Environmental and exergetic evaluation of hydrogen production via lignocellulosic biomass gasification

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ABSTRACT

Gasification is a promising pathway for the conversion of biomass into energy products. In particular, the syngas generated through biomass gasification is of great interest for hydrogen production. Based on an overview of technological options, a base-case system for hydrogen production via biomass gasification is defined, and its environmental and thermodynamic performance is evaluated through a life cycle assessment and an exergetic analysis.

The case study involves poplar gasification in a low-pressure char indirect gasifier, catalytic tar destruction, cold wet gas cleaning, syngas conversion and hydrogen purification. The calculated exergetic efficiency of the plant is 48%, a value comparable to that of conventional coal gasification technologies for hydrogen production. The total exergy loss of the plant (mainly associated with the flue gas streams) is found to be 4.6% of the fuel exergy provided to the overall plant, while 47% of the overall fuel exergy vanishes as exergy destruction within the individual components of the plant.

The life cycle assessment of the system covers from poplar cultivation to hydrogen purification. Seven impact potentials are considered: cumulative energy demand, global warming, ozone layer depletion, photochemical oxidant formation, land competition, acidification and eutrophication. The life-cycle energy balance of the system suggests a relatively promising energy performance. Poplar cultivation and harvesting, biomass pre-treatment and syngas cleaning are identified as the subsystems with the largest contributions to the environmental impacts. Measures to enhance the environmental and energy performance of the system should focus on minimizing the poplar feedstock demand, improving the logistical planning for biomass supply, reducing the natural gas demand of the steam reforming sub-system, and optimizing the electricity demand of the gas cleaning subsystem. Lower consumption levels of fertilizers and diesel for poplar cultivation and harvesting should also be achieved.

1. Introduction

In recent years, there has been an increasing interest in using biomass as an energy source due to rising energy prices caused by fossil fuel shortages and growing energy demands. Moreover, in contrast to fossil fuels, biomass is considered to be a carbon neutral source (Kirubakaran et al., 2009; Nguyen et al., 2013). Thus, biomass-derived fuels are seen as one of the most promising alternatives to conventional fuels. Nevertheless, although carbon dioxide is absorbed during the growth of the biomass, greenhouse gas emissions arise during biomass production, transportation and conversion, as well as during product distribution (Koroneos et al., 2008). Therefore, comprehensive life-cycle thermodynamic and environmental evaluations of biomass energy systems are needed (Moya et al., 2013).

Biomass conversion can be carried out through a wide range of processes, e.g., combustion, pyrolysis, gasification and fermentation. In particular, gasification is considered one of the most promising technologies for the conversion of biomass into electricity, heat and chemical compounds (Campoy et al., 2008). With gasification, biomass is converted into a gaseous fuel (syngas, also called biosyngas) through heating in the presence of a gasifying agent (typically air, oxygen and/or steam). Syngas contains carbon monoxide, hydrogen, carbon dioxide, methane, water and traces of other components, such as tars and dust (McKendry, 2002).

Syngas can be used in a large number of applications, including electricity and/or heat generation and the synthesis of various products. For instance, it can be used to produce ammonia, methanol, hydrogen and diesel (Huber et al., 2006). Specifically,

hydrogen is a clean energy resource that can be used in chemical synthesis, petrochemical reactions, as well as in fuel cells (Tanksale et al., 2010). It is commonly produced through steam methane reforming (SMR) from natural gas, but sustainability concerns have led researchers to investigate other, more environmentally friendly, hydrogen-production methods focused on biomass gasification and syngas upgrading (Corella et al., 2008; Ni et al., 2006; Turn et al., 1998).

In the present study, technological alternatives for biomass gasification are outlined. On the basis of this overview, a base-case system for hydrogen production via biomass gasification is defined. Then, the thermodynamic and environmental performance of the system is evaluated using an exergetic analysis and a life cycle assessment (LCA).

Exergy is the maximum theoretical work that can be obtained when a system is brought to thermodynamic equilibrium with the reference environment, while heat transfer occurs with this environment only (Tsatsaronis and Cziesla, 2004). Exergy remains constant only in reversible processes. An exergetic analysis reveals and quantifies losses that occur in real (irreversible) thermal processes and cannot be accounted for in an energy analysis (Ptasinski, 2008; Tsatsaronis and Cziesla, 2004). This makes exergetic analysis an appropriate method for evaluating the effectiveness of energy conversion processes.

LCA is a well-established methodology to evaluate the environmental impacts of a product over its life cycle. This is achieved by gathering all relevant inputs and outputs of the considered system, evaluating the potential environmental impacts related to these inputs and outputs, and interpreting the results obtained in the inventory analysis and impact assessment phases (ISO, 2006a,b).

Beyond LCA studies that evaluate the cumulative exergy demand category (Dufour et al., 2012), several exergetic LCA studies have already been performed in the field of fuel production systems. For instance, Granovskii et al. (2007) carried out the exergetic LCA of hydrogen production via water electrolysis using renewables. Ozbilen et al. (2012) performed a similar study for nuclear-based hydrogen production through thermochemical water splitting. Similar works have also been conducted for biodiesel (Talens Peiró et al., 2010) and bioethanol (Ofori-Boateng and Lee, 2014). The present study deals with the LCA and exergetic analysis of hydrogen production via biomass gasification.

2. Overview of technological alternatives for biomass gasification

While syngas production via coal gasification has been investigated for many years (Stiegel and Maxwell, 2001), biomass gasification is a relatively new area, currently widely studied due to its potential environmental advantages. Biomass gasification is the thermochemical conversion of biomass into a gaseous fuel in a gasification medium such as air, oxygen and/or steam (McKendry, 2002). It takes place at elevated temperatures, between 500 and 1400 °C, and consists of two stages: pyrolysis and gasification. The former involves the thermal decomposition of the feedstock into volatile hydrocarbons and char, while the latter entails the transformation of these products into syngas (Ciferno and Marano, 2002; Zhang et al., 2010). The operating pressure varies from atmospheric pressure to 33 bar, which highly depends on the plant scale and the final application of the produced syngas (Ciferno and Marano, 2002). High pressures lead to size and efficiency advantages, but at the expense of increased complexity and maintenance costs. Thus, only large-scale processes would be profitable when operating at high-pressure conditions.

The composition of the produced syngas depends on several factors, such as the biomass composition, the gasification technology and the gasifying agent. Air is the most common gasifying agent because it is inexpensive, when compared to oxygen. However, when air is used, the produced syngas presents low energy content due to the dilution effect of nitrogen, with a higher heating value (HHV) of 3.7–6.4 MJ per cubic metre at standard temperature and pressure (m^3 stp; 25 °C, 1 atm) (Li et al., 2004). On the other hand, gasification with oxygen and/or steam produces syngas with an HHV between 9.2 and 16.5 MJ/m^3 stp.

The heat demand of gasification can be supplied directly or indirectly. Direct gasification (or autothermal gasification) is the most common approach. It occurs when partial oxidation of biomass is sufficient to fulfil the heat demand of the process. Otherwise, when an external energy source is used, the process is called indirect gasification (or allothermal gasification) (Belgiorno et al., 2003).

2.1. Biosyngas production

Fixed bed, fluidized bed and indirect gasifiers are the three main types of reactors used for biomass gasification. The most common configurations of these gasifiers are shown in Fig. 1. Even though entrained bed gasifiers constitute a developed technology for coal gasification, they are not considered in this section, because they impose high processing costs when used for biomass gasification (McKendry, 2002).

2.1.1. Fixed bed gasifiers

According to the direction of the flow of the gasifying agent, fixed bed gasifiers can be classified into updraft (counter-current) and downdraft (co-current) gasifiers. Updraft gasifiers (Fig. 1a) are the most mature and simplest type of fixed bed gasifiers. Biomass moves downwards through a bed, while reacting with the gasifying agent that moves in the opposite direction. Gas temperature varies between 500 °C at the exit and 1000 °C at the hearth zone (Ciferno and Marano, 2002; Zhang et al., 2010). The advantages of updraft reactors include suitability for biomass with high moisture content (up to 60%) and high thermal efficiency. The main disadvantage is that the produced syngas contains high amounts of tar, requiring extensive clean-up before it can be used in engines or turbines, or in synthesis applications (Ciferno and Marano, 2002; Zhang et al., 2010). Updraft gasifiers have been successfully operated in various countries − such as Finland and Sweden − since the mid 1980s. An example of this type of reactors is the Bioneer gasifier developed in Finland (VTT, 2002). However, due to the high tar content in the produced syngas, these gasifiers have not been widely studied.

In downdraft gasifiers (Fig. 1b), the gasifying agent moves downwards through the bed, in the same direction as the biomass feedstock. The main advantage is that the produced syngas has low tar content and, therefore, it does not need to undergo extensive clean-up. Reported disadvantages include that biomass with low moisture content (<20%) is required, and that the thermal efficiency is low, because the gas stream leaves the gasifier with a temperature of 900–1000 °C (McKendry, 2002). Additionally, large quantities of unconverted char are produced (McKendry, 2002; Quaak et al., 1999). Although this type of gasifier has been widely investigated (Jaojaruek et al., 2011; Lv et al., 2007; Midilli et al., 2001), its related drawbacks make it unattractive for further development (Ciferno and Marano, 2002).

2.1.2. Fluidized bed gasifiers

Fluidized bed gasifiers typically use a bed of inert material (e.g., sand and alumina) to improve the fluid-dynamic and heat
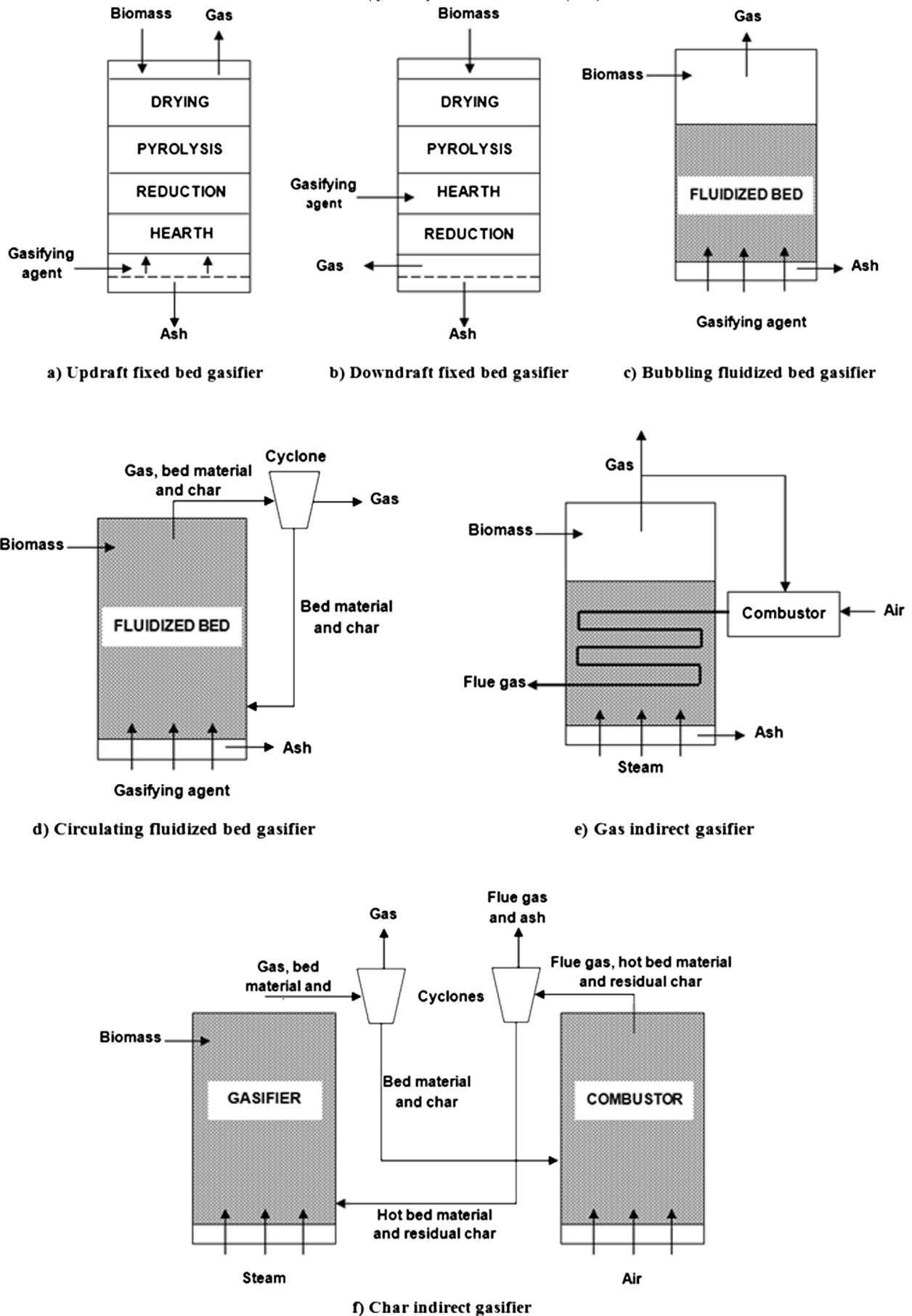
Fig. 1. Configurations of gasifiers.

transmission properties of the system. The biomass feedstock is injected into the bed, mixing rapidly with the bed material. Biomass particles and the bed material are fluidized by the gasifying agent, which flows through the bed, achieving a uniform temperature distribution. Bubbling fluidized bed and circulating fluidized bed gasifiers are the two main types of these reactors, which usually operate at 700–900 °C (Belgiorno et al., 2003).

In bubbling fluidized bed gasifiers (Fig. 1c), the gasifying agent is injected at the bottom of the reactor at a velocity equal to the minimum fluidization velocity, fluidizing the bed material and ensuring intense mixing of the hot bed material. The main advantage of these gasifiers is their suitability for a wide range of biomass particle sizes (Ciferno and Marano, 2002). Moreover, bubbling fluidized bed gasification with air is a relatively simple process for syngas production. For these reasons, these gasifiers have been considered in several studies (Lim and Alimuddin, 2008; Narváez et al., 1996). For instance, Gómez-Barea et al. (2005, 2006) reported the results of pilot-plant experiments on biomass gasification in a 150 kW$_{th}$ air-blown bubbling fluidized bed reactor using different biomass feedstocks, and evaluated the influence of operating conditions on the produced syngas.

Circulating fluidized bed gasifiers (Fig. 1d) are similar to bubbling fluidized bed gasifiers, with the difference that the velocity of the gasifying agent exceeds the minimum fluidization point. Due to this high velocity, an entrainment of the particles in the product gas occurs. The particles are separated in a cyclone at the exit of the reactor and the bed material is returned to the reactor. This type of gasifier has high conversion rates with low contents of tar and unconverted carbon, and is suitable for large-scale applications. Even though these gasifiers can produce more energy, in comparison with bubbling fluidized bed reactors, their heat exchange is less efficient (Ciferno and Marano, 2002; Zhang et al., 2010). The Värnamo demonstration plant in Sweden is based on this technology (Albertazzi et al., 2005).

Fluidized bed gasifiers for hydrogen production have been widely studied (Aznar et al., 2006; Rapagnà et al., 1998). Since the hydrogen content of biomass is around 6 wt%, biomass by itself is not an interesting source of hydrogen. In fluidized bed gasifiers that use steam as the gasifying agent, the hydrogen production can be increased. Unfortunately, the high energy intensity of this technology makes it unattractive. In this context, indirect gasifiers arise as a possible alternative (Corella et al., 2008).

2.1.3. Indirect gasifiers

Indirect gasification can be carried out in two types of reactors: gas indirect gasifiers and char indirect gasifiers. As observed in Fig. 1, in contrast to fluidized bed gasifiers, indirect reactors involve the use of combustors as additional units to provide the required heat. In both gas and char indirect gasifiers, pure steam is the gasifying agent, because it increases the hydrogen content of the syngas. Gas indirect gasifiers (Fig. 1e) use a fluidized bed heated by a hot gas stream from a separate burner, in which a fraction of the syngas is combusted with air to meet the heat requirements. Gas indirect gasification can work with a wide range of feedstocks (Belgiorno et al., 2003).

Alternatively, instead of burning part of the syngas produced, char can be combusted. Char indirect gasifiers (Fig. 1f) consist of two separate reactors: a fluidized bed gasifier and a fluidized bed combustor. Biomass is converted into syngas in the gasifier at 700–900 °C (Göransson et al., 2011). The char and bed material (sand) are separated from the syngas in a cyclone. The resulting solid stream enters the combustor, where the char is burned, thereby heating the sand. The sand is circulated between the two reactors to provide the necessary heat of the gasification. This process has the highest conversion rates and gas yields (Belgiorno et al., 2003).

Some examples of this process are the Battelle biomass gasifier, licensed in the USA by Future Energy Resource Corporation (Ciferno and Marano, 2002; Corella et al., 2008), and the fast internally circulating fluidized bed gasifier developed at the Technical University of Vienna in cooperation with the Austrian Energy & Environment company (Duret et al., 2005; Hannula, 2009). As char indirect gasifiers produce a hydrogen-rich gas with a suitable heating value, further research on their use for hydrogen production is being performed (Mann, 1995; Pfeifer et al., 2004; Shen et al., 2008).

2.2. Biosyngas conditioning

Although syngas consists mainly of CO and H$_2$, it also contains undesirable compounds such as particles, condensable tars, alkali compounds, CO$_2$, H$_2$S, HCl, NH$_3$, HCN and COS. Therefore, syngas must be purified and conditioned to produce a gas with a suitable composition for its final application. Syngas purification also diminishes potential problems in downstream processes (e.g., catalyst poisoning, clogging, etc.). Before cleaning the gas, tar removal is required. In general, tars can be partly removed by thermal/catalytic destruction or condensation. To decrease the tar levels and enhance syngas production and quality, tar removal is performed by thermal/catalytic destruction followed by condensation.

Thermal destruction generally requires temperatures between 900 and 1100 °C, which are usually higher than the temperature of the output stream of the gasifier (McKendry, 2002). Thus, additional energy is needed to heat the gas. Moreover, high temperatures can cause material and economic complications (Huber et al., 2006). Catalytic destruction allows operation at lower temperatures, so that zero or little energy is needed to heat the gas. Hence, it is a more common procedure to reduce tar content than thermal destruction (Huber et al., 2006; McKendry, 2002; Pfeifer et al., 2004). The reaction of tars with H$_2$O, CO$_2$ and/or O$_2$ producing CO, CO$_2$, CH$_4$, H$_2$ and H$_2$O is assisted by catalysts (Huber et al., 2006).

After tar destruction, syngas undergoes cold wet gas cleaning (Göransson et al., 2011; Toonssen et al., 2008). This proven technology includes various stages. First, syngas is cooled and fine particles and condensed alkali compounds are removed by means of filtering devices such as filter bags. In the next stage, residual particles, halides, ammonia and residual tars are removed via scrubbing. Finally, H$_2$S and COS are removed by means of the LO-CAT® process and a ZnO guard bed, in order to avoid catalyst poisoning downstream (Spath et al., 2005). Sulphur concentration can be reduced below 0.1 ppm.

Dry hot gas cleaning constitutes an alternative to cold wet gas cleaning. It is based on the use of a series of sorbent reactors and separators (Sharma et al., 2013). Alkali impurities and halides are removed in the first sorbent reactor. Thereafter, the sorbents and ash are separated in a cyclone. Desulphurization occurs in the second sorbent reactor. A filter is then operated in pulsed or pulseless regime to completely remove all the particles. Finally, the resulting gas stream is passed through a multi-zoned packed bed of different sorbents to capture trace impurities of S, Se, As, Hg, NH$_3$, etc. (Sharma et al., 2013). When compared to cold wet gas cleaning, dry hot gas cleaning can result in a more efficient operation, also avoiding wastewater generation (Göransson et al., 2011; McKendry, 2002). Nonetheless, dry hot gas cleaning presents significant technical challenges associated with the performance of sorbents and particulate filters (McKendry, 2002; Sharma et al., 2013).

2.3. Biosyngas in energy applications

Currently, from an energy perspective, the main uses of syngas are power and heat generation through direct combustion, co-
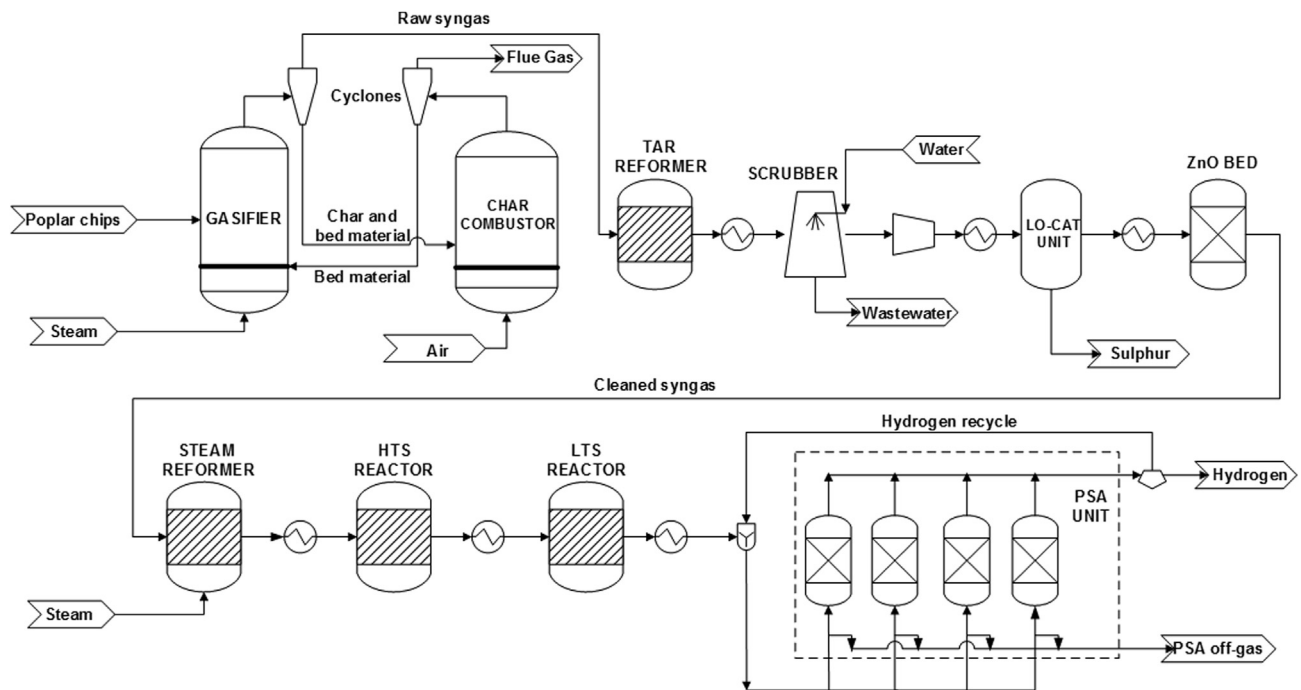
Fig. 2. Diagram of the main processes involved in the base case for biomass gasification.

firing in existing coal power plants, combined heat and power generation, and integrated gasification combined cycles (Boerrigter and Rauch, 2005). Alternatively, syngas can be used in the synthesis of energy products, such as methanol, synthetic fuel, synthetic natural gas (SNG) and hydrogen. Syngas generated through biomass gasification is primarily used for hydrogen production (Kırtay, 2011).

Syngas from biomass gasification using air or oxygen contains between 8 and 14 vol% of hydrogen. However, if steam is used as the gasifying agent, the hydrogen content can reach concentrations ranging from 30 to 60 vol% (Shen et al., 2008). Biosyngas is converted into hydrogen in two main steps: steam reforming (performed due to the methane content of the syngas, usually above 5 vol% [Boerrigter and Rauch, 2005]) and water gas shift (WGS) reaction. The first process (steam reforming) converts methane and higher hydrocarbons into CO and H_2:

$$C_xH_y + x\ H_2O \leftrightarrow x\ CO + (x + y/2)H_2 \qquad (1)$$
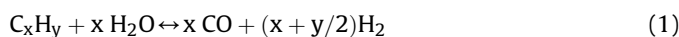
CO is then converted into CO_2 and H_2 by the WGS reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

The WGS reaction is generally performed in two consecutive reactors: a high-temperature reactor (HTS) at 350—500 °C and a low-temperature reactor (LTS) operating at around 200 °C (Huber et al., 2006). The most common catalysts for the WGS reaction are Fe—Cr-based catalysts for HTS and Cu-based catalysts for LTS. Hydrogen is purified by pressure swing adsorption (PSA) (Mann, 1995; Spath et al., 2005).

In addition to hydrogen production, SNG generation from lignocellulosic biomass, via gasification and catalytic methanation, is also being investigated (Steubing et al., 2011; Zhang, 2010). To meet the final SNG specifications, the produced syngas must have a high methane content and a low or zero nitrogen content. An example of this application is the Milena pilot plant in the Netherlands (Zhang, 2010).

Other biosyngas uses are subject to study, but, to date, their relevance is low, when compared to hydrogen production. For instance, research activities on biosyngas transformation into synthetic fuels through the Fischer—Tropsch synthesis are being performed (Huber et al., 2006; Opdal, 2006; Zhang, 2010). However, currently, there are no commercial plants that use biomass for this process, since the syngas must be very clean (Huber et al., 2006; Kumar et al., 2009).

3. Material and methods

3.1. The base case

The goal of this study is to evaluate the exergetic and environmental performance of a base case for biomass gasification. As hydrogen is considered one of the most promising alternatives to fossil fuels, the considered base case is associated with hydrogen production through biomass gasification. Based on the technological alternatives summarized in Section 2, poplar gasification in a low-pressure char indirect gasifier, catalytic tar destruction, cold wet gas cleaning and syngas conversion to hydrogen through SMR and WGS, followed by PSA purification, have been considered. Fig. 2 shows a schematic representation of the base case. Poplar (50% moisture) has been selected as the biomass feedstock due to the current interest in short-rotation plantations (SRP) for the production of second-generation biofuels. SRP poplar can grow with little input and in relatively small areas, thus improving the life-cycle performance of the biofuel (Gasol et al., 2009).

As shown in Fig. 2, the process selected for poplar gasification uses a low-pressure char indirect gasifier designed by Battelle Columbus Laboratory, operating at 870 °C and 1.6 bar (Spath et al., 2005). The heat required for the endothermic gasification is supplied by the bed material that circulates between the gasifier vessel and the char combustor. Steam is used as the gasifying agent, producing a syngas of relatively high hydrogen content, in

Table 1
Composition of the biosyngas after tar reforming (mol%, wet).

Component	Mol% (wet)
H_2	33.4
H_2O	26.5
CO	16.5
CO_2	16.1
CH_4	6.1
Higher hydrocarbons	1.2
Others (NH_3, H_2S, N_2)	0.2

comparison to that produced in air-blown gasifiers. The bed material is synthetic olivine, which promotes tar destruction, thus increasing the syngas yield. The syngas stream exiting the gasifier is sent to the tar reformer, where tars are converted into CO and H_2. This reactor consists of a bubbling fluidized bed that uses olivine as catalytic bed material. After the tar reformer, the syngas is conditioned by cold wet gas cleaning that is preferred to dry hot gas cleaning, which is associated with technical challenges. Elemental sulphur is obtained as a by-product from the cleaning subsystem, which is linked to the LO-CAT® process (48 °C, 30 bar). Thereafter, syngas undergoes SMR (at 850 °C and 30 bar) and high- and low-temperature shift conversion (at 350 °C and 200 °C, respectively). SMR is carried out because the produced syngas contains significant amounts of methane and higher hydrocarbons after tar reforming (Table 1) (Spath et al., 2005). Lastly, the final product (i.e., purified hydrogen) is obtained in a PSA unit that operates at 43 °C and 25.5 bar. The steam reformer is fuelled by the PSA off-gas (primary fuel) and natural gas (secondary fuel), which provides the additional thermal energy required by the reforming process. Since the attractiveness of hydrogen production is highly dependent on its primary energy demand, the conversion technology used and the related environmental impacts, a thorough evaluation of the thermodynamic and environmental performance of the case study must be conducted (Reijnders, 2009; Serrano et al., 2012).

3.2. Introduction to the exergetic analysis

The inefficiencies present within the boundaries of a system are represented by the exergy destruction. Streams that exit the system boundaries and are not further used in the process constitute the exergy losses. To calculate exergy values, a reference environment with a reference temperature, pressure and chemical potential must be defined (exergy reference environment or thermodynamic environment). At the reference state the exergy is zero. The defined reference values remain constant when heat and materials are exchanged between a system and the environment.

Exergy is separated into physical ($\dot{E}^{ph}$) and chemical ($\dot{E}^{ch}$) parts. Physical exergy depends on temperature and pressure and for a stream of matter it is defined by Eq. (3), where h and s are the specific enthalpy and entropy, respectively. The subscript 0 denotes the values at the temperature and pressure of the environment (T_0 and p_0). The temperature and pressure of the environment considered in this study are 15 °C and 1 bar, respectively.

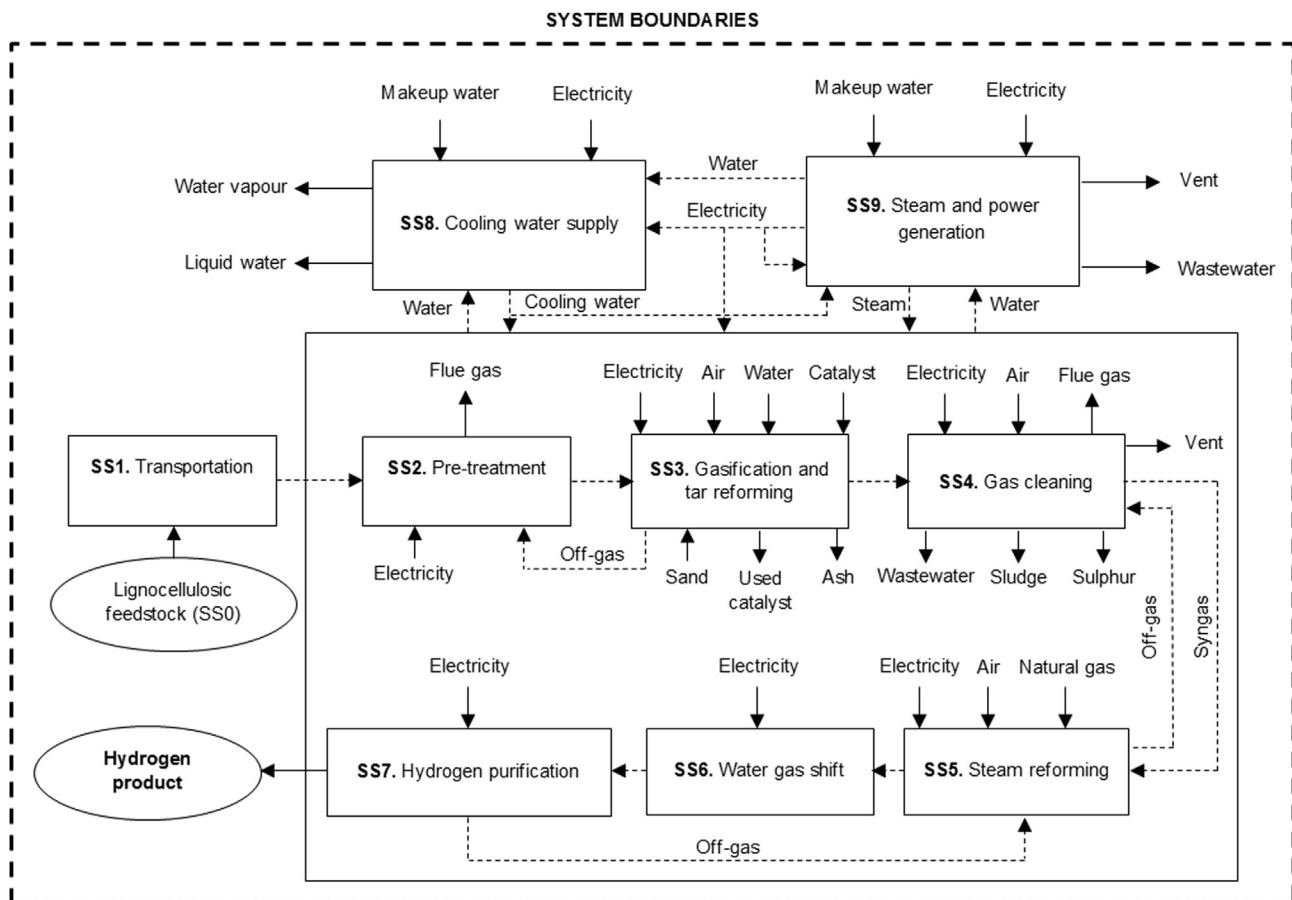$$e^{ph} = (h - h_0) - T_0 \cdot (s - s_0) \tag{3}$$

Fig. 3. Simplified flowchart of the base case study: definition of subsystems (dotted arrows involve flows between subsystems).
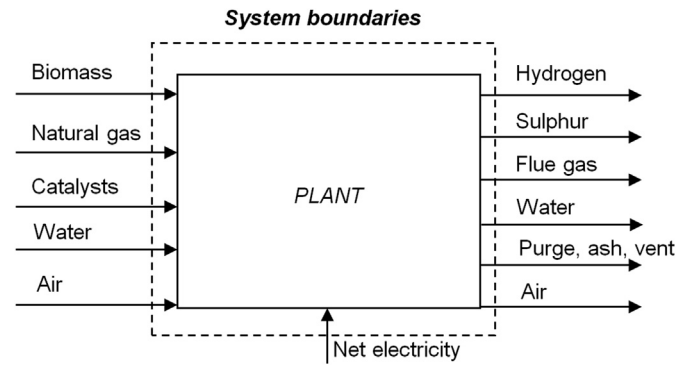
Table 2
Main inventory data for hydrogen production via poplar gasification (FU: 1 m³ stp of purified hydrogen).

Inputs from the technosphere			Outputs to the technosphere		
Materials and fuels			*Products*		
Poplar wood chips (wet basis) (SS0)	2.14	kg	Purified hydrogen	1.00	m³ stp
Magnesium oxide (SS3)	$4.08 \cdot 10^{-5}$	kg	*Avoided products*		
Olivine (SS3)	$3.21 \cdot 10^{-2}$	kg	Sulphur	$8.63 \cdot 10^{-4}$	kg
Process water (SS3)	$4.30 \cdot 10^{-3}$	kg	*Wastes to treatment*		
Natural gas (SS5)	$9.73 \cdot 10^{-3}$	kg	Sand/ash to landfill (SS3)	$4.30 \cdot 10^{-2}$	kg
Makeup water (SS8)	$7.69 \cdot 10^{-1}$	kg	Catalyst to landfill (SS3)	$3.50 \cdot 10^{-4}$	kg
Makeup water (SS9)	$5.99 \cdot 10^{-1}$	kg	Wastewater to treatment plant (SS4)	$1.21 \cdot 10^{-1}$	kg
Energy			Sludge to incinerator (SS4)	$5.82 \cdot 10^{-3}$	kg
Electric energy (SS2)	$9.45 \cdot 10^{-4}$	kWh	**Emissions to water**		
Electric energy (SS3)	$4.63 \cdot 10^{-3}$	kWh	Wastewater (SS8)	$1.48 \cdot 10^{-1}$	kg
Electric energy (SS4)	$2.79 \cdot 10^{-2}$	kWh	Wastewater (SS9)	$4.07 \cdot 10^{-2}$	kg
Electric energy (SS5)	$1.61 \cdot 10^{-4}$	kWh	**Emissions to air**		
Electric energy (SS6)	$1.61 \cdot 10^{-4}$	kWh	Oxygen (SS2)	$6.25 \cdot 10^{-2}$	kg
Electric energy (SS7)	$4.82 \cdot 10^{-4}$	kWh	Nitrogen (SS2)	1.91	kg
Electric energy (SS8)	$1.41 \cdot 10^{-3}$	kWh	Water (SS2)	1.11	kg
Electric energy (SS9)	$8.41 \cdot 10^{-4}$	kWh	Argon (SS2)	$3.26 \cdot 10^{-2}$	kg
Transport by lorry			Carbon dioxide (SS2)	$6.20 \cdot 10^{-1}$	kg
Poplar wood chips to plant (SS1)	$1.71 \cdot 10^{-1}$	t·km	Ammonia (SS2)	$1.57 \cdot 10^{-4}$	kg
Inputs from the environment			Oxygen (SS4)	$3.46 \cdot 10^{-2}$	kg
Air (SS3)	2.58	kg	Nitrogen (SS4)	1.32	kg
Air (SS4)	$2.09 \cdot 10^{-3}$	kg	Water (SS4)	$3.42 \cdot 10^{-1}$	kg
Air (SS5)	1.78	kg	Argon (SS4)	$2.24 \cdot 10^{-2}$	kg
			Carbon dioxide (SS4)	1.40	kg
			Nitrogen dioxide (SS4)	$2.92 \cdot 10^{-5}$	kg
			Water (SS8)	$6.22 \cdot 10^{-1}$	kg
			Carbon dioxide (SS9)	$3.38 \cdot 10^{-4}$	kg
			Ammonia (SS9)	$8.75 \cdot 10^{-5}$	kg

Fig. 4. System boundaries considered in the exergetic analysis.

respectively, are defined and the exergetic efficiency of the plant (ε_{tot}) can be calculated with Eq. (5).

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} \qquad (5)$$

The total exergy destruction of the plant ($\dot{E}_{D,tot}$) is calculated by subtracting its overall product exergy and exergy loss ($\dot{E}_{L,tot}$) from its overall fuel exergy, as in Eq. (6).

$$\dot{E}_{D,tot} = \dot{E}_{F,tot} - \dot{E}_{P,tot} - \dot{E}_{L,tot} \qquad (6)$$

3.3. LCA framework and data acquisition

The functional unit (FU) of the LCA study — i.e., the quantified performance of the product system to be used as the reference unit (ISO, 2006a, 2006b) — is 1 m³ stp of purified hydrogen (at plant). The system boundaries set for the LCA of the base case are shown in Fig. 3. As observed, a cradle-to-gate approach has been followed, starting at the feedstock plantation and finishing at the purification facility. A total of nine subsystems have been defined, viz., feedstock transportation (SS1), pre-treatment (SS2), gasification and tar reforming (SS3), gas cleaning (SS4), steam reforming (SS5), water gas shift (SS6), hydrogen purification (SS7), cooling water supply (SS8), and steam and power generation (SS9). Additionally, poplar cultivation and harvesting has been included as a background subsystem (SS0) that mainly involves land occupation, CO_2 absorption, fertilizer use and diesel consumption (Fan et al., 2011; Gasol et al., 2009). As presented in Fig. 3, a steam cycle is integrated into the system to fulfil the steam requirements, as well as to partly satisfy the electricity demand of the system. In this way, the electricity purchased from the grid is significantly reduced.

An LCA study requires the quantification of the relevant inputs and outputs of a system through its life cycle. In the present study,

Chemical exergy depends on the reference model used for its calculation (Tsatsaronis and Cziesla, 2004). Although available models are arbitrary to some extent, their uncertainties and differences do not affect the conclusions of an exergetic analysis. In this article, the model formulated by Ahrendts is used. The calculation of the chemical exergy is based on the chemical exergy per unit of mass defined in the reference model used. The chemical exergy per mole of a mixture of n gases is calculated by Eq. (4), where e_i^{ch} and x_i stand for the standard molar chemical exergy and the mole fraction of each i substance, respectively.

$$e^{ch} = \sum_{i=1}^{i=n} x_i \cdot e_i^{ch} + R \cdot T_0 \cdot \sum_{i=1}^{i=n} x_i \cdot \ln(x_i) \qquad (4)$$

After the exergies of all necessary streams are known, the fuel and product exergies of the overall process, $\dot{E}_{F,tot}$ and $\dot{E}_{P,tot}$,

Table 3
Composition of biomass and ambient air (wt%).

Biomass		Ambient air	
Composition (wt%, dry basis)		Composition (wt%)	
C	50.88	N_2	74.04
H	6.04	O_2	22.70
N	0.17	Ar	1.26
S	0.09	CO_2	0.05
O	41.90	H_2O	1.95
Ash	0.92		
Lower heating value (MJ/kg)	18.20		
Moisture content (wt%)	50.00		
e^{ch} (MJ/kg; dry and ash free)	20.50		

foreground data have been adapted from a techno-economic report on hydrogen production via poplar gasification (Spath et al., 2005). Table 2 summarizes the main inventory data gathered for the considered base case study. The biomass transportation distance assumed (80 km) has been based on literature data (Iribarren et al., 2012).

Secondary data have been mainly taken from the ecoinvent database (Frischknecht et al., 2007). Background processes include transportation (Spielmann et al., 2007) and the production of chemicals (Althaus et al., 2007) and energy carriers (Dones et al., 2007). Data from specific scientific literature have been used for poplar cultivation and harvesting (SS0) (Fan et al., 2011; Gasol et al., 2009).

4. Results and discussion

4.1. Exergetic analysis

In the exergetic analysis, the sulphur output has been considered as part of the overall product of the system. Thus, the product consists of hydrogen (main product) and sulphur (by-product). Fig. 4 shows a simplified diagram of the system considered in the exergetic analysis.

To calculate the chemical exergy of the streams, their composition must be known. The composition of the biomass is shown in Table 3. Stream data have been derived from Spath et al. (2005) and the incoming and outgoing streams in Fig. 4 may consist of more than one substream.

Based on Eq. (5) and according to the exergies of the considered streams and the power input ($\dot{W}_{in}$), the exergetic efficiency of the plant has been calculated using Eq. (7). The numerator and the denominator of the ratio represent the product and fuel exergies of the plant, respectively. The fuel exergy provided to the overall plant, $\dot{E}_{F,tot}$, involves the biomass, the added natural gas (considered here as pure methane), the air (used as oxidizer), the catalysts used and the power input required to operate the system. The net power input required by the plant is approximately 10 MW. The product exergy of the plant, $\dot{E}_{P,tot}$, includes the hydrogen and the produced sulphur. The calculated stream exergies are shown in Table 4. As observed, although sulphur has been considered as a by-product, its effect on the overall plant efficiency is negligible.

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} = \frac{\dot{E}_{H_2} + \dot{E}_S}{\dot{E}_{biomass} + \dot{E}_{CH_4} + \dot{E}_{catalysts} + \dot{E}_{air} + \dot{W}_{in}} \quad (7)$$

The exergetic efficiency of the plant has been found to be 48%. Since efficiencies of approximately 49% have been reported for the production of hydrogen via coal gasification (Abbas and Wan Daud, 2010; Rosen, 1996; Stiegel and Ramezan, 2006), the biomass gasification system can be considered an attractive alternative as long as environmental advantages are associated with this system. The use of a renewable resource (poplar biomass) and the production of high purity hydrogen (99.9 vol%) should support the suitability of this system.

As shown in Eq. (8), the exergy loss consists of the exergy of streams exhausted to the atmosphere (i.e., the flue gas streams led to the stack, $\dot{E}_{flue\,gas}$), the cooling air used in the compression unit ($\dot{E}_{CA_{out}-CA_{in}}$) and the cooling water used in various parts of the plant ($\dot{E}_{CW_{out}-CW_{in}}$).

$$\dot{E}_{L,tot} = \dot{E}_{flue\,gas} + \dot{E}_{CW_{out}-CW_{in}} + \dot{E}_{CA_{out}-CA_{in}} \quad (8)$$

When calculating the total exergy loss of the plant, some streams, such as the disposed sludge and ash, as well as the vent

Table 4
Specific physical and chemical exergies (e^{ph}, e^{ch}) and overall exergy rates ($\dot{E}_{stream}$) of incoming and outgoing streams.

	e^{ph} (kJ/kg)	e^{ch} (kJ/kg)	$\dot{E}_{stream}$ (kW)
Incoming streams			
Biomass	0.0	$1.0 \cdot 10^4$	$4.7 \cdot 10^5$
Natural gas	0.0	$4.6 \cdot 10^4$	$9.6 \cdot 10^3$
Catalysts	0.0	622.8	427.5
Water	0.0	7.1	72.5
Air	0.0	4.1	119.1
W_{in}	–	–	$1.0 \cdot 10^4$
Outgoing streams			
Hydrogen	$5.0 \cdot 10^3$	$1.2 \cdot 10^5$	$2.4 \cdot 10^5$
Sulphur	5.3	0.0	0.2
Water	101.9	7.6	209.8
Air	0.0	2.2	0.1
Flue gas	156.8	145.8	$2.2 \cdot 10^4$

exhausted from the deaerator have been neglected. In these cases, the chemical exergy is considered to be zero and the physical exergy negligible. The total exergy loss of the plant has been found to be 4.6% of the $\dot{E}_{F,tot}$ and it is mainly associated with the flue gas streams.

According to Eq. (6), 47% of the overall fuel exergy provided to the plant vanishes as exergy destruction. This percentage corresponds to 230 MW and it is constituted by the exergy destruction within the individual components of the plant. Through the overall exergetic analysis of the plant presented here, a general overview of the performance of the plant has been obtained. It is expected that most of the exergy destruction will occur in the components where chemical reactions take place (Bejan et al., 1996; Petrakopoulou, 2010), with the largest part in the gasifier. One common practice to improve the operating efficiency of chemical reactors is to increase the temperature of the reacting streams. However, because most of the exergy destruction within the chemical reactors is unavoidable (Petrakopoulou, 2010), only marginal improvements can be achieved. Further measures depend on the system configuration and its specific potential for improvement that can be revealed using advanced exergy-based methods.

4.2. Environmental characterization

The life cycle impact assessment phase of an LCA study associates life cycle inventory data with a set of environmental impact categories and their corresponding indicators, in order to evaluate the environmental performance of a system (ISO, 2006a, 2006b). The environmental characterization of hydrogen production via poplar gasification has been carried out taking into account seven categories: cumulative energy demand (CED), global warming (GWP), ozone layer depletion (ODP), photochemical oxidant formation (POFP), land competition (LC), acidification (AP) and eutrophication (EP). CED refers to the cumulative non-renewable (fossil and nuclear) energy demand (VDI, 2012), while the other

Table 5
Environmental characterization of the overall system (FU: 1 m³ stp of purified hydrogen).

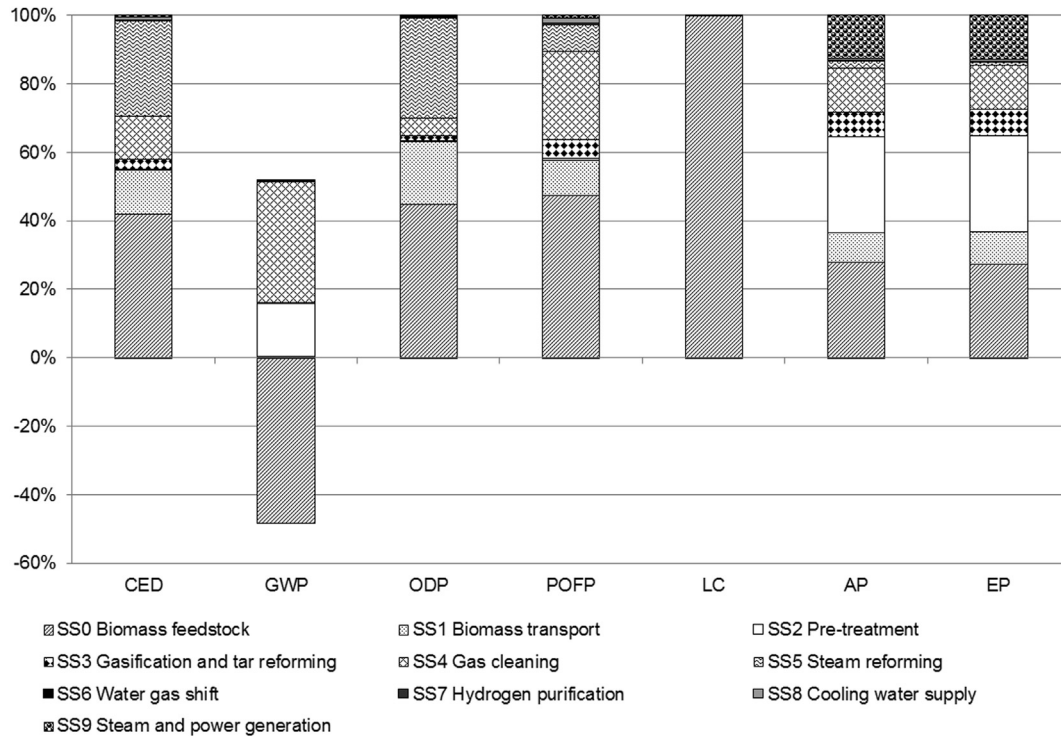|	Whole system	Sulphur credit	Hydrogen
CED (MJ eq)	2.05	$-4.35 \cdot 10^{-3}$	2.04
GWP (kg CO_2 eq)	$1.30 \cdot 10^{-1}$	$-2.76 \cdot 10^{-4}$	$1.30 \cdot 10^{-1}$
ODP (kg CFC-11 eq)	$1.49 \cdot 10^{-8}$	$-3.53 \cdot 10^{-11}$	$1.49 \cdot 10^{-8}$
POFP (kg C_2H_4 eq)	$2.20 \cdot 10^{-5}$	$-1.38 \cdot 10^{-6}$	$2.07 \cdot 10^{-5}$
LC (m²a)	$7.93 \cdot 10^{-1}$	$-1.32 \cdot 10^{-7}$	$7.93 \cdot 10^{-1}$
AP (kg SO_2 eq)	$1.16 \cdot 10^{-3}$	$-3.45 \cdot 10^{-5}$	$1.13 \cdot 10^{-3}$
EP (kg PO_4^{3-} eq)	$2.52 \cdot 10^{-4}$	$-1.45 \cdot 10^{-7}$	$2.52 \cdot 10^{-4}$

Fig. 5. Contribution (%) of the subsystems to the potential environmental impacts allocated to hydrogen.

impact potentials have been computed using the CML method (Guinée et al., 2001). The software SimaPro 7 has been used for the computational implementation of the inventories (Goedkoop et al., 2010).

Table 5 presents the environmental characterization results of the overall hydrogen production system. These results have been shared between the different products generated by the system: hydrogen (main product) and sulphur (marketable by-product). An allocation procedure has been followed to face this multifunctional system (Ekvall and Finnveden, 2001). Since the produced sulphur can be introduced to the existing sulphur market and cover part of its demand, an avoided burden approach has been adopted. The produced sulphur has been assumed to partly replace the conventional production of sulphur (avoided product), preventing, therefore, the related environmental burdens (avoided impacts). Based on this method, an environmental credit has been computed
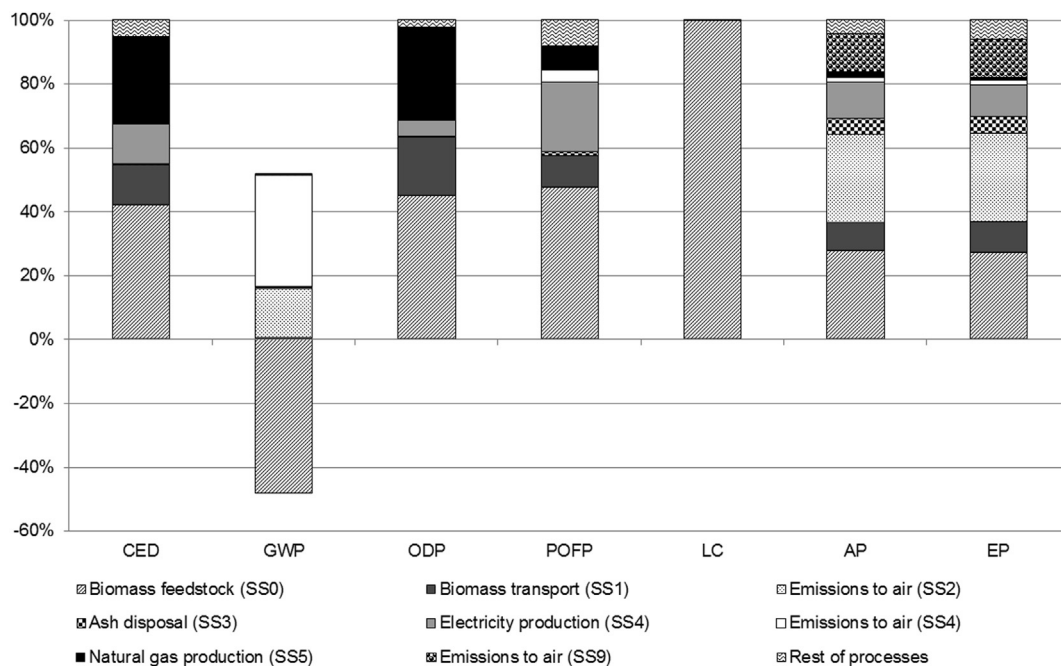

Fig. 6. Contribution (%) of the main processes to the potential environmental impacts allocated to hydrogen.

to account for the generation of the sulphur by-product. The environmental characterization results linked to the hydrogen product in Table 5 have been calculated by subtracting this environmental credit from the impacts of the whole system. As observed, the environmental reduction associated with the sulphur credit is negligible (percentage reduction < 0.25%) for all considered impact categories, with the exception of POFP (6%) and AP (3%).

The use of an LCA approach allows the identification of the subsystems that contribute most to the potential impacts attributed to the produced hydrogen. As shown in Fig. 5, the biomass cultivation and harvesting subsystem (SS0) dominates the LC impact category, also accounting for the highest contributions to POFP (48%), ODP (45%) and CED (42%). Although SS0 also contributes to AP and EP significantly, these categories are dominated by the pre-treatment subsystem (SS2), with a contribution percentage of 28% in both cases. Finally, the gas cleaning subsystem (SS4) has been found to be the subsystem with the highest contribution to GWP. In this category, a desirable effect has been identified for SS0, due to CO_2 absorption during the poplar cultivation stage. This favourable effect of poplar cultivation on the GWP category, as well as the leading role of SS0 regarding LC, agrees with observations from other LCA studies of energy systems that use biomass as feedstock (Hsu, 2011; Iribarren et al., 2012; Susmozas et al., 2013).

Even though biomass transport (SS1), gasification (SS3), steam reforming (SS5) and steam and power generation (SS9) have not been identified as top contributors to any impact category, they should not be disregarded. For instance, SS5 contributes to ODP and CED with more than 25%, SS9 presents contributions of higher than 12% to AP and EP, and SS1 contributes significantly to ODP (18%).

The application of the LCA methodology to hydrogen production via poplar gasification leads to the identification not only of the most contributing subsystems, but also of the specific processes that result in these contributions. Fig. 6 summarizes the contribution of the main processes to the potential environmental impacts attributed to hydrogen.

As observed, direct emissions to air from the pre-treatment subsystem (SS2) are the reason of the high contribution of this subsystem to AP, EP and GWP. It should be noted that the off-gas stream from the gasification subsystem (SS3) is used for biomass drying in the pre-treatment subsystem. Thus, the final emission impacts have been fully attributed to SS2.

Direct emissions to air from the gas cleaning subsystem (SS4) are responsible for the contribution of SS4 to GWP. In addition to poplar cultivation/harvesting/transport and direct emissions to air from SS2 and SS4, other processes with high environmental impact contributions include: (i) the natural gas production linked to SS5 (contribution of 29% to ODP and 28% to CED), (ii) the electricity production associated with SS4 (contribution of 22% to POFP, 13% to CED, 12% to AP and 10% to EP), and (iii) direct emissions to air from SS9 (contribution of 12% to AP and EP). The significant role of electricity is in agreement with previous life-cycle studies on biomass gasification (Koroneos et al., 2008), as well as the leading role of poplar production and direct emissions from the processing plant (Susmozas et al., 2013). Nevertheless, it should be noted that gasification plants could be designed to be (completely) energy self-sufficient (Susmozas et al., 2013).

Based on the CED indicator of the produced hydrogen (Table 5), a preliminary life-cycle energy balance has been carried out. While the total fossil and nuclear energy demand accounts for 2.04 MJ/FU, a total energy output of 10.79 MJ/FU has been estimated according to the lower heating value of the produced hydrogen (Waldheim and Nilsson, 2001). Hence, an energy surplus of 8.75 MJ/FU has been found, which is equivalent to 81% of the potential energy output. Although more thorough energy balances are needed, preliminary results suggest a relatively promising energy performance of hydrogen production via poplar gasification, as also observed in previous studies (Koroneos et al., 2008; Susmozas et al., 2013).

Finally, based on the environmental hot spots identified in this section, actions to (i) minimize the poplar feedstock demand (i.e., attainment of higher conversion efficiencies), (ii) improve the logistical planning for biomass supply, (iii) reduce the natural gas demand of the steam reforming subsystem, and (iv) optimize the electricity demand of the gas cleaning subsystem, are highly recommended to enhance the environmental and energy performance of the system. Improvements related to poplar cultivation and harvesting also are of great value, especially concerning the achievement of lower consumption levels of fertilizers and diesel.

5. Conclusions

Based on an overview of the current alternatives available for biomass gasification, a representative base case was defined: hydrogen production via poplar gasification in a low-pressure char indirect gasifier. The thermodynamic and environmental performance of this case study was evaluated through an exergetic analysis and an LCA.

The exergetic efficiency of the considered plant was found to be 48%. In this respect, the performance of the biomass gasification system is comparable to hydrogen production via coal gasification, while achieving environmental advantages associated with the use of a renewable bioresource (poplar).

Inventory data for the base case were collected to estimate the potential environmental impacts of the system for a selection of seven impact categories. Poplar cultivation and harvesting, biomass pre-treatment and syngas cleaning were found to be the subsystems with the largest contributions to the environmental impacts. Measures to improve the environmental and energy performance of this hydrogen production system should focus on minimizing the poplar feedstock demand, improving the logistical planning for biomass supply, reducing the natural gas demand of the steam reforming subsystem and optimizing the electricity demand of the gas cleaning subsystem. Lower consumption levels of fertilizers and diesel for poplar cultivation and harvesting should also be achieved.

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