Life cycle assessment of hydrogen production from biogas reforming

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11   **Abstract**

12   A H_2 production system via biogas reforming was comprehensively investigated by life

13   cycle assessment (LCA), after identification of the optimal thermodynamic operating

14   conditions computed from a detailed analysis of the involved chemical reactions. The

15   system boundaries for the LCA include biogas production, biogas reforming as well as

16   construction and decommissioning steps. The biogas production data are adapted from a

17   literature review, whereas the reforming inventory data are obtained from process

18   simulation in Aspen Plus™ software. The life cycle inventory data for the H_2 system are

19   computationally implemented into SimaPro 8. Different environmental impact categories,

20   following the ILCD 2011 midpoint impact assessment method, were calculated. An energy

21   analysis is also carried out, based on cumulative energy demand and on non-renewable

22   primary energy consumption as additional impact categories.

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1   The results obtained show that the total greenhouse gas emissions of the system are

2   estimated to be 5.59 kg CO_2-eq per kg of H_2 produced, which represents about half of the

3   life cycle GHG of conventional H_2 production systems via steam methane reforming. Most

4   environmental impacts are influenced by the amount of artificial fertilizer displaced by the

5   digestate as well as by the impact credits for recycling of the plant construction materials

6   and equipment. Overall, the LCA of the biogas-to-H_2 system shows very advantageous

7   results. Accordingly, the authors recommend the use of biogas as an ecofriendly source for

8   sustainable H_2 production.

9

10   *Keywords:* Hydrogen, biogas, steam reforming, environmental impact, thermal efficiency.

11

12   **Nomenclature**

13

AD   anaerobic digestion

ADP   abiotic depletion potential

AP   acidification potential

BG   biogas

Bioeth-ATR-H_2 H_2 production by bioethanol auto-thermal reforming

Bioeth-SER-H_2 H_2 production by bioethanol steam reforming

Biom-gasi-H_2 H_2 production by lignocellulosic biomass gasification

C&D   construction and decommissioning

CED   cumulative energy demand

DMR   dry methane reforming

Electro-H_2 H_2 production by electrolysis

FAO   food and agriculture organization

FC	fuel cells
FEP	freshwater eutrophication potential
FETP	freshwater eco-toxicity potential
FU	functional unit
GHG	greenhouse gas
HTPce	human toxicity with cancer effects
HTPnce	human toxicity with non-cancer effects
HTS	high temperature shift
IRP	ionising radiation potential
ISO	international organization for standardization
LCA	life cycle assessment
LCI	life cycle inventory
LCIA	life cycle impact assessment
LHV	lower heating value
LTS	low temperature shift
LUP	land use potential
MEP	marine eutrophication potential
NER	net energy ratio
NG	natural gas
NRE	non-renewable energy requirement
ODP	ozone depletion potential
PMP	particulate matter potential
POF	photochemical ozone formation
PSA	pressure swing adsorption
SALCA-P	Swiss agricultural life cycle assessment-Phosphorus

SB	system boundaries
SETAC	society of environmental toxicology and chemistry
SG	synthesis gas
SMR	steam methane reforming
TEP	terrestrial eutrophication potential
W	mechanical work
WGS	water gas shift
WRD	water resource depletion
η	thermal efficiency

1. Introduction

Rising concerns about the effects of global warming and gradual depletion of non-renewable fossil fuels have led to increasing interest in H_2 for fuel cell (FC) applications owing to their zero emission and high efficiency [1]. However, more than 50% of the world's total H_2 production is derived from steam methane reforming (SMR) of natural gas (NG) [2]. SMR is a mature and cost effective technology which uses fossil fuel as a feedstock so the amount of CO_2 formed would be the same as that formed by direct combustion of the fuel (NG) [3]. For instance, greenhouse gas (GHG) emission of H_2 production via SMR process is estimated as 13.7 kg eq. CO_2 per kg of net H_2 produced [4]. Also, a typical SMR plant with a capacity of one million m^3 of H_2 per day produces about 0.3–0.4 million standard cubic meters of CO_2 per day [4]. In order to help reduce global warming, the use of raw materials and energy from renewable sources should lessen GHG emissions. A palliative way to achieve this goal would consist in reducing the current use of NG in favor of biogas (BG).

1   BG is the product of the anaerobic digestion (AD) of organic residues from several origins

2   (sewage sludge, food waste, animal manures, crop residues, etc.) and it is basically

3   composed of methane, carbon dioxide and minor species such as hydrogen sulphide,

4   ammonia, humidity, etc. [5]. BG can be directly used as a combustible gas; however, the

5   combustion process of BG to generate heat has a low efficiency. In fact, humidity and

6   CO_2 content of the BG, which dilutes the intake charge, limit the engine peak power due to

7   the decrease in the calorific value of the fuel [6]. As a special case, BG could be used to

8   produce H_2 which would be then supplied to FC [7,8], which reached remarkable progress

9   during the past decade. The utilization of BG as a feedstock for a reforming process to

10   produce H_2 offers several advantages; (i) it is a bio-renewable fuel and can reduce the

11   emission of GHG, (ii) it is easily generated from available local agricultural wastes and

12   residues and (iii) contrarily to combustion, the presence of CO_2 and humidity in BG are

13   advantageous for converting BG into H_2 via steam and dry reforming reactions. In this

14   context, the use of BG as a renewable resource for producing H_2 has been widely

15   investigated in recent years [7,9–11]. Lately, Castillo et al. [11] conducted a steam

16   reforming reaction of a BG mixture with an H_2 permeable palladium–silver membrane

17   reactor under temperatures between 350 and 450 °C and with of reaction side pressure of

18   0.1 to 0.4 MPa. The authors showed that, in the experiment, the reaction with permeation

19   achieved a higher H_2 production than the reaction without permeation in identical

20   operational conditions. Iulianelli and co-workers [7] studied the steam reforming of a

21   model BG mixture for generating H_2 by using an inorganic membrane reactor, in which a

22   composite Pd/Al_2O_3 membrane separates part of the produced H_2 through its selective

23   permeation. The authors show that the BG steam reforming reaction, at 380 °C, 2.0 bar,

24   $H_2O/CH_4 = 3/1$, gas hourly space velocity (GHSV) of 9000 h^{-1} the permeate purity of the

25   recovered H_2 is around 96%, although the conversion (15%) and H_2 recovery (>20%) are

1   relatively low; on the contrary, at 3.5 bar, 450 °C, $H_2O/CH_4 = 4/1$, $GHSV = 11000 \, h^{-1}$ the

2   conversion increases up to more than 30% and the recovery of H_2 to 70%.

3

4   The production of H_2 produced from BG claims to be an environmentally sustainable

5   system. However, significant efforts are still required for its production system to be

6   evaluated from a comprehensive environmental point of view. Currently, life cycle

7   assessment (LCA) is a well-known and widely used method to assess the potential

8   environmental impacts and resources used throughout the entire life cycle of a product or

9   process, including raw material acquisition, production, use, and end-of-life phases as

10   defined by SETAC and coded by ISO 14040 standards [12]. LCA has become an important

11   decision-making tool for promoting new alternative fuels since it can systematically

12   analyse energy use and environmental impacts before implementing a fuel policy [13].

13   Therefore, LCA methodology has been used extensively within the recent decade to

14   evaluate the environmental performance of bioenergy processes [14–16]. Until present,

15   several BG-to-H_2 studies have been published but to the best of our knowledge, research

16   dealing with the LCA of such comprehensive systems is still scarce. Hence, for a complete

17   insight on the environmental performance of BG-to-H_2, it would be necessary to include all

18   the energy and raw materials involved in the entire system. Scientific perception indicates

19   that H_2 generated by BG reforming could potentially lead to environmental improvements.

20   However, this perception should be quantitatively substantiated through a scientifically

21   rigorous investigation.

22

23   The main objective of this study is to measure, via LCA methodology, the energy

24   performance and environmental impact of H_2 production system from biogas reforming. A

25   combination of various assessment tools is applied to comprehensively investigate the BG-

to-H$_2$ system. These tools focus on the BG reforming reactions, simulate the H$_2$ production process, and perform an environmental impact assessment (using LCA methodology). Through the study of chemical reactions, thermodynamically optimal operating conditions at which the BG may be converted to H$_2$ via the steam and dry reforming process can be identified. The recommended thermodynamic conditions obtained are subsequently exploited in the simulation of a real H$_2$ production process. The results of the process simulation are used, thereafter, as inputs to a life cycle inventory and are computationally implemented into SimaPro 8 software [17]. The following environmental and energy parameters were selected to describe the performance of the BG-to-H$_2$ system: Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Human Toxicity with cancer effects (HTPce), Human Toxicity with non-cancer effects (HTPnce), Particulate Matter (PMP), Ionising Radiation (IRP), Photochemical Ozone Formation (POF), Acidification Potential (AP), Terrestrial Eutrophication (TEP), Freshwater Eutrophication (FEP), Marine Eutrophication (MEP), Freshwater EcoToxicity (FETP), Land Use (LUP), Water-Resource Depletion (WRD), Abiotic Depletion Potential (ADP), Cumulative Energy Demand (CED) and Non-Renewable Energy requirement (NRE).

2. Methodology

2.1. BG-to-H$_2$ production system

As described above the aim of this research is to investigate an H$_2$ production system from BG reforming. The considered system comprises two main steps: (1) BG production, and (2) BG reforming.

2.1.1. BG production

The BG production process was adapted from a published article [18]. The BG was produced by AD from farm waste. After collection by trucks, the waste (about 14 t/day)

was fed into an on-site hopper and mixer. The digester feedstock was considered to be a

mixture of manure (7 t/day) and the rest split equally (at 2.33 t/day each) between cheese

whey, waste maize silage and fodder beet. The feedstock passed, firstly, through a

macerator before being pumped into an 800 m^3 AD tank. Within the digester, the feedstock

was agitated and heated up to 40 °C (in anoxic, mesophilic conditions), producing about

2027 Nm^3 of BG per day. The average molar composition of the BG is considered to be

CH_4 (60%), CO_2 (35%), N_2 (3%) and H_2O (2%) [19]. The main coproducts of BG were the

liquid and the solid digestate. The liquid digestate produced in the AD tank was pumped

out into a lagoon and thus stored for use as fertilizer on the farm. The solid digestate was

removed and loaded onto a trailer to be used as fine-grade compost. The BG was piped

from the top of the digester to a 350 m^3 gas storage tank and then to the reforming process.

2.1.2. BG reforming: H_2 production

The H_2 production process basically consists in three main steps [20,21]: (1) synthesis gas

(SG) generation, (2) water gas shift (WGS) and (3) gas purification.

The first step is called reforming; the BG–steam mixture is catalytically converted to SG, a

mixture primarily made up of H_2, CO, CO_2, CH_4 and H_2O. The main reactions occurring in

the reforming reactor, according to the literature [6,22], was considered to be the SMR (Eq.

2) and the dry methane reforming (DMR) (Eq. 3). The overall reforming reaction can be

modeled to reflect the following relationship:

$$BG\ (CH_4) + \alpha\ H_2O + \beta\ CO_2 \rightarrow SG\ (H_2, CO, CO_2, CH_4, H_2O, etc.) \tag{1}$$
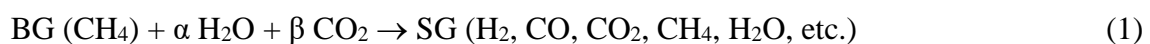
where α and β are the stoichiometric coefficients of water and carbon dioxide, respectively.

The main possible reactions for the BG reforming are as follows:

SMR

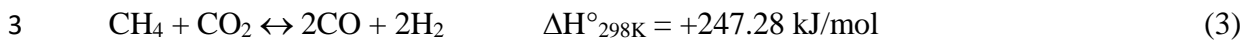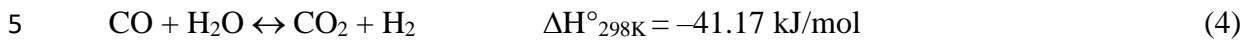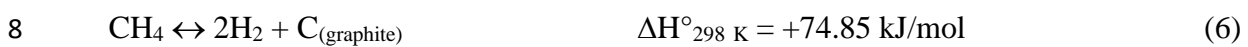1 $$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H°_{298K} = +206.11 \text{ kJ/mol} \qquad (2)$$

2 *DMR*

3 $$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H°_{298K} = +247.28 \text{ kJ/mol} \qquad (3)$$

4 *WGS*

5 $$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H°_{298K} = -41.17 \text{ kJ/mol} \qquad (4)$$

6 *Carbon formation*

7 $$2CO \leftrightarrow CO_2 + C_{(graphite)} \qquad \Delta H°_{298 \text{ K}} = -172.43 \text{ kJ/mol} \qquad (5)$$

8 $$CH_4 \leftrightarrow 2H_2 + C_{(graphite)} \qquad \Delta H°_{298 \text{ K}} = +74.85 \text{ kJ/mol} \qquad (6)$$

9 $$CO + H_2 \leftrightarrow C_{(graphite)} + H_2O \qquad \Delta H°_{298 \text{ K}} = -131.26 \text{ kJ/mol} \qquad (7)$$
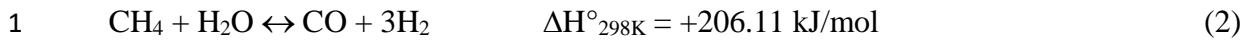
10 The overall reaction in Eq. (1) is highly endothermic and requires a large amount of heat,

11 which is provided by external burners. The SG composition depends on the reformer

12 temperature (T) and pressure (P), as well as the feed composition, expressed by the

13 $CH_4/CO_2/H_2O$ ratio [9,23].

14 *In the second step*, the SG exiting the reformer is passed through a WGS reactor, where the

15 CO reacts with H_2O over a catalyst to form H_2 and CO_2 (Eq. 4). In practice, the WGS

16 reaction takes place in two separate reactors: a High Temperature Shift reactor (HTS),

17 operating between 300 and 400 °C, and a Low Temperature Shift reactor (LTS), operating

18 between 200 and 300 °C [24].

19 The last step is the purification of H_2. The purification process can be achieved through a

20 number of techniques (CO_2 removal using chemical absorption and methanation processes,

21 pressure swing adsorption (PSA), metallic membrane separation, etc.). However, in

22 modern plants H_2 membrane separation has attracted much attention due to its high

23 H_2 purity (>99%) and to its moderate energy consumption.

24

The detailed flowsheet of the H_2 production process from BG reforming is presented in Fig. 1. The process was modeled in Aspen Plus™ process simulation software developed by AspenTech using simulation data from the U.S. Department of Energy (DOE) demonstration SMR facility in the city of Las Vegas [2]. However, previous thermodynamic studies indicate that the sole use of BG with a CH_4/CO_2 ratio >1 (as our case study CH_4 (60%)/CO_2(35%)=1.7) causes significant coke formation resulting in the deactivation of catalysts and subsequent reactor plugging [25,26]. Coke deposition can be reduced during DMR by either using a fluidised-bed in the presence of sufficient oxidizing agents (steam, carbon dioxide, air (O_2)) [23,26,27] or by using excess steam in a fixed-bed reactor [26,28]. In this work, water is added in the reforming reactor for two reasons (i) to prevent deactivation of the catalyst, and (ii) to avoid water addition in the WGS reactor.

Fig. 1.

A detailed flowsheet of the H_2 production process from BG reforming.

Label numbers: **1-6:** Water   7-**10**: BG   **11-16**: SG   **18**: H_2 **17,19,20**: Retentate

21: Air Combustion   **22-24**: Off-Gas.

Carbon (coke) formation is a major barrier for commercial application of BG reforming in the chemical industry, as solid carbon deposits on the surface of the catalyst lead to catalyst deactivation. Carbon formation is significantly affected by the reforming operating temperature and the molar ratios of H_2O/CH_4 and CO_2/CH_4 [26]. Hence, it is important to optimize operating conditions to avoid or at least minimize carbon deposition within BG reforming processes. Therefore, before simulating the BG-to-H_2 process, the reforming reactions are investigated to determine the influence of water addition and reforming temperature on SG composition and coke deposition. The reforming pressure is provided by the operation pressure of the U.S. DOE process (i.e. 10 atm) [2] and the CO_2/CH_4 molar

10

ratio is defined by the current BG composition (i.e. 0.583). During the present study the optimal operating conditions (H_2O/CH_4 ratio and temperature) at which BG may be converted to H_2 have been identified. The choice of these conditions lies in the maximization of H_2 production while minimizing CO concentration in the SG and suppressing coke formation. However, it is important to reduce the CO concentration in the SG in order to reduce the required size of the WGS reactors (the second step of the process) [29]. In the present paper, the equilibrium compositions of the SG were calculated by minimizing the Gibbs free energy with the aid of the Aspen Plus™ software (Aspen Technology, Inc., Burlington, USA) [30]. Indeed, the minimization of the total Gibbs free energy represents a suitable method to compute the thermodynamic equilibrium compositions of any reacting system. This is because the reaction is thermodynamically favored when its total Gibbs free energy, expressed as a function of the component concentrations, temperature and pressure, is at its minimum value [31]. The method of thermodynamic analysis via the minimization of Gibbs free energy used in this study has already been introduced in our previous papers [32,33] and has also been described in detail by other research groups [34,35]. The R-Gibbs reactor model [30] was selected, and the thermodynamic properties were computed using the Soave-Redlich-Kwong (SRK) equation of state (following the thermodynamic models selection criteria, described by Aspen Plus™ reference manual (physical property methods and models [30]). Aspen Plus™ software requires the input of all chemical species potentially present in the reaction system as reactants and products. Accordingly to previously published results [6,9,23], the component list was restricted to CH_4, H_2O, CO, H_2, CO_2, N_2 and $C_{(graphite)}$. It is noteworthy that the equilibrium calculations performed here do not account for the kinetic aspects of the BG reforming reaction.

The H$_2$ production process (depicted in Fig. 1) starts by pumping the inlet water (stream 1→ stream 2) and compressing the BG (stream 9 → stream 10) to the reforming operating pressure (10 atm). Water is then heated before being fed into the reforming reactor (2→6). First, water recovers the calories from the HTS cooler COOL-HTS (2→3), then the hydrogen cooler (COOL-H$_2$) (3→4), it passes through the SG cooler (COOL-SYNG) (4→5) and finally the economizer 1 (ECONO-1) (5→6). The SG leaving the reformer is cooled to 300 °C (HTS inlet temperature) in a heat exchanger (COOL-SYNG). The product stream exiting the HTS reactor is cooled to 200 °C (LTS inlet temperature) in COOL-HTS. The gas leaving the LTS is heated to T = 500 °C (the operating temperature of the hydrogen membrane separation) in the economizer 2 (ECONO-2). Purified hydrogen (reaching 99.99%) is cooled after passing through a heat exchanger (COOL-H$_2$) (17→18), whereas the gas containing un-reacted methane (retentate) is expanded to atmospheric pressure (19→20) before being sent back into the furnace. The endothermic nature of the reforming reaction requires a combustion furnace, which is also fed by a fraction of the inlet BG (7→8). The combustion air (stream 21) is considered to exceed by 10%. The combustion gas (stream 22) passes through two heat exchangers, ECONO-1 and ECONO-2, before being sent back to the digester to maintain the desired temperature (i.e. 40 °C). The simulation was performed under steady state according to the following assumptions:

- Air, BG and water enter the process at temperature T=25 °C and pressure P=1 atm.

- The excess of combustion air is 10%.

- Pressure drops are neglected during operation in all units.

The reforming and the WGS (HTS and LTS) reactors were modeled using the library model RGibbs. The Rstoich model [30] was used to model the combustor required to supply heat to the reformer. The Aspen Plus™ library model HEATX [30] was employed for all of the heat exchangers with two input and output streams. H$_2$ purification was

performed by a membrane separation module that was modeled with the Aspen Plus™

module Sep as an isothermal metallic membrane. The pump, the compressor and the valve

were modeled respectively using the Pump, Compr and Valve library models [30].

2.2. Life cycle assessment of H_2 production from biogas reforming

2.2.1. LCA background

LCA is a standardized methodology for the evaluation of environmental impacts and

resources used throughout a product's life cycle, from raw material acquisition to

production and use phases and finally to waste management (also known as cradle-to-grave

methodology) [12,36].

The methodological framework of LCA, as defined in ISO 14040-14044 standards [12],

includes four interrelated phases: (1) *Goal and scope definition*: Specifies the aims of the

study, the system boundaries (SB), and sets a functional unit (FU) to provide a reference

for all input and output data, (2) *Life cycle inventory (LCI) analysis*: Identifies material and

energy inputs and outputs for all processes within the SB and including calculation and

allocation procedures, (3) *Life cycle impact assessment (LCIA)*: Evaluates the potential

environmental effects related to the results of the LCI, and (4) *Interpretation of the results*:

Evaluates the life cycle model by identifying significant issues based on the results of LCI

and LCIA, considering consistency and completeness, and makes conclusions and

recommendations.

2.2.2. LCA of BG-to-H_2 system

2.2.2.1. Goal and scope definition

a. Goal

The main objective of this study was to evaluate the life-cycle environmental burdens of a

H_2 production system based on BG reforming, in order to identify the environmental hot

spots (the life cycle steps that have a high contribution to the environmental burden). We

will not only identify the environmental impacts but also quantify the energy performance

from a cradle-to-gate perspective.

b. Functional unit, system boundaries, and common assumptions

The FU chosen in this paper is 1 kg of H_2. The SB, illustrated in Fig. 2, were chosen in a

way to include all steps necessary for the operation of the entire system (to deliver the

system's FU). The following life-cycle stages are taken into account:

S1 (AD plant): includes (i) waste collection, (ii) AD plant operation, and (iii) digestate

storage and use.

S2 (H_2 plant): encloses (i) feed conditioning and BG reforming, and (ii) WGS and

purification.

S3 (Construction and Decommissioning (C&D)): includes (i) construction (building and

equipment), and (ii) decommissioning (landfilling, incineration and recycling).

Fig. 2.

Overview of the LCA boundaries of the BG-to-H_2 system.

The BG production by the AD plant implies solid and liquid digestate productions, after

separation of phases. Digestates are commonly stored and used for agricultural crop

productions and are spread over fields as organic fertilizer (N, P and K supplies). The

fertilizing effect of digestate is taken into account in LCA by substitution of mineral

fertilizers (see [37] for a review), while the agricultural use of this residue involves:

- Emissions at agricultural field levels of nitrogen compounds, phosphate and heavy metals due to digestate composition.

- Avoided emissions of substituted mineral fertilizer productions and transport.

- Avoided emissions at agricultural field levels of nitrogen compounds, phosphate and heavy metals due to avoided mineral fertilizer composition.

Nitrogen compound emissions (NH_3, N_2O, NO_x and NO_3^-) and nitrogen mineral fertilizer equivalents were computed using the tool proposed by [38]. Mixtures of substituted mineral fertilizer were determined according to French fertilizer mixtures as performed in [39]. Ammonia and nitrogen oxides (NO_x) avoided emissions were determined according to [40], while nitrate emissions of avoided mineral fertilizer followed FAO guidelines [41]. Phosphate emissions (from spread digestate and avoided fertilizer) were calculated with a simplified SALCA-P model [42]. The phosphorus mineral fertilizer equivalent (MFE) value was assumed to be 0.95. The potassium MFE was fixed at 1.0 (see [39] for details). All heavy metals in AD inputs were assumed to spread with digestate (references values come from [42] except for cheese whey [43]). Avoided heavy metals emissions were determined with values proposed in [39]. No environmental impacts were considered for the feedstock as it was made up from farm waste.

According to literature data, uncontrolled methane emissions from the BG plant due to leakages were estimated to represent 2% of the produced BG [44–46]. The storage of digestate in an open-air lagoon system tends to release both methane and ammonia. These emissions are assumed to be 4.465 kg/ t AD feedstock and 0.115 kg/ t AD feedstock, respectively [18,47]. However, concerning ammonia, a further 0.677 kg/ t AD feedstock of ammonia is released during digestate spreading [18,47]. In the frame of this study, a lifetime of 20 years and 8000 working hours per year were assumed for the system. At the end of their service life, the AD and reforming plants are dismantled and the component

material either landfilled, recycled or incinerated (see Table S.2 (in supplementary material)). The background LCI data was provided by the Ecoinvent default database v3.1 [48], as implemented in Simapro 8.

2.2.2.2. Life cycle inventory (LCI) analysis

BG production data are adapted from the inventory assessment of the LCA impacts related to electricity and heat generation from BG produced by AD, as previously undertaken by Whiting and Azapagic [18], while reforming operating data are obtained from the process simulation in Aspen Plus™. As described by Whiting and Azapagic [18] the feedstock and operational data for the AD plant were provided from the farm owners. The data for construction materials were estimated by scaling up to the 800 m^3 AD of an eco-invent database plant (300 m^3 AD) [48]. The reformer unit weight was achieved from [49] taking into account information about the catalyst system from [50]. However, the construction material requirements (concrete, steel, aluminum, iron, etc.) of the reforming plant were adapted from [51].

2.2.2.3. Life cycle impact assessment (LCIA)

LCI data were computationally implemented into SimaPro 8 [17] to carry out the LCIA. The following environmental and energy indicators were selected to describe the performance of the BG-to-H_2 system: GWP, ODP, HTPce, HTPnce, PMP, IRP, POP, AP, TEP, FEP, MEP, FETP, LUP, ADP, CED and NRE. The characterization models used for the impact calculations are the European ILCD 2011 impact assessment method, elaborated by [52] according to the [53] and the Cumulative Energy Demand method [54], which allows for the assessment of renewable and non-renewable primary energy consumption.

3. Results and interpretation

3.1. Chemical reaction investigation

Fig. 3 illustrates the formation of coke (g C / mole CH_4 in feed) as a function of reforming

temperature for different H_2O/CH_4 operating conditions. There is a great potential for coke

deposits at low H_2O/CH_4 ratios ($0/1 \rightarrow 0.25/1$), for all investigated reforming temperatures.

At a given temperature, an increase in the H_2O/CH_4 ratio lowered the amount of coke

formed; for H_2O/CH_4 ratios greater than 1, no coke can be formed at temperatures above

700 °C. The conclusions agreed with the work of Assabumrungrat *et al.* [55].

Fig. 3.

Thermodynamically predicted coke formation of the BG reforming as a function of

temperature for different H_2O/CH_4 ratios at 10 atm ($CO_2/CH_4 = 0.583$).

Fig. 4 shows the amount of H_2 produced as a function of the H_2O/CH_4 ratio and

temperature. For all considered temperatures, the H_2 yield increases as the H_2O/CH_4

increases from 1/1 to 5/1. This observation is consistent with Le Chatelier's Principle. In

fact, the addition of extra steam (i.e. increase of H_2O/CH_4 ratio) on the reactant side, Eqs (2,

4) tends to shift the equilibrium toward the product side (H_2 production). However, when

the H_2O/CH_4 ratio is greater than 3, the gain in H_2 productivity becomes marginal, as the

reaction consumes excessive amounts of water. The H_2 yield increases as the reforming

temperature increases. It reaches a maximum then slightly decreases. This behavior is the

result of inhibition of the exothermic WGS reaction (Eq. 4).

Fig. 4.

17

1   Moles of H_2 produced per mole of CH_4 in feed as a function of temperature and H_2O/CH_4

2   ratio at 10 atm (CO_2/CH_4 =0.583).

3

4   Fig .5 shows how the increasing temperature led to a rise in CO yields. This result is due to

5   the inhibition of the exothermic WGS reaction by high temperature, leading to a high CO

6   content in the SG. It turns out that a simultaneously high H_2 production and low CO

7   content in the SG is not possible to achieve because the reforming temperature must be

8   high enough to obtain a reasonable H_2 yield. However, the temperature must be as low as

9   possible to minimize the CO content. Regarding the above mentioned results and

10   interpretation of thermodynamic calculations, we recommend, for this BG reforming

11   system, a reforming temperature of 800 °C and a H_2O/CH_4 ratio of 3. These recommended

12   conditions are subsequently used in the simulation of the entire BG-to-H_2 process.

13

14   **Fig. 5.**

15   Moles of CO produced per mole of CH_4 in feed as a function of temperature and H_2O/CH_4

16   ratio at 10 atm (CO_2/CH_4 =0.583).

17

18   **3.2. Process simulation**

19   The simulation of the reforming process by Aspen plus™ provides the properties of the

20   stream (T, P, mole flow, enthalpy, entropy, etc.) at different locations. Table 1 summarizes

21   properties (T, P, mass flow and composition) of the key streams of the process. The

22   estimation of the needed materials for each component of the reforming process, required

23   for LCI, is gathered in Table S.1 (in supplementary material).

24

25   **Table 1**

1   Key stream properties of the reforming process.

2

3   The energetic performance of a reforming system is conventionally evaluated by the

4   thermal efficiency. The thermal efficiency is based on considerations of the first law of

5   thermodynamics and is calculated as the energy output divided by the energy input [2,56]

6   as shown in Eq. (8).

7
$$\eta_{Thermal} = \frac{m_{H2} \times LHV_{H2}}{m_{BG} \times LHV_{BG} + W_{Compressor} + W_{Pump}} \qquad (8)$$

8   where m_i and LHV_i are the mass flow and the Lower Heating Value of species "i",

9   respectively; W_i is the mechanical work of component "i".

10   The thermal efficiency of the BG reforming process is 76.8%, which indicates that

11   approximately three quarters of the energy fed into the process is finally recovered in the

12   useful product (H_2) and that the remaining incoming process energy is vented in the off-gas

13   (steam 24). The thermal efficiency of the process remains within the range of values

14   reported in the literature and relative to SMR system (Simpson and Lutz (66.65%) [2],

15   Rosen 86% [57], Bargigli et al. (77%) [58], Hajjaji et al. (70.03%) [59]).

16

17   **3.3. LCA results**

18   Tables 2 and 3 present the main inventory data of the BG-to-H_2 system. These data

19   themselves constitute a key outcome of this study.

20

21   **Table 2**

22   Main inventory data (per kg H_2) subsystems 1 and 3.

23

24   **Table 3**

25   Main inventory data (per kg H_2) subsystems 2 and 3.

Table 4 shows the characterization results, computed using the ILCD method, for the

production of 1 kg of H_2. Five impact categories are detailed in this interpretation section:

GWP, ADP, AP, Eutrophication Potential (TEP, FEP and MEP) and CED (renewable and

non-renewable). These are among the most common and well-established impact

categories for assessing bioenergy systems in LCA studies [60–62].

Table 4

LCIA results for the production of 1 kg of H_2.

The total GHG emissions of the system are estimated to be approximately 5.59 kg CO_2-eq

per kg of H_2 produced. According to table 4, GHG emissions were mainly derived from the

AD plant (96%), especially due to methane losses at the BG production plant (20%) and to

methane emissions from the digestate during its storage (80%). However, CO_2 emissions

from the H_2 plant (resulting from BG reforming) are assumed to be biogenic and are

therefore not included in the assessment [63,64].

In an effort to increase our understanding of the opportunities of the BG-to-H_2 process, we

compare, in Fig. 6, the life cycle GHG emissions of BG-to-H_2 system with other

alternative routes for H_2 production: H_2 production by conventional SMR system (SMR-

H_2) [65], H_2 production by lignocellulosic biomass gasification (Biom-gasi-H_2) [66], H_2

production by electrolysis (Electro-H_2) [67], H_2 production by bioethanol autothermal

reforming (Bioeth-ATR-H_2) [59] and H_2 production by bioethanol steam reforming

(Bioeth-SER-H_2) [59]. However, these comparisons remain relatively rough as they cannot

be carried out consistently to due to the different methodologies applied for H_2 production.

As suggested in Fig. 6, the BG-to-H_2 system can represent a good alternative in terms of GHG emissions, as it only emits about half of the GHG life cycle of a conventional H_2 production system (SMR). This performance could be further improved by controlling lost methane during AD operation (methane leakage) and escaped methane during digestate open-air lagoon storage. However, in modern AD plants the digestate is now sent to a storage tank. The resulting residual gas can therefore be collected, thus further increasing the environmental improvements and profitability of the BG plant.

Fig. 6.

GHG emissions of different hydrogen production technologies.

Fossil fuel, metal, and minerals are used in H_2 production systems. The ADP is an impact category that measures the use of these abiotic reserves. As observed in Table 4, there is an overall reduction in the depletion of non-renewable resources by –120 mg Sb eq. /kg of H_2. This negative impact on ADP is due to the credits for mineral fertilizers (N, P, K) displaced by the use of AD plant sub-products (digestate) as organic fertilizer (as described above). This implies that the production of mineral fertilizers (the avoided product) consumes considerable amounts of abiotic resources, resulting in a negative ADP impact for the BG-to-H_2 system. A reduction (about 2%) in the ADP impact is also due to the credits for the recycling of the plant equipment and construction materials. However, the construction of the plants (building and equipment) bears a significant contribution to the ADP impact (about 20%). This is mainly attributed to the use of abiotic resources (steel, copper, concrete, etc.) during building and equipment manufacture.

BG-to-H_2 production systems emit substances that cause acidification. Acidification is a process that occurs in the atmosphere when acidifying compounds such as NO_x, SO_x, and NH_3 react with water vapor to form acids. These acids reach the ground in the form of acid rain which has important impacts on the soil, groundwater, materials and ecosystems. Almost all of the AP impact (estimated at 0.29 mol H^+ eq.) is attributed to the AD plant system. This can be explained by the ammonia produced during digestate spreading (34.56 g NH_3/ kg of H_2) and escaped during its open-air lagoon storage (5.89 g NH_3/ kg of H_2). It is noteworthy that the avoidance of mineral fertilizer was not sufficient to offset the strong emissions of ammonia. Consequently the AP impact remains unfortunately positive. Also due to ammonia losses, the AD plant is responsible for 100% of TEP and 86% of MEP, estimated at 1.33 molc N eq. / kg of H_2 and 6.60 g N eq. / kg of H_2, respectively (see Table 4). The production of H_2 via BG reforming also contributes to the FEP impact, although this impact (expressed kg P eq.) is fully compensated by the use of AD plant by-products (avoidance of the production of mineral fertilizer). The production of these would cause large amounts of phosphorus (P) to be released into the fresh water.

The CED indicator is a good proxy for the overall environmental impact [68]. The CED is applied to investigate the use of non-renewable NRE (fossil, nuclear, biomass from primary forests) and renewable (biomass from agriculture, wind, solar, geothermal, water) sources supporting the investigated process. Here, CED is used to compute energy consumption throughout the life cycle of H_2 and to identify the most energy consuming steps of BG-to-H_2 system. In this case, it is noteworthy that BG is not included as an energy input in the CED term. Indeed, BG is an intermediate product of the production system in this life cycle. It is produced by the system (AD plant) to be employed, subsequently, for H_2 generation (reforming plant).

As described in Table 4, a total of 4.97 MJ eq. is required to produce one kg of H_2 in which 4.15 MJ-eq is non-renewable (NRE) and the remaining part (i.e. 0.82 MJ eq.) is renewable. Table 4 clearly illustrates that the highest energy demand during the life cycle of H_2 is dominated by the H_2 plant subsystem, especially due to the consumption of electricity in the reforming process (for compressing and pumping the reformer feed). There is a saving in the energy demand of -3.94 MJ eq. / kg H_2 in the AD plant due to the credits for mineral fertilizers displaced by the digestate. Furthermore, there is a reduction (-1.48 MJ eq. / kg H_2) due to the credits for the recycling of the plant construction materials and equipment. By contrast, a total of 3.78 MJ eq. / kg H_2 was used for the plant building and equipment manufacture.

Alongside the CED indicator, the net energy ratio (NER) is computed to provide a comprehensive picture of the energetic performance of the entire BG-to-H_2 system. The NER, which is a measure of ''useful energy'' (total energy output) production by the system per unit of nonrenewable energy consumption (NRE), is defined in Eq. (9) [69]. The total energy output of the BG-to-H_2 system is 120 MJ (LHV of H_2 produced).

$$NER = \frac{LHV_{H2}}{NRE} \qquad (9)$$

The NER of H_2 produced by the BG-to-H_2 system is 28.88, implying that for each unit of energy consumed to produce H_2, 28.88 units of energy were obtained. Therefore the BG-to-H_2 system presents a net energy gain. It is noteworthy to emphasize that the NER value for NG reforming is lesser than one (about 0.57) [70].

4. Conclusion

In the present study, a various assessment tools were combined to comprehensively investigate a H_2 production system via BG reforming. These tools are employed to study

the BG reforming reactions, simulate the entire H_2 production process, and perform an

environmental impact assessment (using LCA methodology).

The main findings of this investigation are summarized as below:

- At a given reforming temperature, an increase in the H_2O/CH_4 ratio lowered the amount of

produced coke; for H_2O/CH_4 ratios greater than 1, no coke could be formed at temperatures

above 700 °C.

- The recommended conditions for BG reforming that were determined for maximizing

hydrogen production while minimizing the methane and carbon monoxide contents and

coke formation, could be achieved at reforming temperatures of 800 °C and a H_2O/CH_4

ratio of 3.

- The thermal efficiency of the reforming process was 76.8%, which remains within the

range of values reported in the literature and relative to conventional NG reforming.

- The LCA indicated that the AD plant subsystem represents the most influential subsystem.

- The total GHG emissions of the system are estimated to be approximately 5.59 kg CO_2-

eq per kg of H_2 produced, which corresponds to about half of the life cycle GHG of

conventional H_2 production systems (SMR).

- There is an overall economy in the depletion of non-renewable resources due to the credits

for mineral fertilizers (N, P, K) displaced by the use of AD plant sub-products (digestate) as

organic fertilizer. However, the construction of the plants (building and equipment) still

bears a significant contribution to the ADP impact (about 20%).

- The highest energy demand during the life cycle of H_2 is dominated by the H_2 plant

subsystem, especially due to the consumption of electricity in the reforming process (for

compressing and pumping the reformer feed).

- Most environmental impacts are influenced by the amount of artificial fertilizer displaced by the digestate as well as by the impact credits for recycling of the plant construction materials and equipment.

In general, the LCA results of BG-to-H_2 system show that this technique remains very advantageous. Accordingly, the authors recommend the use of BG as an ecofriendly source for sustainable H_2 production.

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Table captions

3

Table 1

Key stream properties of the reforming process.

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Table 2

Main inventory data (per kg H_2) subsystems 1 and 3.

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Table 3

Main inventory data (per kg H_2) subsystems 2 and 3.

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Table 4

LCIA results for the production of 1 kg of H_2.

15

1

2 **Figure captions**

3

4 **Fig. 1.**

5 A detailed flowsheet of the H_2 production process from BG reforming.

6 Label numbers: **1-6:** Water   7**-10**: BG   **11-16**: SG   **18**: H_2 **17,19,20**: Retentate

7 **21**: Air Combustion   **22-24**: Off-Gas.

8

9 **Fig. 2.**

10 Overview of the LCA boundaries of the BG-to-H_2 system.

11

12 **Fig. 3.**

13 Thermodynamically predicted coke formation of the BG reforming as a function of

14 temperature for different H_2O/CH_4 ratios at 10 atm ($CO_2/CH_4 =0.583$).

15

16 **Fig. 4.**

17 Moles of H_2 produced per mole of CH_4 in feed as a function of temperature and H_2O/CH_4

18 ratio at 10 atm ($CO_2/CH_4 =0.583$).

19

20 **Fig. 5.**

21 Moles of CO produced per mole of CH_4 in feed as a function of temperature and H_2O/CH_4

22 ratio at 10 atm ($CO_2/CH_4 =0.583$).

23

24 **Fig. 6.**

25 GHG emissions of different hydrogen production technologies.

26

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Table 1.

Properties of key streams of the reforming process.

Stream	1 (Water)	7 (BG)	8 (BG comb.)	9 (BG ref.)	11 (SG)	18 (H_2)	21 (Air comb.)	24 (off-gas)
T (°C)	25	25	25	25	800	226.8	25	370.6
P (atm)	1	1	1	1	10	1	1	1
Mass flow (kg /h)	87.42	97.17	26.06	71.10	158.53	11.53	220.50	393.56
Composition (% mol.)								
CH_4	0	60.0	60.0	60.0	1.8	0.0	0.0	0.0
CO_2	0	35.0	35.0	35.0	10.3	0.0	0.0	26.4
H_2O	100	2.0	2.0	2.0	32.1	0.0	0.0	27.4
N_2	0	3.0	3.0	3.0	0.8	0.0	79.0	46.1
CO	0	0.0	0.0	0.0	12.6	0.0	0.0	0.0
H_2	0	0.0	0.0	0.0	42.5	100.0	0.0	0.0
O_2	0	0.0	0.0	0.0	0.0	0.0	21.0	0.1

Table 2

Main inventory data (per kg H_2) subsystems 1 and 3

Inputs from the technosphere		
AD plant operation		
Manure	(S1)	25.51 kg
Waste maize silage	(S1)	8.50 kg
Fodder beet	(S1)	8.50 kg
Cheese whey	(S1)	8.50 kg
Electricity	(S1)	4054.96 kJ
Construction		
Concrete	(S3)	500.47 g
Reinforced steel	(S3)	18.18 g
Chromium steel	(S3)	2.18 g
Copper	(S3)	0.20 g
Laminated timber	(S3)	9.22 g
High-density polyethylene	(S3)	0.08 g
High-impact polystyrene	(S3)	0.95 g
Polyvinyl chloride	(S3)	0.13 g
Synthetic rubber	(S3)	0.51 g
Outputs to the technosphere		
BG	(S1)	7.18 Nm^3
Digestate	(S1)	42.82 kg
Avoided products		
Fertilizer, as N	(S1)	57.81 g

Fertilizer, as P	(S1)	67.23 g
Fertilizer, as K	(S1)	179.84 g
Outputs to the environment		
CO_2, biogenic	(S1)	90.42 g
CH_4, biogenic	(S1)	284.19 g
NH_3	(S1)	40.45 g

Table 3

Main inventory data (per kg H_2) subsystems 2 and 3

Inputs from the technosphere		
Feed conditioning & BG reforming		
BG	(S2)	7.18 Nm^3
Water	(S2)	7.58 kg
Air	(S2)	19.12 kg
Electricity	(S2)	1952.82 kJ
Construction		
Building		
Concrete	(S3)	227.90 g
Steel	(S3)	72.81 g
Aluminum	(S3)	0.60 g
Iron	(S3)	0.89 g
Equipment		
Feed conditioning & BG reforming		
Steel	(S3)	0.72 mg
Steel high alloy	(S3)	2.78 mg
Alumina	(S3)	0.96 mg
Cast iron	(S3)	0.64 mg
Steel low alloy	(S3)	0.30 mg
WGS & purification		
Steel	(S3)	4.00 mg
Steel high alloy	(S3)	0.13 mg

Aluminum	(S3)	1.12 mg
Alumina	(S3)	2.13 mg
Iron	(S3)	1.65 mg
Cast iron	(S3)	0.66 mg
Nickel	(S3)	0.15 mg
Steel low alloy	(S3)	18.22 mg

Outputs to the technosphere

H_2	(S1)	1 kg

Outputs to the environment

CO_2, biogenic	(S1)	13.43 kg

Table 4.

LCIA results for the production of 1 kg of H_2.

Impact category	Total	AD plant	H_2 plant	C & D
GWP (kg CO_2 eq)	5.59	5.38	5.99×10^{-2}	0.15
ODP (kg CFC-11 eq)	1.53×10^{-8}	-4.84×10^{-8}	5.11×10^{-8}	1.26×10^{-8}
HTPnce (CTUh)	2.76×10^{-7}	-1.53×10^{-8}	2.71×10^{-8}	2.64×10^{-7}
HTPce (CTUh)	8.64×10^{-9}	-1.72×10^{-7}	3.67×10^{-9}	1.77×10^{-7}
PMP (kg $PM_{2.5}$ eq)	5.25×10^{-3}	5.09×10^{-3}	3.47×10^{-5}	1.24×10^{-4}
IRP (kg U_{235} eq)	1.23	0.78	0.44	1.58×10^{-2}
POF (kg NMVOC eq)	-1.46×10^{-3}	-2.16×10^{-3}	1.61×10^{-4}	5.39×10^{-4}
AP (molc H^+ eq)	0.29	0.29	3.66×10^{-4}	9.31×10^{-4}
TEP (molc N eq)	1.33	1.33	5.43×10^{-4}	2.26×10^{-3}
FEP (kg P eq)	-6.02×10^{-5}	-1.88×10^{-4}	1.27×10^{-5}	1.15×10^{-4}
MEP (kg N eq)	6.60×10^{-3}	5.66×10^{-3}	6.12×10^{-4}	3.29×10^{-4}
FETP (CTUe)	4.85	-4.11	1.08	7.88
LUP (kg C deficit)	-2.37	-3.05	6.62×10^{-2}	0.61
WRD (m^3 water eq)	-1.67×10^{-3}	-3.25×10^{-3}	1.33×10^{-3}	2.48×10^{-4}
ADP (kg Sb eq)	-1.20×10^{-4}	-1.54×10^{-4}	3.16×10^{-6}	3.03×10^{-5}
CED (MJ eq)	4.98	-3.94	6.72	2.19
NRE (MJ eq)	4.15	-3.84	6.42	1.57

Synthesis gas (SG) generation   **Water Gas Shift (WGS)**   **Purification**

Reformer

HTS (300-400 °C) **LTS** (200-300 °C)

Feed

SG

H₂

Heat exchanger   Heat exchanger

Recycled gas

Raw materials

Emissions

| Material | Electric Energy |

S1: AD plant

Waste collection → AD plant operation → Digestate storage & use

S2: H$_2$ plant

Feed conditioning & BG reforming → WGS & purification → **H$_2$**

S3: Construction & decommissioning

Construction
- Building
- Equipment

Decommissioning
- Landfilling
- Incinerating
- Recycling

System boundaries