



Article

Life Cycle Performance of Hydrogen Production via Agro-Industrial Residue Gasification—A Small Scale Power Plant Study

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Abstract: This study evaluates the environmental profile of a real biomass-based hydrogen production small-scale (1 MW_{th}) system composed of catalytic candle indirectly heated steam gasifier coupled with zinc oxide (ZnO) guard bed, water gas shift (WGS) and pressure swing absorber (PSA) reactors. Environmental performance from cradle-to-gate was investigated by life cycle assessment (LCA) methodology. Biomass production shows high influence over all impact categories. In the syngas production process, the main impacts observed are global warming potential (GWP) and acidification potential (AP). Flue gas emission from gasifier burner has the largest proportion of total GWP. The residual off gas use in internal combustion engine (ICE) leads to important environmental savings for all categories. Hydrogen renewability score is computed as 90% due to over 100% decline in non-renewable energy demand. Sensitivity analysis shows that increase in hydrogen production efficiency does not necessarily result in decrease in environmental impacts. In addition, economic allocation of environmental charges increases all impact categories, especially AP and photochemical oxidation (POFP).

Keywords: hydrogen production; biomass gasification; life cycle assessment; environmental impact

1. Introduction

Growing concerns about climate change, rising costs of fossil fuel, and the geopolitical uncertainty associated with an uninterrupted energy supply have motivated individuals, organizations and nations to look for substitutes that are clean and renewable [1,2]. Hydrogen (H₂) is, currently, considered as one of the leading candidates in the search alternatives to fossil fuels (FF) [3]. Nevertheless, H₂ is only an energy carrier like electricity and not a primary energy source. It can be produced from a wide variety of energy sources, such as natural gas, coal, biomass, solar (thermal and photovoltaic), etc. [4] and act as a unique energy hub providing low or zero emission in energy use to all energy consuming sectors [5]. However, the environmental performance of hydrogen-production systems highly depends on the type of primary energy and conversion technology used [6]. Among several renewable energy sources, bio-hydrogen is gaining a lot of attraction because of its conversion efficiency with less pollutant generation [7]. In particular, hydrogen production through lignocellulosic biomass residues gasification

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is a promising pathway in terms of global warming impacts and energy security [8–10]. However, although lignocellulosic biomass is a renewable resource, its use does not guarantee an appropriate environmental performance [11] and, even under strategies of using agriculture and forestry residues to avoid emissions from direct and indirect land use change, the feedstock use can potentially cause negative environmental impacts [12]. Therefore, it is requisite to analyze entire biomass to hydrogen production process considering the impacts from the cultivation to the conversion plant.

LCA is a well-established methodology to evaluate the environmental impacts of a product over its life cycle. It is often used to determine the greenhouse gas footprint and minimum selling price in several kinds of processes and in particular regarding biomasses [13]. This is achieved by: (i) gathering all relevant inputs and outputs of the considered system; (ii) evaluating the potential environmental impacts related to these inputs and outputs; and (iii) interpreting the results obtained in the impact assessment phase [14]. Hence, LCA is a viable tool to identify environmental hotspots and find approaches that enhance environmental results related to the products [15,16]. The LCA application to energy is becoming increasingly important for evaluating which technology is more affordable and more sustainable [17]. LCA often demonstrated the benefits of replacement of oil with bioenergy systems [18] not only for energy but also for refinery scopes [19]. Despite the potential role of LCA in sustainable development of energy systems [20], few LCA studies have been carried out on H₂ production from biomass [8,9,21,22]. In these papers, agricultural and forestry waste that feed oxygen/steam fixed or circulating fluidized bed coupled with tar cracker/reformer/scrubber, sulfur removal systems, steam reformer and water gas shift reactors have been assessed. Kalinci et al. [9] evaluated two different large scale gasification systems, circulating fluidized bed and fixed bed gasifiers coupled with tar reformer, water gas shift (HTS (High Temperature Shift), MTS (Medium Temperature Shift), and LTS (Low Temperature Shift)) and PSA reactors. In this study, impacts were just evaluated in term of kg CO₂. Moreno and Dufour [21] investigated environmental efficiency of a 131 MW_{th} power plant that applied a fixed bed gasifier with steam reformer, WGS and PSA. Susmozas et al. [8] assessed biomass gasification via circulating fluidized bed gasifier and SMR technology for hydrogen production in a medium size power plant. ZnO reactor and steam reformer were not included. Finally, Suwatthikul et al. [22], after the model implementation, by means of ASPEN Plus, a simulation software for chemical process, of a steam gasification system and its validation, developed a LCA comparing conventional gasification and energy self-sufficient gasification in terms of GWP and marine aquatic ecotoxicity.

Since biomass resources are typical of a distributed nature and are limited by low energy density, perishability and complexity of the supply chain, distributed power plants offer significantly better energy security and possibility to exploit the full potential than the equivalent centralized plant [23,24]. To sustain development of these distributed units, reliable, high efficient and low environmental impact small scale power plants have to be developed [24]. Thus, it is important to conduct a LCA of hydrogen production at small scale systems. Previous literature regarding this specific topic is missing and, therefore, the contribution of the present study is relevant because it deals with LCA of hydrogen production via small scale biomass plant realized during four-year project of UNIfHY (UNIque gasifier for HYdrogen production) [25]. In this case study, almond shell, which represents agro-industrial residue, is used as feedstock, and a catalytic candle indirectly heated steam gasifier coupled with zinc oxide (ZnO) guard bed, water gas shift (WGS) and pressure swing absorber (PSA) reactors is considered as conversion technology. Almond shell has been chosen because it has the most suitable characteristics to this thermochemical process, as explained by Bocci et al. [24]. The chemical characterization of any feedstock to be used in a gasification process is an important step for qualifying the process itself in terms of conversion efficiency (mass and energy) and presence of potential poisoning elements. In this paper, almond shells have been selected as representative of agro industrial residue because, as a food industry derived biomass source, they are largely available, have a limited cost of supply, do not have potential poisoning elements and have already been tested in the UNIfHY project [25].

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The article is organized as follows: after the Introduction, Section 2 describes the methodology used; Section 3 reports a description of the conceptual organization of the gasification system within the model; Sections 4 and 5, respectively, present and discuss the main results of the work; and Section 6 reports the conclusions.

2. Methodology

2.1. The Life Cycle Assessment

LCA is a methodology for the comprehensive evaluation of the impact that a product (good or service) has on the environment throughout its life cycle [14]. This method presents a holistic approach for a comprehensive environmental assessment, following a standardized method which guarantees reproducibility of results [14,26].

2.1.1. Goal and Scope Definition

The environmental impacts and energy requirements of the whole process aimed at hydrogen production from the almond shell by means of gasification process and the subsequent use for electricity have been determined. In addition, environmental hotspots were identified to reduce the impact and improve the environmental and energy profiles. StimaPro 8.1 software, developed by PRé Consultants, was used for the environmental evaluation of the process.

2.1.2. Functional Unit and System Boundaries

The functional unit (FU) expresses the function of the system in quantitative terms and provides the reference to which all the inputs and outputs of the product system are calculated [14]. The functional unit selected for this assessment was the production of 1 MJ of hydrogen (purity: 99.99%).

A cradle-to-gate LCA has been performed including feedstock production, gasification, H_2 purification and electricity generation from off-gas.

2.1.3. Inventory Data Acquisition

The most effort-consuming step in the execution of LCA studies is the collection of inventory data to build the Life Cycle Inventory (LCI). High quality data (input and output) are essential for a reliable evaluation [27].

Inventory data for the bioenergy production plant are collected from foreground data of a pilot plant and form questionnaire filled out by designer, producer and operators of the equipment and gasifier plant. In feedstock production phase, on farm emissions derived from fertilizer application have also been modeled following the IPCC (Intergovernmental Panel on Climate Change) guidelines [28]. Temporary storage of carbon in tree biomass, and carbon storage in orchard soils, is accounted for based on net annual changes in carbon stored or emitted. The average soil carbon accumulation in almond orchards was estimated as 624 kg of carbon ha⁻¹ year⁻¹. More detailed information concerning these calculations can be found in [29]. Emissions from fuel combustion in both bioenergy plant and agricultural machinery have been calculated according to Tier 1 method described in IPCC guidelines. The fuel consumption does not include the extraction stage. The inventory involves the distribution of fuel to the final consumer including all necessary transports. In the off-gas management subsystem presented in the following paragraph, the derived emissions from CHP were calculated with the emission limits reported by [30].

2.1.4. Impact Assessment

According to some criteria defined for selecting the impact assessment methods, such as the scientific robustness, which considers the level of uncertainty, development that occurs over time, their application in LCA practice and the European environmental policy goals, the midpoint CML method is chosen to assess hydrogen production system (Fuel cell and Hydrogen-Joint Undertaking 2011).

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In line with [31–33], four midpoint categories were taking into account: acidification potential (AP), eutrophication potential (EP), global warming potential (GWP) and photochemical oxidation potential (POFP). The cumulative (non-renewable) fossil and nuclear energy demand (CED) of the whole life cycle was also quantified [34].

2.2. Hydrogen Renewability

The concept of renewability has firstly been introduced by Neelis et al. [35] and, as an indicator, it can assist decision makers to choose fuel with superior renewability character. According to cumulative energy demand (CED) method, renewable and non-renewable energy involved in whole life cycle can be counted. The index represented for this cycle is shown in Equation (1), [35]:

$$Hydrogen\ renewability[\%] = \frac{renewable\ energy\ input}{(renewable\ energy+nonrenewable\ energy\ inputs)} \tag{1}$$

2.3. Sensitivity Analysis

In addition, sensitivity analysis has been performed to assess the influence of change in hydrogen production efficiency and environmental charge allocation on the model results. Among the factors that affect hydrogen production, the steam to biomass ratio (S/B) has been chosen [36,37]. Therefore, study results have been compared with those considering S/B equal to 1 and 1.5, respectively. Experimental conditions for these different ratios are found in [38]. Alternatively, an economic allocation between hydrogen and electricity produced in the bio-energy plant was assumed. According to [39,40], allocation percentages for hydrogen and electricity in economic basis were 96% and 4%, respectively.

3. Description and Model of the Gasification System

The present system is based on a 1 MW $_{th}$ innovative gasification system [41–43]. Figure 1 shows the CHEMCAD, a simulation software for chemical process, flowsheet of the system with the indirectly heated gasifier here considered. To realize the 1 MW $_{th}$ system with Steam–Oxygen gasifier, the depicted plant in Figure 2 is used.

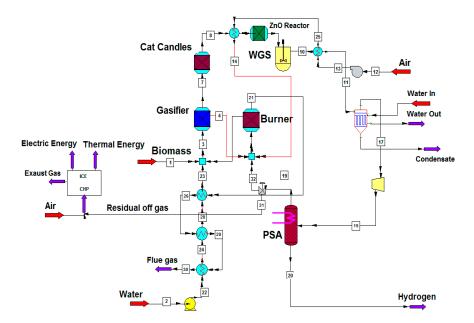


Figure 1. Flow sheet of the plant evaluated in this study.

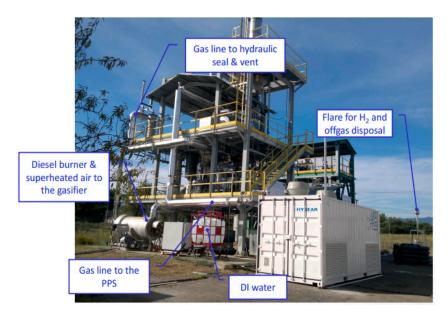


Figure 2. A picture of the plant.

The system is divided into four subsystems. First is the Biomass production (SS1). The bioenergy plant operation has been divided into two main stages: from biomass to syngas representing the syngas production stage (SS2) and from syngas to hydrogen representing the syngas conversion stage (SS3). All inputs and outputs demanded for the plant operations are included to consider the related environmental burdens. The last subsystem is composed of the off-gas management (SS4). Figure 3 illustrates the system boundaries and the considered processes.

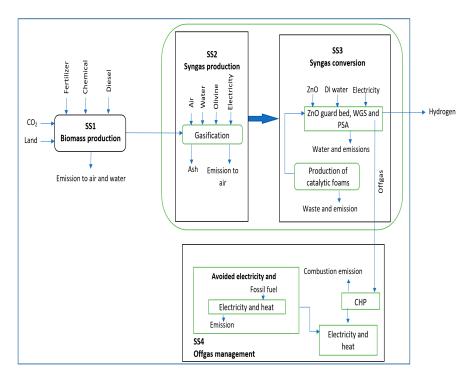


Figure 3. Life cycle boundaries for hydrogen production system.

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3.1. Subsystem 1: Biomass Production

In Subsystem 1, all the biomass production processes were considered, comprising main crop planting, fuels consumed by agricultural machinery, requirements of fertilizer, pesticides and water for irrigation, transportation, fuel consumed in factory and biomass collection [29,44,45]. The global inventory data for this subsystem are reported in Table 1. Since waste production is not the goal of farming, it is required to designate all outputs (main products and waste) of cultivation and adapt allocation method to account only for the environmental burdens allocated to waste [21,27]. In this study, environmental charges of cultivation stage are allocated using market prices (1% of charge associated to waste).

Input from Technosphere **Output to Technosphere** Materials and Fuels **Products and Coproducts** 0.257 kg Diesel 0.017 kg Kernel (main product) 0.025 kg Nitrogen fertilizer Almond shell 0.144 kg Energy Other Co-products 0.74 kg0.037 kWh Electricity Input from nature Water 800 kg Output to environment Emissions to air Nitrogen oxides $0.45 \times 10^{-3} \text{ kg}$ Methane $0.35 \times 10^{-6} \text{ kg}$ Carbon dioxide $0.0087 \, \text{kg}$ Emissions to water $2 \times 10^{-4} \text{ kg}$ Nitrogen oxides

Table 1. Global inventory data (per 1 MJ_{H2}) for Subsystem 1.

3.2. Subsystem 2: Syngas Production

The main operating conditions of the entire power plant are listed in Table 2 [38]. In addition, almond shell characterization and syngas composition are shown in Tables 3 and 4, respectively.

Parameters (Unit)	Value
Power (kW _{th})	1000
Biomass feeding rate (kg/h)	200
Steam feeding rate (kg/h)	100
Electricity consumption (kW)	
Start up	4
water pump	0.61
Air blower	13
Syngas blower	3
Syngas Compressor	36
Gasification T (°C)	850
S/B	0.5
Combustor T (°C)	950
Olivine between combustor/gasifier (kg/h)	1000

Table 2. Operating conditions of the gasifier.

Table 3. Almond shell characterization [46].

Bulk Density (kg/m³)	Humidi (%wt)	ty Ash (%wt)	Volatile Matter (%wt)	Fixed Carbon (%wt)	C (%)	Н (%)	N (%)	O (%)	CI (%)	S (%)
450	12	1.2	80.6	18.2	47.9	6.3	0.32	44.27	0.012	0.015

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Compositions (Unit)	Value	
Gas yield (Nm ³ dry/kg _{bio,daf})	1.45	
H_2 (% _{dry})	44	
CH_4 (% $_{drv}$)	10	
CO (% _{dry})	28	
CO ₂ (% _{dry})	18	
$H_2O(\%_{wet})$	16	
$C_6H_6 (g/Nm^3_{dry})$	4.11	
C_7H_8 (g/Nm 3 dry)	0.68	
$C_{10}H_8 (g/Nm^3_{dry})$	0.68	
MJ/Nm ³ dry	11.4	

Table 4. Syngas composition.

Syngas production stage involves the gasification process. Gasification is performed in a 1 MW $_{\rm th}$ Indirectly heated Bubbling Fluidized Bed gasifier (IBFB), working under mentioned conditions in Table 2 for 7000 operating hours (even if during the project only 120 h of pure hydrogen production has been achieved). Indirectly heated bubbling fluidized bed with tar reforming inside the gasifier was chosen in this study since this configuration provides a synthesis gas with higher hydrogen content than fluidized and fixed bed gasifiers [6,36,41,47–49]. The 1 MW $_{\rm th}$ gasifier built and experimented in the research project is an oxygen bubbling fluidized bed gasifier. Thus, we considered the same technology running in indirectly heated configuration.

First, tar and methane are treated and the cleaning process of synthesis gas from particles is carried out by 60 Catalytic Filter Candles (CFC) allocated in the gasifier freeboard. This is an innovative method adapted and tested during the two European research projects called UNIQUE [50] and UNIfHY [25]. In the gasification process, both electricity and heat are requisite. The electricity consumed in the syngas compressor and in the air blower is taken directly from the Italian national grid. Thermal energy is required to preheat the air, heat the water, and generate and overheat the steam, and is provided by syngas and flue gas cooling. Owing to the indirectly heated configuration, hot bed material (olivine) from the combustor is circulated back to the gasifier supplying the thermal power needed for the gasification reactions. Carbon dioxide emissions from flue gas have been considered.

3.3. Subsystem 3: Syngas Conversion

In the syngas conversion stage, the produced syngas has been used in a portable purification station (PPS), which generates the H_2 . This unit combines a ZnO reactor (to remove the sulfur compounds within syngas), a WGS reactor (to convert CO into further H_2) and a PSA membrane reactor (to separate H_2 from the other syngas components). Since atmospheric pressure gasification is more suitable for small-scale applications, the conventional WGS that operates at high pressure has been substitute with ceramic foams catalytic WGS operating at atmospheric pressure. The use of a ceramic foam with a wide catalytic surface area impregnated with catalyst eliminates the need to operate at high pressure for high conversion efficiency [36].

The ZnO data have been considered but this unit is not present in the flowsheet because the trace elements have not been considered in the simulation. The heat from the heat exchangers in PPS is recovered to meet low temperature thermal need.

All inputs and outputs needed for the hydrogen production unit (PPS), such as electricity, ZnO, de-ionized water and WGS Cu foams, are included. Additionally, the derived emissions from burning off-gas (such as nitrogen oxides, carbon dioxide, and sulfur dioxide) were considered. Construction of gasifier plant with 20-year life time has also been considered within the subsystem boundaries. The details of catalysts production are extracted from a questionnaire filled out by the University of Strasburg, a partner of UNIfHY project. The materials and energy inputs required for the catalysts production to be used in a 1 MW_{th} power plant are presented in Table 5.

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Parameters (Unit)	Value
Number	20
Size (cm)	D: 70
	H: 10
Material and Energy	
Water (kg)	800
Cerium nitrate (kg)	367
Heat (MJ)	12,000
Lifetime (year)	3

500 500

Emission to water

 NO_{x} (kg)

Cerium nitrate solution (L)

Copper nitrate solution (L) Emission to air (kg)

Table 5. Material and energy employed for catalysts production.

During the 20-year lifetime of power plant, the catalysts with three-year lifetime need to be replaced seven times. To integrate this production phase into the model, the energy and materials required for these catalysts (Table 5) have been multiplied by seven and divided by the total energy output produced during 20 years.

The main inventory data for hydrogen production via almond shell gasification are shown in Table 6.

Table 6. Main inventors	v data for hydroge	n production via	almond shell	gasification per FII
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Input from	Technosphere	Output to	Technosphere
Material	s and fuels	Products at	nd coproducts
Almond shell (SS1)	0.144 kg	Hydrogen	1 MJ
Diesel (SS2)	$3.55 \times 10^{-5} \text{ kg}$		
Water (SS2)	0.144 kg	Avoide	d product
De-ionized water (SS3)	0.128 kg	Avoide	a product
Zinc oxide (SS3)	$1.3 \times 10^{-4} \text{ kg}$	Electricity	0.26 kWh
Cu foam (SS3)	$3 \times 10^{-7} \text{P}$		
Energy			
Electricity (SS2)	0.014 kWh	Emissi	ons to air
Electricity (SS3)	0.027 kWh	Emussi	ons to an
Input from nature		Nitrogen oxide (SS2)	$1 \times 10^{-9} \text{ kg}$
Input ir	om nature	Methane (SS2)	$1.7 \times 10^{-8} \mathrm{kg}$
Olivine (SS2)	0.00027 kg	Carbon dioxide (SS2)	0.16 kg
	· ·	Water (SS2)	0.15 kg
		Sulfur dioxide (SS4)	$2 \times 10^{-6} \text{ kg}$
		Nitrogen oxide (SS4)	$2.5 \times 10^{-5} \mathrm{kg}$
		Emissio	n to water
		Wastewater (SS3)	0.05 kg
		Solid waste flows	
		Ash (SS2)	$1.6 \times 10^{-3} \text{ kg}$
		Olivine (SS2)	$2.7 \times 10^{-4} \text{ kg}$
		Insulation (SS2)	$5.5 \times 10^{-7} \text{ kg}$
		Hydrogen Sulfide (SS3)	$5 \times 10^{-5} \text{ kg}$

3.4. Subsystem 4: Off-Gas Management

In the syngas conversion process, off-gas is co-produced from PSA and is mainly used in the burner (syngas production process). This subsystem involves the use of the residual off gas into a conventional Combined Heat and Power system (CHP, via an Internal Combustion Engine, ICE). Under the conditions mentioned in Table 2, with respect to the total energy output: the energy content

of residual off-gas represents 12%; the H₂ represents 43%; and the thermal energy losses are 45% (8% in flue gas and another 37% mainly due to the heat of the cooling water and condensate) (Figure 1).

According to previous energy study of the authors [38] and Fremaux et al. [37], it is inferred that the residual off-gas decreases with higher S/B ratio (e.g., with S/B greater than 1.5–2, depending on the PSA efficiency, the off-gas is completely used in the burner). In particular, the global efficiency is limited by the thermal losses and by the PSA compressor consumption. The hydrogen efficiency is limited by the PSA efficiency and by the absence of a methane reformer. Thus, to increase the hydrogen efficiency, high temperature hydrogen membrane separation that works at low pressure (as Palladium membranes) including methane reforming are considered but, up to now, are still in a development phase. Indeed, the hydrogen efficiency is about 38%, while the global efficiency (considering hydrogen, residual off gas and the useful heat) is about 70%.

The production of off-gas, under the fixed gasification and conditioning parameters (residence time, temperature, catalysts, etc.) mainly depends on S/B ratio and PSA efficiency. Being the PSA efficiency a technological parameter rather than an operational parameter, only the variation of S/B has been considered in the following sensitivity analysis.

The off-gas use for CHP was considered within the system boundaries together with the consequently avoided conventional electricity production, while heat generation has been disregarded. Indeed, electricity can be used for own demand and injected to the grid, meanwhile the heat produced by CHP can only be used if there is a near low temperature heat demand. In accordance to ISO standards, allocation procedure is avoided by system expansion in this LCA study.

During biomass-based hydrogen production, hydrogen and off-gas are coproduced. The hydrogen was considered as the main product, although the produced electricity from off-gas can be sold to the national grid. In fact, it is considered as an avoided input in the base case of this study. In other words, the system is expanded rather than allocated. Therefore, hydrogen production was only addressed as the base case. In addition, impacts derived from the production and transmission of the avoided electricity were also included within the subsystem boundaries in this case.

4. Results

Table 7 summarizes the LCA characterization results for the different subsystems under study per functional unit. Positive values are environmental burdens while negative values signify environmental credits or benefits accrued from carbon dioxide uptake and the substitution of electricity from national grid.

Category	Unit	Total	SS1	SS2	SS3	SS4
GWP	Kg CO ₂ eq	0.042	-0.12	0.19	0.11	-0.14
EP	Kg PO ₄ eq	2.6×10^{-4}	5×10^{-4}	3.6×10^{-5}	3.3×10^{-6}	-2.8×10^{-4}
AP	Kg SO ₂ eq	-4.5×10^{-4}	2×10^{-4}	1.3×10^{-4}	1.5×10^{-5}	-8×10^{-4}
POFP	Kg C ₂ H ₄ eq	-1.8×10^{-5}	6×10^{-6}	2.7×10^{-6}	3.3×10^{-6}	-3×10^{-5}
CED	MJ eq	-0.46	0.39	0.14	0.3	-1.3

Table 7. Characterization results corresponding to the production of 1 MJ_{H2}.

Figure 4 displays the relative contributions of each subsystem to the environmental results for the studied system. According to these results, the biomass production (SS1) shows high influence over the environmental profile, especially in term of EP with a contribution of 60%. This result is mainly related to the emissions derived from fertilizer application. In addition, the large amount of energy required to produce fertilizer causes intense fossil energy consumption in feedstock production phase. Contrarily, this subsystem achieves a positive effect on GWP owing to the CO_2 uptake by photosynthesis. Therefore, the emission of $120 \text{ g } CO_2$ eq per functional unit is avoided. The main environmental impacts of the syngas production (SS2) are observed on GWP (34%) and AP (15%),

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mostly related with flue gas emitted from gasifier combustor and feedstock supply. The syngas conversion (SS3) has relatively lower impact on GWP (19%) than the other categories.

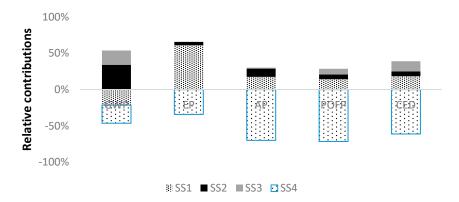


Figure 4. Relative contributions from subsystems involved to each impact category.

SS4 covers the energy generation from off-gas and its utilization as electricity. Thus, the production of electricity from the grid is avoided. As shown in Table 7, it leads to environmental benefits in terms of all the analyzed categories. In the following, a detailed assessment per subsystem has been carried out to recognize in detail the main contribution to these environmental outcomes.

As displayed in Figure 5, impact of fertilizers in SS1 is notable in EP, AP and POCP categories with a contribution greater than 84% because of drastic energy consumption in production of nitrogen fertilizer required. Irrigating orchard, owing to diesel and electricity requirements in irrigation, has also impact on AP and POFP with 5% and 15%, respectively. Regarding GWP, the fixation CO₂ by photosynthesis can offset the GHG emitted throughout the cultivation system which are chiefly derived from fertilizer production.

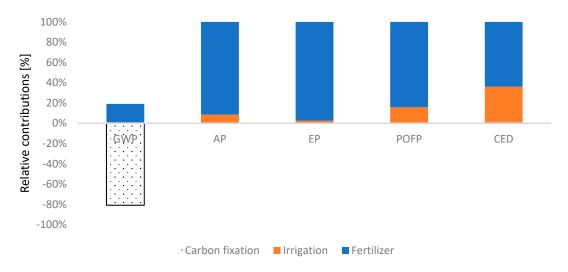


Figure 5. Breakdown of contributions from process involved in Subsystem 1.

With regard to the syngas production process (SS2), flue gas emission from gasifier burner has the largest proportion of total GWP (55%). By virtue of carbon fixation of feedstock, this impact eventually experiences a massive decrease.

The other categories (AP, POFP and EP) are significantly influenced by feedstock supply process. Moreover, the electricity required to run the gasification has been taken from the Italian grid; its production turns out as second large contributor for AP and POFP categories with 16% and 23%,

respectively. Eighty percent of the electricity consumption in SS2 is due to the air blower to provide air needed for gasification process.

In SS3, the syngas production phase impacts on all the environmental categories. In particular, for EP, it impacts with 97% related to feedstock and fertilizer consumption. The materials used for syngas conversion to hydrogen have minor impact on this subsystem. Among them, the Cu foam production has higher environmental impact than the other materials accounting for almost the 3.6% of the impact on AP and POFP.

In SS4, the emissions from the CHP (SO_2 and NO_x) have been estimated according to emission limits legislated by European Commission. Carbon dioxide released by off-gas burning is biogenic and it is not treated as a net source of carbon dioxide by IPCC. The detailed information is indicated in Table 8. The avoided emissions from electricity production and transmission, as shown in Figure 6, have the greatest negative impact on all categories.

Input from Technosphere		Output to To	echnosphere
Materials ar	nd fuels	Avoided products	
Off-gas (from SS3)	1.33 MJ	Electricity	0.26 kWh
		Output to e	nvironment
		Emissio	ns to air
		Sulfur dioxide	$2 \times 10^{-6} \text{ kg}$
		Nitrogen oxide	$2.5 \times 10^{-5} \text{ kg}$

Table 8. Global inventory data (per 1 MJ_{H2}) for Subsystem 4.

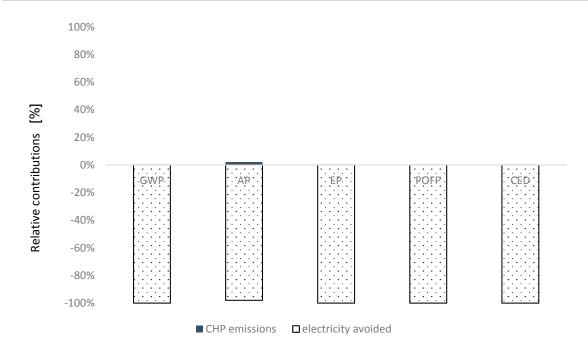
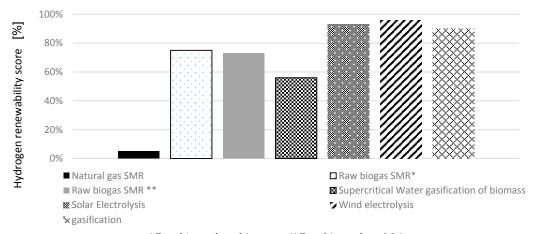


Figure 6. Breakdown of contributions from process involved in Subsystem 4.

The renewability score of hydrogen under the conditions considered in our study has been fixed at 90%, which is close to the values defined for wind and solar based hydrogen production, 96% and 93%, respectively [51]. In fact, high energy saving in SS4 leads to achieving this appreciative value.

To calculate the renewability score in the current study, the energy content of biomass as the renewable energy was considered 18 MJ/kg $_{\rm biomass}$ [46]. Therefore, the consumption of 0.144 kg biomass per 1 MJ $_{\rm H2}$ equals to 2.6 MJ biomass-renewable energy consumption. According to the cumulative energy demand indicator (Table 7), 0.46 MJ energy per 1 MJ $_{\rm H2}$ would be saved in the

whole life cycle. In fact, the electricity produced from off-gas leads to 1.3 MJ energy saving per 1 MJ_{H2} . The non-renewable energy of whole life cycle has been calculated as $0.22 \, MJ/MJ_{H2}$ considering 43% contribution of off-gas treatment subsystem (SS4) to save energy. On the other hand, if SS4 were excluded from the model, the H_2 renewability could be expressed as 75%. In other words, off gas treatment can improve hydrogen renewability by 15%. According to [6] and Table A1 in Appendix A, other approaches for hydrogen production are compared in Figure 7.



* Raw biogas from bio-waste ** Raw biogas from Maize

Figure 7. Hydrogen renewability for each technology [6].

5. Discussion

In this section, the results obtained in our study for the GWP, AP and EP impact categories are compared with other LCA studies. To simplify these comparisons, our results are presented using the same functional units as other studies (0.042 kg CO_2 eq per MJ_{H2} , 0.45 kg CO_2 eq per Nm^3_{H2} or 15.96 CO_2 eq g/s).

Kalinci et al. [9] reported values of GWP as $17.13 \, \text{CO}_2$ eq g/s in the CFBG system and $0.175 \, \text{CO}_2$ eq g/s in the DG system. In this study, the production of pine wood as feedstock for H_2 production in Proton Exchange Membrane (PEM) fuel cell vehicle were defined into system boundary. H_2 compression and transportation have been found as the main sources of environmental impact. Although the authors consider more subsystems and a wider system boundary, their result for the CFBG (comparable with our system) is just marginally higher than the one of our system. This is justified by the kind of biomass used, which does not need cultivation process and has a greater carbon fixation.

Moreno and Dufour [21] reported values for the GWP concerning different biomasses. Economic allocation has been considered to designate relevant emissions to waste biomass in orchard products. They found that use of allocation approach leads to decrease in CO_2 fixation and carbon credits of waste, since it is distributed between fruit with 90–99% of total price and waste. Therefore, the GWP, for almond pruning, by considering or not the allocation has been determined as 1.5 and 0.18 kg CO_2 eq per Nm^3 of hydrogen, respectively and GWP for vine pruning by considering or not the allocation 1.1 and 0.2 kg CO_2 eq per Nm^3 of hydrogen, respectively. In this estimation, non-converted CH_4 has been recovered into system to provide energy needs. The emissions estimated in this study are slightly lower than the ones in our study due to the use different type of gasifier. In fact, in line with results obtained by [9], fixed bed gasifier released lower emission than fluidized bed gasifier.

Thus, differences on the feedstock and the system boundaries have influence on the results and explain the variations in relation with other studies.

In other research [52], the CO_2 emitted from raw biogas reforming under two different feedstocks (maize and bio waste) was assessed. The GWP value is estimated to be 0.046 kg CO_2 eq. per 1 MJ_{h2}

for maize-based biogas and 0.037 kg CO_2 eq. if bio waste is used as feedstock. The emissions from fertilizer supply and use of diesel for farming machines in maize cultivation are mainly responsible for these values. These results are quite similar to the system investigated in this study. However, the value reported to generate H_2 by natural gas SMR was 0.1 kg CO_2 per 1 MJ_{H2} [6,53,54]. Therefore, 0.058 kg CO_2 per 1 MJ_{H2} can be reduced if waste biomass gasification is utilized to produce hydrogen.

Regarding the other impact categories, remarkable differences have been identified. In terms of AP and EP, Moreno and Dufour [21] reported $0.006~kg~SO_2$ eq and $0.008~kg~SO_2$ eq a

Thus, Table 9 summarizes the differences with the reviewed studies.

GWP	AP	EP	F 1. (. 1	Handling	D. C.
kg CO ₂ /Nm ³ H ₂	kg SO ₂ /Nm ³ H ₂	kg PO ₄ /Nm ³ H ₂	Feedstock	Multifunctional Process	Reference
0.45	-0.0048	0.0028	Almond shell	System expansion	Our result
1.5	0.0009	0.0054	Almond pruning	Economic allocation	[21]
0.18	0.008	0.045	Almond pruning	-	[21]
1.1	0.001	0.005	Vine pruning	Economic allocation	[21]
0.2	0.006	0.03	Vine pruning	-	[21]
$kg CO_2/MJ_{H2}$	$kg SO_2/MJ_{H2}$	$kg PO_4/MJ_{H2}$	1 0		
0.042	-4.5×10^{-4}	2.6×10^{-4}	Almond shell	System expansion	Our result
0.046	-	-	Maize-biogas	-	[52]
0.037	-	-	waste-biogas	-	[52]
0.1	-	-	Methane	-	[6,53,54]
$g CO_2/s$	-	_			. , , 1
15.96	-	-	Almond shell	System expansion	Our result
17.13	-	_	Pine wood	- 1	[9]

Table 9. Comparative synoptic of this and previous researches.

Sensitivity Analysis

Sensitivity analysis has been performed to assess influence of H_2 productivity and the allocation method used in the model. As mentioned in Section 2, among several factors affecting H_2 productivity, the steam to biomass ratio (S/B), (see Section 3.4) has been chosen to assess hydrogen production. In Figure 8, the current status characterizes the gasification system presented in Section 3 (S/B = 0.5). This status has been compared with the LCA output considering the S/B ratio equal to 1 and 1.5 (Table 10). Therefore, the results of this study have been compared with results related to S/B 1 and 1.5. The experimental conditions for these different ratios are found in [38].

Composition (Unit)	Outlet	Gasifier	Outlet WGS		
	S/B 1	S/B 1.5	S/B 1	S/B 1.5	
Gas yield (Nm³ _{dry} /kg _{bio,daf})	1.63	1.72	1.9	2	
$H_2(\%_{dry})$	49	51	58	60	
CH ₄ (% _{dry})	7	6	7	5	
CO (% _{drv})	24	23	3	2	
CO ₂ (% _{dry})	20	20	32	33	
H ₂ O (% _{wet})	34	46	40	50	
C_6H_6 (g/Nm 3 dry)	5.51	6.97	4.7	6	
C_7H_8 (g/Nm 3 dry)	1.23	1.53	1.05	1.3	
$C_{10}H_8 (g/Nm^3_{dry})$	0.33	0.77	0.29	0.66	

Table 10. Syngas composition in outlet of gasifier and inlet of WGS.

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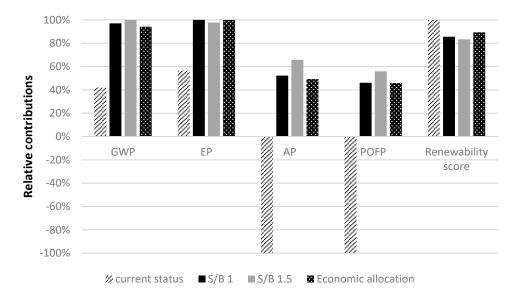


Figure 8. Sensitive analysis results for increase in hydrogen production.

According to Table 10, increasing the steam to biomass ration improves gas yield and H_2 production but also the CO_2 and H_2O content. The gas yield and H_2 production increase is more relevant than the increase of inert gas, because the LHV of the syngas increases [36].

Figure 8 shows that, in cases of S/B 1 and 1.5, impacts are higher (from 60% of GWP to around 100% for AP and POFP). Numerical values related to Figure 8 are presented in Table 11. This is due to the decrease in electricity production and subsequently decrease in environmental benefits (see Section 4). In addition, regarding renewability score, the case of S/B 0.5 shows the best performance. The economic allocation case, where environmental impacts are allocated to H₂ and electricity, shows environmental improvements compared with the case of S/B 1 and 1.5 but always higher than the case of S/B 0.5. This means that increase in hydrogen production not necessarily results in diminution of environmental impacts on the contrary these impacts can grow. Rise in hydrogen produced leads to fall in off-gas volume, electricity obtained and its avoided impacts. These results clarify role importance of by-products in environmental efficiency of hydrogen production. In addition, as the Italian electric profile includes high fraction of non-renewable sources in [27], which results that more than 65% is generated from non-renewable sources, mainly natural gas, oil and hard coal, renewability of hydrogen can be affected by decline in avoided grid derived electricity demand, which entails consumption of fossil-based electricity due to drop in off-gas volume.

Impact Category	Unit	Scenarios				
imput cutegory	Cint	Current Status	S/B 1	S/B 1.5	Economic Allocation	
GWP	Kg CO ₂ eq	0.042	0.097	0.1	0.094	
EP	Kg PO ₄ eq	2.6×10^{-4}	4.6×10^{-4}	$4.4 imes 10^{-4}$	4.5×10^{-4}	
AP	Kg SO ₂ eq	$-4.5 imes 10^{-4}$	$2.3 imes 10^{-4}$	2.9×10^{-4}	2.2×10^{-4}	
POFP	$Kg C_2H_4 eq$	-1.8×10^{-5}	8.3×10^{-6}	1×10^{-5}	8.2×10^{-6}	
Renewability score	%	90	77	75	80	

Table 11. Comparison of different scenarios.

Decentralized power plants entail environmental benefits despite the technical and economic challenges for this scale of power plant. Indeed, investment cost per power unit of small scale power plants is higher than large scale plants and there are higher requirements for the technological development of these small-scale power plants (thermal balance, etc.). Moreover, hydrogen production cost can be higher (10 euro/kg) compared with large scale production cost (1-2 euro/kg).

On the other hand, the energy, economic and environmental impacts of the biomass transportation are relatively lower due to avoiding distribution and because CHP and CCHP systems can also be more applicable for small scale power plants as heating and cooling production is more effortlessly distributed and usable. In fact, currently, hydrogen production systems at large scale can be more technically and economically applicable, but they impose higher impacts.

6. Conclusions

This study evaluates the environmental characteristics of hydrogen and electricity production in an innovative small-scale biomass gasification plant. The LCA methodology has been applied to assess the environmental performance of this production scenario.

Real input and output flows for the whole system have been identified and managed in detail from a cradle-to-gate perspective. This study showed that the biomass production phase influences all impact categories, which is a unanimous result of previous research. Furthermore, due to multifunctional nature of this process and considering byproduct converted into electricity as well as no auxiliary energy consumption, these environmental impacts massively decrease. Negative values in AP, POFP and CED illustrate this improvement. Following this result, a sensitivity analysis was conducted to assess the influence of the variations in hydrogen and byproduct volume on environmental impacts. The S/B ratio has been chosen as parameter affecting both off-gas and hydrogen production because it is commonly recognized as the main factor in the analysis of performance of gasification process. Results indicate that, although increase in hydrogen production can directly reduce all environmental impacts, this implies a fall in off-gas volume, which indirectly leads to increased impacts for all categories. As a result, in the considered production system, the environmental effects cannot be univocally represented by hydrogen production rate because relevance of byproducts produced plays an even more important role. In this line of research, development of system boundary into bio-refinery products can also lead to higher reduction in environmental footprints of hydrogen production system. In addition, the sensitivity analysis shows that allocation method also highly affects the system profile. Allocation of environmental charges can considerably overestimate results. Results of this work have a relevant impact with respect to previous literature works regarding hydrogen production by means of biomass gasification because it has analyzed the effect of some design parameters on the environmental impact of the overall system, quantifying the contribution, for each category, of the different configurations.

Finally, despite the limits of small scale hydrogen production system, many potential advantages of this category can be enumerated. Therefore, a highly efficient small-scale power plant with low environmental burden needs to be developed to tackle the low energy density and perishability of biomass.

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Nomenclature

AP acidification potential
CED Cumulative Energy Demand
CFC Catalytic Filter Candles
CHP Combined Heat and Power

CCHP Combined Cooling Heating and Power

EP eutrophication potential

FU Functional Unit

GWP global warming potential

IBFB Bubbling Fluidized Bed gasifier

ICE Internal Combustion Engine

LCA Life Cycle Assessment

LCI Life Cycle Inventory

LHV Low Heating Value

POFP photochemical oxidation potential

PSA Pressure Swing Adsorber SMR Steam Methane Reforming

SS1 Subsystem1
SS2 Subsystem2
SS3 Subsystem3
SS4 Subsystem4
WGS Water Gas Shift

Appendix

Table A1. Energy demand per kWh_{H2} and H₂ renewability score [6].

Scenario	Fossil Energy (kWh Primary Energy)	Nuclear Energy (kWh Primary Energy)	Renewable Energy (kWh Primary Energy)	H ₂ Renewability Score (%)
Natural gas	2.3	0.5	0.14	5
Wind electrolysis	0.06	0.03	2	96
SCWG	1.2	0.4	2.1	56
Raw biogas SMR	0.6	0.4	3	75
Raw biogas SMR-maize	0.6	0.5	3	73

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