

## Environmental implications of biohydrogen based energy production from steam reforming of alcoholic waste

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1 **Environmental implications of biohydrogen based energy production from steam reforming**  
2 **of alcoholic waste**

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11  
12 **Abstract**

13 Nowadays, there is an increasing demand for energy in the world. With an energy system still  
14 based on fossil fuels, a paradigm shifts towards clean energy production based on available  
15 renewable resources is necessary. Hydrogen is a high-quality energy carrier that can be used  
16 with great efficiency and is expected to acquire a great importance in the next generation of  
17 fuels. This study aims to analyze the potential environmental impacts associated with the  
18 steam reforming of alcoholic waste from distilleries to produce clean electricity by using the  
19 Life Cycle Assessment methodology. The main findings from this study reported that the global  
20 environmental profile is better than other alternatives more common as sanitary landfill or  
21 incineration. In terms of some impact categories as Abiotic and Ozone Depletion, Acidification  
22 and Eutrophication, steam reforming of alcoholic waste performed better profiles than other  
23 processes that produce hydrogen from diverse feedstocks.

24 **Keywords:** Alcoholic waste; Environmental profile; LCA; SOFC; Biohydrogen

## 25 **Abbreviations**

LCA	Life Cycle Assessment
SS	Subsystem
CC	Climate change
OD	Ozone depletion
TA	Terrestrial acidification
FE	Freshwater eutrophication
ME	Marine eutrophication
HT	Human toxicity
POF	Photochemical oxidant formation
PMF	Particulate matter formation
TET	Terrestrial ecotoxicity
FET	Freshwater ecotoxicity
MET	Marine ecotoxicity
FD	Fossil depletion
WW	Wastewater
WGS	Water Gas Shift
PSA	Pressure Swing Adsorption
ISO	International Organization for Standardization

26

## 27 **1. Introduction**

28 Currently, global energy production is based on the use of fossil fuels such as coal, oil and  
29 natural gas (Rossetti et al., 2015a) and accounts for approximately 65% of global GHG  
30 emissions (Uusitalo et al., 2017). Dependence on the use of fossil fuels as an energy resource  
31 has caused environmental problems of global impact, such as air pollution in terms of emission  
32 of pollutants and particles, as well as the depletion of natural resources, among others (Hajjaji  
33 et al., 2016; Reyes-Valle et al., 2015), which leads to adverse consequences for society in terms  
34 of human health and damage to the ecosystem (Valente et al., 2019). So much so that the  
35 2030 Agenda and the 17 Sustainable Development Goals (SDGs) set by the United Nations

36 includes ensuring access to affordable, reliable and sustainable energy for all. This objective  
37 aims at guaranteeing universal access to energy service, substantially increasing the share of  
38 renewable energy in the global energy mix and doubling the rate of improvement in energy  
39 efficiency. This is why the paradigm shift towards clean energy production must be based on  
40 available renewable resources (Da Costa-Serra and Chica, 2018).

41 In recent years, numerous alternatives to the use of traditional fossil fuels have been  
42 proposed, such as the production of biofuels, bioalcohols, hydrogen or any type of renewable  
43 energy (Balat, 2011). In particular, biomass is one of the renewable energy sources that has  
44 experienced strong growth in recent years, due to its global availability and diversity (Spiridon  
45 et al., 2016; Tian et al., 2018). Biofuels derived from biomass offer a number of advantages  
46 over their oil-based counterparts according to Demirbas (2008): they can be considered carbon  
47 neutral after-combustion by fixing carbon during biomass growth, close to a carbon-neutral  
48 balance, so that they contribute to achieving sustainability goals. For this reason, numerous  
49 initiatives have been developed in the development of conversion technologies based on  
50 resources derived from biomass (Unrean et al., 2018).

51 Focusing on the different types of fuels, hydrogen is a high quality energy carrier that can be  
52 used with high efficiency (Frolov et al., 2013) and is expected to acquire great importance in  
53 next generation fuels (Alipour-Moghadam et al., 2014). This fact, together with declining fossil  
54 fuel reserves, steadily rising prices and increasing pollution make hydrogen a very attractive  
55 product for meeting global energy demand (Khaodee et al., 2011).

56 However, the environmental profile of hydrogen-based energy systems is as "clean" or "dirty"  
57 depending on the scheme of conversion (Rabenstein and Hacker, 2008). The traditional  
58 schemes producing H<sub>2</sub> from natural gas are a major source of CO<sub>2</sub>, with emissions of  
59 approximately 10-12 kg of CO<sub>2</sub> per kg of H<sub>2</sub> (Spath and Mann, 2001). Traditional plants produce  
60 hydrogen by catalytic steam reforming of natural gas, which is a mature technology and is the

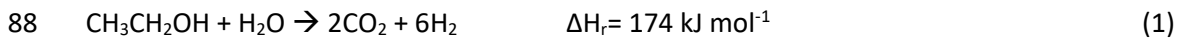
61 pathway by which most hydrogen is produced today. Because of this, reducing CO<sub>2</sub> emissions  
62 associated with hydrogen production would result in a considerable reduction of pollution  
63 (Salkuyeh et al., 2018).

64 In this sense, fuel cells technology and the use of hydrogen are proposed as one of the most  
65 promising environmental solutions in relation to the reduction of global emissions (Díaz  
66 Alvarado and Gracia, 2010). Fuel cells are devices that electrochemically convert chemical  
67 energy from fuels into electricity (Morales et al., 2010). Among the different types of fuel cells,  
68 the Solid Oxide Fuel Cell (SOFC) is the most efficient, due to its high operating temperatures  
69 and the fact that it is not poisoned with CO (Hernández and Kafarov, 2009). When this type of  
70 battery is used, an efficiency around 50% can be obtained (Strazza et al., 2015); in addition, an  
71 efficiency of 70% can be achieved if cogeneration system is used (Strazza et al., 2010).

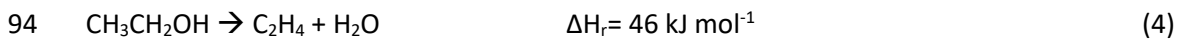
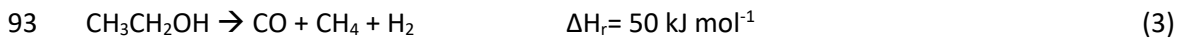
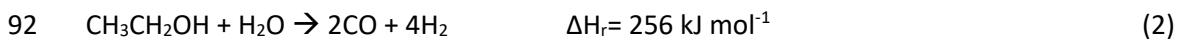
72 Hydrogen production from renewable sources such as poplar (Susmozas et al., 2016) or willow  
73 wood (González-García et al., 2012), sugar cane (Halleux et al., 2008), sweet potato (Costa et  
74 al., 2018), sorghum (Aguilar-Sánchez et al., 2018) or sugar beet (Luo et al., 2009) have been  
75 investigated as the first actions to achieve a significant reduction of environmental impacts  
76 (Salkuyeh et al., 2018). Hydrogen can be obtained from different feedstocks through steam  
77 reforming (Braga et al., 2016; López et al., 2019; Zheng et al., 2019), autothermal reforming  
78 (Khila et al., 2017; Spallina et al., 2018; Xue et al., 2017) and aqueous phase reforming  
79 (Coronado et al., 2018; Esteve-Adell et al., 2017; García et al., 2018), among them, steam  
80 reforming is the most common, as almost 90% of H<sub>2</sub> is produced by natural gas reforming. It  
81 also has the highest conversion efficiency, around 70% (Haryanto et al., 2005).

82 Steam reforming of natural gas is the most popular method for producing commercial  
83 hydrogen that currently covers about 50% of global hydrogen demand (Anzelmo et al., 2018)  
84 and is sometimes referred to as steam methane reforming (SMR). Steam reforming is an  
85 endothermic process based on the reaction of gas with steam at high temperature and

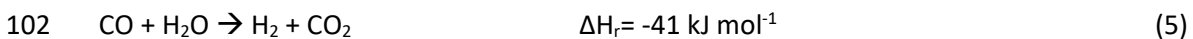
86 moderate pressure. In this way, the chemical reaction taking place leads to hydrogen and  
87 carbon dioxide (Reaction 1):



89 However, depending on the reaction mixture and operating conditions in the reactor, another  
90 route can be followed, producing undesirable products (Ni et al., 2007), such as carbon  
91 monoxide (Reaction 2), methane (Reaction 3) or ethylene (Reaction 4):



95 Once the process is complete, the output stream must undergo purification treatment to avoid  
96 the presence of by-products such as methane and carbon monoxide. The removal of CO is an  
97 important step because it normally poisons the catalyst in fuel cells, that is why CO is removed  
98 first by the Water Gas Shift (WGS) reaction (Reaction 5). WGS is an exothermic and reversible  
99 reaction usually used in industry to produce high purity hydrogen (Alamolhoda et al., 2019).  
100 Normally, 90% of the CO outflowing from the steam reforming reactor can be converted to  
101 CO<sub>2</sub> (Rossetti et al., 2015b).



103 Following this stage, the Pressure Swing Adsorption (PSA) process separates hydrogen from  
104 the rest of the components of the gas stream with 85% efficiency, obtaining H<sub>2</sub> with 99% purity  
105 (Susmozas et al., 2013), and whose energy content is usually higher than that of the natural  
106 gas used for reforming.

107 The implementation of other alternatives of hydrogen production can be considered from  
108 alternative raw materials, such as alcohols (Rossetti et al., 2015a). In addition to steam  
109 reforming of ethanol, studies have been published on steam reforming of different types of

110 alcohol with the aim of producing hydrogen. Some of these alcohols are butanol (Kumar et al.,  
111 2018), propanol (Wang et al., 2015), methanol (Tian et al., 2017) or glycerol (Menezes et al.,  
112 2018) but, even so, the use of ethanol for this purpose offers the best opportunity to produce  
113 hydrogen from renewable sources (Ramírez and Homs, 2008), especially if this ethanol is  
114 derived as residue from other processes. Specifically, the alcoholic wastes from the wine  
115 industry results an attractive raw material due to 65% of world wine production is managed by  
116 European winegrowers mostly small and medium-sized wineries according to the Comité  
117 Européen des Entreprises Vins (CEEV, 2016). Wine production generates large amounts of solid  
118 and liquid wastes, with a serious impact on the environment when they are not adequately  
119 treated. The liquid wastes are processed in distilleries to obtain purified alcohols, but in these  
120 processes, alcoholic purges without commercial value containing impurities separated from  
121 the good quality alcohols are generated. Thus, the process here analysed aims to raise  
122 awareness of the potential of these by-products and their valorization activities as a  
123 sustainable way to produce hydrogen.

124 The main objective of the study is to analyze the potential environmental impacts associated  
125 with the steam reforming of alcoholic waste from distilleries. Quantifying the consumption of  
126 material and energy resources during the life cycle makes it possible to estimate potential  
127 changes and emissions to the environment. The main product of the process is hydrogen ( $H_2$ ),  
128 along with a certain amount of carbon monoxide (CO), carbon dioxide ( $CO_2$ ), methane ( $CH_4$ )  
129 and ethylene ( $C_2H_4$ ), which accounts for a proportion lower than 30%. This output stream is  
130 used to produce energy in a 3 kW SOFC.

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

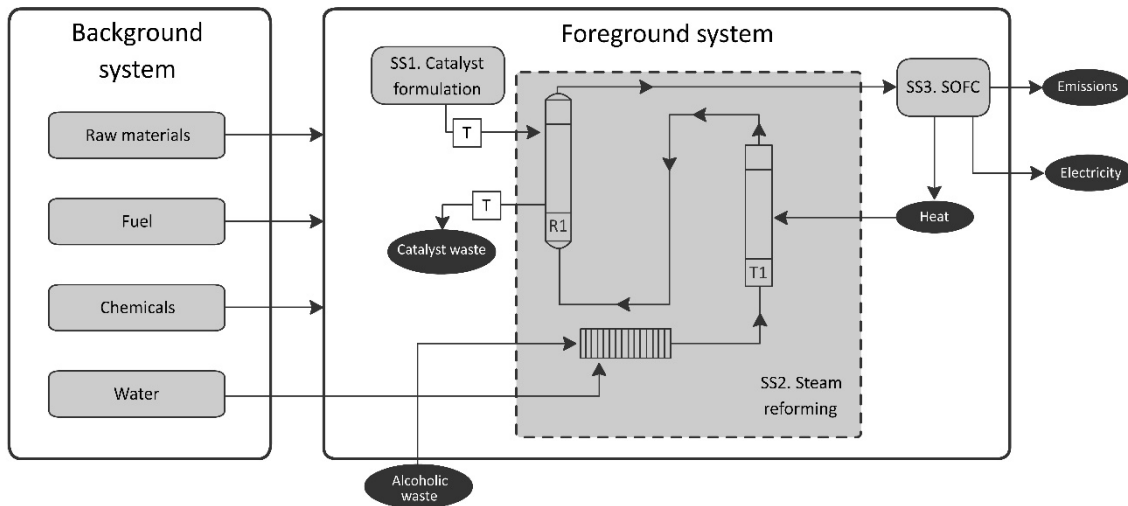
### 132 *2.1. Definition of goal and scope*

133 The Life Cycle Analysis methodology has been considered as a fundamental tool in the analysis  
134 of the environmental profile associated with the steam reforming of alcoholic waste from

135 distilleries in order to identify key environmental performance indicators. In distilleries, alcohol  
136 can be extracted from some wines that cannot be marketed. During this distillation process,  
137 an ethanol-rich fraction is obtained, but also a residual fraction that remains in the distiller's  
138 tail, which is the residue used in this study.

139 Figure 1 presents the block diagram of the process, identifying the system boundaries, the  
140 different subsystems considered and the main inputs and outputs of the system.

141 No infrastructure process was considered in the evaluation, since the environmental impacts  
142 per process unit, from installation, construction, decommissioning, infrastructure, machinery,  
143 etc., have been considered negligible during the lifetime of this type of facilities. This has been  
144 a common practice in other life cycle assessment studies of biorefineries (Jeswani et al., 2015;  
145 Karlsson et al., 2014). However, this study has taken into account the manufacture of the  
146 catalyst and the SOFC phase, due to the fact that their useful life is clearly shorter than that of  
147 large installations.



148

149 **Figure 1.** System boundaries of the reforming system for the valorization of the alcoholic  
150 waste. Caption: T: Transport; R1: Reforming reactor; T1: Heat exchanger.



151 The foreground system includes the process units that are the direct object of this study. For  
152 the purposes of the study, three subsystems (SS) have been considered, which are detailed  
153 below:

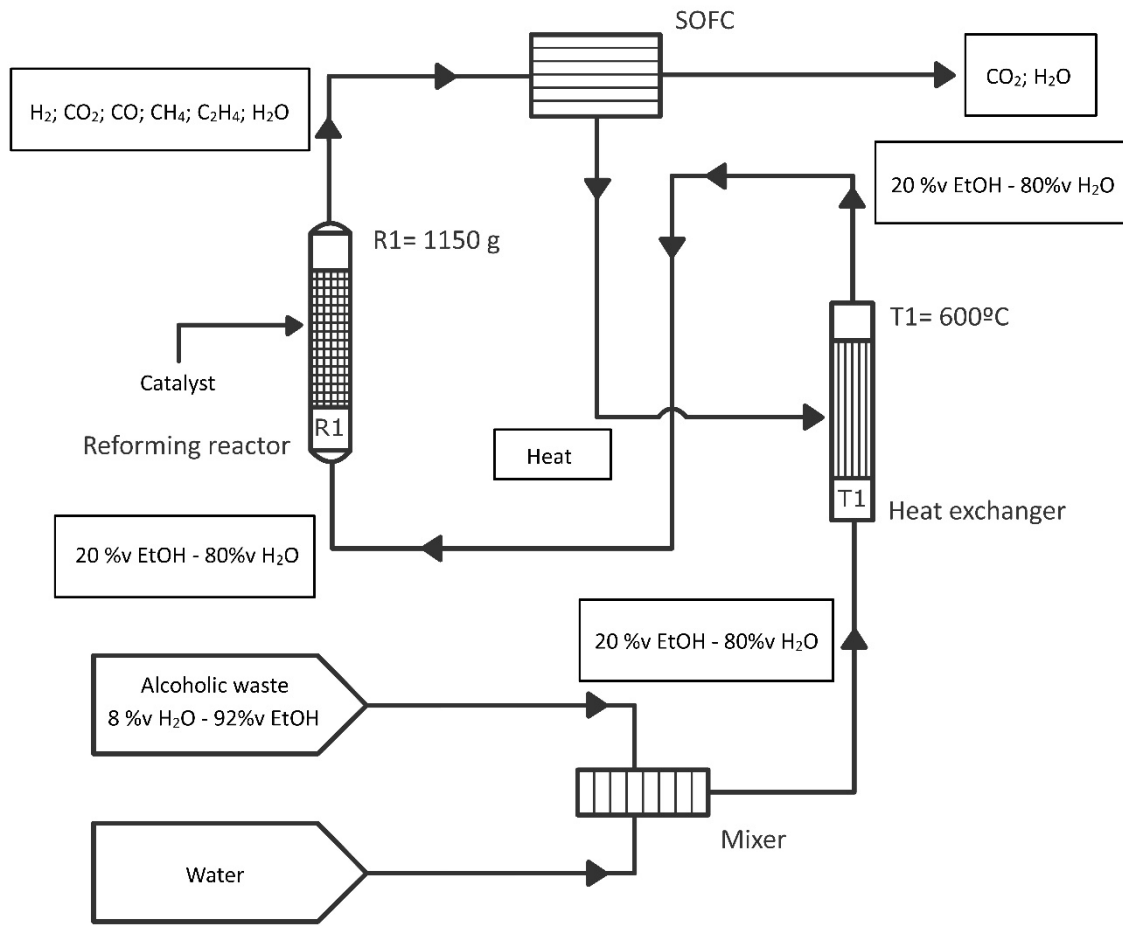
154 Subsystem 1: Catalyst formulation. This subsystem considers all the materials necessary for the  
155 manufacture of the catalyst used in the reforming reactor (Menor et al., 2017). The catalyst is  
156 composed of a sepiolite base with Nickel (15% weight) and Lanthanum (1% weight). Its  
157 considered useful life is 20 months, regenerating every 4 months. The transport of the catalyst  
158 to the plant is also considered, taking as distance 100 km.

159 Subsystem 2: Steam reforming. This process includes all the inputs needed to perform the  
160 steam reforming process. These inputs are mainly electricity, water and alcohol residues from  
161 distilleries. The transport of alcoholic waste to the plant is not included, as this type of facility  
162 is designed to be included in the distillery. The waste produced in this subsystem is the catalyst  
163 spent at the end of its useful life and is considered 100 km as the average transport to the  
164 landfill.

165 Subsystem 3: SOFC. This subsystem includes the net production of electricity in the SOFC using  
166 the SS2 gas stream as feed. At the exit of this subsystem, CO<sub>2</sub> and H<sub>2</sub>O emissions are derived  
167 from the reactions taking place with CO and CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> inside the SOFC. The electricity  
168 produced is fed into the grid. The SOFC works at a high temperature of around 600°C and  
169 produces a large amount of heat, as represented in Figures 1 and 2, this heat is redirected to  
170 the system and used to heat the stream entering the reforming reactor. This subsystem  
171 includes the SOFC manufacturing stage. Gas stream purifying processes are not included  
172 because SOFC are not poisoned by the presence of CO (Hernández and Kafarov, 2009). This  
173 type of device directly provides electricity from the chemical reaction taking place. The  
174 electrodes of this type of battery are catalytic, so they are relatively stable and are not  
175 consumed (Fragiacomo et al., 2018).

176 The Background System includes the production of raw materials, fuel, chemicals and water  
177 used in the process, as well as the consumption of fuel used in the transportation of materials.  
178 As the basis for the calculation of Functional Unit (FU), the treatment of 1 tonne of alcoholic  
179 waste in the facility was chosen, which will be taken as a reference for all the inputs and  
180 products of the system as well as the emissions, energy consumption and transport associated  
181 with this process (ISO, 2006a, 2006b).

182 The description of the steam reforming process is presented in detail in Figure 2. The waste  
183 from the distillery enters the plant with approximately 92% v/v ethanol, to which water is  
184 added to reach 80% v/v water and 20% v/ ethanol. The steam-to-carbon molar ratio (S/C ratio)  
185 used in most cases is 3:1 (Jeon et al., 2018), but in this case a steam-to-carbon ratio of 6:1 was  
186 considered. This steam-to-carbon ratio increases the production of CO<sub>2</sub> and H<sub>2</sub> and reduces the  
187 formation of the undesirable products mentioned in Equations 2-4, but increases the heat  
188 necessary to vaporize the water/ethanol mixture. However, since this heat is supplied by the  
189 residual heat produced in the SOFC, the use of additional fuel is not necessary. The stream  
190 passes through a heat exchanger where it is heated up to 600°C, the temperature required for  
191 the inlet stream of the reforming reactor. The output of the reactor is a gas stream comprised  
192 by H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O and a minor proportion of C<sub>2</sub>H<sub>4</sub>. This stream is fed to the SOCF, where  
193 heat and electricity are produced. The high temperature stream is recycled in the system to  
194 heat the water and ethanol feed, reducing energy consumption. The electricity produced is fed  
195 into the grid.



196

197 **Figure 2.** Detailed scheme of Subsystem 2, showing the composition of the different streams  
 198 and their temperature.

199 *2.2. Data acquisition and life cycle inventory*

200 Life cycle inventory involves the collection of qualitative and/or quantitative input/output data  
 201 for the system. In the case of Subsystem 1, catalyst manufacturing data were obtained from a  
 202 previous study about the formulation of a sepiolite-based catalyst with the addition of Ni  
 203 (Menor et al., 2017), although the amount of catalyst used is a primary data. In relation to the  
 204 Steam Reforming Subsystem, all the information on the consumption of the process comes  
 205 from primary data, except electricity consumption, which was obtained from a study about the  
 206 life-cycle assessment of biomass gasification as an alternative to steam methane reforming for  
 207 hydrogen production (Susmozas et al., 2013); where an electric consumption of 1.35 kWh per  
 208 kg H<sub>2</sub> produced was considered. Finally, the inventory of Subsystem 3 has been obtained from

209 various scientific publications. (Strazza et al., 2015, 2010) conducted several studies to assess  
 210 the environmental profile of two SOFC systems: one with 230 kW and other one with 20 kW  
 211 system. (Lee et al., 2015) obtained the environmental impact of a 100 kW SOFC power  
 212 generation system. The different life cycle inventories published in the above-mentioned  
 213 manuscripts were adapted to the characteristics of the battery used in the study. Background  
 214 system processes have been taken from Ecoinvent® database. Tables 1-3 present the life cycle  
 215 inventory of the different subsystem considered in this study.

216 **Table 1.** Life cycle inventory for Subsystem 1. Catalyst formulation per FU

Inputs from Technosphere		Outputs to Technosphere	
<b>Materials</b>	<b>kg</b>	<b>Products</b>	<b>kg</b>
MiliQ water	2.63	Catalyst to SS2	$8.15 \cdot 10^{-2}$
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	$6.05 \cdot 10^{-2}$	<b>Wastes</b>	<b>l</b>
La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	$2.54 \cdot 10^{-3}$	Wastewater	2.63
Sepiolite	$6.84 \cdot 10^{-2}$		
<b>Energy</b>	<b>kWh</b>		
Electricity	0.72		
<b>Transport</b>	<b>kg·km</b>		
Catalyst to plant	8.15		

217

218 **Table 2.** Inventory for subsystem S2. Steam Reforming per FU

Inputs from Technosphere			
<b>Materials</b>	<b>kg</b>	<b>Energy</b>	<b>MWh</b>
Water	4470	Electricity	$2.49 \cdot 10^{-1}$
Alcoholic waste	1000	<b>Transport</b>	<b>kg·km</b>
Catalyst from SS1	$8.15 \cdot 10^{-2}$	Catalyst waste to landfill	8.15
Outputs to Technosphere			
<b>Products</b>	<b>kg</b>	<b>Waste</b>	<b>kg</b>
Gas stream to SS3	5509	Catalyst waste to landfill	$8.15 \cdot 10^{-2}$

219

220

221

222 **Table 3.** Life cycle inventory for Subsystem SS3. SOFC per FU

<b>Inputs from Technosphere</b>			
<b>Materials</b>	<b>kg</b>	<b>Materials</b>	<b>kg</b>
LaMnO <sub>3</sub>	10.05	Polyethyleneglycol	0.03
LaCrO <sub>3</sub>	0.15	Dibutylphthalat	0.03
Zirconium chloride	1.96	Water, deionised	2.32
Yttrium chloride	0.29	Nitric acid	13.45
Zirconium oxide	0.18	Chlorine	1.61
Nickel oxide	0.18	Petroleum coke	0.26
Nickel	2.36·10 <sup>-4</sup>	Urea, as N	6.61
Ethanol	0.44	Gas stream from SS2	5509
Polyvinilbutyral	0.07	<b>Transport</b>	<b>kg·km</b>
<b>Energy</b>	<b>MJ</b>	Freight rail	31.92
Heating, natural gas	50.76	Lorry > 16t	5.67
Spray drying, natural gas	560.71	Transoceanic freight	202.09
<b>Outputs to Technosphere</b>		<b>Outputs to Nature</b>	
<b>Products</b>	<b>MWh</b>	<b>Emissions</b>	<b>kg</b>
Electricity	1.81·10 <sup>-1</sup>	CO <sub>2</sub> , biogenic	1800
		CO <sub>2</sub>	33.10
		H <sub>2</sub> O	5810

223

224 *2.3. Life Cycle Impact Analysis: Methodology*

225 Simapro 8.5.2 (PRé Consultants, 2017) has been the software used for the implementation of  
 226 the Life Cycle Inventory. To analyze the inputs and outputs of the Life Cycle Inventory, the  
 227 Classification and Characterization guidelines defined by ISO 14040 and ISO 14044 (ISO, 2006a,  
 228 2006b) were followed. The environmental results have been presented in terms of the  
 229 following impact categories of the ReCiPe methodology: Climate Change (CC), Ozone Layer  
 230 Depletion (OD), Terrestrial Acidification (TA), Freshwater Eutrophication (FE), Marine  
 231 Eutrophication (ME), Human Toxicity (HT), Photochemical Oxidant Formation (POF), Particulate  
 232 Matter Formation (PMF), Terrestrial Ecotoxicity (TET), Freshwater Ecotoxicity (FET), Marine  
 233 Ecotoxicity (MET) and Fossil Fuel Depletion (FD).

234

235 **3. Results and Discussion**

236 *3.1. Environmental characterization*

237 The environmental characterization of the alcoholic waste steam reforming resulted in the  
 238 impacts reported in Table 4. All impacts in Table 4 are attributed to the Functional Unit (1  
 239 tonne feedstock).

240 **Table 4.** Characterized results of the system per FU

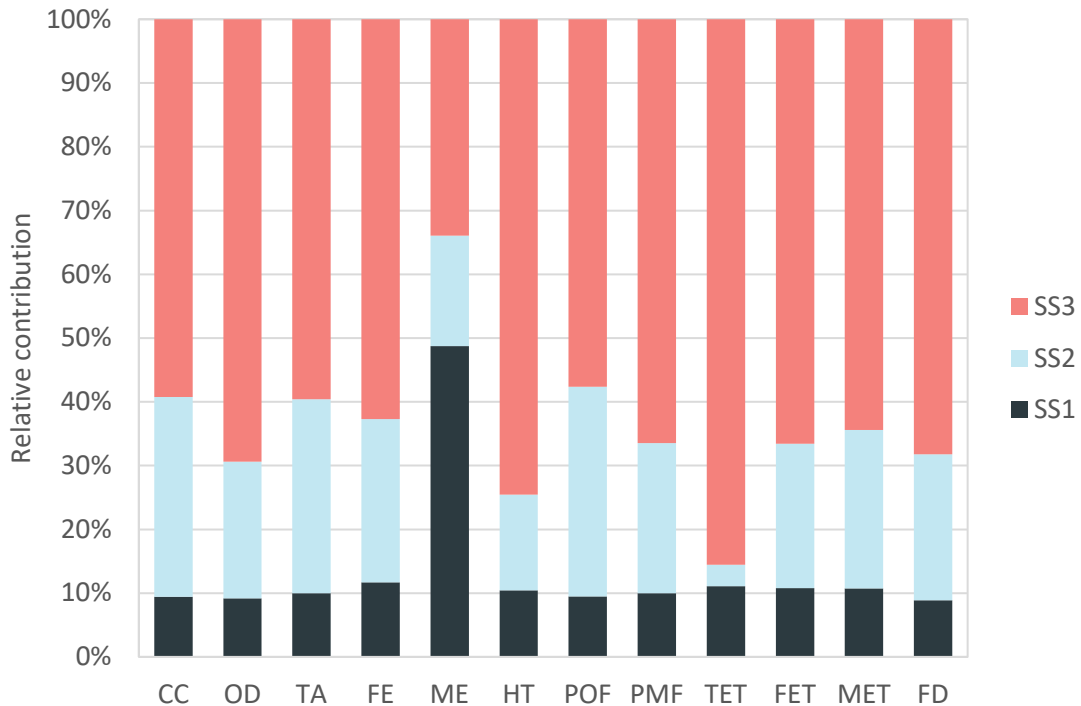
Impact category	Units	SS1	SS2	SS3	Total
CC	kg CO <sub>2</sub> eq	33.08	109.91	207.79	350.78
OD	kg CFC-11 eq	$5.98 \cdot 10^{-6}$	$1.40 \cdot 10^{-5}$	$4.52 \cdot 10^{-5}$	$6.52 \cdot 10^{-5}$
TA	kg SO <sub>2</sub> eq	0.22	0.67	1.32	2.21
FE	kg P eq	$1.41 \cdot 10^{-2}$	$3.09 \cdot 10^{-2}$	$7.56 \cdot 10^{-2}$	$1.21 \cdot 10^{-1}$
ME	kg N eq	$6.08 \cdot 10^{-2}$	$2.16 \cdot 10^{-2}$	$4.23 \cdot 10^{-2}$	$1.25 \cdot 10^{-1}$
HT	kg 1,4-DB eq	17.11	24.57	122.23	163.91
POF	kg NMVOC	0.10	0.35	0.62	1.07
PMF	kg PM10 eq	0.10	0.24	0.66	1.00
TET	kg 1,4-DB eq	$1.04 \cdot 10^{-2}$	$3.15 \cdot 10^{-3}$	$8.05 \cdot 10^{-2}$	$9.41 \cdot 10^{-2}$
FET	kg 1,4-DB eq	0.76	1.59	4.67	7.01
MET	kg 1,4-DB eq	0.61	1.42	3.68	5.71
FD	kg oil eq	11.65	30.11	89.78	131.55

241

242 The SOFC is the main contributor to the Climate Change (CC) category, since this subsystem  
 243 comprises several processes necessary for the manufacture of the main components. In SS3,  
 244 direct emissions into the atmosphere are quantified, directly from the alcoholic stream,  
 245 residue produced from grape fermentation. Therefore, CO<sub>2</sub> emissions from SS3 should not be  
 246 considered as fossil carbon, but as biogenic CO<sub>2</sub>. This decision agrees with a study on the  
 247 production of hydrogen and electricity by reforming supercritical water from bioglycerol  
 248 feedstock (Galera and Gutiérrez-Ortiz, 2015). If CO<sub>2</sub> was not considered biogenic, direct CO<sub>2</sub>  
 249 emissions would represent almost 60% of environmental impact in the climate change  
 250 category. Therefore, the final impact on this category would be 2146 kg CO<sub>2</sub> eq per tonne of  
 251 alcoholic waste processed at the facility.

252 The Ozone Layer Depletion category has fairly low values in all subsystems. Freshwater and  
253 Marine Eutrophication (FE and ME) show similar behavior, as they are influenced by the same  
254 type of substances. The impact value in these categories is relatively similar in all subsystems,  
255 which makes the final impact value low. Human Toxicity (HT) and Fossil Depletion (FD) have  
256 relatively high levels compared to the rest of the impact categories. The reason is the  
257 formulation of catalysts and the manufacture of SOFC, since heavy metals and hazardous  
258 substances are required that cause a high impact in the HT category. As for the FD category, its  
259 value is related to the high consumption of fossil fuels associated with the formulation of  
260 catalysts and the manufacture of SOFC.

261 The specific contribution of each subsystem to the impacts calculated for the system is shown  
262 in Figure 3. The manufacture and operation of the SOFC (SS3) was found to dominate almost  
263 all impact categories, with percentages ranging from 57.7% in Photochemical Oxidant  
264 Formation (POF) to 85.6% in Terrestrial Ecotoxicity (TET). Additionally, the steam reforming  
265 subsystem (SS2) showed a significant contribution to Climate Change (31,3%), Terrestrial  
266 Acidification (30,4%) and Photochemical Oxidant Formation (32,9%). The remaining subsystem  
267 (SS1) accounted for a contribution percentage around 10%, except for ME, where the  
268 contribution was higher than 45%.



269

270 **Figure 3.** Relative contribution (%) of the different subsystems to the total environmental  
 271 impact

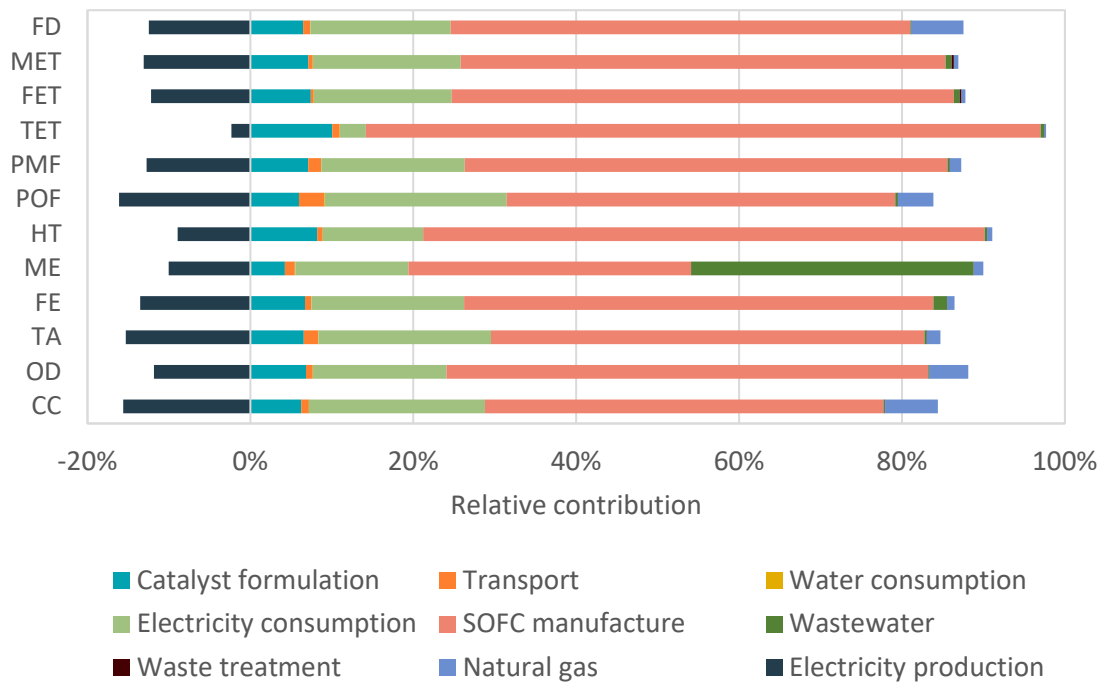
272 In order to highlight the processes with the highest environmental impact on the life cycle  
 273 performance of the system, the individual contributions to the impact are broken down in  
 274 Figure 4. These results show that SOFC manufacturing is the major contribution in almost all  
 275 impact categories, except for ME. Therefore, the manufacture of SOFC is the main hotspot of  
 276 the system and must have the highest priority in the improvement actions from the  
 277 environmental point of view.

278 The second largest contributor to the total environmental impact is electricity consumption,  
 279 with contributions percentage ranging from 15% in HT to 32.9% in POF. If electricity  
 280 production is taken into account, its contribution to environmental impact decreases  
 281 significantly to 4.2% and 9.1% in HT and POF, respectively. The formulation of catalysts  
 282 presented a uniform distribution of environmental impacts in all categories, with contributions  
 283 always below 10.6%. The consumption of natural gas to heat the process is only responsible  
 284 for a maximum of 9.4% in CC and 8.5% in FD, but in the rest of the impact categories, their



285 contributions never exceed 6%. The rest of the substances (transport, water consumption and  
 286 waste treatment) contributed practically insignificantly to the environmental impact.

287 Wastewater treatment is the main contributor to the ME impact, due to the high amount of  
 288 nitrogen-based compounds such as nitrites and nitrates that are discharged in the treated  
 289 effluent. This may explain, as seen in Figure 3, why the main contributor to the ME impact  
 290 category is SS1, due to the wastewater generated during the formulation of the catalyst.



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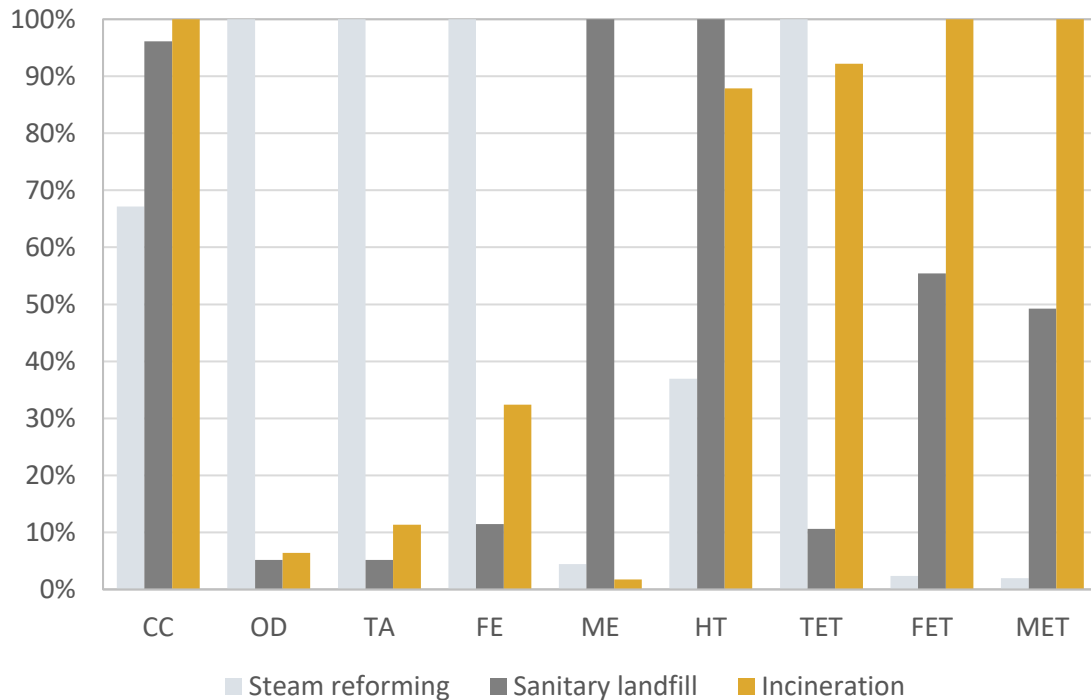
292 **Figure 4.** Relative contribution (%) of the components of alcoholic waste steam reforming to  
 293 the overall impact

294 The environmental profile of alcoholic waste steam reforming is mainly due to two factors. On  
 295 the one hand, the use of a raw material that is considered waste from another process and  
 296 therefore has no associated environmental impact. On the other hand, the production of  
 297 electricity makes it possible to obtain environmental credits that promote a better  
 298 environmental profile.

299

300                    *3.2. Sensitivity analysis*

301    In order to compare the environmental characterization results of some alternative waste  
302    treatments to steam reforming, a sensitivity analysis was performed. The methods selected for  
303    this analysis were landfill and incineration. Note that the inventory data for incineration and  
304    landfill were taken from the Ecoinvent® database. Figure 5 depicts the environmental  
305    performance of the alternative treatments for the alcoholic waste considered. As noted, the  
306    steam reforming scenario potentially implied a more acceptable environmental profile than  
307    the other scenarios, except for Ozone Layer Depletion, Terrestrial Acidification, Freshwater  
308    Eutrophication and Terrestrial Ecotoxicity. In particular, steam reforming makes it possible to  
309    reduce GHG emissions by 33% compared to incineration and by 30% compared to landfill.  
310    Steam reforming is the largest contributor to OD impact for the emission of harmful gases to  
311    the stratospheric ozone layer during some operations such as electricity generation or  
312    chemical production. Regarding Terrestrial Acidification and Freshwater Eutrophication, steam  
313    reforming presents the worst environmental performance. The consumption of Ni-based  
314    compounds in the manufacture of SOFC and some processes derived from the extraction of  
315    lanthanum for SOFC are the responsible processes of the poor performance in TA and FE  
316    respectively. With respect to TET, steam reforming has worse results, but if the three  
317    ecotoxicity categories (TTE, MET and FET) are considered, the environmental impact of steam  
318    reforming is lower, improving 95.8% with respect to incineration and 97.8% with respect to the  
319    sanitary landfill.



320

321 **Figure 5.** Comparative environmental profile of the alternative treatments for alcoholic waste  
 322 considering 1 tonne as functional unit

323

### 3.3. Comparative analysis

324

In addition to the basic scheme, a comparison was made with some processes published in the

325

scientific literature. The FU was changed to 1 kg of hydrogen produced in the plant with 99.9

326

vol% purity by steam reforming (Figure 6), in agreement with other reforming studies using

327

other raw materials for hydrogen production (Hajjaji et al., 2016, 2013; Khila et al., 2016;

328

Susmozas et al., 2016, 2015, 2013), thus allowing the comparison of the environmental profile

329

of different processes. Therefore, the new facility configuration does not consider the

330

operation of the SOFC, consequently the output stream of the system is led to a purification

331

system: First, the WGS process removes carbon monoxide and produces a small amount of

332

additional hydrogen. Additionally, in a COPROX reactor the remaining CO can be further

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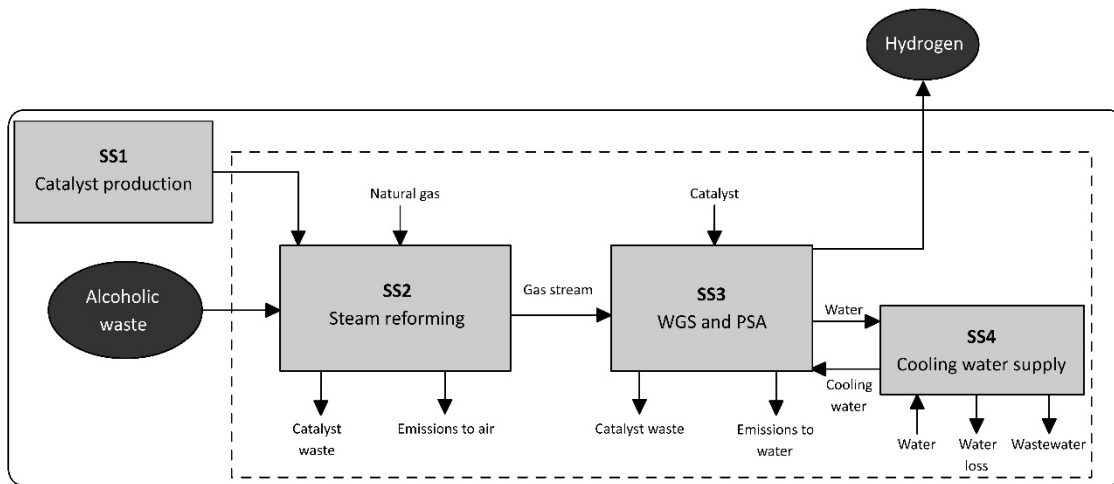
reduced to CO<sub>2</sub> in the presence of oxygen. Finally, the PSA process separates H<sub>2</sub> from the rest

334

of the gases in the stream, obtaining H<sub>2</sub> with 99% purity. Therefore, two additional subsystems

335

were introduced to purify the output hydrogen stream (SS3) and provide cooling water (SS4)



336

337 **Figure 6.** New flowchart considered to compare the steam reforming of alcoholic waste with  
 338 other published studies.

339 The following processes have been considered: SMR-H<sub>2</sub>: Steam reforming of methane obtained  
 340 from natural gas (Susmozas et al., 2013). PG-H<sub>2</sub>: Poplar biomass gasification. The system  
 341 includes the cultivation of poplar and its transport to the plant. Once in the plant are included  
 342 all the operations necessary to obtain hydrogen and the production of electricity from the  
 343 steam produced in the system (Susmozas et al., 2013). PG&C-H<sub>2</sub>: Gasification of poplar  
 344 biomass, as mentioned above, but includes carbon fixation during the cultivation stage  
 345 (Susmozas et al., 2016). GSR-H<sub>2</sub>: Glycerol reforming, obtained as a co-product of biodiesel  
 346 production by transesterification of rapeseed oil. Carbon sequestration during oil production is  
 347 considered (Susmozas et al., 2015). BSR-H<sub>2</sub>: Biofuel reforming, including also carbon fixation  
 348 produced during the growth of biomass used for biofuel (Susmozas et al., 2015). SBR-H<sub>2</sub>: Steam  
 349 reforming of bioethanol, including bioethanol production (Hajjaji et al., 2016). BAR-H<sub>2</sub>:  
 350 Autothermal reforming of bioethanol (Khila et al., 2016).

351 In order to carry out the comparative analysis, life cycle inventories were modified. In relation  
 352 to the type and quantity of reaction catalyst, the WGS data were obtained from (Compagnoni  
 353 et al., 2017). All the necessary data to measure the inputs and outputs in SS3. WGS and PSA

354 and SS4. Cooling water supply were obtained from (Susmozas et al., 2015, 2013). Inventory  
 355 data of WGS, PSA and Cooling water supply can be found in Table 5.

356 **Table 5.** New life cycle inventory to compare the steam reforming of alcoholic wastes with  
 357 other published processes

Inputs from Technosphere		Outputs to Technosphere	
<b>Materials</b>	<b>kg</b>	<b>Products</b>	<b>kg</b>
Alcoholic waste	5.42	H <sub>2</sub>	1.00
Water	24.21	<b>Emissions</b>	<b>kg</b>
SR catalyst	4.41·10 <sup>-4</sup>	CO <sub>2</sub>	8.16
WGS catalyst	1.11·10 <sup>-3</sup>	CH <sub>4</sub>	0.45
<b>Energy</b>	<b>kWh</b>	C <sub>2</sub> H <sub>4</sub>	9.41·10 <sup>-3</sup>
Electricity	1.36	CO	1.97
<b>Transport</b>	<b>t·km</b>	<b>Wastes</b>	<b>kg</b>
Road	0.48	SR catalyst to landfill	1.11·10 <sup>-3</sup>
		WGS catalyst to landfill	4.41·10 <sup>-4</sup>
		Wastewater from WGS	4.61

358

359 The results of the comparison between steam reforming of alcoholic residues and other  
 360 related processes are presented in terms of the impact categories of the CML methodology  
 361 Global warming potential (GWP – kg CO<sub>2</sub> eq), Depletion of abiotic resources (ADP – kg Sb eq),  
 362 Ozone layer depletion (ODP – kg CFC-11 eq), Photochemical oxidation (POFP – kg C<sub>2</sub>H<sub>4</sub> eq),  
 363 Acidification potential (AP – kg SO<sub>2</sub> eq) and Eutrophication potential (EP – kg PO<sub>4</sub><sup>3-</sup>). The  
 364 magnitudes of the environmental impacts of hydrogen production systems are displayed in  
 365 Table 6, in order to simplify the comparative study, the results are scaled to 100 and  
 366 represented in Figure 7. For example, alcoholic waste steam reforming shows the best results  
 367 in terms of ADP, ODP, AP and EP, but performs worse in GWP and has the worst result in POFC.

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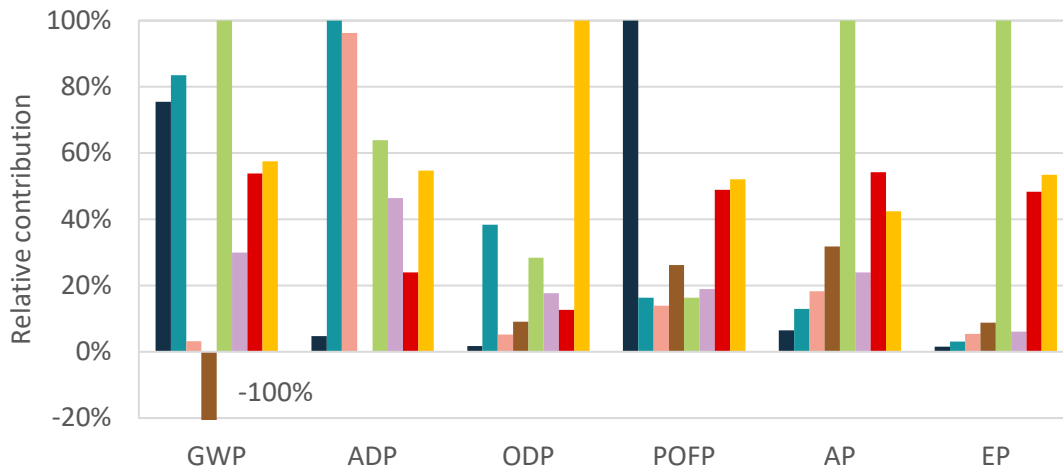
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370

371 **Table 5.** Summarized results of comparative life cycle assessment

Processes	GWP	ADP	ODP	POFP	AP	EP	Reference
Present study	9.55	$4.25 \cdot 10^{-3}$	$5.29 \cdot 10^{-8}$	$3.17 \cdot 10^{-3}$	$4.20 \cdot 10^{-3}$	$8.11 \cdot 10^{-4}$	Present study
SMR-H <sub>2</sub>	10.60	$8.90 \cdot 10^{-2}$	$1.20 \cdot 10^{-6}$	$5.18 \cdot 10^{-4}$	$8.40 \cdot 10^{-3}$	$1.64 \cdot 10^{-3}$	(Susmozas et al., 2013)
PG-H <sub>2</sub>	0.41	$8.57 \cdot 10^{-2}$	$1.62 \cdot 10^{-7}$	$4.40 \cdot 10^{-4}$	$1.19 \cdot 10^{-2}$	$2.85 \cdot 10^{-3}$	(Susmozas et al., 2013)
PG&C-H <sub>2</sub>	-14.60	---	$2.85 \cdot 10^{-7}$	$8.31 \cdot 10^{-4}$	$2.07 \cdot 10^{-2}$	$4.60 \cdot 10^{-3}$	(Susmozas et al., 2016)
GSR-H <sub>2</sub>	12.70	$5.69 \cdot 10^{-2}$	$8.90 \cdot 10^{-7}$	$5.16 \cdot 10^{-4}$	$6.51 \cdot 10^{-2}$	$5.26 \cdot 10^{-2}$	(Susmozas et al., 2015)
BSR-H <sub>2</sub>	3.79	$4.13 \cdot 10^{-2}$	$5.54 \cdot 10^{-7}$	$6.00 \cdot 10^{-4}$	$1.56 \cdot 10^{-2}$	$3.20 \cdot 10^{-3}$	(Susmozas et al., 2015)
SBR-H <sub>2</sub>	6.81	$2.13 \cdot 10^{-2}$	$3.96 \cdot 10^{-7}$	$1.55 \cdot 10^{-3}$	$3.53 \cdot 10^{-2}$	$2.54 \cdot 10^{-2}$	(Hajjaji et al., 2016)
BAR-H <sub>2</sub>	7.27	$4.87 \cdot 10^{-2}$	$3.13 \cdot 10^{-6}$	$1.65 \cdot 10^{-3}$	$2.76 \cdot 10^{-2}$	$2.81 \cdot 10^{-2}$	(Khila et al., 2016)

372



373

374 **Figure 7.** Comparison (in %) of different reforming processes to obtain hydrogen. Caption: Dark  
 375 Blue: Present studio; Light Blue: SMR-H<sub>2</sub>; Pink: PG-H<sub>2</sub>; Brown: PG&C-H<sub>2</sub>; Green: GSR-H<sub>2</sub>; Purple:  
 376 BSR-H<sub>2</sub>; Red: SBR-H<sub>2</sub>; Yellow: BAR-H<sub>2</sub>.

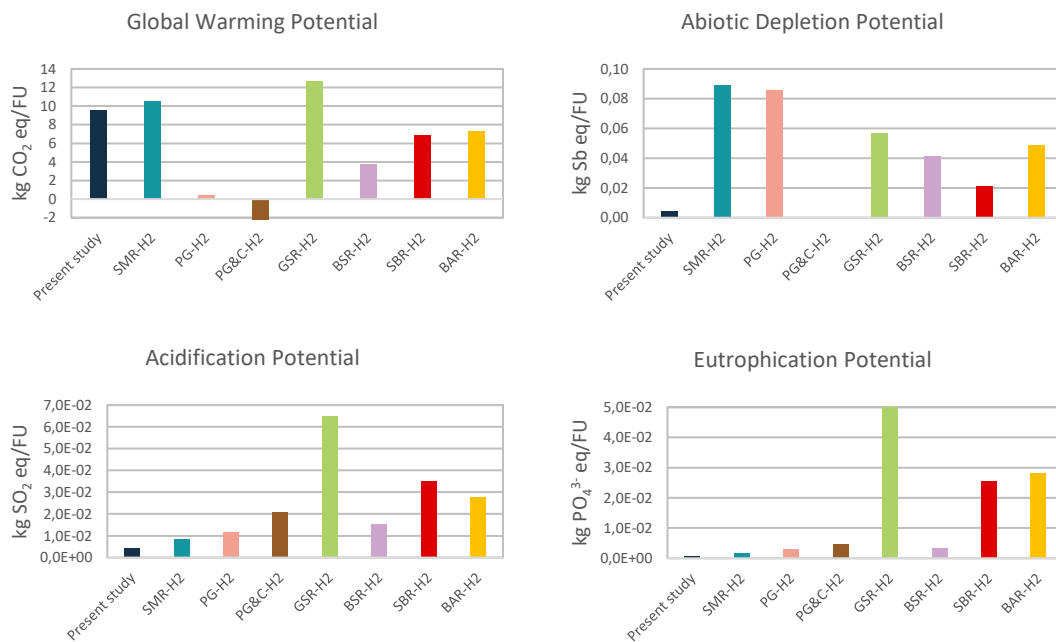
377 The comparison between the present study and other published processes is possible because  
 378 the environmental performance of the different studies is published in some LCA studies with  
 379 a methodological framework consistent with this study. Steam reforming of alcoholic residues  
 380 has the highest value in POF, due to direct emissions of CH<sub>4</sub>, which occur in relatively high  
 381 quantities during steam reforming. However, this process performs well in terms of ODP with a  
 382 value around 2% of BAR-H<sub>2</sub>, which is the process with the worst environmental performance in  
 383 this category.

384 Four impact categories are detailed in this section: Depletion of abiotic resources (ADP),  
385 Acidification potential (AP), Eutrophication potential (EP) and Global warming potential (GWP).  
386 These are the most common and well-established categories for assessing bioenergy systems  
387 in LCA studies (Cherubini and Strømman, 2011; Muench and Guenther, 2013; Peters et al.,  
388 2015). The total GHG emissions of the system are estimated at approximately 9.55 kg CO<sub>2</sub> eq  
389 per kg of H<sub>2</sub> produced. As can be seen in Figure 8.a, this value is relatively higher than that of  
390 other technologies but is considerably lower than that of a conventional H<sub>2</sub> production system  
391 (SMR-H<sub>2</sub>). Approximately 90% of these emissions are attributed to direct methane emissions  
392 from the reforming reactor, as CH<sub>4</sub> is 21 times more likely to affect GWP over a 100-year  
393 period, according to IPCC. The lowest value in this category corresponds to PG&G-H<sub>2</sub>, since this  
394 process considers CO<sub>2</sub> capture during biomass cultivation. This explains the importance of  
395 system boundaries in an LCA study, since PG&G-H<sub>2</sub> covers from biomass cultivation to  
396 hydrogen production with CO<sub>2</sub> capture. However, in the present study the limit of the system  
397 ranges from alcoholic residues entering the plant to the production of electricity, so carbon  
398 sequestration during biomass cultivation is not considered.

399 Some metals, minerals and fossil fuels are used in all H<sub>2</sub> production systems. Figure 8b shows  
400 that fossil methane to hydrogen system (SMR-H<sub>2</sub>) has the greatest impact on ADP, as expected,  
401 due to the large consumption of fossil fuels in the reforming process. H<sub>2</sub> produced from  
402 bioethanol consumes considerable non-renewable resources throughout the life cycle when  
403 ethanol production phases are considered (Hajjaji et al., 2013). However, in this study, steam  
404 reforming of alcoholic waste (mainly ethanol) is the best process in terms of ADP because this  
405 ethanol is a waste derived from another process that has no associated impact. With respect  
406 to Acidification Potential and Eutrophication Potential (Figure 8c and 8d), steam reforming of  
407 alcoholic waste presents the best results. The processes with the highest impact in these  
408 impact categories are those that take into account the cultivation phase (SBR-H<sub>2</sub>, BAR-H<sub>2</sub> and

409 GSR-H<sub>2</sub>), mainly due to the use of fertilizers containing nitrate, ammonia and phosphate in the  
 410 production of bioethanol from wheat or biodiesel from rapeseed oil.

411



412

413

**Figure 8.** Comparison of the environmental impacts in GWP, ADP, AP and EP categories

414

#### 4. Conclusions

415

From a life cycle perspective, the results suggest that this type of energy systems that produce

416

hydrogen from alcoholic waste through steam reforming has good environmental

417

performance. Overall, steam reforming of this type of alcoholic waste for energy production

418

could play a significant role in future energy systems.

419

The SOFC is the main contributor to environmental impact in most impact categories.

420

Analysing the different processes, the manufacture of SOFC is the process with the greatest

421

environmental impact in all impact categories except in ME, where wastewater treatment is

422

the main contributor. The sensitivity analysis shows the promising performance of this waste

423

treatment, since the treatment of 1 tonne of alcoholic waste produces 351 kg of CO<sub>2</sub> eq, this

424

result is 33% and 30% better than incineration and sanitary landfill respectively.

425

It is clear that Life Cycle Assessment is a useful tool to determine the environmental

426

performance of steam reforming of alcoholic waste to produce electricity. However, these



427 results have been obtained by evaluating the data taken on a laboratory scale, and more  
428 studies on a larger scale will be needed in the future to determine a more accurate estimate of  
429 the actual environmental profile of the process.

430 Comparative analysis has allowed us to compare this process with others related to the  
431 production of hydrogen from different raw materials. Although steam reforming has some  
432 poor results in GWP and POF due to methane emissions, its environmental performance is  
433 generally better than other processes published in the scientific literature.

434

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