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Hydrogen Production from Fossil Fuels: Life Cycle Assessment of Technologies with Low Greenhouse Gas Emissions

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ABSTRACT: Because of the existence of infrastructures all around the world, the use of fossil resources as raw materials for hydrogen production can be a midterm solution in the implementation of hydrogen as a transport fuel. Therefore, the fuel processing technology used for the production of hydrogen should produce the lowest amount of greenhouse gases, with the highest energy efficiency and the lowest environmental impact. In this work, several options for hydrogen production from fossil fuels are evaluated: steam reforming, autothermal reforming of hydrocarbons, coal gasification, and methane decomposition. A system for the capture of CO₂ is supposed to be integrated in the reforming and gasification processes. This study evaluates the overall life cycle greenhouse gas emissions, the fossil energy consumption, and the environmental impact for the current and future energy scenarios. The autothermal reforming, decomposition of natural gas, and coal gasification are the best options from all of the points of view, while extrapolations to future scenarios predict very similar impacts. The economic analysis of methane decomposition processes reveals that the carbon selling price and the conversion of methane are the main factors influencing the cost-efficiency of produced hydrogen.

1. INTRODUCTION

Hydrogen has been proposed as one of the potential energy carriers for future energy scenarios because several advantages are achieved when it is used: high yields in fuel cells, clean combustion without emissions of CO₂, NO_x, or SO_x, and feasible storage of the intermittent renewable energy sources.^{1,2} As known, hydrogen can be produced from a wide variety of primary energy sources and production technologies.³ Steam reforming of hydrocarbons (mainly methane, from natural gas), coal, or heavy petroleum fraction gasification and water electrolysis are the more common techniques used today. The latter, used for producing high-purity hydrogen, is unfeasible not only economically but also environmentally because it consumes as much electricity with the related greenhouse gas (GHG) emissions as obtained from the electrical grid mostly based on fossil fuels. In fact, these emissions are quite higher than those obtained for the steam reforming of methane.⁴ The solution for this technology is to use a renewable origin of the electricity, such as photovoltaic or wind sources. This kind of system has been evaluated, and a good behavior was observed, but the scale of the hydrogen application is quite low if compared to the hypothetical hydrogen needs for its use in transportation.^{5,6}

It can be assumed that hydrogen will be obtained from renewable sources (water or biomass) using renewable energy in the long term, but in the short term, the fossil fuels are the most realistic alternatives to implement the "hydrogen economy". Some studies showed that the GHG emissions associated with hydrogen are similar to those from current gasoline-product

systems if their application for transportation are compared.⁷ Therefore, carbon capture and sequestration would be needed to minimize them.

In this paper, we evaluate several alternatives for obtaining hydrogen from different fossil resources, which are apparently the most efficient raw materials to produce hydrogen in a higher scale, with a comprehensive perspective of the production scheme by means of life cycle assessment (LCA) tools. The assessed raw materials are natural gas (automaintained decomposition, steam reforming, and autothermal reforming), petroleum derivative processes (steam reforming of ethanol, gasoline, and diesel), and coal (gasification). The evaluation is focused on the GHG emissions, with special attention on the fossil energy use in the product system. The projections made by the International Energy Agency (IEA) for the future have been employed for evaluating the potential evolution of each technology. In addition, their global environmental impacts are also estimated through two assessment methods: IMPACT2002+ and Ecoindicator 95.

2. SYSTEM DESCRIPTION

2.1. Chemistry of the Fuel Processing. Natural gas is assumed to be produced through the typical upstream processing.

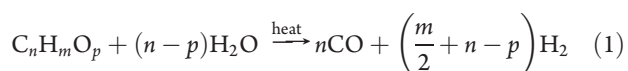
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Gasoline and diesel are obtained in a crude oil refinery. Ethanol is produced by the hydrolysis of ethylene, which is obtained by steam cracking in an oil refinery. Coal comes from conventional mining techniques. The fuel processing technologies assessed in this work are shown in Table 1.

2.1.1. Steam Reforming of Hydrocarbons. The reforming of hydrocarbons with steam has been deeply analyzed for hydrogen production because a small reformer can be installed in a fuel station without changing the infrastructures for hydrocarbon distribution.⁸ Figure 1 shows the block diagram for the assumed steam reforming for any hydrocarbon. The raw material is preheated and fed to the reformer. The reforming reaction (eq 1) is highly endothermic, and the usual reactor employed is direct-flame-heated, which implies a fuel consumption, usually natural gas.



The primary gas produced is mainly composed of CO and H₂. Subsequently, the water–gas shift reaction (WGSR) (eq 2) is carried out to increase the hydrogen production.



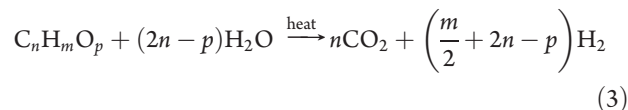
The WGSR is accomplished in two stages: high-temperature shift (HTWGS) and low-temperature shift (LTWGS), with intermediate cooling to overcome the equilibrium restrictions. Fe₂O₃–Cr₂O₃–CuO is used as a catalyst for the high-

Table 1. Assessed Processes for Hydrogen Production from Fossil Resources

process	raw material	code
steam reforming	natural gas	SR-NG
autothermal reforming	natural gas	ATR-NG
autocatalytic decomposition	natural gas	AD-NG
steam reforming	ethanol	SR-ET
autothermal reforming	ethanol	ATR-ET
steam reforming	gasoline	SR-G
steam reforming	diesel	SR-D
gasification	coal	CG

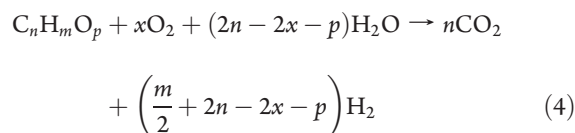
temperature stage, whereas for the low-temperature transformation, the catalyst is CuO–ZnO–Al₂O₃. Operation temperatures have been considered to be 773 and 573 K, respectively.⁹ The same operation conditions for this reaction are assumed for autothermal reforming and coal gasification.

Therefore, the overall reaction of the steam reforming process is



The produced CO₂ is separated from hydrogen by means of a pressure swing adsorption (PSA) unit. Hydrogen is obtained with great purity, 99.99%, and can be fed to a fuel cell. The exhaust gas, mainly composed by unreacted methane and hydrogen, is recycled to the reactor, except a small purge to avoid impurity accumulations. This recycling allows us to obtain a process conversion of 99%.

2.1.2. Autothermal Reforming. The autothermal reforming consists of the same above-described reforming reactions for producing hydrogen, but a part of the fuel reacts with oxygen to obtain the heating energy needed in the reforming reaction, which is endothermic. The general reaction of the autothermal reforming, including the WGS reaction, is usually written as



The value of x depends upon the composition of the hydrocarbon. Ahmed and Krumpelt⁸ calculated the value of the enthalpy of the methane reforming reaction as a function of x .

$$\Delta H_{298}^\circ = 60472 - 136634x \text{ (cal/mol)} \quad (5)$$

For 298 K, the process would be autothermal when the value of x is greater than 0.44; the higher the x ; the more exothermic the reaction.

2.1.3. Coal Gasification. The gasification of coal with steam presents more complex reaction pathways than the reforming of

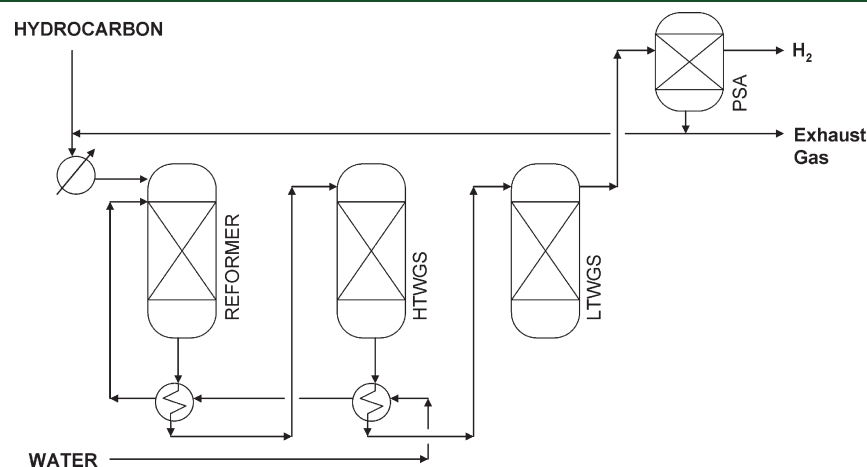
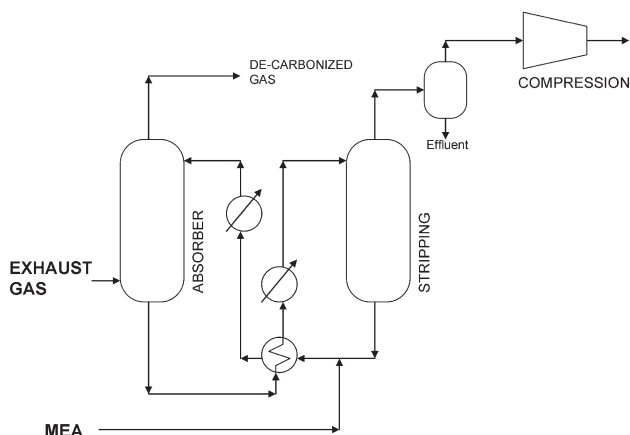


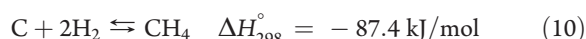
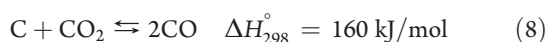
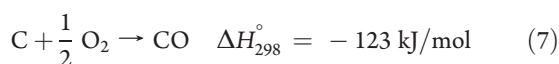
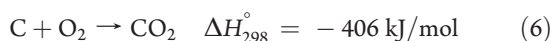
Figure 1. Hydrogen production by steam reforming of hydrocarbons.

Table 2. Main Emissions from a Coal Gasifier

parameter	emission value per N m ³ of H ₂
particulates (g)	8.0
NO _x (g)	5.8
SO _x (g)	2.9

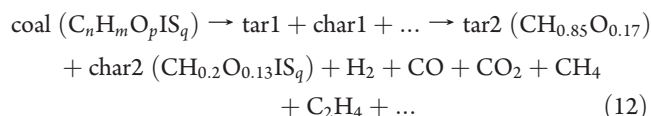
Figure 2. Amine process for the capture of CO₂.

other hydrocarbons. These reactions are

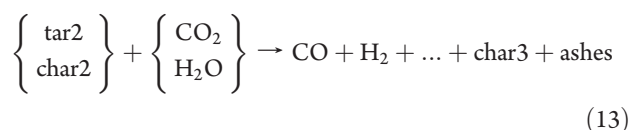


The net balance of this reaction system is clearly exothermic. According to the literature,¹⁰ one of the possible mechanisms of coal gasification is as follows.

(i) fast pyrolysis (IS = inorganic species):



(ii) reactions with steam and/or CO₂:



(iii) Reactions of light hydrocarbons and CO with steam to produce hydrogen (reactions 1, 2, and 3).

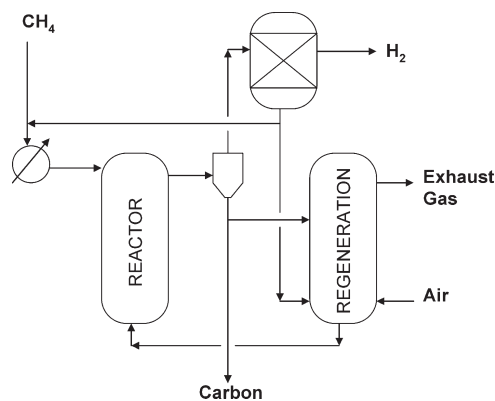
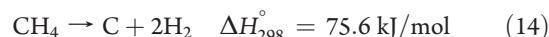


Figure 3. Block diagram of the methane decomposition for the production of hydrogen.

This mechanism explains how coal is gasified and the generation of ashes and other byproducts that increase the environmental impacts of the process. The temperature for the gasification process is 900 °C (typical value for high carbon conversion). Moreover, it has also been assumed that suspended particulate material and gases are being produced. Emissions coming from this process (Table 2) have been reported by Ruether et al.¹¹

2.1.4. Carbon Capture and Storage (CCS). The above-mentioned processes produce CO₂ as a reaction byproduct. In this paper, CO₂ mitigation in the hydrogen production technologies from fossil resources is being analyzed; therefore, a CCS system is included (Figure 2). Carbon dioxide is captured by absorption with monoethanolamine (MEA). Then, CO₂ is stripped, and the amine solution recovered is recycled to the absorber. Purified CO₂ is compressed to 25 MPa for its injection in an exhausted oil field.^{12,13}

2.1.5. Methane Decomposition. The decomposition of methane corresponds to the reaction



This reaction only produces 2 mol of hydrogen/mol of methane, which is lower than the ratio obtained from the steam reforming of methane. The produced carbon is solid, and its deposition can deactivate the performance of any metal catalyst.¹⁴ The reaction is also catalyzed by carbonaceous materials with high yields.^{15–17} This kind of catalysts could be obtained from the processing of the produced carbon in the same reaction. Therefore, the catalysis process is regarded as automaintained. The block diagram is shown in Figure 3. It was proposed by Muradov and Veziroglu¹⁴ and analyzed by Dufour et al.¹⁸

The carbon content of the processed hydrocarbon is directly captured as solid C. This solid is separated from the gas stream with a cyclone series. Then, hydrogen is obtained with 99.99% purity in a PSA unit, and the reject is partially recycled to the reactor. The other part of the recycled stream is used as fuel for heating purposes in the regeneration of carbon, which consists of the surface gasification of carbon. Thus, the process produces a small amount of CO₂.

2.2. Mass and Energy Balances. The assumed operation conditions and the conversion achieved in each process are shown in Table 3. The pressure was fixed for all of the processes at 1 MPa, except for methane decomposition that was fixed at 0.2 MPa.

Table 3. Reaction Temperature, Fuel Conversion, and Yield to Hydrogen for Each Assessed Process

process	reaction temperature (K)	fossil fuel conversion in the reactor (%) ^a	fossil fuel efficiency (%)
SR-NG	1123	88.7	43
ATR-NG	1123	99 ^b	50
AD-NG	1123	50	47.5
SR-ET	1023	99	40
ATR-ET	1023	99 ^b	58
SR-G	1023	73	35
SR-D	1023	55	25
CG	1173	98	84

^a Assumed at equilibrium. ^b Combustion reaction is accounted.

Table 4. Results of the Mass and Energy Balances of the Assessed Production Methods (Results Per N m³ of Hydrogen)

parameter	unit	SR-NG	ATR-NG	AD-NG	SR-ET	ATR-ET	SR-G	SR-D	CG
natural gas	kg	0.24	0.37	0.39					
ethanol	kg				0.50	0.60			
diesel	kg							0.56	
gasoline	kg						0.29		
coal	kg								0.39
heat (as natural gas)	kg	0.23	0.04	0.04	0.24	0.02	0.33	0.35	
steam consumption	kg	0.55	0.24		0.77	0.29	1.46	2.2	1.04
water consumption	kg	0.10	0.55		0.01	0.88	0.02	0.01	0.82
electricity (compression)	MJ	0.52	0.80	0.55	0.48	0.70	0.45	0.40	−0.74
electricity (CCS)	MJ	0.46	0.37		0.58	0.44	0.57	1.0	0.47
MEA consumption	kg	3.0×10^{-3}	1.5×10^{-3}		3.2×10^{-3}	1.2×10^{-3}	3.8×10^{-3}	0.02	2.4×10^{-3}
avoided steam	kg	0.23	0.68	0.53	0.19	0.42	0.25	0.45	0.7

The fossil fuel efficiency is the energy contained in the hydrogen related to the energy in the raw material along with the heat consumed in the process, with the latter being expressed as natural gas [energy in H₂/(energy in raw materials + heat as natural gas)]. In the case of gasoline and diesel, two surrogate compounds have been employed as those used by Pereira et al.¹⁹ and Docter and Lamm.²⁰ For diesel, C_{13.4}H_{26.3} was used, although some thermodynamic properties of C₁₃H₂₈ were employed (heat capacity, density, etc.). For gasoline, the chosen surrogate was that proposed by Docter and Lamm, *n*-heptane.¹⁸ The results for the inputs and outputs of the processes are shown in Table 4.

As a general rule, the higher the hydrogen/carbon atom ratio, the higher the production of hydrogen and the higher the efficiency.⁸ Thus, CH₄ from natural gas would be the best fuel for hydrogen production. If the processes from natural gas are evaluated, it can be seen that the consumption of the fossil resource is quite similar when the inputs as reagents and heat are added. The main difference lays on the rest of the processes; for the reforming options, there is an important steam and water consumption. This fact is avoided in the decomposition of methane. Likewise, the need for electricity is lower for this process because the CO₂ capture and storage is not necessary. The avoided steam is the steam that can be recovered from the excess of heat of some streams. Although, technically, the produced steam cannot be totally used, it is considered as a “negative” contribution to the balances of the processes, reducing the amount of energy required from the overall life cycle. The processes from oil-derived products (ethanol, gasoline, and diesel processing) seem to have worse behavior than others. In

the case of diesel and gasoline, the worst behavior is observed. These have high electricity, steam, and heat consumption, while the avoided production of steam is also the lowest.

The case of coal gasification has an important advantage: the process is exothermic.¹¹ Apart from the heat that can be obtained from the produced hydrogen, there is an excess of energy that can be recovered as electricity. In the process simulation, we have estimated a net production of 0.74 MJ N^{−1} m^{−3} of produced hydrogen; 0.47 MJ has to be subtracted, because it is consumed in the compression process of the CCS system. Therefore, 0.27 MJ of electricity N^{−1} m^{−3} of H₂ is being produced, which is quite similar to 0.3 MJ N^{−1} m^{−3} of H₂, the value estimated by Ruether et al.¹¹ (they reported 12 MW for a production of 318 tons of H₂/day).

3. METHODOLOGY

3.1. LCA. LCA is a fundamental tool for evaluating the environmental performance of energy systems, in not only the environmental impact calculation context but also the quantification of life cycle energy balances.^{21,22} It also provides unique perspectives to policymakers²³ to drive new research to the best environmentally friendly options. In the field of hydrogen technologies, some important studies have been published; for example, LCA for transportation systems,^{24,25} where the hydrogen fuel cell system is compared to conventional diesel, kerosene, or natural gas systems. Other studies^{22,26,27} are focused on production processes. In this work, we assess the performance of hydrogen production technologies from fossil fuels from a life cycle perspective.

Table 5. IMPACT2002+ Categories, Indicators, and Weights Used for Final Score Estimation

damage category	midpoint category	midpoint reference substance	damage factor	indicator	weighing factor
human health	carcinogens	kg of C ₂ H ₃ Cl	2.8×10^{-6}	DALY ^a /kg of C ₂ H ₃ Cl	1
	non-carcinogens	kg of C ₂ H ₃ Cl	2.8×10^{-6}	DALY/kg of C ₂ H ₃ Cl	
	respiratory inorganics	kg of PM2.5 equiv	7×10^{-4}	DALY/kg of PM2.5 equiv	
	ionizing radiation	Bq C-14	2.1×10^{-10}	DALY/Bq C-14	
	ozone layer depletion	kg of CFC-11 equiv	1.05×10^{-3}	DALY/kg of CFC-11 equiv	
	respiratory organics	kg of C ₂ H ₄ equiv	2.1×10^{-6}	DALY/kg of C ₂ H ₄ equiv	
ecosystem quality	aquatic ecotoxicity	kg of TEG water	5.0×10^{-5}	PDF ^b m ² year/kg of TEG water	1
	terrestrial ecotoxicity	kg of TEG soil	7.9×10^{-3}	PDF m ² year/kg of TEG soil	
	terrestrial acid/nitri	kg of SO ₂ equiv	1.04	PDF m ² year/kg of SO ₂ equiv	
	land occupation	m ² organic arable	1.09	PDF m ² year/m ² organic arable	
climate change	global warming	kg of CO ₂	1	kg of CO ₂ /kg of CO ₂	1
	non-renewable energy	MJ primary	1	MJ primary/MJ primary	
resources	mineral extraction	MJ surplus	1	MJ primary/MJ surplus	1

^aDALY = disability adjusted life years. ^bPDF = potentially disappeared fraction.

LCA methodology is an essential tool for the evaluation of processes claiming GHG emission mitigation. An example of that is the biomass processing; although it can be thought of as a carbon-free technology, there are studies that assign to the biomass processing the same carbon dioxide emissions as those produced from fossil fuel transportation schemes.²⁸ Therefore, when a new technology is proposed as carbon-free, a life cycle perspective has to prove it. In the same way, the pollution associated with new production schemes has to be evaluated. A life cycle approach not only evaluates the GHG emissions or the energy use but also the pollution associated with other fields, such as the depletion of the ozone layer, the eutrophication of aquatic systems, the acid rain effect, the biodiversity, the consumption of water, etc.

This paper assesses the production of hydrogen by, theoretically, clean processes from fossil fuels, i.e., those that minimize GHG emissions. A life cycle perspective will reflect how deep is the reduction of emissions, the change in the fossil energy consumption, and how other environmental aspects may have varied. The selected functional unit is 1 N m³ of hydrogen (99.99% purity) for all of the cases. System boundaries and factors considered for LCAs are focused on the raw material, energy acquisition, and manufacturing stages. The construction materials needed to erect the production plants are also considered. The software of PRé Consultants, SimaPro 7.1, was used to perform the assessment, and the Ecoinvent 2.0 database was used to calculate the life cycle inventory.

The whole upstream chain, previous to the production process, is covered. This means that raw material extraction, treatment, distribution, and transportation are also considered in the life cycle analysis. The mass and energy balances of the production stage, shown in Table 1, were calculated from simulation of reaction networks. The impact of raw material extraction, treatment, and distribution were taken from the database Ecoinvent 2.0. The geographical scope is considered to be an European average; therefore, the accuracy of the used database is considered appropriate.

3.2. Assessment Methods. The global warming potential (GHG emissions) was measured with the Intergovernmental Panel for Climate Change (IPCC) method, reviewed in 2007²⁹ and with a time scope of 100 years. The fossil energy use was measured with the cumulative energy demand (CED) method, and the single score of the environmental method was calculated with the IMPACT2002+ method and compared to Ecoindicator 95.

3.2.1. IPCC 2007 Global Warming Potential, 100 Years. This method measures the amount of equivalent CO₂ corresponding to the different gaseous emissions from a life cycle point of view. The characterization factors are proposed for a list of substances²⁹ contributing to climate

Table 6. Ecoindicator 95 Categories, Indicators, and Weights in the Final Score

impact category	category indicator	weighing factor
greenhouse effect	kg of CO ₂	2.5
ozone layer	kg of CFC11	100
acidification	kg of SO ₂	10
eutrophication	kg of PO ₄ ³⁻	5
heavy metals	kg of Pb	5
carcinogens	kg of B(a)P	10
winter smog	kg of SPM	5
summer smog	kg of C ₂ H ₄	2.5
pesticides	kg of a.s.	25

change, where the impact is measured as the equivalent amount of carbon dioxide that would produce the same impact as 1 kg of the evaluated substance. The stability of the emissions is a key factor to calculate the global warming potential; therefore, three sets of factors are proposed for three different time scopes: 25, 100, and 500 years. The midterm, 100 years, has been chosen for this assessment.

3.2.2. CED. This method is focused on the use of energy in each stage of a life cycle.³⁰ It was developed in the mid 1970s as a consequence of the energy crisis, and it was aimed to detect the stages of a life cycle where main savings could be achieved. The method has a strong link with the environmental impact; therefore, it has to be employed as a complement of other assessment methods.³¹ In this research, this variable was estimated from the fossil energy input to the life cycle.

3.2.3. Single Score Methods. These assessment methods are used to calculate a single score of the environmental impact of each alternative during its whole life cycle. They classify the environmental impacts into categories, estimating the impact to be equivalent to that produced from reference substances. For that purpose, characterization factors are needed. Factors are defined using the relative importance of a substance for an impact category in comparison to the reference substance [e.g., methane has a characterization factor to the reference substance (CO₂) of 7.6 (w/w) in the category of global warming potential for a time horizon of 500 years²⁹]. Finally, a single score for environmental impact is obtained by applying a weighting factor to each category and summing the final results.

The first method used in this work is IMPACT2002+. The data collected from the inventory of the life cycle is assigned to 14 impact categories, which are linked to 4 damage categories (human health, ecosystem quality, climate change, and resources). IMPACT2002+ is a

Table 7. Prospects of Electricity Generation Share Per Energy Source and Per Scenario

scenario	C + O (%) ^a	G (%) ^a	N (%) ^a	H (%) ^a	B (%) ^a	R (%) ^a
current 2009	33	19	34	6	2	4
WEO baseline 2030	31	29	17	6	8	8
WEO alternative 2030	16	27	28	8	10	11
ETP baseline 2050	55	21	8	9	3	4
ETP ACT 2050	16	29	19	13	5	18
ETP BLUE 2050	13	25	23	12	6	21

^a C + O, carbon + oil; G, gas; N, nuclear; H, hydro; B, biomass; and R, renewable.

combination of several methods. It was built by adding the categories of IPCC, CED, Ecoindicator 99, and CML to IMPACT2002+. Table 5 shows the categories, indicators, and weights used for estimating the final score.

One of the categories of this method is non-renewable energy, and this includes the fossil fuels that are consumed in high amounts as raw materials in each process. The possible high importance of it can shadow the influence of other categories. Therefore, Ecoindicator 95 was selected as a second assessment method, because it only includes environmental and human health categories. Table 6 shows the categories, indicators, and weighing factors used in the method.

3.3. Future Energy Scenarios. The analysis was extended from the current data to the future scenarios proposed by the IEA to observe how the technologies may perform differently because of different future energy scenarios and different GHG emission generation rates.

3.3.1. World Energy Outlook (WEO). WEO analysis is performed by the IEA each year, and it reflects the prospective analysis of climate change policies in Organisation for Economic Co-operation and Development (OECD) countries, oil and gas supplies, and other issues. In this work, the 2008 version was employed.³² It proposes two scenarios:

(1) WEO baseline case. Some moderate policies on climate change are assumed, but they are strongly restricted by economic factors.

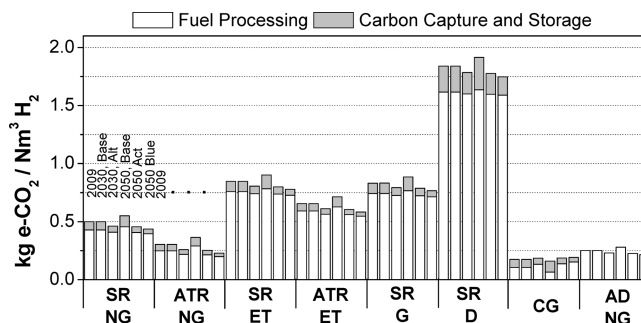
(2) WEO alternative case. In this case, more ambitious environmental policies are applied. Safety in energy supply and CO₂ mitigation are the key issues.

3.3.2. Energy Technology Perspective (ETP). This study comes from IEA, as in the case of the WEO but with a special focus on the role of technologies rather than on the role of policies.³³ The baseline is the extension of WEO2008 baseline to 2050, by assuming that economic growth changes after 2030 as the population growth slows and the economies of developing countries begin to mature. ACT scenarios are those that optimize energy production toward achieving the same emissions of CO₂ in 2050 as in 2005. BLUE scenario assumes that CO₂ emissions in 2050 are half of 2005 emissions. Both scenarios consider the application of optimistic and ambitious policies on climate change. ACT and BLUE are only possible if the whole world participates on these policies.

3.3.3. Electricity Generation. The main factor that varies the energy balance of the LCA is the energy mix employed for electricity generation. Electricity is consumed in the different processes mainly associated with gas compression operations. This occurs at carbon dioxide storage, PSA, and steam compression. On the other hand, the needed heat for each process is considered to be mainly obtained by combustion of an excess of natural gas. For countries in the OECD–Europe geographical area, the assumed production mix for electricity generation corresponding to the different scenarios is shown in Table 7.

4. RESULTS

4.1. GHG Emissions. The results from the assessment of the GHG emissions are shown in Figure 4. Coal gasification has the

**Figure 4.** Current and future projections of GHG emissions associated with each assessed process for hydrogen production.

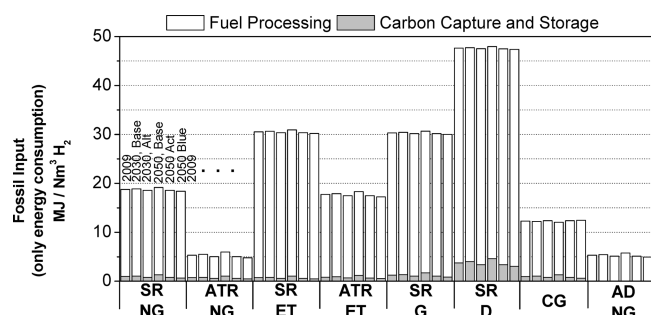
best performance because of the great amount of avoided emissions, i.e., CO₂ that is not emitted because electricity is not consumed. In general, results indicate that GHG emissions of coal gasification increase slightly when the scenario is more environmental friendly (i.e., 2030 alternative or 2050 BLUE). The lower emissions of coal gasification are correlated to non-produced electricity. Then, if the production of electricity is cleaner (from renewable resources), the positive effect associated with the avoided electricity consumption is smaller. With regard to the contribution of the CCS process to the total CO₂ emissions, it is observed that its contribution is much lower than that corresponding to fuel processing in all cases. Thus, the implementation of capture and storage technologies leads to a significant reduction of total GHG emissions for all of the systems evaluated because the amount of retained CO₂ is much higher than that emitted for the capture and storage processes, as demonstrated in previous works.¹⁸ Finally, the contribution of these processes to the total CO₂ emissions changes slightly with the energy scenario because of the different prospects of electricity generation share.

Along with coal gasification, processes with the lowest emissions are the methane automaintained decomposition (AD-NG) and the autothermal reforming of natural gas (ATR-NG). Both options involve the emission of 0.25 kg of CO₂ (half of the value obtained for SR-NG). Emissions from the ATR process are lower than those for conventional steam reforming because part of the natural gas is directly burned into the reactor to supply the heat needed for the reforming reaction and the fuel economy is better than that of the direct flame heating of tube reactors of steam reforming. The results for AD-NG show that this option leads to less emissions than the reforming reaction with a capture system, SR-NG, because AD-NG avoids the need for CCS techniques.

Table 8 presents results of CO₂ mass balance for processes that use coal and natural gas as raw materials (CG, SR-NG, AD-NG, and ATR-NG), detailing the contribution of the principal steps for hydrogen production: emissions associated with raw material (extraction, transport, and storage), steam consumption, fuel consumption (only for heating), and electricity consumption. Finally, avoided CO₂ emissions related to the production of steam that can be converted into electricity are also displayed. As observed, necessary amounts of coal and steam for the gasification lead to higher CO₂ emissions than that corresponding to natural gas and steam requirements in SR-NG, AD-NG, and ATR-NG processes. However, the high quantity of steam produced in the coal gasification (because it is an exothermic process) compensates these emissions, leading to the lowest value of CO₂ emitted.

Table 8. CO₂ Emissions (kg of equiv CO₂ N^{−1} m^{−3} of H₂) for the Main Steps of CG, SR-NG, AD-NG, and ATR-NG Processes (CCS Step Is Not Included) for Scenario 2009

process	total	raw material (NG or coal)	steam consumption	heat (NG)	other consumptions ^a	avoided emissions
SR-NG	0.426	0.144	0.128	0.136	0.072	−0.054
ATR-NG	0.245	0.219	0.055	0.021	0.109	−0.159
AD-NG	0.256	0.227	0.000	0.024	0.085	−0.080
CG	0.100	0.114	0.244	0.000	0.003	−0.262

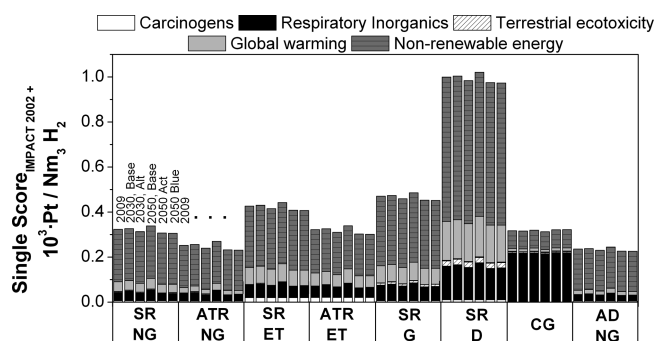
^a Principally water and electricity.**Figure 5.** Current and future projections of fossil energy input to each assessed process for hydrogen production.

Oil-based processes produce higher amounts of CO₂ than others. In this case, the low value of H/C ratios noticeably influences the efficiency of the process and, therefore, the production of CO₂. Besides, the life cycle of the raw material is quite significant, that is, the case of the impact of the diesel life cycle with several energy-demanding operations, which has higher contribution to the emissions than the life cycle of gasoline or ethanol. Again, the ATR option produces lower emissions because of the better fuel economy.

The influence of the proposed energy scenarios on the amount of CO₂ emitted is quite low for all of the processes shown in Figure 4. However, for these cases, the worst scenario is the baseline of both studies (WEO 2030 baseline and ETP 2050 baseline) because a slight decrease of CO₂ emissions is obtained when more environmentally friendly situations are used for LCA calculations. Despite this, these most optimistic scenarios do not show any significant improvement. That means that the technology currently producing high amounts of GHG gases will also produce important emissions in the future. Then, a special focus should be made in the fuel processing technology and in the selection of the raw material.

4.2. Fossil Energy Use. Figure 5 represents the use of fossil resources as energy input to the processes. In the calculation, the use of hydrocarbons as raw materials (e.g., as reactive) for hydrogen production was subtracted. As observed before, the change of the scenario slightly influences the fossil fuel consumption of hydrogen production. The lowest input from fossil resources would correspond to the highest efficiency; this is the case of natural gas in the ATR-NG and AD-NG processes. Then, it is deduced that the life cycle energy efficiency is better when the autothermal processes are considered. Coal processing seems to be also more energy efficient than other options because of its exothermic character. Again, CCS processes are responsible for less fossil resource consumption than fuel processing technologies.

4.3. Environmental Impact. As mentioned above, the IMPACT2002+ method was used to obtain the single score for the

**Figure 6.** Current and future projections of the single score of the environmental impact of each assessed production process through IMPACT2002+.

overall environmental impact. This method has 14 categories for the calculation of the environmental impact; however, only 5 have a significant influence (Figure 6), and 3 are responsible for more than 95% of the total impact. The value of the “non-renewable energy category” is calculated in relation to the total available reserves of the studied fossil fuel. In general, the use of fossil energy is the main drawback of these technologies because fossil fuels are mainly consumed as raw material in the hydrogen production process or when the raw material is obtained (ethanol, gasoline, or diesel). This can be especially relevant for methane decomposition, because the fossil energy category sums 80% of the total impact, mainly because of the lower H₂/CH₄ ratio produced in the reaction (reaction 14) in comparison to steam reforming processes. The low contribution for coal gasification is due to the larger reserves of this fossil fuel. The “global warming” category sums, in equivalent units, the amount of GHG emissions. Its overall influence on the environmental impact is lower than that corresponding to other significant categories. This result was expected, because the purpose of the study is to assess hydrogen production processes with minimal CO₂ emissions. Concerning “respiratory inorganics”, the presence of particulate matter in the emissions from the life cycle of all of the considered fossil fuels makes this category important in the final assessed impact. Natural gas has the minimum contribution to this category. The contribution of the “respiratory inorganics” category grows because the processes are based on heavier compounds, becoming very relevant for coal gasification. Finally, “carcinogens” and “terrestrial ecotoxicity” categories are contributed by processes based on derived oil products (ethanol, gasoline, and diesel) because of the impacts associated with the production of some secondary products during their manufacturing.

Future projections have weak influence on the single score calculated with the IMPACT2002+ method. Therefore, it may be deduced that the reduction of the environmental impact must be achieved by shifting technologies for the use of fossil resources.

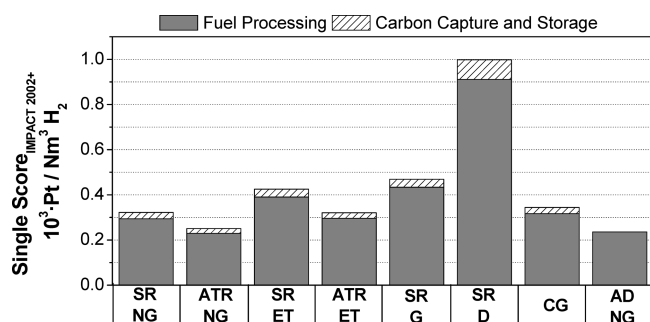


Figure 7. Single score of the environmental impact for each assessed process. The contribution of the CCS system is differentiated.

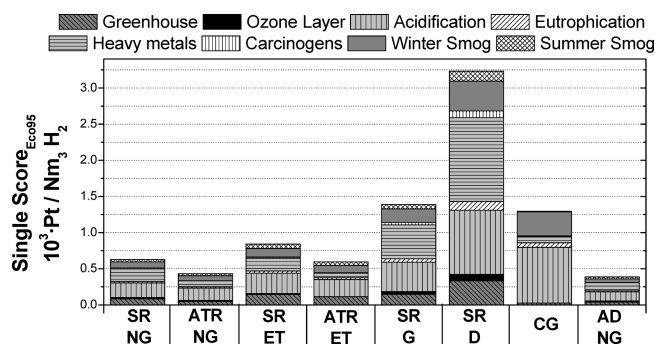


Figure 8. Single score of the environmental impact of each assessed production process through Ecoindicator 95.

The contribution of the CCS system has also been assessed and is shown in Figure 7. The contribution derived from the performance of the CCS system is small. The optimal use of energy and the recycling of the amine solution (MEA) contribute to this result. The main impact is observed for the carbon capture of oil derivatives and is proportional to the use of MEA and electricity in the process (shown in Table 4).

As known, when a single score is given to the environmental impact of a life cycle, the method selected for the calculation has a strong influence on the final results. In particular, we want to remark the contribution of the category “non-renewable energy”. As fossil resources are being used, the scarcity of them increases. Therefore, the contribution of this category minimizes the influence of other environmental or health impacts. As previously explained, another assessment method has been studied to skip this problem, Ecoindicator 95 (see Table 6). The results obtained are shown in Figure 8. With this new assessment method, coal gasification is the third process in terms of environmental impact produced by acidification, eutrophication, and winter smog. The three categories are directly related to the nature of the raw material used, coal, which produces high particulate matter, SO₂, and NO_x emissions because of the much higher content on S and N than the other fossil fuels. In this case, the positive effect achieved with this process by avoiding electricity consumption (and thus CO₂ emissions) is not so remarkable because the weighing factors of Ecoindicator 95 promote the contribution of the acidification, eutrophication, and winter smog with regards to the GHG emissions.

The processes based on diesel and gasoline again show the highest impact, mainly by the contributions of GHG, acidification, winter smog, and heavy metals. The first three factors are mainly

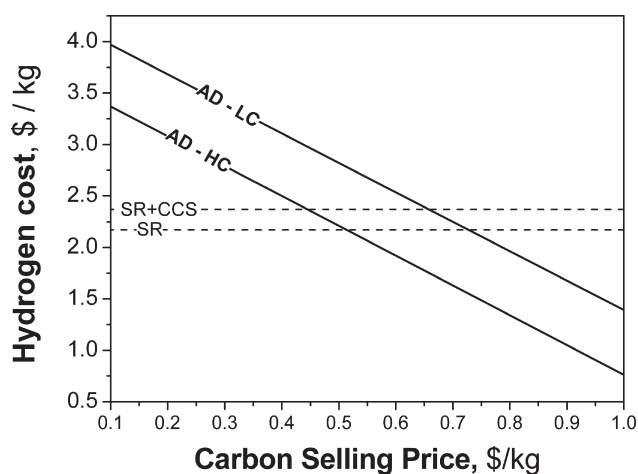


Figure 9. Hydrogen cost as a function of the carbon selling price for low conversion (LC) and high conversion (HC) of methane.

due to the higher emissions related to higher energy consumption during the production of these compounds and their processing to obtain hydrogen. Acidification is also related to the sulfur content of the initial raw material (oil). Finally, heavy metals come from the extended use of catalysts and equipment during the process life cycle (transformation of oil into hydrogen). The ethanol-based processes also have significant impacts because of the original raw material, crude oil, but at a lower extent than diesel or gasoline because ethylene requires fewer processes than those fuels in its manufacturing. Autothermal reforming shows again a better environmental profile than the conventional steam reforming because of a better fuel economy, as previously explained. The natural-gas-based processes present the best performance, because the raw material used has the lowest N and S content and the processes need less energy. The best performing processes are the auto-maintained decomposition and autothermal reforming, with a small difference for the first one, because of the lower emissions produced during the process and the better fuel economy.

According to all of the results evaluated, the automaintained decomposition of natural gas seems to be the best option. Besides, the most suitable way to capture CO₂ is prevention, i.e., to store it as solid C, even better than the CO₂ absorption system, which may have higher environmental impact. However, there is an economical drawback that should be overcome: the huge amounts of solid C that would be produced. Figure 9 shows the hydrogen cost calculated for each carbon selling price for high conversion (HC, 90%) and low conversion (LC, 30%). This estimation was made with the H2A model. As seen, the price of the solid carbon has a strong influence on the costs of hydrogen. For the studied conversion (50%), a selling price of around \$0.6/kg will be necessary to equal the costs from steam reforming coupled to CCS techniques. The produced carbon has high purity and quality, and its price can reach \$1/kg. Nevertheless, a production plant of hydrogen with methane decomposition technology can easily saturate the carbon market. Then, new use for carbon must be searched with a non-energy purpose. Several proposals, as construction material or soil remediation, have been made.¹⁴

5. CONCLUSION

Automaintained decomposition and autothermal reforming of natural gas are the best processes for hydrogen production from

fossil fuels after assessing GHG emission mitigation, energy consumption, and total environmental impact. Nevertheless, the automaintained decomposition lacks applications for the huge amounts of solid carbon co-produced, and its economy feasibility strongly depends upon the carbon selling price. In general, natural gas is the best raw material in comparison to crude oil or coal. Nevertheless, coal gasification has the advantage of co-producing a high amount of energy as heat that can be used for electricity generation or directly as thermal energy, avoiding the use of other fuels. This is translated on reduced GHG emissions and low environmental impacts and energy use. If fossil fuel depletion is not considered, the environmental impact of this process increases, overpassing the ethanol-based processes. All of the crude-oil-derived raw materials, especially diesel and gasoline, show the worst performance mainly because of the necessary processes for obtaining these fuels from the crude oil (catalytic cracking, catalytic reforming, alkylation, etc.). Ethanol produced by hydrolysis of ethylene shows better indicators than those for other oil-derived raw materials, because less processes are involved in its manufacture.

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NOMENCLATURE

AD = automaintained decomposition

ATR = autothermal reforming

CCS = carbon capture and storage

CED = cumulative energy demand

CG = coal gasification

D = diesel

ET = ethanol

G = gasoline

GHG = greenhouse gas

IMPACT = impact assessment of chemical toxics

IPCC = Intergovernmental Panel for Climate Change

LCA = life cycle assessment

NG = natural gas

PSA = pressure swing adsorption

SR = steam reforming

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