Environmental profile and sustainability of hydrogen production technologies: the PHISICO2 program

Javier Dufour [1,2,]*, David Serrano [1,2], José L. Gálvez[3]. and Graciano Martínez[3]

[1] Instituto IMDEA Energía, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain
[2] Universidad Rey Juan Carlos, Department of Chemical and Environmental Technology. ESCET.c/ Tulipán s/n, 28933 Móstoles (Madrid), Spain
[3] National Institute of Aerospace Technology (INTA), Renewable Energies Area, Crtra. Ajalvir Km 4, 28850 Torrejón de Ardoz (Madrid), Spain

*javier.dufour@urjc.es

Abstract Regarding climate change mitigation, safety in energy supply and energy independence of regions, hydrogen has been anticipated as a good alternative. Natural gas steam reforming is the conventional way to obtain it, but a huge amount of CO_2 is produced. The PHISICO2 Programme studied several ‘clean’ alternatives: methane decomposition, solar two-step thermochemical cycles and photodecomposition of water. LCA has been employed to evaluate their environmental profile and to compare them to conventional processes. Results indicate that water photodecomposition has the best environmental performance. Unfortunately, it is highly dependent on its efficiency and materials durability. Processes with fossil resources also show a good environmental behaviour. Methane decomposition produces high quality carbon as by-product. Thermochemical cycles are quite sensitive to process yield and materials lifetime.

1 Introduction

Main energy policies within Europe seek climate change mitigation, the increase of energy efficiency and the sustainability of the energy market, also by increasing the share of renewable sources of energy and clean fuels. Hydrogen has been pointed as a fuel with great potential, as its combustion is clean, it has a significant heating value and its storage can solve the seasonal character of renewable energy. As well, hydrogen is regarded as a long-term solution for transport. In order to drive the shift to this fuel, current research focuses mainly in environmentally-friendly production processes, safe storage and transport methods and hydrogen fuel cells with a long lifetime. Hydrogen production is usually performed by steam reforming of methane, main component of natural gas. So, this production scheme consumes an important amount of non-renewable resources and other manufacturing schemes should be developed.

The assessment of new, environmentally friendly, hydrogen production methods should be performed from a life cycle perspective. This would assure an effective research work to address real environmental hotspots and avoiding the reallocation of environmental impacts without achieving a real improvement. So, life cycle assessment tools are used in this paper to evaluate the environmental behaviour of several hydrogen production methods, with a focus on the consumption of non-renewable resources, greenhouse gases (GHG) emissions and exergy consumption, which reflects the availability of work. Assessed technologies were proposed in the PHISICO2 program, an initiative from Madrid regional government for the development of new hydrogen production technologies where strong regional research groups are playing an important international role. These technologies are methane decomposition, water thermochemical decomposition, and water photoelectrolysis. These three innovative techniques to produce hydrogen were also compared to commercially available technologies: steam reforming of methane and electrolysis. This paper presents preliminary results from the assessment of each technology.

2 Systems Definition

A life cycle assessment was performed accordingly to the ISO 14040:2006 standard. As production technologies are compared, system burdens do not cover storage, distribution and use phases of hydrogen. Raw materials extraction, manufacturing of materials and its distribution were considered and data for these processes were taken from secondary sources, mainly Ecoinvent 2.0. Electricity generation was studied separately, as it is quite relevant for the study of electrolysis processes and for all the compression stages. The geographical scope is the European level and the electricity generation mix was taken from IEA data [1].

2.1 Methane decomposition

The process is based on the route proposed by Muradov et al. [2] and its impact in the life cycle assessment of produced hydrogen with several catalysts was analyzed by Dufour et al. [3,4]. Methane, coming from natural gas, is decomposed in hydrogen and solid carbon. This reaction is endothermic and needs a high temperature (more than 1400 ºC) at low pressures to produce hydrogen. Therefore, catalysts are needed in order to lower heating energy demand. Metallic compounds allow reducing temperature to 600-700°C, but poisoning of catalysts with produced solid carbon reduces significantly the conversion. The option of carbonaceous materials [5] as catalysts is quite interesting, as part of the produced carbon can be a raw material to replace exhausted catalyst. Then, the process could be considered automaintained. For this paper, carbon catalysts will be considered. Separation of hydrogen and methane is made by PSA and the catalysts is regenerated by surface partial oxidation. Energy balance reveals that 3 MJ of heat (as natural gas burned in boiler) per Nm^3 of hydrogen are consumed. As well, 0.67 MJ of electricity are needed for the compression stages and 0.5 kg of steam can be produced from excess heat recovery.

2.2 Water photoelectrolysis

Photoelectrolysis is the decomposition of water to produce hydrogen and oxygen by an electric current generated by the solar irradiation of a photosensitive material. Many materials are photosensitive [6] but only few fulfil the requirements on durability, efficiency, manufacturing costs and process maintenance costs in order to achieve a sustainable process. For this paper, a mixture of cadmium sulfide, cadmium oxide and zinc oxide (CdS-CdO-ZnO) was studied in the yield terms proposed by Navarro et al. [7]. The process is quite simple and the layout of the device can be very similar to a solar panel with water flowing inside inner channels. The optimum yield of the process is achieved by means of a sacrificial agent, Na_2S, which also acts as the electrolyte. Achieved energy efficiency is quite low: only 0.5% was assumed for this assessment. Currently, higher efficiencies have been achieved (5-10%). The process is consuming about 6,000 m^2a per Nm^3 H_2, so an impact on soil and biodiversity may occur when using this technology.

2.3 Water decomposition through two stage thermochemical cycles

This process is based on water decomposition through solar thermal energy by using a redox material in a two-stage process: nickel ferrite, $NiFe_2O_4$, as defined by Kodama et al. [8]. This compound is exposed to solar thermal radiation and it is reduced at very high temperature (1773 K). The reduced phase is hydrolized with water in order to produce hydrogen. This reaction is exothermic and it is carried out at lower temperatures (1273 K). In total, both reactions need about 32 MJ of heat from a solar concentrator per Nm^3 H_2. The process consumes 0.5 kg of argon per Nm^3 of hydrogen as carrier gas in order to remove the oxygen from the reduction reactor, avoiding recombination of the reduced phase and displacing equilibrium to the formation of products.

2.4 Reference technologies

Two processes are taken as reference technologies for the production of hydrogen: steam methane reforming and water electrolysis with electricity from grid, photovoltaic panels and wind mills. For the steam reforming of methane from natural gas, the mass and energy balance made by Spath et al. [9] was considered and an amine process to capture CO_2 generated was added [10]. The energy consumption of this process is 1.2 MJ of heat (from natural gas burning) per Nm^3 of H_2 and 1.1 MJ of electricty is consumed at the compression processes. Excess heat is considerable and its recovery, with a 60% efficiency, would produce 1.24 kg of high pressure steam per Nm^3 of hydrogen. Electrolysis process was assumed to have the same mass and energy balance as that proposed by Ivy [11]. The electricity need is about 18 MJ per Nm^3 H_2, which may be obtained from the grid (assumed as the European average), from photovoltaic panels and from wind mills.

2.5 Assessment methods

The functional unit for the assessment is 1 Nm^3 of hydrogen. The European average was taken as the geographical scope and the assessment does not considered further stages than production with a quality standard suitable for feeding hydrogen fuel cells. The life cycle primary energy demand was assessed using the Cumulative Energy Demand method. The IPCC methodology from 2007 was used to calculate GHG emissions and the availability of work, defined as exergy, through the whole chain was assessed with the developed Cumulative Exergy Demand method. Non incompatibilities of data used in the assessment were observed for this study. For the evaluation of the impact on energy resources, calculated parameters were used. First, renewability of hydrogen accounts for the total share of renewable energy input in relation to total primary energy consumption of the whole life cycle. This indicator would reflect the renewable character that may be allocated to the produced hydrogen. As it is taking into account all the embodied primary energy consumption, it would help to identify where renewable energy sources really contribute to generate renewable hydrogen. Exergy efficiency is also an important parameter. This indicator is the relationship between hydrogen exergy content (i.e. its specific free energy content, 10.8 MJ per Nm^3 H_2) and the life cycle exergy input. For the calculation of exergy input, it has to be considered only non-renewable exergy, as renewable available work is considered to be unlimited. Then, this efficiency parameter may be higher than one, which means that the process is producing net work from resources. If it is lower than 1, the life cycle is consuming exergy from natural, non-renewable resources. Finally, it is reminded that the assessment on GHG emissions, primary energy consumption and exergy efficiency is not enough to evaluate the environmental performance of assessed processes. Other environmental pressures may derive from the assessed hydrogen life cycle options and, so, further work will be done in this respect.

3 Results and Discussion

Figure 1 shows the high amount of GHG emissions allocated to the production of hydrogen from electrolysis process when electricity is assumed to be fed from the average European grid (Grid-E). Solar electrolysis (Solar-E) and the two stages thermochemical decomposition of water (TSTC) has negligible contribution from production processes if it is compared to the emissions associated to materials manufacturing. Therefore, materials durability and the impact produced in their life cycle would be essential factors for the assessment.

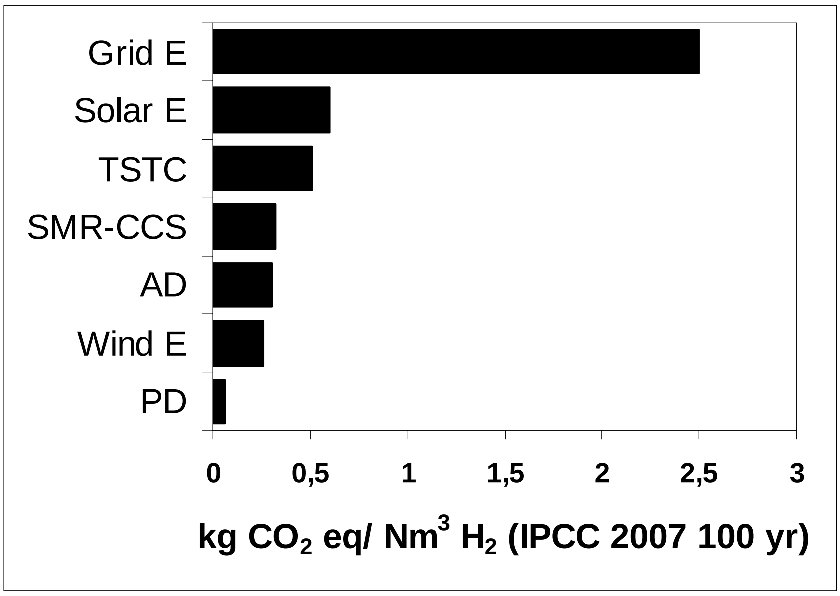

Fig.1: **GHG gases emissions from assessed options (PD: water photodecomposition, E: Electrolysis, AD: Methane decomposition, SMR: Steam Methane Reforming, CCS: Carbon Capture and Storage, TSTC: Two stage thermochemical cycle)**

Lowest impact comes from photoelectrolysis of water: the main reason is that this technology is quite simple if compared to other multistage processes. The two main assumptions that may influence the final impact of this process are the relatively long durability assumed for the cell (10000 h) and the flow of sacrificial agent, which may be higher in real-scale processes (lab scale performance was considered in the mass balance). For processes commercially available, the best performer is the electrolysis coupled with wind turbines, while the steam reforming of methane is still responsible for an important amount of emissions, even with a carbon capture and storage. As well, hydrogen produced from the thermal decomposition of methane performs better than natural gas reforming. Previous studies [3,4] have already shown the possibilities of that hydrogen production route. As well, methane automaintained decomposition would perform better if renewable sources are considered: for instance, changing the raw material, which may come from biomass processing, and also changing the source to supply the heating energy demand, which may come from solar thermal processes. These solutions may also be proposed for the low renewability of hydrogen produced by this method, as shown in Figure 2.

Renewability is defined by Neelis et al. [12] to compare the different life cycle character of hydrogen produced by electrolysis and steam reforming of natural gas. In this paper, the results from that reference are proved, as the renewability of hydrogen from electrolytic hydrogen from wind energy is highly renewable. In these LCA studies, none of the assessed technologies would achieve a 100% value of renewability as there would be always an input of fossil sources (e.g. in the materials life cycle). Water photodecomposition seems to give a very important renewable character to hydrogen, due to the assumed characteristics of photocatalysts. As expected, hydrogen from natural gas processes is not renewable and the grid electrolysis has a significant renewable character, but it is only due to the contribution of renewables to the grid (approx. 10%).

Solar processes also contribute largely to increase hydrogen renewable character, as the main energy source in the life cycle is a renewable resource.

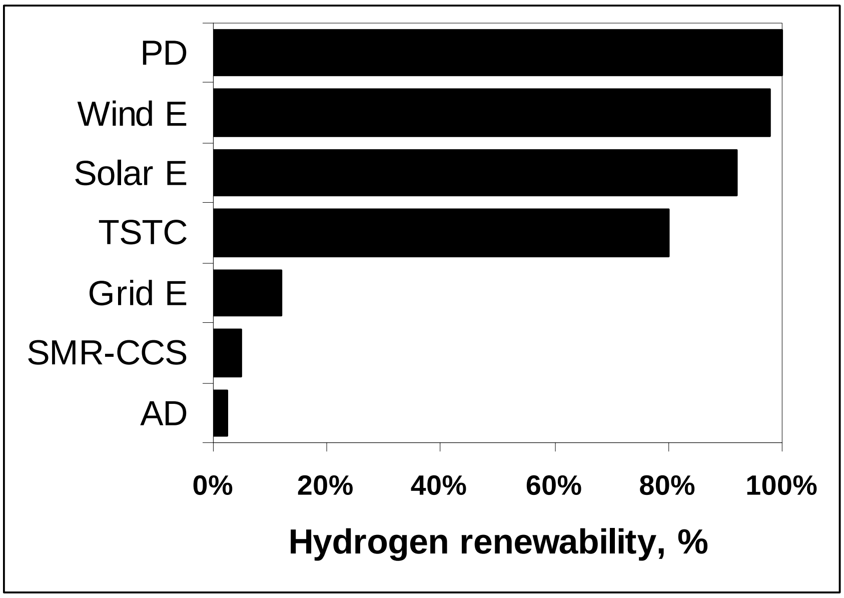

Fig.2: **Hydrogen renewability from assessed options (PD: water photodecomposition, E: Electrolysis, AD: Methane decomposition, SMR: Steam Methane Reforming, CCS: Carbon Capture and Storage, TSTC: Two stage thermochemical cycle)**

In Table 1, exergy efficiency results are shown. As expected, processes based on fossil sources and water grid electrolysis are net consumers of primary available work (i.e. exergy). None of the solar processes based on photovoltaics or thermochemical cycles produces net exergy, as their life cycle efficiency values are lower than 1. A lot of exergy is embodied in materials of solar installations, due to the impact of their manufacturing processes. This result confirms the findings from other references [13,14], where the combination of solar photovoltaics and water electrolysis has a value of 0.69 for the life cycle exergy efficiency.

Tab.1: Exergy efficiency of assessed processes

Process	**Exergy Efficiency**
Electrolysis (EU Grid)	0.2
Automaintained decomposition	0.4
Steam reforming of natural gas	0.58
Electrolysis (PV)	0.65
Two stages thermal decomposition of water	0.72
Electrolysis (Wind Turbine)	4.8
Water photoelectrolysis	9.6

The electrolysis coupled with wind is producing net exergy (4.8 exergy MJ per non renewable exergy MJ input), as well as water decomposition (9.6), although this process is still not commercially available and the aforementioned assumptions have a significant influence on its performance.

Finally, this paper should be regarded as a short extraction from a more comprehensive study performed under the PHISICO2 programme of the regional government of Madrid. Energy and Greenhouse gases have a direct and clear link between them and are very relevant for the perception of hydrogen as energy carrier. Nevertheless, other environmental pressures have to be carefully analysed. A better understanding of the real environmental impact of current research activities should be considered essential for the development of new technologies, especially regarding new energy carriers.

4 Conclusions

The environmental impact of different life cycle options for hydrogen, focused on different production technologies, was analysed. Three new processes, still in a development phase, were investigated in three main environmental categories: greenhouse gases emissions, renewable character of hydrogen and life cycle exergy efficiency. Methane decomposition produces less direct or indirect carbon dioxide emissions than steam methane reforming. Hydrogen produced from water two stages thermochemical decomposition has similar performance to commercial electrolytic hydrogen produced from solar photovoltaic electricity. These processes have high life cycle carbon emissions and low exergy efficiency (they are net consumers of exergy) mainly due to the embodied energy consumption of the materials used for the installations. Water photoelectrolysis shows a quite promising performance, similar to electrolysis coupled with wind turbine electricity, but is still dependent on the process yield and on the durability of materials.

5 References

[1] International Energy Agency, IEA. World Energy Outlook. 2006. Ed. by OECD/IEA, Paris.

[2] Muradov, N., Veziroglu, T.N., From hydrocarbon to hydrogen-carbon to hydrogen economy. *International Journal of Hydrogen Energy*, Vol. 30, 2005, 225-237

[3] Dufour, J., Serrano, D.P., Gálvez, J.L., Moreno, J., García, C. Life Cycle Assessment of processes for hydrogen production: Environmental feasibility and reduction of greenhouse gases emisiones. *International Journal of Hydrogen Energy*, Vol. 34, 2009, 1370-1376

[4] J. Dufour, J.L. Gálvez, D.P. Serrano, J. Moreno, G. Martínez, Life cycle assessment of hydrogen production by methane decomposition using carbonaceous catalysts, *International Journal of Hydrogen Energy*, Vol. 35, 2010, 1205-1212

[5] Serrano, D.P., Botas, J.A., Guil-López, R., H_2 production from methane pyrolysis over commercial carbon catalysts: kinetic and deactivation study. *International Journal of Hydrogen Energy*, Vol. 34, 2009, 4488-4494

[6] Rajeshwar, K., McConnell, R., Licht, S., EDS. Solar Hydrogen Generation. Solar Hydrogen Generation. Toward a Renewable Energy Future. Ed. By Springer Science, New York, 2008.

[7] Navarro, R.M., del Valle, F., Fierro, J.L.G., Photocatalytic hydrogen evolution from CdS-ZnO-CdO systems under visible Light irradiation: effect of thermal treatment and presence of Pt and Ru cocatalysts. *International Journal of Hydrogen Energy*, Vol. 33, 2008, 4265-4273

[8] Kodama, T., Gokon, N., Thermochemical Cycles for High-Temperature Solar Hydrogen Production, *Chemical Reviews*, Vol. 107, 2007, 4048-4077

[9] Spath, M.L., Mann, M.K., Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming. *NREL Technical Report NREL/TP-570-27637*, 2001. Available at www.osti.gov/bridge

[10] Odeh, N.A., Cockerill, T.T., Life Cycle GHG assessment of fossil fuel power plants with carbon capture and storage. *Energy Policy*, Vol. 36, 208 367-380

[11] Ivy, J., Summary of electrolytic Hydrogen Production. *NREL Report MP-560-36734*, 2004, available at www.nrel.gov

[12] Neelis, M.-L., van der Kooi, H.J.; Geerlings, J.J.C., Exergetic life cycle análisis of hydrogen production and storage systems for automotive applications. *International Journal of Hydrogen Energy*, Vol. 29, 2004 537-545

[13] Granovskii, M., Dincer, I., Rosen, M.A.; 2007. Exergetic life cycle assessment of hydrogen production from renewables. Journal of Power Sources, 167, 461-471

[14] Dincer, I., Rosen, M.A., Exergy, Ed. By Elsevier, Oxford, 2008