Life Cycle Assessment of Natural gas-based Chemical Looping for Hydrogen Production

GHGT-12

Life Cycle Assessment of Natural gas-based Chemical Looping for Hydrogen Production

Letitia Petrescu[a]*, Christoph R. Müller[b] , Calin-Cristian Cormos[a],

[a]*Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Street, RO-400028 Cluj -Napoca, Romania*
[b]*Laboratory of Energy Science and Engineering, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland*

Abstract

Hydrogen production from natural gas, combined with advanced CO_2 capture technologies, such as iron-based chemical looping (CL), is considered in the present work. The processes are compared to the conventional base case, i.e. hydrogen production via natural gas steam reforming (SR) without CO_2 capture. The processes are simulated using commercial software (ChemCAD) and evaluated from a technical point of view considering important key performance indicators such as hydrogen thermal output, net electric power, carbon capture rate and specific CO_2 emissions. The environmental evaluation is performed using Life Cycle Analysis (LCA) with the following system boundaries considered: i) hydrogen production from natural gas coupled to CO_2 capture technologies based on CL, ii) upstream processes such as: extraction and processing of natural gas, ilmenite and catalyst production and iii) downstream processes such as: H_2 and CO_2 compression, transport and storage. The LCA assessment was carried out using the GaBi6 software. Different environmental impact categories, following here the CML 2001 impact assessment method, were calculated and used to determine the most suitable technology. Sensitivity analyses of the CO_2 compression, transport and storage stages were performed in order to examine their effect on the environmental impact categories.

Keywords: "LCA; CCS; Chemical Looping; Natural gas"

* Corresponding author. Tel.: +4-026-459-3833; fax: +4-026-459-0818
 E-mail address: letitiapetrescu@chem.ubbcluj.ro

1. Introduction

Hydrogen can play an important role as an energy carrier in a sustainable, reliable, and cost-effective energy future [1]. Hydrogen is currently produced from a variety of primary sources such as natural gas, naphtha, heavy oil, methanol, biomass, wastes, coal, solar, wind, and nuclear [2]. According to Muradov's prediction prevision, fossil fuels will remain the dominant source for hydrogen production over the next few decades [3]. Hydrogen production from fossil fuels is a practical process, but the associated emission of large quantities of CO_2 has to be reduced [4]. Combining hydrogen production based on fossil fuels with carbon capture and storage (CCS) is a major research topic in the development of innovative energy conversion processes [5]. Natural gas is the dominating feedstock for hydrogen production. The reason for this is that natural gas is abundant, available in most parts of the world, has the highest hydrogen content of all fossil fuels, and is of low cost [6]. The dominant H_2 production technology on a large scale is the SR of natural gas, which is responsible for around 50% of the H_2 produced worldwide [7]. Natural gas reforming is a mature technology used in the refinery and chemical industries for large-scale H_2 production [8]. Beside SR, there are also innovative methods for hydrogen production from natural gas e.g. hydrogen production from natural gas combined with advanced CO_2 capture technologies, such as CL. The CL technology for hydrogen production uses oxygen carriers e.g. iron-based materials [5, 9]. The present paper deals with the natural gas conversion based on CL process and on the natural gas SR combined with CL. Ilmenite is used as an oxygen carrier in the CL processes. The focus of this paper lies on the environmental assessment of different hydrogen production processes based on natural gas (using SR and/or CL technologies). As hydrogen gains popularity, the question remains: how sustainable is the production of hydrogen? To measure sustainability, scientists commonly use Life Cycle Assessment (LCA) - the internationally standardized method that quantifies the environmental impacts of a product or service [10]. In this work the conventional SR and innovative CL methods for hydrogen production were analyzed from a LCA point of view.

Nomenclature

ADP	Abiotic Depletion Potential
AP	Acidification Potential
BFW	Boiler Feed Water
CL	Chemical Looping
CCS	Carbon Capture and Storage
EP	Eutrophication Potential
FAETP	Freshwater Aquatic Ecotoxicity Potential
GWP	Global Warming Potential
HTP	Human Toxicity Potential
HTS	High Temperature Shift
LCA	Life Cycle Analysis
LCI	Life Cycle Inventory
LTS	Low Temperature Shift
MAETP	Marine Aquatic Ecotoxicity Potential
NG	Natural Gas
ODP	Ozone Layer Depletion Potential
POCP	Photochemical Ozone Creation Potential
PSA	Pressure Swing Absorption
PSRK	Predictive Soave Redlich Kwong
SR	Steam Reforming
SRK	Soave Redlich Kwong
TEG	Tri-ethylene-glycol
TETP	Terrestric Ecotoxicity Potential

2. Plant configurations, simulation assumptions and technical key performance indicators

The three case studies investigated in the present paper are:
Case 1: Hydrogen production from natural gas using SR technology;
Case 2: Hydrogen production based on CL natural gas conversion;
**Case 3**: Hydrogen production based on SR combined with CL.

2.1 Description of **Case 1***: Hydrogen production from natural gas using SR technology*

Hydrogen production via catalytic steam reforming of natural gas is a mature technology and is the means by which most of hydrogen is made today [11]. Reforming is a catalytic operation, and the catalysts employed are poisoned by even trace amounts of sulfur [12]. Thus, the natural gas is pre-treated in order to convert any sulphur compounds to H_2S [11]. Subsequently, H_2S is adsorbed in a ZnO bed and reacts to form ZnS, which is removed as a solid waste. After pretreatment, the natural gas together with steam are sent to the steam reformer. The reaction taking place here is:

$$H_2O + CH_4 \rightarrow CO + 3H_2 \qquad (r_1)$$
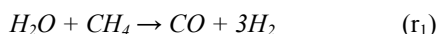
This is a highly endothermic reaction. In order to generate the heat required for the reforming reaction, natural gas is burned with air in the furnace. The synthesis gas from the reformer is rich in H_2 and CO. After the reformer, the gas mixture passes through a heat recovery step and is fed into a water-gas shift reactor to produce additional H_2 [6].The water gas shift (WGS) reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (r_2)$$
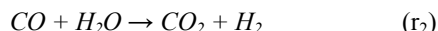
can be used to increase the H_2 content [12]. Normally, two WGS stages (HTS - high temperature shift and LTS - low temperature shift) are used to reduce the CO content to a level of approximately 0.2-0.4 vol. The reaction is exothermic and occurs at temperatures ranging from 200 to 400°C [6]. The two stages for CO conversion are considered in the present study. The hydrogen obtained in the HTS and LTS steps is purified further using a pressure swing absorption (PSA) unit. The H_2 obtained in the process is compressed up to 60 bar. The process simplified schema for *Case 1* is presented in Fig. 1.
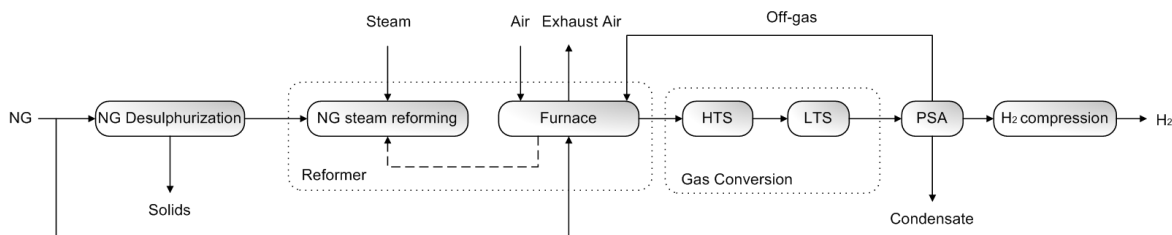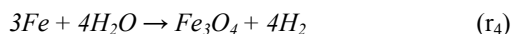

Fig. 1. Block diagram for *Case 1*: Hydrogen production from natural gas using SR (without CCS)

2.2 Description of **Case 2***: Hydrogen production based on chemical looping natural gas conversion*

In this technology, natural gas together with the solid oxygen carrier (ilmenite) is sent to the fuel reactor. The following reaction takes place at 750 - 900°C [13]:

$$4Fe_2O_3 + 3CH_4 \rightarrow 8Fe + 3CO_2 + 6H_2O \qquad (r_3)$$
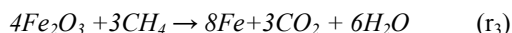
After water condensation and separation, the gaseous stream from the fuel reactor, is sent to the drying and compression stage where CO_2 is dried using Tri-ethylene-glycol (TEG) and compressed to 120 bar being ready for storage. The solid stream containing the reduced metal is re-oxidized with steam to a metal oxide to close the redox cycle. The steam reactor operates at 500 - 700°C [13]; the chemical reaction taking place is:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \qquad (r_4)$$

The gaseous and solid streams are separated and the product of the process (H_2) is compressed to 60 bar. The solid coming from the steam reactor, i.e. Fe_3O_4 is transformed to Fe_2O_3 in the air reactor (combustor) as follows:

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \qquad (r_5)$$
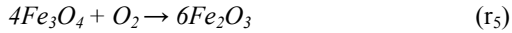
This reactor operates at 950 - 1150°C [13]. The Fe_2O_3 is recycled back to the fuel reactor. A small amount of solids (1%) is removed after oxygen carrier deactivation. The process simplified schema for **Case 2** is presented in Fig. 2.

Fig. 2 Block diagram for *Case 2*: Hydrogen production based on CL natural gas conversion

2.3 Description of **Case 3**: Hydrogen production based on steam reforming combined with chemical looping

The starting raw material for this technology is again natural gas. Sulfur is removed from the natural gas (prior to the reformer). Subsequenty, process steam is added to methane, which is converted to H_2, CO and CO_2. The gas is purified by CO_2 removal in an iron-based CL process to produce a h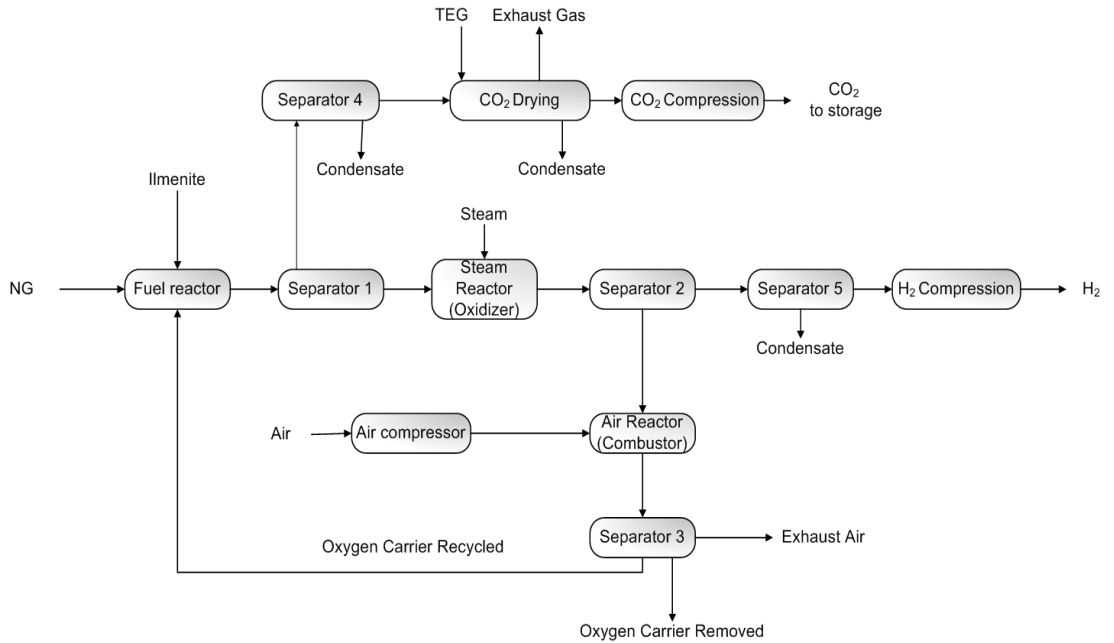igh quality H_2 product. The first part of the process is simmilar to **Case 1**. Syngas from the natural gas SR together with the solid oxygen carrier (ilmenite) are sent to the CL line. The reactions that occur in the CL section (fuel reactor, steam reactor, air reactor) are the same as in **Case 2** (r_3, r_4 and r_5). The process simplified schema for **Case 3** is presented in Fig. 3.
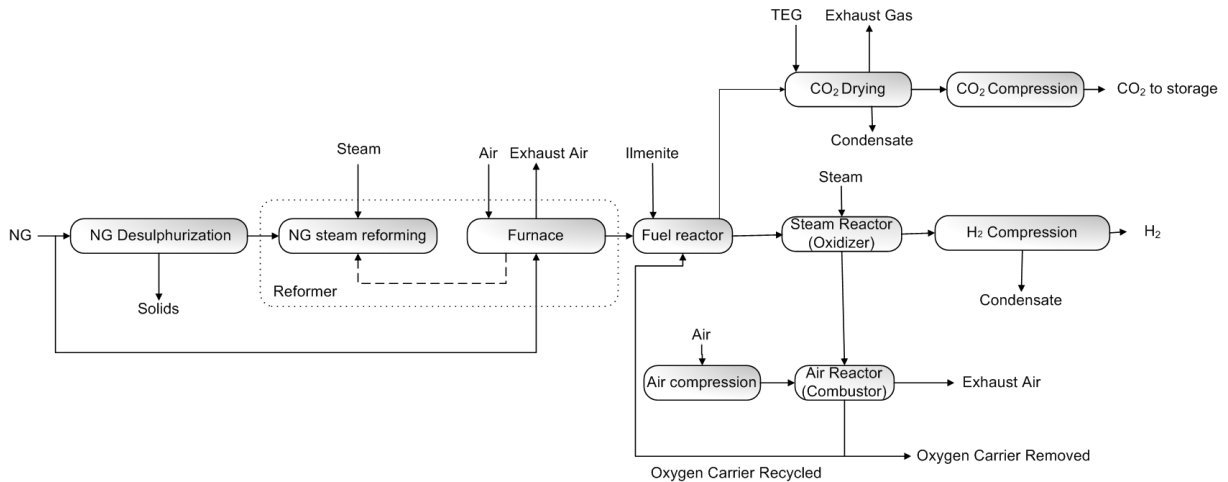
Fig. 3 Block diagram for **Case 3**: Hydrogen production based on SR combined with CL

2.4 Design assumption, process simulation and technical key performance indicators

The main design assumptions for the cases under investigation are presented in Table 1.

Table 1. Design Assumptions (**Case 1-3**)

Unit Operation	Parameter	Value
Natural gas desulphurization (**Case 1- 3**)	Temperature (^{o}C)	350
	Adsorbent- ZnO	
Natural gas reformer (**Case 1**)	Pressure (bar)	30
	Outlet temperature (^{o}C)	900
HTS (**Case 1**)	Temperature (^{o}C)	430
	Catalyst composition (% wt.)	
	Fe_2O_3	88
	Cr_2O_3	9
	CuO	3
	CO Conversion (%)	70
LTS (**Case 1**)	Temperature (^{o}C)	275
Chemical Looping (**Case 2-3**)	Catalyst composition- same as HTS	
	Chemical looping agent- Ilmenite	
	Fuel reactor parameters (bar/ ^{o}C)	30 / 700 - 750
	Steam reactor parameters (bar/ ^{o}C)	28 / 700 - 800
	Air reactor parameters (bar/ ^{o}C)	26 / 850 -1000
	Pressure drop fuel and steam reactors (bar)	1
H$_2$ compression (**Case 1-3**)	Delivery pressure (bar)	60
	Compressor efficiency (%)	85
	Delivery pressure (bar)	120
CO$_2$ Drying and Compression (**Case 2-3**)	Compressor efficiency (%)	85
	Solvent used for CO$_2$ drying -TEG	
	ΔTmin. (^{o}C)	10
Heat exchangers (**Case 1-3**)	Pressure drop (% of the inlet pressure)	1 - 2

The above described processes were simulated using ChemCAD version 6.0.1 process simulator [14]. The Soave Redlich Kwong (SRK) method was selected to model the thermodynamic properties for **Case 1** and the predictive Soave Redlich Kwong (PSRK) method was used for **Case 2** and **Case 3.** The mass and energy balances derived from the simulation were used to calculate key technical performance indicators. The key performance indicators, their definition as well as their correspondent calculation formula, have been previously defined by

Cormos [15]. The obtained results are summarized in Table 2.

Table 2. Technical key performance indicators (KPI) for **Case 1 - 3**

KPI	Units	**Case1**	**Case2**	**Case3**
Natural gas flowrate	kg/h	31371.58	30632.79	46219.51
Natural gas LHV	MJ/kg	46.73	46.73	46.73
Thermal energy of the feedstock – LHV (A)	MW_{th}	407.26	397.66	600.01
Gross electric power output (B)	MW_e	17.02	17.53	68.41
Hydrogen output (C)	MW_{th}	300	300	300
Hydrogen compression	MW_e	4.18	3.97	4.33
Carbon capture & compression	MW_e	-	1.98	1.88
Total ancillary power consumption (D)	MW_e	6.26	7.99	6.21
Net electric power output (E = B - D)	MW_e	10.76	9.54	62.2
Net electrical efficiency (E/A * 100)	%	2.64	2.39	10.37
Hydrogen efficiency (C/A * 100)	%	73.66	75.44	49.99
Cumulative energy efficiency	%	76.30	77.83	60.37
Carbon capture rate	%	0	99.25	68.5
CO_2 specific emissions (hydrogen and power)	kg/MWh	267.39	1.94	212.83

In terms of fuel consumption, the NG flow rate varies in the range 30-47 t/h, as shown in Table 2. The NG flow rate is particularly high in **Case 3**, where additional quantities of NG are required to provide the heat for the reforming reaction. The same situation occurs in **Case 1**. Regarding the ancillary power consumption of various plant sub-systems two important aspects can be noticed: on the one hand, an increase power consumption in the hydrogen compression sub-systems based on reforming technology (**Case 1** and **Case 3**) and, on the other hand, a higher power consumption for the CO_2 compression sub-system for **Case 2**. The lowest ancillary power consumption is registered in **Case 3**. The evaluated plant concepts generate 300 MW_{th} of H_2. The hydrogen efficiency is around 75% for **Case 1** and **Case 2** and decreases significantly in the case of combining those two technologies **Case 3.** Here, the hydrogen efficiency is around 50%. Besides H_2, electric power is also generated in the systems under investigation. The net electric power varies in the range 9–63 MW_e and the net plant electrical efficiency varies in the range 2–10.5%. The carbon capture rate is almost 100 %, i.e. 99.25% in **Case 2**, while, for **Case 3**, it reaches only 68.5%. The capability of capture almost the total carbon content of the feedstock and lower plant complexity streamlines the attractiveness of the direct chemical looping option (**Case 2**). The specific CO_2 emissions of the evaluated plant concept with CCS (**Case 2** and **Case 3**) are in the range of 2-213 kg/MWh. For comparison, the case without CCS (**Case 1**) has specific CO_2 emissions of about 268 kg/MWh.

3. Life Cycle Assessment (LCA)

LCA provides a comprehensive view of the environmental aspects of the product or process and it refers to the major activities in the course of a product's life from its manufacture, use, and maintenance, to its final disposal. A "cradle-to-grave" approach was assumed for the three cases under investigation. "Cradle-to-grave" begins with the gathering of raw materials to creating the product and ends at the point when all materials are returned to the earth [16]. In order to deal with the complexity of LCA, the International Standards Organization (ISO) established a methodological framework called ISO 14044 for performing LCA studies, which comprises four phases: Goal and Scope, Life Cycle Inventory (LCI) analysis, Life Cycle Impact Assessment (LCIA) and Interpretation [17]. Those steps are detailed in the next part.

3.1 Goal and scope of the study, system boundaries, limitations and LCA main assumptions

The primary goal of this study is to quantify and analyze the total environmental aspects of hydrogen production from natural gas using SR and/or CL. For this aim, the following strategy is proposed: i) to provide a detailed assessment of each pathway step, from raw materials extraction to H_2 production, as well as, H_2 and CO_2 transport and storage; ii) to provide a comparison of the environmental efficiency of the processes under study. The present LCA studies were conducted step by step, based on the energy and material consumption of each unit process which derived from the ChemCAD process simulator. A requirement of the study is that the plants are self-sufficient in all their utilities; this implies that electricity must be produced to drive the machinery.

The scope of the study includes the definition of the following characteristics: function of the system, functional unit, geographical and temporal context, system boundaries, main assumptions and limitations. The functions of the systems considered in the present study are: the production of 300 MW_{th} of hydrogen as well as the production of power (10.76 MW_e for **Case 1**, 9.54 MW_e for **Case 2**, 62.2 MW_e for **Case 3**). The functional unit is 1MW of H_2 and power produced. The plants are supposed to be located in Romania, Europe, in 2020, implying that all technology configurations are subject to further technological improvement. The system boundaries include:

i) H_2 production from natural gas conversion coupled to CO_2 capture technologies based on CL;
ii) upstream processes such as: extraction and processing of natural gas, ilmenite and catalyst production;
iii) downstream processes such as: H_2 and CO_2 compression, transport and storage.

The following aspects are not covered in the present format of the study: 1) the construction of the infrastructure (e.g. plant, pipelines, roads, railways); 2) the construction of trains and trucks used for transportation; 3) human activities as well as labour costs associated with the number of employees at each step. The main assumptions made are detailed below.

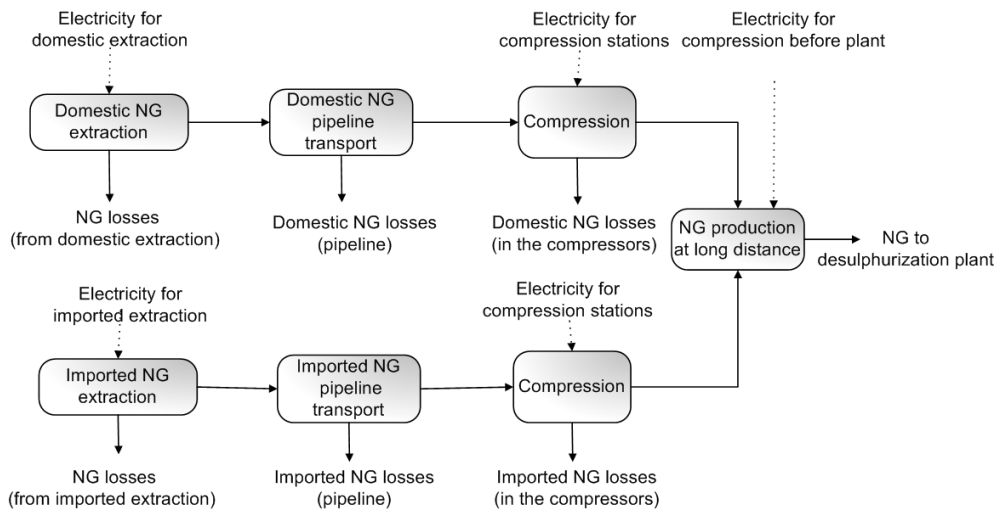The schema presented in Fig. 4 was considered for the natural gas supply chain for all cases.

Fig. 4 Natural gas supply chain (**Cases 1 - 3**)

Some fraction of the NG extracted was considered for the production of electricity required to power the extraction stage. For the domestic extraction of 1 m^3 of natural gas 0.02 m^3 have been considered. A quantity of 0.016 m^3 is requested to extract 1 m^3 for imported natural gas [18]. The domestic natural gas is from Romania, the imported natural gas comes from Russia. We assumed that 70% of the natural gas is domestic and 30% is imported. It is further assumed that the gas was transported via a pipeline network. A distance of 300 km was considered from the extraction site to the plant location for the domestic natural gas. A distance of 3000 km pipeline was considered for the imported natural gas to the national pipeline. A quantity of 0.1% leakage was considered for domestic transport; 0.2% for imported transport. The schema presented in Fig. 5 was considered for the ilmenite supply chain (**Cases 2-3**).
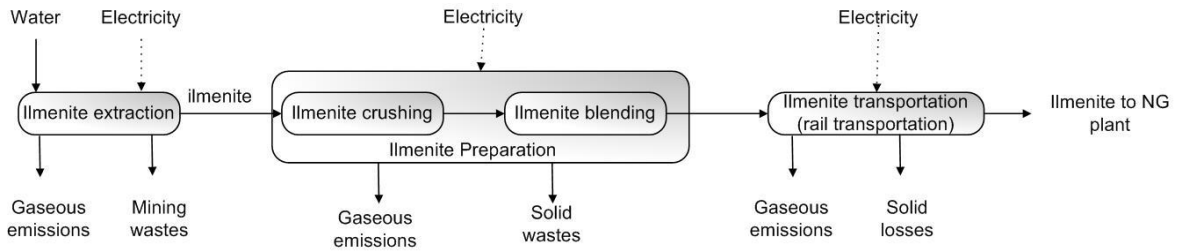
Fig. 5. Ilmenite supply chain (**Cases 2-3**)

The quantities of water, electricity, diesel and explosives necessary to extract and concentrate one tone of ilmenite are taken from literature [19]. The prepared ilmenite (extracted and concentrated) is transported by train over a distance of 200 km.

For the present work it is assumed that H_2 is delivered by pipeline. Hence, a high pressure is required to ensure long distance transport from production sites to end-users with low energy consumption. Ideally, the pressure should be equal to the distribution network pressure of 60-70 bar. One possibility for rapidly expanding the hydrogen delivery infrastructure is to adapt part of the natural gas delivery infrastructure to accommodate hydrogen. Converting natural gas pipelines to carry a blend of natural gas and hydrogen (up to about 20% hydrogen) may require only modest modifications to the pipeline; converting existing natural gas pipelines to deliver pure hydrogen may require more substantial modifications [20]. A percentage of 0.1% of the H_2 produced in the plants is supposed to be lost during transport. H_2 is transported over a distance of 1000 km. The compressor stations are located every 100 km. The pressure drop is supposed to be 10 bar/100 km. The electricity necessary for compression was also included in the analysis.

The CO_2 transport and storage (**Case 2-3**) supply chain is presented in Fig. 6
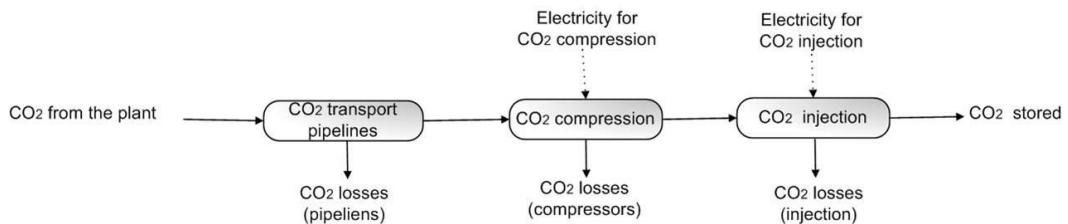

Fig. 6. CO_2 supply chain (**Cases 2-3**)

The CO_2 captured from the processes is supplied to the transport chain at 120 bar and it is transported over a distance of 800 km via pipelines in order to be stored in the sea (it is supposed to be stored in the Black Sea-depth storage at 2000 m). Some data related to the transport are: the fugitive emissions through the pipeline are 2.32 t CO_2/km/year; the fugitive emissions through the compressors are 23.2 t CO_2/MW/year; 40 MW contrigual compressor and a pressure drop of 0.006 MP/km was considered; a distance of 100 km has been considered between two compressor stations; the compression power is 111 kWh/ t CO_2 (400 MJ/ t CO_2); the injection power is 7 kWh/t CO_2; 0.1% CO_2 is proposed to be considered as losses during the injection process [21].

3.2 Life Cycle Inventory (LCI) and Impact Assessment

The LCI correspondent to each step was performed taken into account the material and energy balances derived from the process simulator and the assumptions presented previously. For example, the LCI table containing the inputs and outputs for **Case 2**, for the hydrogen production step, is presented in Table 3.

Table 3. LCI for **Case 2**, hydrogen production step

Input	Unit	Value	Output	Unit	Value
NG	30632.79	kg/h	CO_2 to storage	79285.77	kg/h
Ilmenite	571536.7	kg/h	H_2	9092	kg/h
Air	298606	kg/h	Ilmenite removed:		
BFW	145080	kg/h	Ferric Oxide	3765.73	kg/h
TEG	2700	kg/h	Titanium Dioxide	1883.71	kg/h
Power consumption	7.99	MW_e	Ilmenite recycled	565886.7	kg/h
			Condensate	80664	kg/h
			Exhaust Gas:		
			CO_2	599.68	kg/h
			N_2	0.06	kg/h
			H_2O	36.03	kg/h
			Exhaust Air:		
			N_2	22903.99	kg/h
			O_2	2776.01	kg/h
			Steam to CL	97281	kg/h
			BFW	47799	kg/h
			TEG	2700	kg/h
			Hydrogen	300	MW_{th}
			Electricity	17.53	MW_e

LCI for CO_2 transport and storage for **Case 2** is also presented (see Table 4).

Table 4. LCI for **Case 2**, CO_2 transport and storage step

Input	Unit	Value	Output	Unit	Value
CO_2 from plant	79285.77	kg/h	CO_2 stored	77970.4	kg/h
Electricity for compressors	31615.32	MJ	CO_2 losses pipeline	247.47	kg/h
Electricity for injection	1964.84	MJ	CO_2 losses compressors	989.86	kg/h
Injection pressure	120	bar	CO_2 losses injection	78.05	kg/h
Pressure drop	48	bar			
Pipeline distance	800	km			
No. of compressor stations	8	-			
Storage depth	2	km			
Distance between compression stations	100	km			

An impact assessment was carried out in order to identify the environmantal impacts that arrise from the LCI. The LCA software GaBi version 6.0 [22] was used to evaluate the environmental impacts of inventory aspects and to create product assemblies and life cycles for the three cases under investigation. The CML 2001 method assessment, developed by the Center of Environmental Science at Leiden University, was considered in the present study. The description of the environmental indicators considered in the CML 2001 method are reported in the literature [17].

3.3 Results and discussions

Ten environmental impact categories were evaluated. The values of the environmental impact categories for **Cases 1-3** are reported in Table 5.

Table 5. LCA results (**Case 1-3**) according to CML 2001

KPI	Units	Case1	Case2	Case3
GWP	kg CO_2-Equiv./MW	701.13	240.09	494.25
AP	kg SO_2-Equiv./MW	0.34	2.25	2.28
EP	kg Phosphate-Equiv./MW	0.01	0.15	0.16
ODP	kg R11-Equiv./MW	$5.58*10^{-9}$	$4.72*10^{-8}$	$4.79*10^{-8}$
ADP elements	kg Sb-Equiv./MW	$3.81*10^{-5}$	$1.35*10^{-4}$	$1.47*10^{-4}$
ADP fossil	MJ/MW	4785.67	6679	8012.69
FAETP	kg DCB-Equiv./MW	0.216	1.13	1.21
HTP	kg DCB-Equiv./MW	1.79	14.78	14.98
PCOP	kg Ethene-Equiv./MW	0.024	0.13	0.13
TEP	kg DCB-Equiv./MW	0.072	1.72	1.75

There are large differences in terms of GWP between the cases with CCS (**Case 2** and **Case 3**) and the case without CCS (**Case 1**). Obviously, the case without CCS has the highest GWP caused by the CO_2 released into the atmosphere. The total GWP value for **Case 1** is 701.13 kg CO_2-Equiv./MW. From this value 301.06 kg CO_2-Equiv./MW comes from the H_2 production process, 268.67 kg CO_2-Equiv./MW comes from H_2 transport process and 131.14 kg CO_2-Equiv./MW comes from the catalyst production process. Comparing the two cases with CCS, in terms of GWP, it can be noticed that the GWP value in **Case 3** is higher, i.e. more than double, than in **Case 2**. Possible explanations for this behavior are: i) the exhaust stream coming out from the furnace emits 41268 kg/h of CO_2 in **Case 3** vs. only 600 kg/h of CO_2 are released in **Case 2** and ii) the quantity of CO_2 emitted during ilmenite preparation is larger in **Case 3** than in **Case 2**, i.e. 1683 kg vs. 1402 kg. The quantities of CO_2 lost during the CO_2 transport and storage step (via pipelines, compressors and injection) are the same for both cases. Regarding AP, the best value is obtained in **Case 1** (0.34 kg SO_2-Equiv./MW). For this case 0.319 kg SO_2-Equiv./MW comes from the H_2 production process and the rest, 0.022 kg SO_2-Equiv./MW, comes from the H_2 transport step. For **Case 2**, the total value of AP is 2.25 kg SO_2-Equiv./MW. The contributions of various steps to the AP value is as follows: 1.34 kg SO_2-Equiv./MW comes from the H_2 production process, 0.598 kg SO_2-Equiv./MW is due to the ilmenite production process, 0.286 kg SO_2-Equiv./MW are due to CO_2 transport and storage and 0.021 kg SO_2-Equiv./MW corresponds to the H_2 transport. In **Case 3**, the total AP value is 2.28 kg SO_2-Equiv./MW. The H_2 production process contributes 1.42 kg SO_2-Equiv./MW to the total value, 0.598 kg SO_2-Equiv./MW is due to the ilmenite production process, 0.245 kg SO_2-Equiv./MW comes from the CO_2 transport and storage step and a small contribution to the total value, i.e. 0.019 kg SO_2-Equiv./MW, are due to H_2 transport. The EP impact category has the highest values in the CCS cases due to the ilmenite production process which generates around 83% of the EP. Other impact categories such as ODP and ADP elements have low values in all three cases. ADP fossil has the lowest impact in **Case 1**: 4785.67 MJ/MW. From this value 4772.12 MJ/MW is due to the SR process and only a small part, equivalent to 12.56 MJ/MW, to the H_2 transportation step. ADP fossil has the highest value in **Case 3** (8012.69 MJ/MW) because this case consumes the highest quantity of natural gas (see Table 2). The contribution of different life cycle steps to the ADP fossil for **Case 3** is: 7203 MJ/MW correspond to the H_2 generation process, 640 MJ/MW is due to the ilmenite production, 158 MJ/MW is due to the CO_2 transport and storage and 11.6 MJ/MW to the H_2 transport. The contribution of different life cycle steps to the total ADP fossil (6679 MJ/MW), for **Case 2** is: 5841 MJ/MW corresponds to hydrogen production process, 640.43 MJ/MW is due to the ilmenite production, 184.14 MJ/MW is due to the CO_2 transport and storage and 13.61 MJ/MW to the H_2 transport. The best values of the three impact indicators linked to the lethal concentration LC_{50}, FAETP, HTP, TEP is obtained also in **Case 1**. From Table 6 it can be noticed a higher human toxicity corresponding to the CCS cases compared to the base case.

PCOP impact category has almost the same value for **Case 2** and **Case 3**, but this value is five times more than the PCOP value of the base case (**Case 1**).

Starting from Spath and Mann definitions [11] two efficiencies and two ratios were adapted and calculated for the hydrogen and power generation. The results obtained are presented in Table 6.

Table 6. Efficiencies and ratios (**Case 1-3**)

	Calculation Formula	Units of measure	**Case 1**	**Case 2**	**Case 3**
(a) Life Cycle Efficiency (LCE)	$LCE=(EH_2+E_e-E_u-E_f)/E_f$	%	-27.51	-38.82	- 53.57
(b)External energy efficiency (EEE)	$EEE=(EH_2+E_e-E_u)/E_f$	%	72.49	61.18	46.33
(c) Net energy ration	$NER=(EH_2+E_e)/E_{ff}$		0.76	0.77	0.6
(d) External energy ratio	$EER=(EH_2+E_e)/(E_{ff}-E_f)$		218.23	219.37	213.18

EH_2 = Energy in the hydrogen; E_u = Energy consumed by all upstream processes required to operate the hydrogen plant
E_f = Energy contained in the natural gas fed to the hydrogen plant; E_{ff}= Fossil fuel energy consumed within the system (e);
E_e= Electric power generation.
(a)   Includes the energy consumed by all of the processes.
(b)   Excludes the heating value for the natural gas feedstock from the life cycle efficiency formula.
(c)   Illustrates how much energy is produced for each unit of fossil fuel energy consumed.
(d)   Excludes the energy of the natural gas to the hydrogen plant.
(e)   Includes the natural gas fed to the hydrogen plant since it is consumed within the boundaries of the system.

The energy in the natural gas is higher than the energy content of the hydrogen and power produced. Therefore, the LCEs are negative. This reflects the fact that because natural gas is a non-renewable resource, more energy is consumed by the system than it is produced. The best value for this indicator is obtained in **Case 1**. In calculating the EEE, the energy content of the natural gas is not included, making the result of this measure positive [11]. The best value for this indicator is again obtained in **Case 1**. The NER shows the quantity of energy produced (hydrogen and power) when one energy unit of fossil fuel is consumed. The best value for NER is obtained in **Case 2**. EER shows the rate of energy consumption by the upstream process steps. Higher efficiencies and energy ratios are desired for any process, not only in terms of economics, but in terms of reduced resources, emissions, wastes and energy consumption [11]. The best value for EER is again obtained in **Case 2**.

3.5 Sensitivity analysis

A sensitivity analysis on the CO_2 transport and storage step for **Case 2** is reported in Table 7. The distance from the sink to the storage site was modified from 400 to 1200 km in order to see the changes of this variable on the CO_2 losses (through pipeline, compressors and injection process) and, implicitly, the effect of this variable on the total GWP.

Table 7. Sensitivity analysis for CO_2 transport and storage step (**Case 2**)

Parameter	400 km	800 km	1200 km
CO_2 input flowrate (kg/ h)	79285.77	79285.77	79285.77
CO_2 losses pipeline (kg)	124	247.47	371.2
CO_2 losses compressors (kg)	494.92	989.86	1484.76
CO_2 losses injection (kg)	78.66	78.05	77.43
CO_2 stored (kg)	78588.18	77970.4	77352.38
GWP (kg CO_2-Equiv./MW)	238.08	240.09	242

The CO_2 losses through the pipeline as well as the CO_2 losses through compressors increase proportionally with the pipeline length. There is a slight decrease in the CO_2 loss during the injection process because less CO_2 is injected. The quantity of CO_2 stored decreases with an increase in pipeline length. It can be also noticed, from Table 8, that there is not a great modification on the total GWP (GWP generated by all the life cycle steps: NG supply chain, hydrogen production process, hydrogen transport and CO_2 transport and storage step reported to one MW of hydrogen and electricity produced) with the modification of the pipeline length.

4. Conclusions

Natural gas conversion based on CL process as well as the natural gas SR combined with CL using ilmenite as the oxygen carrier were considered in the present study. These processes were compared to the conventional SR process. The processes are evaluated, in the first instance, from a technical point of view considering some important key performance indicators. Evaluated plant concepts generate 300 MW_{th} of H_2. The carbon capture rate is almost 100% (99.25%) in **Case 2**, while for **Case 3** it reaches only 68.5%. The capability of capturing almost the entire carbon of the feedstock and lower plant complexity streamlines once more the attractiveness of the direct chemical looping option (**Case 2**). The specific CO_2 emissions of the evaluated plant concepts with CCS (**Case 2** and **Case 3**) are in the range of 2-213 kg/MWh. For comparison, the case without CCS (**Case 1**) has specific CO_2 emissions of about 268 kg/MWh.

The focus of the present work lies on an environmental evaluation of the processes using Life Cycle Analysis (LCA). A "cradle-to-grave" approach was assumed for the three cases under study. The system boundaries considered in the LCA include: i) hydrogen production from natural gas conversion coupled to CO_2 capture technologies based on CL; ii) upstream processes such as the extraction and processing of natural gas, ilmenite and catalyst production; and iii) downstream processes such as H_2 and CO_2 compression, transport and storage. The LCA assessment was carried out using the GaBi 6 software. Life Cycle Inventory (LCI) analysis, Life Cycle Impact Assessment (LCIA) and Interpretation, the four steps of LCA are presented in detail. Ten environmental impact categories, according to the CML 2001 impact assessment method, were defined, calculated and compared. The most significant environmental impact categories are the GWP and ADP fossil. The best value for GWP is obtained in **Case 2**, 240.04 kg CO_2-Equiv./MW. ADP fossil has the lowest impact in **Case 1**: 4785.67 MJ/MW. A sensitivity analysis on the CO_2 transport and storage step, viz. on the pipeline length, and implicitly on the CO_2 losses through the pipeline, compressors and injection process, was also performed leading to the conclusion that such a modification does not have a large contribution on the total GWP.

Acknowledgements

References

[1] Melaina M. W., Antonia O., and Penev M., Blending Hydrogen into Natural Gas Pipeline Networks: A Review of Key Issues, Technical Report, NREL/TP-5600-51995, March 2013.9 (http://www.nrel.gov/docs/fy13osti/51995.pdf last acces July 2014)
[2] Navarro R. M., Pena M. A., Fierro J. L. G., Hydrogen Production Reactions from Carbon Feedstocks: Fossil Fuels and Biomass, Chemical Reviews 107 (2007), 3952−3991.
[3] Muradov N., How to produce hydrogen from fossil fuels without CO_2 emission, International Journal of Hydrogen Energy 18 (1993) 211-215.
[4] Kurokawa H., Shirasaki Y., Yasuda I., Energy-Efficient Distributed Carbon Capture in Hydrogen Production from Natural Gas, Energy Procedia 4 (2011) 674–680.
[5] Cormos C.C., Petrescu L., Cormos A.M., Assessment of Hydrogen Production Systems based on Natural Gas Conversion with Carbon Capture and Storage, Proceedings of the 24th European Symposium on Computer Aided Process Engineering – ESCAPE 24, Budapest, Hungary (2014).
[6] Steinberg M., Energy carriers and conversion systems, Vol. 1, Hydrogen production from fossil fuels, Encycolpedia of Life Support Systems (EOLSS), http://www.eolss.net/sample-chapters/c08/E3-13-02.pdf (last acces july 2014)

[7] Metz B., Davidson O., de Coninck H, Loos M, Meyer L. IPCC special report on carbon dioxide capture and storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge (NY, USA): Cambridge University Press; 2005: p. 442.

[8] IEA. Energy Technology Analysis. CO2 capture and storage – A key carbon abatement option, 2008 http://www.iea.org/publications/freepublications/publication/CCS_2008.pdf (last access july 2014).

[9] Martínez I., Romano M.C., Fernández J.R., Chiesa P., Murillo R., Abanades J.C., Process design of a hydrogen production plant from natural gas with CO2 capture based on a novel Ca/Cu chemical loop, Applied Energy 114 (2014) 192–208.

[10] Lazanovski

[11] Spath P.L., Mann M.K., Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming, NREL, 2001.

[12] Molburg J.C., Doctor R.D., Hydrogen from Steam-Methane reforming with CO_2 capture, 20th Annual International Pittsburgh Coal Conference, Pittsburg, 2003.

[13] Fan, L.S. Chemical looping systems for fossil energy conversions. Wiley-AIChE 2010.

[14] Chemstations, Process Flowsheet Simulator. User guide Chemstations Inc., 2008, Huston, USA.

[15] Cormos, C.C., Integrated assessment of IGCC power generation technology with carbon capture and storage (CCS), Energy 42 (2012), 434-445.

[16] Environmental Protection Agency, US-EPA, Life Cycle assessment: Principles and Practice, 2006.

[17] Korre A., Nie Y., Durucan S., Life cycle modelling of fossil fuel power generation with post-combustion CO2 capture, International Journal of Greenhouse Gas Control 4 (2010) 289–300.

[18] Life Cycle Analysis of selected Hydrogen and Electricity Production pathways, Towards Hydrogen and Electricity Production with Carbon Dioxide Capture and Storage, DYNAMIS Project, 2007.

[19] Roth W., Atmaca T., Mori G. Stoffmengenflüsse und Energiebedarf ausge-wählter mineralischer Rohstoffe, Teilstudie Eisen, Geologisches Jahrbuch, Sonderhefte, Reihe H., heft SH6, Hannover (1999).

[20] Hydrogen Transport by Pipeline. www.roads2hy.com (last acces July 2014).

[21]Koornneef, J., Van Keulen T., Faaij, A., Turkenburg W. Life cycle assessment of a pulverized coal power plant with post-combustion capture, transport and storage of CO2. International Journal of Greenhouse gas Control 2 (2008) 48-467.

[22] PE International, GaBi Manual, 2012 http://www.gabi-software.com/fileadmin/GaBi_Manual/GaBi_6_manual.pdf (last access july 2014).