario I with only  
212 one remarkable difference. In this scenario the autohydrolysis liquors obtained in the centrifugation  
213 step (SS2) are directly sent to the concentration unit (SS5), so that the antioxidants are not finally  
214 extracted (**Figure 1b**).

215

216 <**Figure 1b** around here>

217

218 • Scenario III: the scenario I is extended including an enzymatic hydrolysis step (SS8) of the  
219 cellulose from the delignification treatment (SS7) to obtain glucose (susceptible of being used in the  
220 production of ethanol by a fermentative via). For this purpose, the delignified solid (enriched in  
221 cellulose) is mixed with water at a liquid to solid ratio of 30 w/w, and the enzymatic hydrolysis is  
222 carried out by the addition of cellulase (Celluclast 1.5 L) at a ratio of 25 FPU<sup>1</sup> per g of dry solid, and  $\beta$ -  
223 glucosidase (Novozymes 188) at a ratio of 5 IU<sup>2</sup> per FPU of cellulase during 48 h at 48.5 °C. Citric  
224 acid-sodium citrate buffer is used at 0.05 N to maintain the medium at pH~ 4.85. The fraction of  
225 cellulose that is not converted (so called solid waste fraction **in Figure 1c**) is separated by  
226 centrifugation (SS9) as additional product stream for energy production. The production of this energy  
227 is included within the system boundaries of this scenario (SS14). Moreover, an avoided product  
228 approach is considered with regard to the production of the same amount of electricity (taking into  
229 account the Spanish electricity profile) as well as heat (considering its production from natural gas) in  
230 a combined heat and power (CHP) unit.

231

232 &lt;Figure 1c around here&gt;

233

234 • Scenario IV: in this case, the scenario III is extended with the incorporation of an alcoholic  
235 fermentation (SS11) of the glucose that is converted into ethanol and CO<sub>2</sub> as displayed in **Figure 1d**.  
236 For this goal, the strain *Saccharomyces cerevisiae* DSM 70449, obtained from the DSMZ collection  
237 (Braunschweig, Germany), is used in the fermentation. For the inoculum preparation, cells of *S.*  
238 *cerevisiae* are grown (SS10) at 30 °C and 120 rpm for 24 h in a medium containing 10 g glucose/L, 5 g  
239 peptone/L, 3 g malt extract/L, and 3 g yeast extract/L. After growth, cells are recovered by  
240 centrifugation, resuspended in a phosphate buffer solution and inoculated to achieve a concentration  
241 of 2.5 g yeast/L (dry weight basis) in the medium together with the nutrients (without glucose) to start  
242 the fermentation. The fermentation is carried out at 35 °C and 120 rpm for 48 h. Once the fermentation  
243 is completed, the yeast cells are separated from the medium containing the ethanol by centrifugation  
244 (SS12). The spent yeast cells of *S. cerevisiae* could be used as a cheap nitrogen source in other  
245 biotechnological processes (Rivas et al., 2004). In this study, the further management of this biomass

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<sup>1</sup> FPU - Filter Paper Activity

<sup>2</sup> U: unit of enzymatic activity. It is defined as the amount of enzyme catalyzing the formation of 1  $\mu$ mol of D-galacturonic acid per minute at 37 °C and pH5.

246 based stream has not been considered within the system boundaries since it is out of the factory  
247 scope. Finally, to obtain ethanol for chemical uses it is necessary to carry out a purification step of the  
248 fermentation broth. Among all the alternatives available for this purpose, in this research we have  
249 selected a process of distillation (SS13). The data of energy consumptions of this stage were obtained  
250 from the database of Aspen Plus® of our research group. Taking into account the perspective  
251 considered concerning the solid waste fraction management obtained in SS9 (avoided energy  
252 production), the same approach has been established for the ethanol obtained in SS13. Thus, avoided  
253 ethanol production has been computed in the environmental evaluation.

254

255 <Figure 1d around here>

256

257 • Scenario V: the scheme proposed in this scenario is similar to the Scenario I with only one  
258 difference in the delignification stage (SS6). In this case, an organosolv pre-treatment is performed to  
259 obtain cellulose and lignin as isolated fractions (see **Figure 1e**). In summary, the organosolv process  
260 is performed at a liquid/solid of 8 kg/kg (oven dried basis) with ethanol at 50% (w/w) at 200 °C in a 1.5  
261 L stainless steel PARR reactor during 90 min (Dávila et al., 2017c). At the end of the treatment, the  
262 reactor is cooled down and the suspension is filtered obtaining two streams: the black liquor (liquid  
263 fraction) and the delignified solid (solid fraction). The lignin is obtained by precipitation from the black  
264 liquor with three volumes of acidified water and then is filtered and washed several times with water  
265 until neutralization. The delignified solid is washed several times with water and filtered.

266

267 <Figure 1e around here>

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### 269 **2.3 Inventory data acquisition**

270 The transparency in communicating LCA results as well as the limitations that influence their quality  
271 is a mandatory issue for the credibility of any LCA study. A consistent environmental assessment  
272 requires the collection of high quality Life Cycle Inventory (LCI) data. In this study and regardless of  
273 the valorizing scenarios under evaluation, inventory data for the foreground systems (i.e. direct inputs

274 to and outputs from each subsystem) such as electricity requirements in all equipment (reactors,  
275 fermenter, distiller, centrifuges, membrane units and freeze-dryers), chemical doses – when  
276 necessary (H<sub>2</sub>SO<sub>4</sub>, NaOH, ethyl acetate, ethanol), tap water, nutrients and enzymes consumption  
277 correspond to primary data which have been directly taken from the semi-pilot plant taking into  
278 account the average data per batch (100 kg vine shoots – dry matter). As previously indicated, specific  
279 batches have been performed for each valorization route to compile all mass and energy data. The  
280 foreground data for this paper were measured and verified, thus reliable. The data timeline is one year  
281 and the data are geographically representative of the semi-pilot plant under study.

282 All electricity requirements have been directly estimated considering the power of the equipments as  
283 well as the duration of their use in order to obtain the specific requirement for each subsystem. A  
284 summary of primary data managed for each valorizing scenario is displayed in **Table 2**.

285 <**Table 2** around here>

286 With regard to the wastewater treatment plant where the wastewater produced in the different  
287 activities is treated, secondary data have been managed since this stage is not performed within the  
288 semi-pilot plant although it is located on the surroundings. The corresponding inventory data have  
289 been taken from the ecoinvent database © (Doka, 2007).

290 Concerning the background processes, the inventory data corresponding to the production of the  
291 different inputs to the systems (electricity from Spanish grid, chemicals, nutrients and tap water), have  
292 been taken from Ecoinvent © database version 3 (Werner et al., 2016). Regarding the production of  
293 electricity, the process included in the database has been updated using data for the average  
294 electricity generation and import/export data from Spain in 2014 (Red Eléctrica de España, 2014).  
295 Moreover, inventory data related with the process in which the solid fraction is valorized into energy  
296 (SS14) in Scenario III and Scenario IV have been taken from Dones et al. (2007). Data for enzyme  
297 production have been found in Nielsen et al. (2007) and Feijoo et al. (2017).

298 Since bioethanol is also produced as co-product in Scenario IV and bioethanol can be used for energy  
299 and chemical purposes, a system expansion perspective has been assumed and the production of this  
300 amount of ethanol by means of a conventional way has been included within the system boundaries  
301 and considered as “avoided product”. The data managed have been taken from Jungbluth et al.  
302 (2007). The same perspective has been assumed regarding to the solid waste fraction produced in  
303 Scenarios III and IV in the centrifugation stage (SS9). Inventory data managed regarding the avoided  
304 heat production corresponds to the production of heat from natural gas as fossil source (Dones et al.,  
305 2007). Regarding electricity, the production of electricity in the national grid has been computed as  
306 previously described. Detailed information with regard to the background processes managed is  
307 summarized in **Table 3**.

308 <**Table 3** around here>

#### 309 **2.4 Impact assessment methodology**

310 The characterization factors reported by the Centre of Environmental Science of Leiden University -  
311 CML 2001 method v2.05 (Guinée et al. 2002) have been considered in this study for the analysis. It is  
312 an impact assessment method which restricts quantitative modelling to early stages in the cause-  
313 effect chain to limit suspicions or uncertainties. Results are grouped in midpoint categories according  
314 to common mechanisms (e.g., global warming) or commonly accepted groupings (e.g., ecotoxicity)  
315 (Guinée, 2002). The following impact categories have been evaluated: abiotic depletion potential  
316 (ADP), acidification potential (AP), eutrophication potential (EP), global warming potential (GWP),  
317 ozone layer depletion potential (ODP), human toxicity potential (HTP), freshwater aquatic ecotoxicity  
318 potential (FEP), marine aquatic ecotoxicity potential (MEP), terrestrial ecotoxicity potential (TEP) and  
319 photochemical oxidation potential (POP). The choice of these environmental impacts is because all  
320 together give a full and comprehensive overview of the environmental effects related to the activities  
321 involved in the valorization schemes under evaluation. In addition, this selection should allow the  
322 comparison with other studies where environmental profiles of other valorization systems were also  
323 environmentally evaluated (González-García et al., 2016b, 2017). SimaPro 8.2.0.0 has been the

324 software used for the computational implementation of the inventory data and estimation of the  
325 characterization stage (PRé Consultants, 2017).

### 326 **3. Interpretation of results and discussion**

#### 327 **3.1. Global environmental results**

328 First of all, the environmental burdens of the different scenarios proposed for the analysis have been  
329 quantified to estimate the comparative profiles and to identify the most environmentally friendly one,  
330 that is, this scenario that reports the lowest environmental burdens. Next, the main environmental  
331 *hotspots* have also been identified since the environmental improvements should be proposed under  
332 their consideration.

333 From the analysis of data summarized in **Table 2** for the different valorization routes as well as taking  
334 into account the description of the considered strategies, it is evident that they share a number of  
335 steps in common such as autohydrolysis (SS1), centrifugation (SS2), concentration and freeze drying  
336 (SS5) and wastewater treatment (SS6). Although the delignification step (SS7) is also present in all  
337 the routes, the delignification strategy considerably differs between Scenario I-IV (alkaline  
338 delignification) and Scenario V (organosolv), being different not only in terms of operating conditions  
339 but also taking into account the goals. Whereas alkaline delignification allows a higher delignification  
340 ratio deriving on a solid stream rich on cellulose and susceptible to be used for glucose obtaining by  
341 enzymatic hydrolysis, the organosolv based delignification does not allow achieving a high percentage  
342 of lignin removal; however, this procedure enables to extract a lignin less modified.

343 Additional stages (enzymatic hydrolysis, inoculum preparation, fermentation, distillation, ...) have been  
344 computed taking into account the desired final products. Therefore, the specificity of the final products  
345 is different between scenarios.

346 **Figure 2a** displays the comparative environmental profiles for the different valorization scenarios  
347 proposed for study in terms of each impact category selected for assessment. According to the results

348 reported, two scenarios derived on the worse results in different impact categories: Scenario IV in  
349 ADP, AP, EP, GWP, ODP, HTP, FEP and MEP and, Scenario V in TEP and POP. Thus, two  
350 scenarios (I and II) show similar environmental profiles with no outstanding differences (reductions  
351 ranging from 3% to 8% depending on the impact category for Scenario II with regard to Scenario I).  
352 However, the valorization strategies considerably differ between them. As displayed in **Figure 1a**, the  
353 liquid fraction from the centrifugation step (SS2) rich in antioxidant compounds and hemicellulosic  
354 oligosaccharides is further processed by means of an extraction and decantation unit to obtain both  
355 components separately (hemicellulosic oligosaccharides and antioxidant extract). On the contrary (see  
356 **Figure 1b**), this stream is not further treated and both components with market applications cannot be  
357 separated, obtaining a mixed stream.

358 <**Figure 2a** around here>

359 Among the outstanding differences on the environmental profiles, it is important to highlight that an  
360 increment on the number of valorization steps included in the valorization route involves higher energy  
361 and chemical requirements which derives on worse environmental profiles. Thus, it must be taken into  
362 account that if enhancing “closing the loop” strategies under a biorefinery concept through better  
363 recycling and re-using the waste streams, the worse environmental burdens obtained as result from  
364 their higher intensive stages would be balanced out. However, this trend on the results is also linked to  
365 the functional unit selected to report the environmental results which is the amount of waste biomass  
366 valorized per batch. Therefore, it could be expected according to the available literature that this trend  
367 would entirely change if a unit based on the economic revenues was considered (González-García et  
368 al., 2016b; 2017) since the increment of valorization routes derives on more pure streams with  
369 economic and industrial value.

### 370 **3.2. Contributions per subsystems involved**

371 **Figure 2b** displays the distribution of environmental burdens per subsystems involved in the different  
372 valorization strategies of vine shoots into high added value products. Firstly, two scenario must be

373 analyzed in detail, these are Scenario I and Scenario V since stages such as SS1-SS6 are common in  
374 both scenarios and only differences are identified in terms of SS7 contributions.

375 <Figure 2b around here>

376 According to **Figure 2b.(1)** and **Figure 2b.(5)**, activities involved in SS7 intended for delignification of  
377 the solid fraction from SS2 are the environmental *hotspots* with contributions ranging from 29% to 77%  
378 and from 46% to 96% respectively for Scenario I and Scenario V, depending on the category.  
379 Moreover, the effect from SS7 in the profile associated with Scenario V is more outstanding in  
380 categories such as EP, HTP, TEP and POP (see **Figure 3**), which is directly linked to the  
381 delignification procedure, in this case organosolv which is expected due to the chemicals requirement  
382 in this case, ethanol.

383 <Figure 3 around here>

384 The alkaline delignification involves a ratio liquid:solid of 10 kg/kg considering NaOH 12% (w/w) at 124  
385 °C during 105 min. The organosolv stage is performed at a liquid/solid of 8 kg/kg with ethanol at 50%  
386 at 200 °C during 90 min. These different operating conditions derive on a different electricity  
387 consumption (7.4 times higher in Scenario I than in Scenario V) and chemical doses which are  
388 summarized in **Table 2**. In the case of Scenario I, the large electricity requirements in the autoclave is  
389 the main responsible of the impacts derived from SS7 as displayed in **Figure 4a**, which contribute  
390 from 75% to 96% of the total. On the contrary in Scenario V, the production of the ethanol  
391 requirements is the key issue with contributing ratios ranging from 72% to 100% of the total burdens  
392 derived from SS7 (see **Figure 4b**). Thus, further improvements should be focused on optimizing the  
393 electricity consumption and the ethanol requirements in Scenario I and V, respectively. In addition,  
394 alternative chemicals to ethanol in the organosolv process could also be evaluated.

395 <Figure 4 around here>

396 Contributions from SS1 (autohydrolysis) and SS5 (concentration and freeze drying) in scenarios I and  
397 V are also remarkable as depicted in **Figures 2b.1** and **2b.5**. In both cases, electricity requirements in  
398 the reactor and the freeze dryer are the key issues responsible of these results.

399 Regarding Scenario II, improvements on the global environmental profile of up to 8% are identified  
400 with regard to Scenario I (**Figure 2a**), although pure oligosaccharides and antioxidant extract based  
401 streams are not obtained. The main responsible of these results is the avoidance of SS3  
402 (oligosaccharides extraction) and SS4 (ethyl acetate recovery), both of them with electricity  
403 requirements.

404 Scenario III reports a more complex valorization scheme with enzymatic hydrolysis and energy  
405 production as the main new incorporated activities to obtain glucose liquors as well as heat and  
406 electricity from the solid waste fractions. As expected, the incorporation of these processes within the  
407 system boundaries of the valorization route derives on higher environmental burdens that is, on a  
408 worse environmental profile than Scenario I as depicted in **Figure 2a**. Having a look into the  
409 distribution of the environmental burdens derived from Scenario III, three stages can be managed as  
410 environmental *hotspots* as displayed in **Figure 2b.3**. These are SS5 (concentration and freeze drying)  
411 and SS7 (delignification) – in the same line as the previous scenario presented and, SS8 (enzymatic  
412 hydrolysis) –specific to this one. The key issues responsible of the contributions of SS5 and SS7 are  
413 once again the electricity requirement in the freeze dryer and in the autoclave, respectively. Regarding  
414 SS8, the distribution of contributing burdens is depicted in **Figure 5**. Electricity requirement for the  
415 agitation as well as the consumption of both enzymes and buffer are the key factors considered as  
416 environmental *hotspots*. The effect from these factors depends on the category evaluated. Thus,  
417 production of the enzymes required in the hydrolysis is the responsible of near 100% in categories  
418 such as MEP and TEP and around 60% in ODP. The enzymes production process requires large  
419 amount of energy as well as chemicals (Feijoo et al., 2017) which are responsible of these high  
420 impacts. In the remaining categories, the main contributor is the production of electricity requirement,  
421 directly taken from the national grid and which presents a fossil origin. Production of buffer reports  
422 outstanding contributions (ranging from 15% to 20%) in AP, EP, GEP, HTP, FEP and POP mainly  
423 because of the background activities involved in its production.

424 Scenario IV reports a full valorization scheme with enzymatic hydrolysis, fermentation (including  
425 inoculum preparation), energy production and distillation as the main incorporated processes to obtain  
426 bioethanol for chemical applications as well as heat and electricity from solid waste fractions. Once  
427 again, the incorporation of these activities within the valorization route derives on higher environmental  
428 burdens that is, on a worse environmental profile than Scenario I as depicted in **Figure 2a**. However,  
429 comparing all the scenarios, Scenario IV reports the worst environmental results in only five  
430 categories, ADP, EP, GWP, FEP and MEP. Looking into the distribution of the environmental burdens  
431 derived from Scenario IV (**Figure 2b.4**), SS8 is the environmental key factor followed by SS7, SS11  
432 (fermentation) and SS13 (distillation). It is important to highlight in this scenario the environmental  
433 credits associated with the avoided processes specifically in terms of TEP and POP. In this case, the  
434 avoided production of ethanol is the main responsible of this positive effect. As in Scenario III, the  
435 production of the enzymes requirement for the hydrolysis is the responsible of the high contributions of  
436 SS8. Electricity requirement in the autoclave, fermenter and distiller are the key issues responsible for  
437 SS7, SS11 and SS13 contributing burdens, respectively.

438 Finally, if the profiles from Scenario III and IV are compared –since the second one involves the  
439 integration of additional biorefining activities, the profiles are increased 1.3-1.7 times in all the  
440 categories except in MEP and TEP, where negligible differences are identified. The increment of the  
441 environmental burdens is related with the additional activities included in Scenario IV as indicated in  
442 **Figure 2b.4**. In MEP and TEP the effect of these activities is negligible since the main responsible of  
443 the environmental burdens is SS8, which is a shared activity in both scenarios.

### 444 **3.3. Discussion of results**

445 According to the results displayed above, it can forecast that “closing the loop” strategies to introduce  
446 biorefinery strategies and thus, better recycling and re-using the waste streams from production  
447 systems should derive on the worse environmental profiles (see **Figure 2a**) in numerous impact  
448 categories since the number of valorizing activities is increased and therefore, the chemicals and  
449 energy requirements. However, it must be taken into account that this expected behavior is also  
450 related with the functional unit selected to report the environmental results. If a functional unit based

451 on economic approach was considered, where not only the production amount of the different added-  
452 value products was considered but also the potential revenues associated to their market, a different  
453 environmental performance could be expected (González-García et al., 2016b, 2017) balancing out  
454 the worse environmental burdens obtained as result from their higher intensive stages. Therefore, the  
455 analysis has been completed with an economic functional unit and 1€ of economic revenue has been  
456 selected to report the environmental profiles. However in this analysis only three scenarios will be  
457 managed and these are Scenario I, Scenario IV and Scenario V. Scenario II is excluded since there is  
458 not an increment on the valorization strategies regarding Scenario I. Scenario III is not considered  
459 since the glucose liquors should be further valorized into bioethanol, which is carried out in Scenario  
460 IV. A description of market prices of the different coproducts obtained in the different scenarios is  
461 displayed in **Table 4**.

462 <**Table 4** around here>

463 However and in contrast to what it was expected, no differences have been found on the  
464 environmental behavior regardless the functional unit considered. Therefore, Scenario IV reports the  
465 worst profile in all the impact categories except in terms of TEP and POP, where Scenario V is the  
466 worst option as displayed in **Figure 6a**. The low market prices for ethanol, electricity and heat together  
467 with their low yields, unlike the other co-products, derive on negligible alterations on the economic  
468 revenue per batch. Therefore, the effect of their production is not outstanding on the economic  
469 functional unit.

470 <**Figure 6** around here>

#### 471 *Electricity requirements*

472 Electricity requirements in the different valorization routes have been identified as environmental  
473 *hotspot* and thus, as area of significance and influence on the environmental profiles. There is a  
474 potential to improve the profiles through implementing improvements on energy consumption as well  
475 as on the efficiency of the production schemes. Thus, the access to electricity grid mix with a better

476 environmental profile (i.e., reducing the use of fossil sources and promoting the use of renewable  
477 ones) would considerably improve the environmental results corresponding to the valorizing schemes  
478 under evaluation. However and, given the novelty of the bio-based technologies, there are doubts and  
479 discrepancies concerning the choice of electricity mix as a strategic factor for enhancing the  
480 environmental profiles of bioproducts (Collet et al., 2011; Moussa et al., 2016). In our case studies, the  
481 semi-pilot plant is located in Spain and all electricity requirements are directly taken from the Spanish  
482 electricity grid.

#### 483 *Organosolv chemicals: sensitivity analysis*

484 Taking in mind the results obtained for the organosolv based scenario (Scenario V), the ethanol  
485 requirement in the pre-treatment is considered an environmental *hotspot* being the responsible of the  
486 highest environmental burdens regardless the impact category (contributing ratios ranging from 36%  
487 to 95% of the global results depending on the category). However and according to the literature  
488 (Martín et al., 2011), alternative chemicals could be managed in the pre-treatment stage under  
489 organosolv conditions. Therefore, different alternative scenarios have been proposed with the aim of  
490 studying their effect on the environmental impacts associated to this stage.

491 The base scenario, which corresponds to the original case study (Scenario V), is named as scenario  
492 A. Scenarios B and C correspond to the use of glycerol-water at 60% (v/v) and ethylene glycol-water  
493 at 60% respectively, as they are both chemicals typically used in organosolv treatments (Martín et al.,  
494 2011, González et al., 2008).

495 The outcomes of the sensitivity analysis (**Figure 6b**) showed that scenario B yields to the highest  
496 environmental burdens, except for ADP, HTP, MEP and POP categories. Scenario C is the worst  
497 option in terms of ADP and MEP, being Scenario A (the case base) the responsible of the highest  
498 impacts in HTP and POP. Thus, the use of glycerol as organosolv solvent is not recommended from  
499 an environmental point of view in line with the results obtained.

500 Scenario C could be classified as the best option if it is compared to the other two scenarios since  
501 environmental improvements are reported in terms of seven of the ten categories analyzed,  
502 Consequently, it would be convenient the use of ethylene glycol as solvent instead of ethanol. This  
503 selection is also supported by the consideration of the normalization phase (Guinée et al. 2002), which  
504 allows us to compare all environmental impacts using the same scale as well as to add the  
505 normalization values of impact categories to obtain a single number per scenario. According to it, the  
506 normalization values are:  $1.40 \cdot 10^{-7}$ ,  $1.77 \cdot 10^{-7}$  and  $9.38 \cdot 10^{-7}$  for Scenario C, Scenario A and Scenario B  
507 respectively.

#### 508 *Comparison with literature*

509 Nowadays the interest on the biorefinery concept is receiving special attention for multiple reasons  
510 mainly due to a great fraction of energy carriers and materials come from fossil fuel refineries  
511 (Cherubini, 2010), as well as because the European Commission is adopting strategies to “closing the  
512 loop” of product life cycles in industrial production systems from a circular economy approach. By  
513 applying the “closing the loop” strategy the production of waste could be reduced, the environmental  
514 profiles could be improved and the the economic profits could increase (Liguori et al., 2016). Different  
515 types of products can be obtained such as fuels, fibres (Nascimento et al., 2016), fine chemicals  
516 (Ekman and Börjesson, 2011), antioxidants (Ekman et al., 2013) and even proteins (Halloran et al.,  
517 2016). However, special attention is currently being paid on oligosaccharides production due to their  
518 interest as prebiotic functional food ingredients (González-García et al., 2016b) and biomaterials  
519 (Gullón et al., 2016).

520 In this sense, several studies can be found in the literature where LCA methodology has been applied  
521 to determine the environmental improvements linked to biorefinery strategies (Ekman and Börjesson,  
522 2011; Ekman et al., 2013; González-García et al., 2016b; 2017). However, only some studies can be  
523 found focused on the environmental analysis of the oligosaccharides production at semi-pilot scale, as  
524 driving force of the valorization schemes. González-García et al. (2016b) reported the environmental  
525 analysis of different schemes under thermal treatment conditions of wood chips valorization into  
526 soluble saccharides of polymeric and oligomeric nature (also known as galactoglucomannas) or

527 levulinic acid as the main products. González-García et al. (2017) considered the production of pectin-  
528 derived oligosaccharides from sugar beet pulp valorization under thermal and enzymatic treatments.  
529 To the best of our knowledge, no other environmental studies have been published in this topic. Both  
530 studies were performed from a cradle-to-gate approach, excluding from the system boundaries further  
531 uses as well as distribution. Therefore, no studies can be found in the literature in which the  
532 production of xylooligosaccharides –as in this study-, had been previously environmentally evaluated.  
533 Although different types of oligosaccharides streams have been assessed in the literature which  
534 involve different uses and properties (galactoglucomannans, pectin based and xylooligosaccharides in  
535 our study), a comparative environmental profile in terms of greenhouse gases emission throughout the  
536 whole life cycle (that is, carbon footprint) is proposed for consideration in this section. The carbon  
537 footprint is compared per kilogram of oligosaccharide produced and the results are displayed in  
538 **Figure 6c.**

539 According to Figure 6c, the carbon footprint ranges from 49 to 218 kgCO<sub>2</sub>eq·kg oligosaccharide<sup>-1</sup>. The  
540 best profiles are obtained in scenarios A and B, which correspond to the production of pectin-based  
541 oligosaccharides under thermal and enzymatic treatments considering a waste from sugar industry as  
542 raw material (González-García et al., 2017). The worst profiles correspond to the extraction of  
543 galactoglucomannans from residual wood waste under thermal treatment conditions (scenario C and D)  
544 (González-García et al., 2016b). The remaining scenarios (E-I) correspond to the xylooligosaccharides  
545 extraction from vine shoots considering different thermal pre-treatments and different valorization  
546 routes. Thus, the carbon footprints allocated to the systems under evaluation in this study are between  
547 the previous studies available in the literature.

548 Other limitations in performing a LCA comparison (when possible) could be the availability of the  
549 environmental profile assessment in terms of different impact categories (midpoint vs endpoint), the  
550 use of different system boundaries or even the consideration of system expansion approaches. The  
551 ISO 14040 (2006) standard establishes that all limitations and assumptions must be transparently  
552 defined, addressed and clearly presented in line with the goal and scope of the study.

553

#### 554 **4. Conclusions**

555 Biorefining systems cannot be per se favourable from an environmental perspective since according to  
556 the literature, they can be high intensive chemicals and energy demanding systems, deriving on high  
557 impacts on the environment. The use of renewable waste as raw material in biorefining activities under  
558 efficient and optimized conditions could be crucial to make future high added compounds and  
559 processes more sustainable not only from environmental but also from an economic perspective. The  
560 degree of waste valorization of the foreground systems is linked to the desired purity of the final  
561 product. The range of carbon footprint results ( $\text{kgCO}_2\text{eq}\cdot\text{kg oligosaccharide}^{-1}$ ) reported in this study  
562 must be carefully compared to others available in the literature since depending on the type of  
563 oligosaccharide, the production system requires complex and intensive foreground processes coming  
564 into larger impacts. The valorizing routes analyzed in this study appear to be attractive options to  
565 produce high-added value products with multiple applications from an agro-industry residue available  
566 in large amounts in Mediterranean countries. According to the outcomes, further research should be  
567 focused on improving the current valorizing techniques at semi-pilot scale specifically in terms of  
568 chemicals and electricity requirements (efficiency of the production process). LCA methodology can  
569 be considered as a valuable and useful tool to support decision making strategies, specifically for  
570 systems under development such as the one reported in this study. Other issues that can affect the  
571 implementation of biorefineries are policy issues and incentives as well as legislation. It is important to  
572 take into account that implementing a biorefinery approach could be considered as a way to manage  
573 renewable wastes, avoiding their disposal which involves a cost for companies. Finally, the intention of  
574 this study is not to provide an outright answer regarding the potential environmental profiles of high  
575 added value products since they are not generalizable but also to contribute to the understanding of  
576 the main issues responsible of these results.

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