

# **Renewable hydrogen production. The role of Solar Thermal Water Splitting.**

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Thesis for the Degree of Master of Science

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## ABSTRACT

In a context of environmental crisis and depletion of conventional energy resources, the current energy model based on fossil fuels is obsolete and needs to be redefined and redesigned. Hydrogen economy can represent a good alternative. To get it, developing carbon-free renewable hydrogen production processes will be crucial. This Master Thesis is focused on the ones using solar thermal energy to split water. At first, world's energy situation is analyzed to introduce the need of alternatives like hydrogen. Then, main hydrogen production processes are classified and discussed. Nowadays 96% of hydrogen production is based on decarbonizing fossil fuels. Even though, there are different renewable alternatives developed or under developing, which are expected to take a main role in the middle and long term. Among them, thermochemical cycles are a good solution to split water using solar thermal energy, especially two-step cycles like ZnO/Zn. Taking this one as an example, viability of a large-scale hydrogen production implementation using thermochemical cycles is analyzed at different levels: solar technology, energetic efficiency and economical status and perspective. I conclude that this process is viable nowadays, except for the economical level. It requires financial support in the first states of its commercial development, but not necessarily in its middle and long term. In those, could represent a great pathway to produce carbon-free renewable hydrogen.

**Key words:** hydrogen production, thermochemical cycles, decarbonisation, solar thermal energy, carbon-free energy.

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# 1. INTRODUCTION.

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Hydrogen, as an energy carrier, will be analysed in this master thesis, focusing on its production processes from water using solar thermal energy.

## 1.1. OBJECTIVES.

The **main objective** of this work is to reach an understanding of renewable solar thermal hydrogen production from water. I will contextualize it in the current scenario of energy consumption and hydrogen production, and I will analyse feasibility of large-scale application using this technology.

To accomplish it, the following **secondary objectives** are proposed:

- To have a general overview about the world energy situation, and to assess the need for changing the current model to justify the searching for a new energy carrier as the hydrogen.
- To classify the main hydrogen production processes nowadays, and provide a deeper analysis of the ones using solar thermal energy, in order to decide which one could be more interesting in the future.
- To analyse viability of a large-scale application using solar thermal energy, studying it at different levels as the solar technology requirement, the energetic efficiency or economical status and perspectives.

For the first two objectives, the methodology is based on literature surveys. The third objective also requires bibliographic information, but will be supported on the use of information obtained before (in chapters 1 and 2) and the performance of some calculations.



## 1.2. PRELIMINARY CONCEPTS.

Before talking about the energy sector and the role played by hydrogen, it is necessary to define some preliminary concepts.

### **Primary energy source, energy carrier and feedstock:**

The first thing to point out is that hydrogen is not a primary energy source but an energy carrier, as it is electricity.

**Primary energy sources** are those that are found or stored in nature. In this group are included biomass, coal, oil, natural gas, sunlight, wind, water, uranium used in nuclear power, geothermal energy and potential energy from the Earth's gravity. [1]

An **energy carrier** is defined by ISO 13600 as a “substance or a phenomenon that can be used to produce mechanical work or heat or to operate chemical or physical processes” [2]. It is therefore a manufactured product that requires an energy input to be elaborated, and it can further be released controllably. Some examples are gasoline, bioethanol, electricity or hydrogen. The great advantage of this last one over electricity is that hydrogen can be stored directly, while electricity requires the use of batteries or other indirect applications.

A **feedstock** is the resource from which the energy carrier is extracted [1]. As an example, bioethanol is an energy carrier obtained using biomass as a feedstock. Hydrogen itself is an energy carrier with several possible feedstocks, such as coal, oil, natural gas, biomass or water.

### **Energy types:**

Another important concept when talking about energy is its classification depending on its use.

**Primary energy:** as defined above, it is the energy that comes directly from nature. Some examples are fossil fuels, wind or sunlight. If it cannot be used directly, it has to be converted into secondary or final energy before consumption.

**Secondary energy:** it is the energy converted to be transported or transmitted. Some examples are refined oil, electricity or hydrogen.

**Final energy:** it is the energy that can be used directly, and it is available for the final user. Some examples are gasoline, electricity or hydrogen.

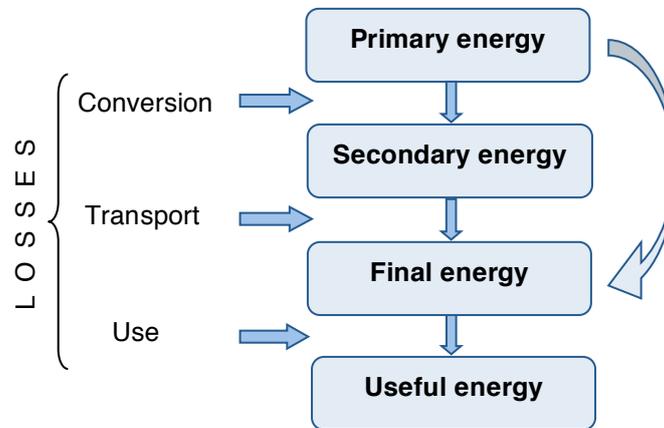
**Useful energy:** it is the usable energy in a final use application. Some examples are heat from a radiator, light from a bulb or mechanical energy in a vehicle.

As an example of this terminology, the solar energy could be the primary energy to obtain hydrogen, using electrolysis as a conversion process. This hydrogen would be a secondary energy until it is



transported to a hydrogen station. Then, a car could use this final energy form to produce mechanical energy, a useful energy form. All this definitions are schematically represented in Figure 1.

**Figure 1:** Energy types depending on its use.



Source: own elaboration.

Take into account that converting energy from one type to another always implies losses. So, going down in this list represents a smaller amount of energy than the precedent forms. This will be an important fact to consider when analysing data about energy consumption.

**Resources and reserves:**

Finally, a differentiation between resources and reserves is needed. For this purpose, some definitions from U.S. Geological Survey [3] are shown below:

**Resource:** “A concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth’s crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible.”

**Identified Resources:** “Resources whose location, grade, quality and quantity are known or estimated from specific geologic evidence.”

**Reserve Base:** “That part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth.”

**Reserves:** “That part of the reserve base which could be economically extracted or produced at the time of determination”. So, simplifying, reserves are this part of resources that is identified and recoverable.



## 1.2. ENERGY CONSUMPTION: STATE-OF-THE-ART.

Primary energy consumption worldwide has grown dramatically over the past 100 years. The high level of development reached by our society has been made possible by the use of coal, oil and natural gas. The greatest advances of the last two centuries have been linked, in one way or another, to a large increase in energy consumption from fossil fuels [4] (see Figure 2). This development has resulted in several problems, as it is supported in an energy system that is vulnerable, socially unbalanced and highly detrimental to the environment.

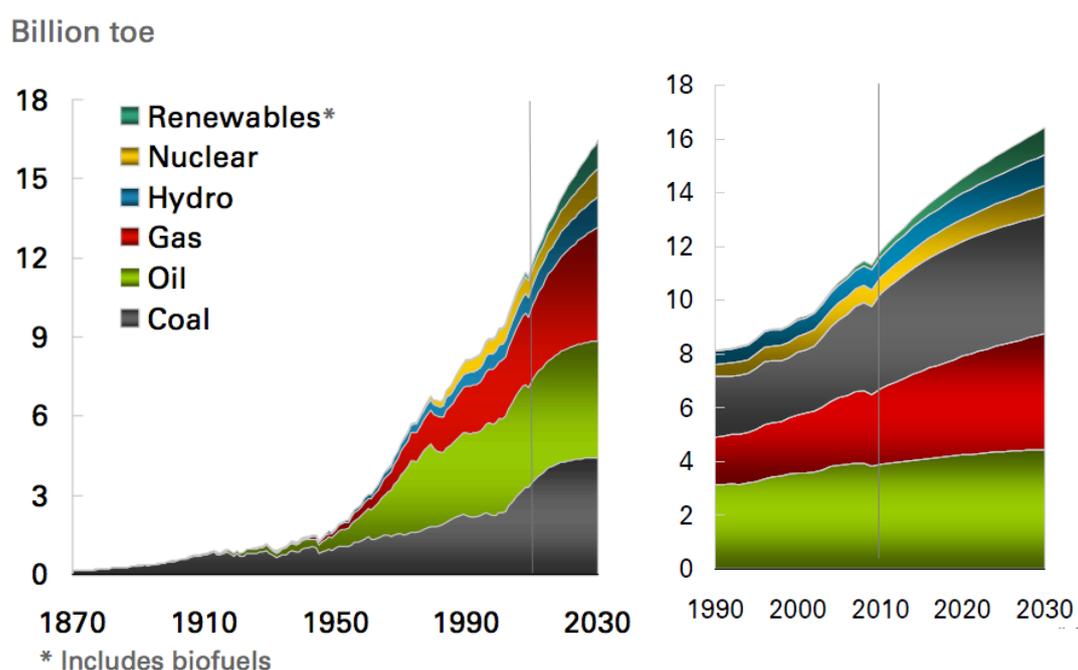
Problems are more evident today, because many of the resources used are limited and their reserves are becoming worryingly low. As an example, it seems clear that the peak oil production has been already reached [5][6], and the coal peak production is predicted for 2025 [7]. With all of this it seems that the current energy model is becoming obsolete.

Hydrogen as an energy carrier has a strong relation with energy sector, and both developments will be closely linked. In this paragraph, a general overview about world energy situation will be given, in order to contextualize subsequent studies.

### 1.2.1. PRIMARY ENERGY CONSUMPTION.

With the development of the industrial society and the population growth, in the last 100 years, energy consumption has experienced a dramatic increase. In this period, society has gone from consuming one billion tonnes of oil equivalent (toe) in 1910 to overcome the border of the 12 billion toes in 2010 [8] [9], as showing Figure 2.

**Figure 2:** *World primary energy consumption.*

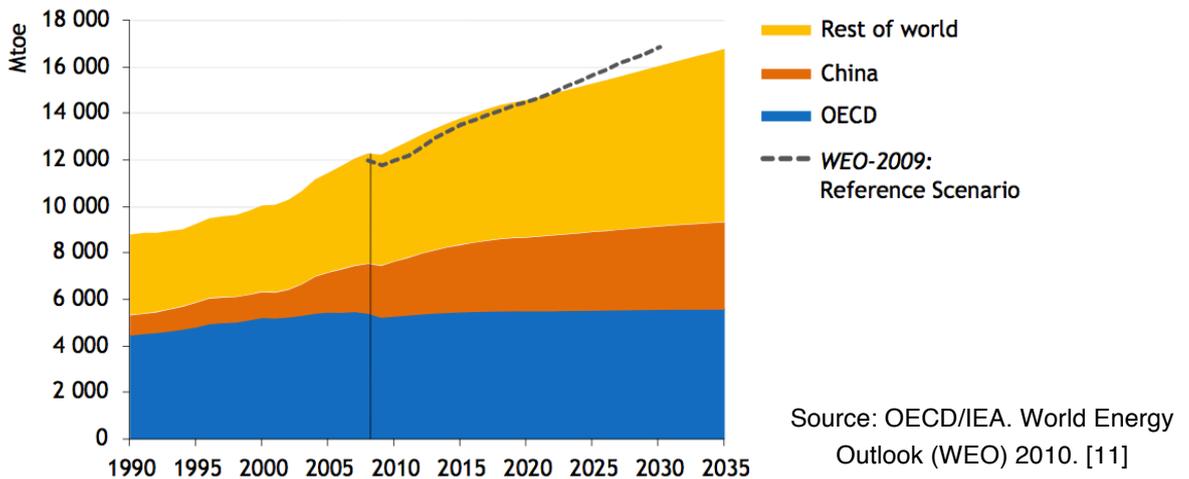


Source: BP Energy Outlook 2030. [9]



In 2009, a turnaround was experienced, with the first decrease since 1982. Despite that, in 2010 there was a strong growth of 5.6%, which represents the highest, recorded since 1973 [10]. As can be seen below in Figure 3, the forecast for the next 20 years are equally troubling. It is expected a similar growth rate for this period [8] [9].

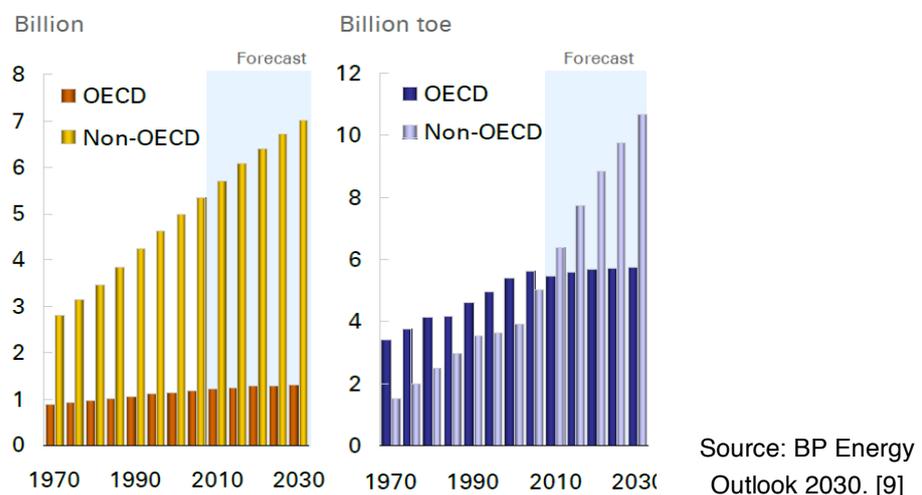
**Figure 3:** World primary energy consumption forecast to 2035.



This growth will be different between regions. On one side the more developed countries, basically represented by the OECD ones, will stabilize their consumption. Even that, they already has a really high energy consumption rate. There are examples such as Europe, which for historical reasons have a greater awareness in energy saving and efficiency, but there are also opposite cases like United States.

On the other side developing countries, represented by non-OECD ones, will not stop their development at the cost of using fewer resources. In Figures 3 and 4, it can be seen how, accompanied by a clear population growth, they will also experience a huge increase in energy consumption. This phenomenon is already shown in countries like China, Russia, Brazil or India.

**Figure 4:** World population (left) and world primary energy consumption (right) forecast to 2030, differentiating between OECD and non-OECD countries.



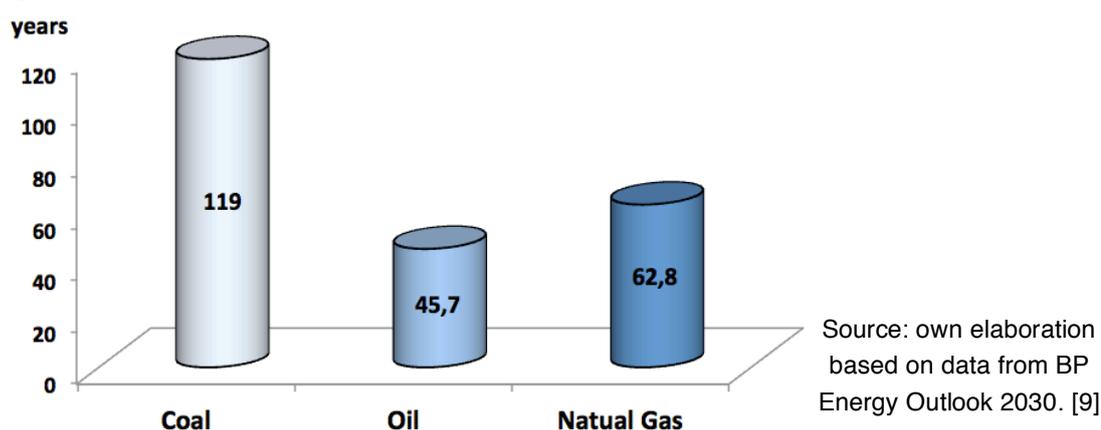


### 1.2.2. OBSOLESCENCE OF THE MODEL: THE NEED FOR A NEW PARADIGM.

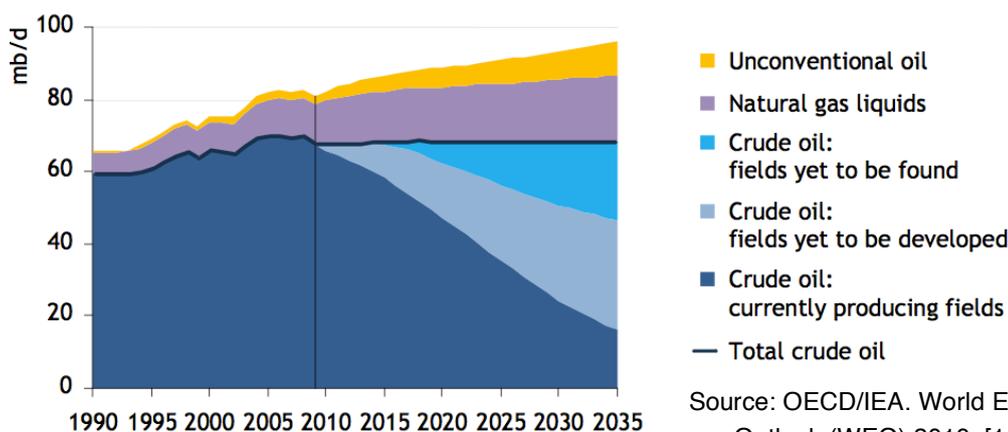
Considering world energy consumption, it is clear that the current model and the growth rate that characterizes it are unsustainable. The need for a new paradigm emerges not only for this high level of energy consumption, but also due to other problems like resources exhaustion, environmental consequences or social inequities of the model.

The first factor is the expected duration of proved fossil fuel reserves, which accelerates the obsolescence of the model. As it has been seen before, a dependence on this primary energy sources is clear. That is worrying not only because the strategic weakness that represents, but also because it is a non-renewable energy source and actually it is proved that reserves are not far from exhaustion. With the current consumption rate oil, it is predicted to last less than 50 years. Values for oil and coal, shown in Figure 5, are also an important concerning. Recent studies show how the crude oil peak has already been reached [5] [6] (see Figure 6<sup>1</sup>), and how the coal peak is also close to the predicted value for 2025 [7].

**Figure 5:** Proved fossil fuels reserves, in years with current consumption rate.



**Figure 6:** World oil production by type in the New Policies Scenario.<sup>1</sup>

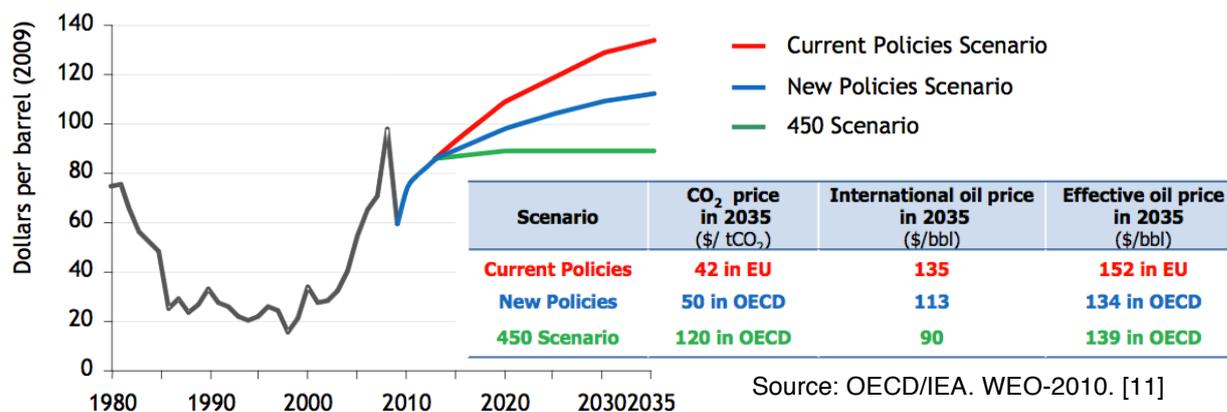


<sup>1</sup>**Scenarios considered in WOE: New Policies Scenario:** “assumes cautious implementation of recently announced commitments and plans, even if yet to be formally adopted, and provides benchmark to assess achievements and limitations of recent developments in climate and energy policy”. **Current Policies Scenario:** “takes into consideration only those policies that had been formally adopted by mid-2010” **450 Scenario:** “depicts a world in which collective policy action is taken to limit the long-term concentration of greenhouse gases in the atmosphere to 450 parts per million of CO<sub>2</sub>-equivalent (ppm CO<sub>2</sub>-eq)” [9] [12]



Furthermore, this is not just a capacity issue, but also an economical problem. This shortage of reserves implies an important increase in energy prices in the future, as it can be seen with the oil example in Figure 7. Even in the best possible scenario, effective oil prices considering CO<sub>2</sub> prices will be over 130 dollars per barrel.

**Figure 7: international oil price assumptions.**

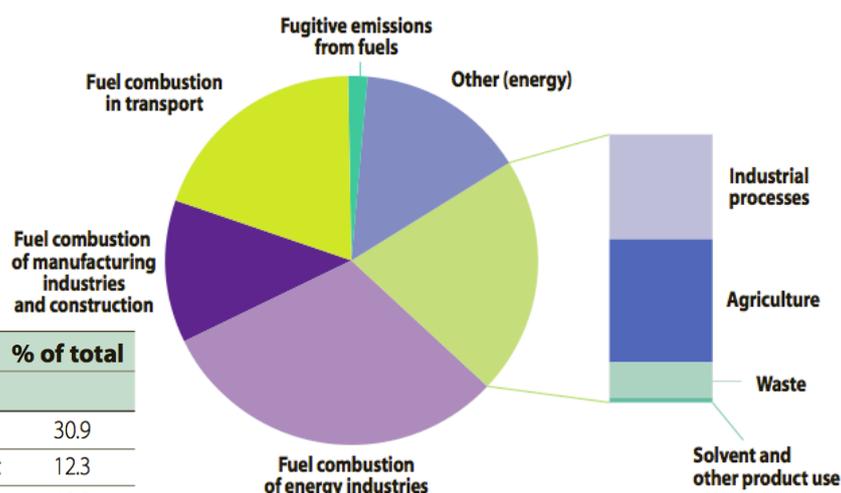


Another important factor is the environmental consequences of the current energy model. One of the main indicators is the greenhouse gases (GHG) emission, especially CO<sub>2</sub>, which is responsible for the climate change being experienced worldwide.

A first thing to determine is the contribution of the energy sector in those emissions. That is reflected in Figure 8 and Table 1, taking European Union in 2008 as an example. It can be seen as energy related activities, where hydrogen would be decisive, are primarily responsible for almost an 80% share [12].

**Figure 8 and Table 1: EU-27 greenhouse gas emissions, breakdown by sector, 2008.**

Sector	% of total
<b>Energy related</b>	
Fuel combustion of energy industries	30.9
Fuel combustion of manufacturing industries and const	12.3
Fuel combustion in transport	19.5
Fugitive emissions from fuels	1.7
Other (energy)	14.7
<b>Non-energy related</b>	
Industrial processes	8.3
Agriculture	9.6
Waste	2.8
Solvent and other product use	0.2

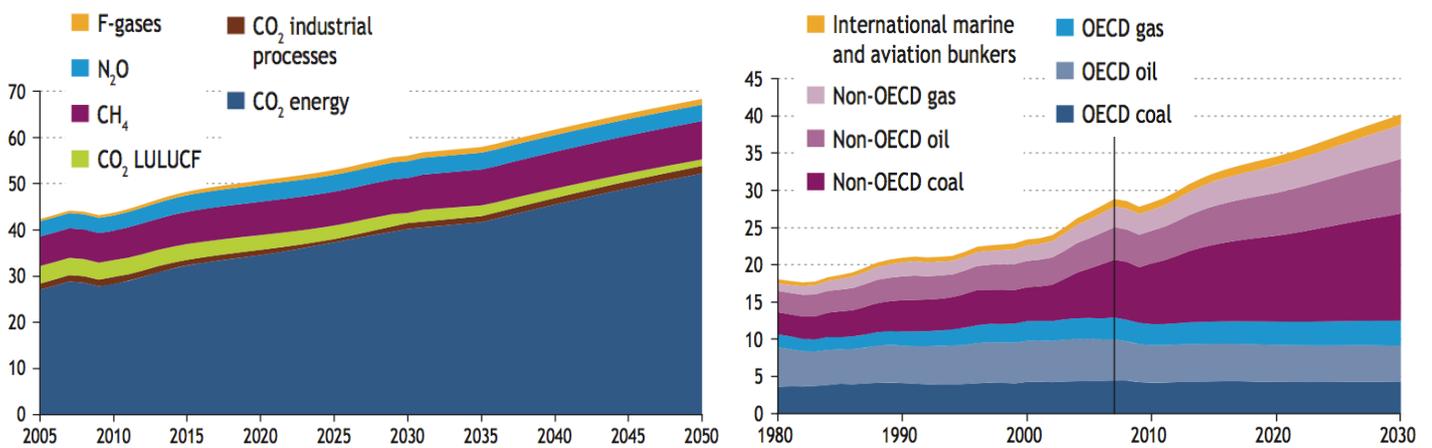


Source: EU. Eurostat..[12]



When it is looking at data on emissions (Figure 9), it can be seen that not only they are worryingly high at present day, with all the negative environmental consequences that implies, but also that the tendency for next years it is not been expected to change if no measures are taken. This is another clear sign that the energy model must be redefined. In the GHG emissions figure (left), it can be seen how CO<sub>2</sub> has a main participation, as a consequence of actual levels in fossil fuel consumption. Also in CO<sub>2</sub> emissions figure (right), it can be checked again that future development in emergent regions will lead to an increase in energy consumption, with the increase consequences in emissions if they use the current energy model.

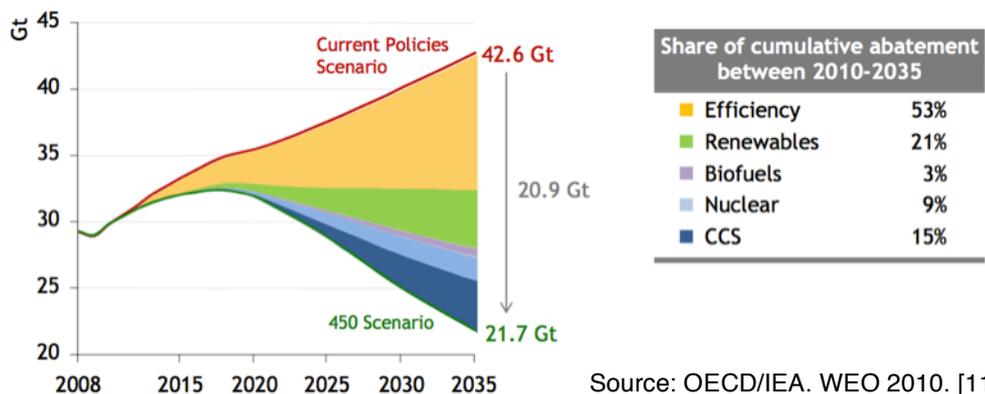
**Figure 9:** World anthropogenic greenhouse-gas emissions by source (left, in Gt CO<sub>2</sub>-equivalent) and energy-related CO<sub>2</sub> emissions by fuel and region (right, in Gt CO<sub>2</sub>) in the WEO Current Policies Scenario.



Source: OECD/IEA. World Energy Outlook (WEO) 2009. [8]

As the need for changes is obvious from the above data, it is interesting to consider another possible evolution in emissions if a different path is taken. For that, WEO 450 Scenario can be taken as an objective, and it can be compared with Current Policies Scenario as shown in Figure 10. To achieve this goal, it is clear that the energy efficiency has to be the main objective. Then, when we talk about hydrogen, the improvement of technological processes will be highly important, from its initial production to its end use. New energy sources and carbon capture and storage (CCS) will also play a main role. They will be especially considered in chapter 2 where I will analyse hydrogen production.

**Figure 10:** World energy-related CO<sub>2</sub> emission savings by technology in the WEO 450 Scenario, relative to the Current Policies Scenario.

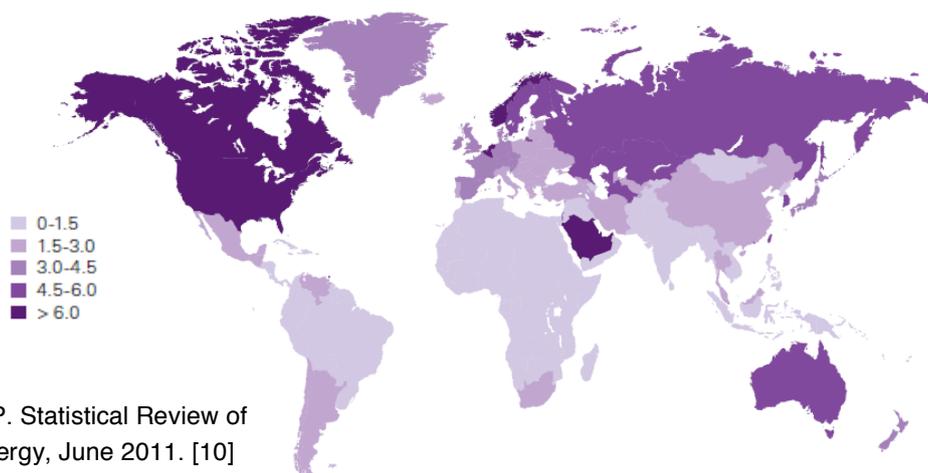


Source: OECD/IEA. WEO 2010. [11]



Finally, social inequities derived from the application of the model should be considered as a third factor, even when this work is focused on a technical point of view. Those are again mainly due to the strong dependence from fossil fuels, that often promotes unfair policies towards society and the environment. During the last century, it has been many times demonstrated that geopolitical disparity in distribution of resources and demand generates strong unbalances, with really negative consequences. This is reflected, as an example, in Figure 11, which shows energy consumption per capita in the world in 2010.

**Figure 11:** Primary energy consumption per capita (tep) in 2010.



Source: BP. Statistical Review of World Energy, June 2011. [10]

As long as fossil fuels dependence lasts, these social inequities will continue existing, and might even be enhanced. They represent a last social aspect that confirms the need for changing the current energy model, and the need for finding a new paradigm of energy use in which the hydrogen potential can play an important role.

### 1.2.3. HYDROGEN ECONOMY MODEL AS A POSSIBLE ALTERNATIVE.

So far, the need of changing current energy model has been reflected in different ways, and now, when considering good paths to follow, many alternatives can be suggested. One of them, that is gaining widespread support around the world, is the use of hydrogen.

In 2002 Jeremy Rifkin published "The Hydrogen Economy" [4]. It is a work of reference when considering changes in economic and energy sectors. It is a concept that has been used before, but Rifkin's publication was one of the greatest impacts, and has been highly relevant.

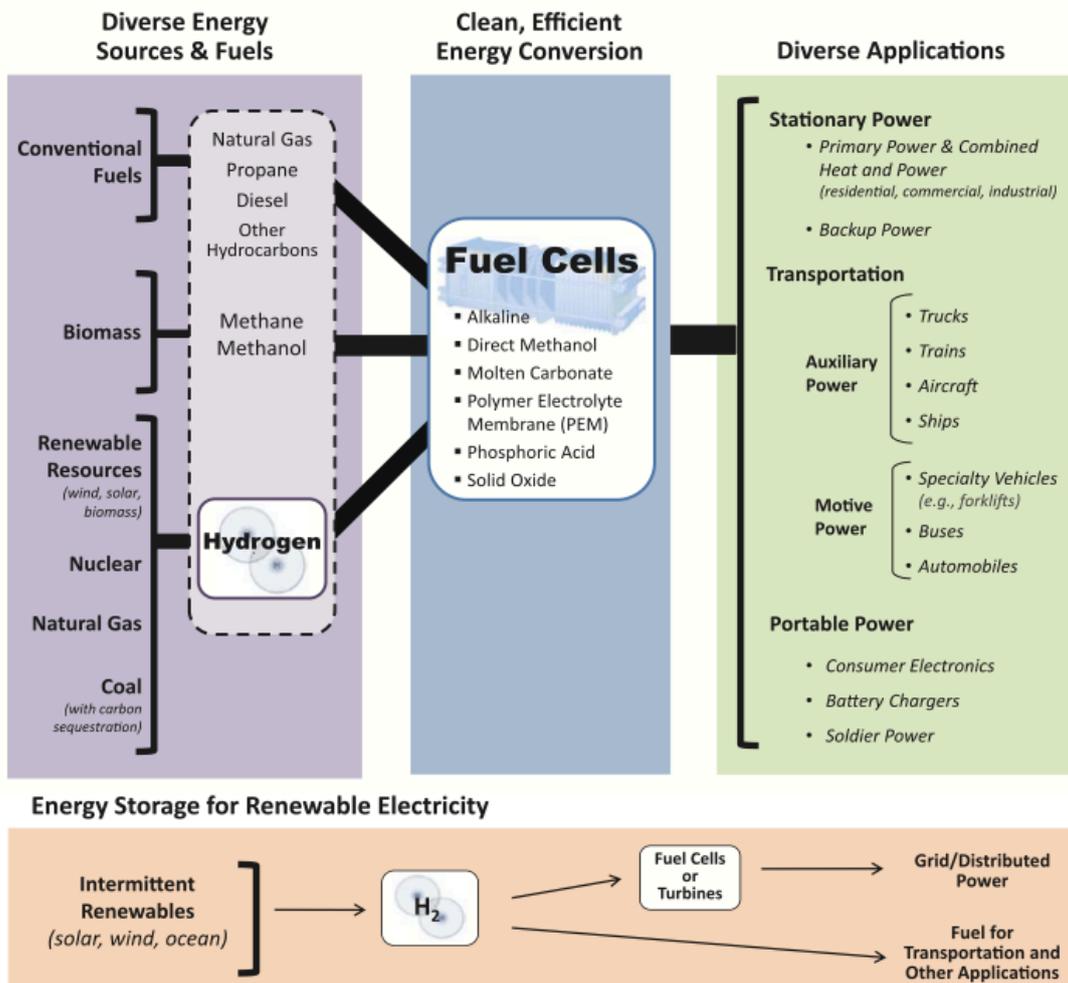
*Hydrogen Economy* proposes a social, economical and technological model in which renewably generated hydrogen has a main role, with great influence in almost all levels of our society, as it has energy itself. In his book, Rifkin presents many interesting ideas about this new paradigm. As an example, one of the most outstanding and groundbreaking refers to energy production and distribution. The author argues that we are accustomed to be unidirectional when using energy:



consumers always buy it from an energy company, which can establish trade rules leaving consumer without decision capacity. A proposed alternative is to create a hydrogen exchange network, which Rifkin calls Worldwide Hydrogen Energy Web (WHEW) and that is analogous to Internet in exchanging information. Each person may be both a consumer and producer, and could sell the surplus production to the grid.

Rifkin's work is a reflection of growing relevance of this energy model, but there are many more. Nowadays many institutions are studying and developing this concept, from governments to private companies. OECD, through the International Energy Agency (IEA), represents an example. In 1977 its member countries created the Hydrogen Implementing Agreement (HIA), an R&D co-operation programme on hydrogen technologies, and in April 2003 the Hydrogen Co-ordination Group (HCG) was established, an advisory policy committee on hydrogen and fuel cells [13]. The U.S. Department of Energy (DOE), through the Hydrogen and Fuel Cells Program, shows another one of the many examples. They are doing also an important work in R&D, Figure 12, from his Hydrogen and Fuel Cells Program Plan [14], is a good reference for understanding the use of hydrogen and fuel cells within the proposed model.

**Figure 12: U.S. DOE schematic about hydrogen and fuel cells use.**



Source: U.S. DOE. The Department of Energy Hydrogen and Fuel Cells Programme Plan. [14]



### 1.3. HYDROGEN CHARACTERISTICS.

Hydrogen is the simplest, the lightest and the most abundant chemical element of the universe. Hydrogen is the first of the periodic table and its atom, symbol H, is composed of one proton and one electron. As a single atom it is very reactive, so it is usually found forming diatomic molecules (H<sub>2</sub>), and when mixed with enough oxidant it becomes a combustible mixture. At normal conditions of temperature and pressure (NTP<sup>1</sup>), it is a colourless, odourless and tasteless gas. Some of its main physicochemical properties are shown in Table 2. [15] [16] [17] [18]

**Table 2: Hydrogen properties.**

Properties	Value	Units
Name	Hydrogen	-
Symbol	H	-
Atomic number	1	-
Atomic weight	1,00797	-
Electro configuration	1s <sup>1</sup>	-
Melting point	-259,2	°C
Boiling point	-252,7	°C
Density (NTP <sup>1</sup> )	0,08375	kg/m <sup>3</sup>
Specific volume (NTP <sup>1</sup> )	11,94	m <sup>3</sup> /kg
Viscosity (NTP <sup>1</sup> )	8,813·10 <sup>-5</sup>	g/cm-sec
Diffusion coefficient in air (NTP <sup>1</sup> )	0,610	cm <sup>2</sup> /s
Thermal conductivity (NTP <sup>1</sup> )	0,1825	W/m-K
Enthalpy (NTP <sup>1</sup> )	3858,1	kJ/kg
Entropy NTP (NTP <sup>1</sup> )	53,14	J/g-K
Specific heat at constant pressure, Cp (NTP <sup>1</sup> )	14,29	J/g-K
Specific heat at constant volume, Cv (NTP <sup>1</sup> )	10,16	J/g-K
Auto ignition temperature	585	°C
Flammable range in air	4,0 – 75,0	vol%
Lower Heating Value <sup>2</sup> (LHV)	120,21	MJ/kg
Higher Heating Value <sup>3</sup> (HHV)	142,18	MJ/kg

Source: Own elaboration based on: McGraw-Hill [15], Rajeshwar, K.; McConnell, R.; Licht, S.; Rajeshwar, K. [16] U.S. DOE. Hydrogen Analysis Resource Centre. [17] [18]

<sup>1</sup>NTP (normal temperature and pressure) = 20 °C (68 °F) and 1 atmosphere [17]

<sup>2</sup>LHV: “The low heating value (also known as net calorific value) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which assumes the latent heat of vaporization of water in the reaction products is not recovered.” [18]

<sup>3</sup>HHV: “The high heating value (also known as gross calorific value or gross energy) of a fuel is defined as the amount of heat released by a specified quantity (initially at 25°C) once it is combusted and the products have returned to a temperature of 25°C, which takes into account the latent heat of vaporization of water in the combustion products.” [18]



As it is going to be considered as an energy carrier, it is also interesting to compare its characteristics with other fuels, as shown in Table 3.

**Table 3:** Comparative properties of hydrogen and fuels.

Properties	Units	Hydrogen <sup>1</sup>	Methane <sup>1</sup>	Propane <sup>1</sup>	Methanol <sup>1</sup>	Ethanol <sup>1</sup>	Gasoline <sup>2</sup>
<b>Chemical Formula</b>	-	H <sub>2</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>x</sub> H <sub>y</sub> (x = 4 – 12)
<b>Molecular Weight</b>	-	2,02	16,04	44,1	32,04	46,07	100 - 105
<b>Density (NTP<sup>3</sup>)</b>	kg/Nm <sup>3</sup>	0,0838	0,668	1,87	791	789	751
<b>Viscosity (NTP<sup>3</sup>)</b>	g/cm-sec	8.81·10 <sup>-5</sup>	1,10·10 <sup>-4</sup>	8,012·10 <sup>-5</sup>	9,18·10 <sup>-3</sup>	0,0119	(3,7 – 4,4)·10 <sup>-3</sup>
<b>Normal Boiling Point</b>	°C	-253	-162	-42,1	64,5	78,5	27 - 225
<b>Vapour Specific Gravity (or Relative Density) (NTP<sup>3</sup>)</b>	air=1	0,0696	0,555	1,55	Not applicable	Not applicable	3,66
<b>Flash Point</b>	°C	< -253	-188	-104	11	13	-43
<b>Flammability Range in Air</b>	vol%	4,0 – 75,0	5,0 – 15,0	2,1 – 10,1	6,7 – 36,0	4,3 – 19	1,4 – 7,6
<b>Auto Ignition Temperature in Air</b>	°C	585	540	490	385	423	230 - 480

Source: Adapted from: U.S. DOE. Hydrogen Analysis Resource Centre. [19]

<sup>1</sup> Properties of the pure substance

<sup>2</sup> Properties of a range of commercial grades

<sup>3</sup>**Normal conditions** are defined by IUPAC as “a qualitative term, dependent on the preference of the investigator; it often implies ambient pressure and "room temperature"”. [20] When working with hydrogen, usual values for **normal conditions of temperature and pressure (NTP)** are 293,15 K (20 °C) and 1 atmosphere.

It should not be confused with **standard conditions**: “An exact value, or a concept, that has been established by authority or agreement”. IUPAC **standard conditions of temperature and pressure** for gases (**STP**) are 273.15 K (0 °C) and pressure of 10<sup>5</sup> Pascal. IUPAC also recommends that the former use of the pressure of 1atm as standard pressure (equivalent to 1.01325 x 10<sup>5</sup> Pa) should be discontinued. [20]

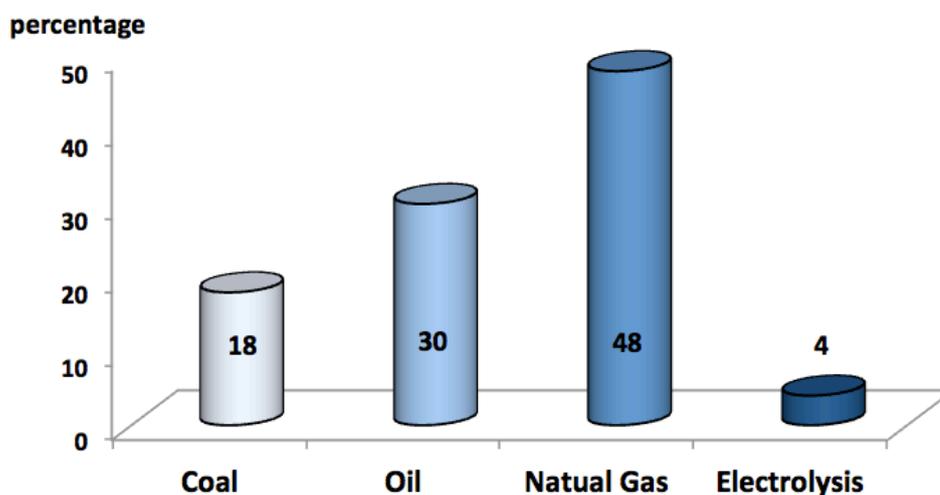


## 2. HYDROGEN PRODUCTION TECHNOLOGIES

After a general overview on hydrogen as an energy carrier, it is time to focus in the hydrogen production technologies. The first part of the chapter will consist of a description of the main production processes, differentiating between those using fossil fuels as a feedstock and those based on renewable sources. The second part will be focused on solar thermal hydrogen production from water.

At present, hydrogen is mainly produced from fossil fuels (96%), and just a small part comes from water electrolysis. In 2006 the production was some 65 million tones, and the forecast for 2011 was around 81 million tones. The main sources of hydrogen that has been used until now are shown in Figure 13: 48% was produced from natural gas, 30% from oil, 18% from coal and just 4% from water electrolysis. [21][22]

**Figure 13:** Present world hydrogen production percentages.



Source: own elaboration based on data from: Suresh B.; Yoneyama M.; Schlag S. [21]  
International Energy Agency (IEA). [22]



This important participation of fossil fuels comes from the higher level of development of its production processes. It is a technology with many years of experience in the chemical industry. Even though, this trend is predicted to change in next years, when renewable sources will take a key role in the middle and long term. As it has been seen before, a change in the energy model is needed, and also developing other hydrogen production processes will be critical to achieve sustainability. In this chapter will be discussed the most important ones, and a summary is given in Table 4.

**Table 4:** *Hydrogen production technologies.*

Production Technology				Hydrogen source (feedstock)	Energy source	
FOSSIL FUELS	2.1.1	Steam reforming (SR)		CO <sub>2</sub> CAPTURE	Natural Gas	NG combustion Solar thermal
	2.1.2	Partial oxidation (POX) and Autothermal reforming (ATR)			Natural Gas / Oil	NG / Oil combustion
	2.1.3	Gasification			Coal / "Biomass"	Coal / "Biomass" combustion Solar thermal
	2.1.4	Thermal decomposition (cracking)		C CAPT.	Natural Gas / Oil	NG combustion Solar thermal
RENEWABLE SOURCES	2.2.1	Water electrolysis	Alkaline electrolysis		Water	Electricity from Renewables / Nuclear / Fossil fuels
			PEM electrolysis			
			High temperature electrolysis			
	2.2.2	Photo-electrolysis (photolysis)		Solar		
	2.3	Thermal water splitting	Thermal dissociation (thermolysis)			Solar thermal
			Thermochemical cycles			Solar thermal Nuclear
2.2.3	Photo-biological production (Biophotolysis)		Water + algae / bacteria	Solar		

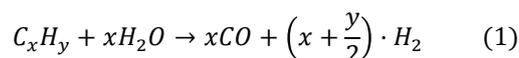
Source: own elaboration based on: International Energy Agency (IEA) [13], Steinfeld, A. [23] [24], Steinfeld, A and Palumbo R. [25], Bellona [26], Abengoa [27]



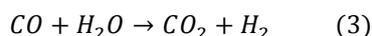
## 2.1. HYDROGEN PRODUCTION FROM FOSSIL FUELS.

### 2.1.1. STEAM REFORMING (SR).

Steam reforming consists of decarbonisation of light hydrocarbons. This is an endothermic catalytic reaction, where an organic molecule is mixed with water vapour and a catalyser to obtain hydrogen, assisted by thermal energy. The first step separates the organic molecule into hydrogen and carbon monoxide (CO), at temperatures between 750-1000 °C and a pressure around 25 bar. The general reaction is:

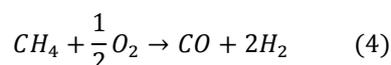


The steam reforming of natural gas is actually the cheapest and the most common industrial production process. It has a reaction (2) that follows the structure of the general one (1). The resulted gas has approximately 12% of CO, which can be converted into CO<sub>2</sub> and H<sub>2</sub> with a catalytic water-gas shift reaction (3):



### 2.1.2. PARTIAL OXIDATION (POX) AND AUTOTHERMAL REFORMING (ATR).

Partial Oxidation (POX) is the combustion of hydrocarbons with a reduced amount of oxygen. The reaction in this case is exothermic, so there is no need for external heating. For methane it is expressed as:



Autothermal Reforming (ATR) is a combination between partial oxidation (POX) and steam reforming (SR) in which hydrocarbons are mixed with both oxygen and steam. Part of the reaction is endothermic, so the proportion between oxygen and steam is controlled to avoid the need of any external energy. That makes the reaction more complex than (2) and (4), but it also produces CO and H<sub>2</sub>.

Those processes are not only used with natural gas, but also with heavy hydrocarbons such as oil. In this case, its low fluidity and often high content of sulphur makes steam reforming inappropriate.

Temperature and pressure of the different reactions depend on the kind of process and the fuel used. As an example, ATR with natural gas has a range of temperatures of 950-1100 °C, and a pressure that can reach 100 bar. In all cases, the CO produced in the reaction can be further converted into H<sub>2</sub> with the water-gas shift reaction (3).



In the case of natural gas, a comparison between this processes and steam methane reforming (ATM) is shown in Table 5.

**Table 5:** Comparison between SMR and ATR/POX in H<sub>2</sub> production from natural gas.

Technology	SMR	ATR or POX
Benefits	High efficiency Emissions	Smaller size Costs for small units
Challenges	Costs for large units Complex system Sensitive to natural gas qualities	Simple system Lower efficiency H <sub>2</sub> purification Emissions/flaring

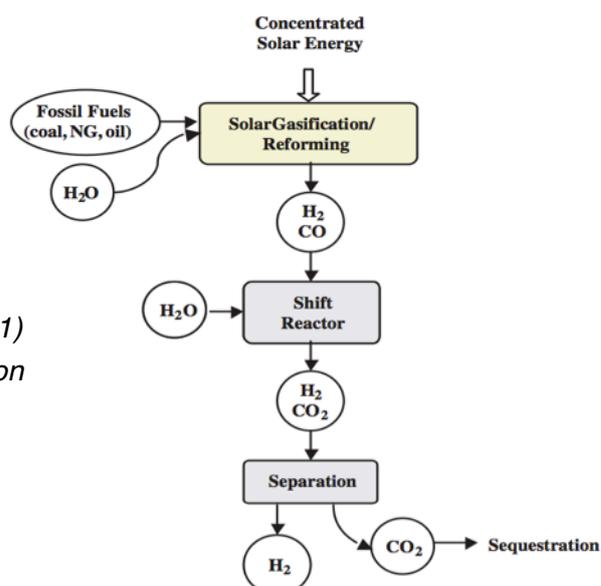
Source: International Energy Agency (IEA). [13]

### 2.1.3 COAL GASIFICATION.

Gasification consists on decarbonisation of heavy hydrocarbons, with the same general reaction as for steam reforming (1). It can be done with different processes and fuels, but the most common is the coal gasification, represented with the following reaction:



It is an endothermic reaction, so external heat is needed as with steam reforming. It produces CO, and once again it can be converted into CO<sub>2</sub> and H<sub>2</sub> as described in reaction (3). A schematic of both coal gasification and steam reforming processes, where different products routes are shown, is represented in Figure 14:



**Figure 14:** Schematic of steam reforming (2.1.1) and coal gasification (2.1.2) hydrogen production processes using solar thermal energy.

Source: Steinfeld, A. [24]

Coal is the fossil fuel with the lowest ratio hydrogen-carbon, so it produces more CO<sub>2</sub> per mole of H<sub>2</sub>. Despite this, as well as in the other processes seen until now, H<sub>2</sub> with low emissions can be produced



with capture and storage of CO<sub>2</sub>, as explained below. This process can also be done with biomass as a renewable source, following the same general equation (5). However, no commercial plants exist today, as there are still several developments needed to achieve competitiveness.

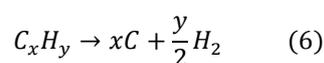
### CO<sub>2</sub> capture and storage:

All the processes explained up now uses fossil fuels to obtain hydrogen. In a huge simplification they consist of separating C from H<sub>2</sub> by heating them up, a decarbonisation process that also generates CO and CO<sub>2</sub>. As seen before, CO can be further transformed into H<sub>2</sub> and CO<sub>2</sub> using equation (3), but finally something has to be done with CO<sub>2</sub> to avoid high emissions levels.

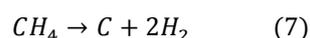
To achieve a sustainable hydrogen production, CO<sub>2</sub> has to be captured and stored. The capture is produced during the hydrogen production process, using different methods. The conventional technology is based on amine absorption, but there are others being developed, such as selective membranes or sorbents. Once captured, CO<sub>2</sub> must be deposited permanently. It can be done in geological formations like empty oil and gas fields or in aquifers.

#### 2.1.4. THERMAL DECOMPOSITION (CRACKING).

Thermal dissociation, or cracking, means a thermal decomposition of hydrocarbons. It is possible to separate hydrogen and carbon by heating without oxygen, but very high temperatures are needed. The general reaction for thermal dissociation is expressed as:

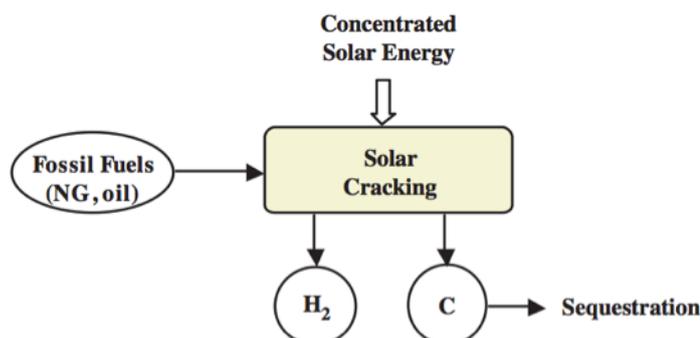


And the specific one for methane is:



Like in all this fossil fuel based processes, other compounds may be formed depending on the composition of the feedstock and in the reaction kinetics. Even that, thermal decomposition has two clear resulting products. One is a gas rich in hydrogen, which has to be purified before being used. The other is a condensed phase rich in carbon, which can be captured to avoid its release into the environment. A schematic of the processes is represented in Figure 15:

**Figure 15:** Schematic of thermal decomposition or cracking (2.1.4) using solar thermal energy.



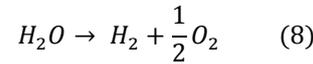
Source: Steinfeld, A. [24]



## 2.2. HYDROGEN PRODUCTION USING RENEWABLE SOURCES.

### 2.2.1. WATER ELECTROLYSIS.

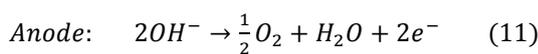
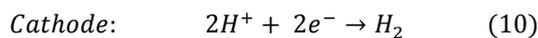
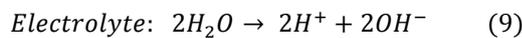
Electrolysis is a chemical reaction in which water is separated into oxygen and hydrogen when an electric current passes through it, according to equation (8).



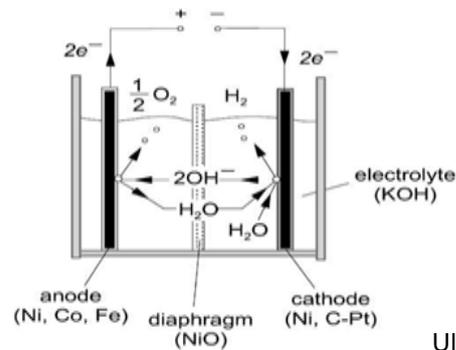
The device used in this process is called electrolyser, and it is usually classified according to the electrolyte it uses. As showed in Table 4, two of them stand out over the rest: alkaline electrolysis and PEM electrolysis. High temperature electrolysis is also being seriously considered, since it can be done using waste heat from other processes to achieve better global efficiencies.

#### Alkaline electrolysis:

Alkaline electrolyzers have a liquid alkaline electrolyte, such us KOH (potassium hydroxide), that flows through the cell. Using electricity, hydrogen is produced in the cathode and oxygen in the anode, as shown in Figure 16. Partial reactions to achieve global reaction (8) are also shown below:



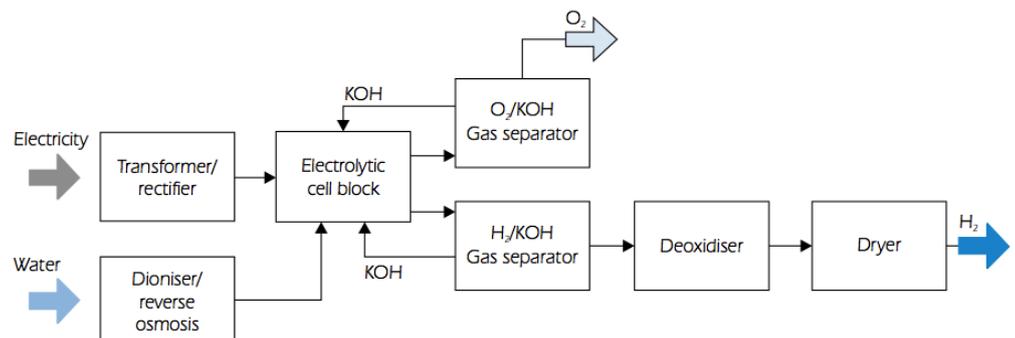
**Figure 16:** Schematic diagram of an alkaline electrolyser cell.



Source:  
Ulleberg, O. [28]

These electrolyzers have been used in industry for a long time, being a proved technology available in a commercial scale with efficiencies around 70-80% [26]. They are suited for stationary large-scale application, and can work at pressures up to 25 bar. The main components of an alkaline electrolyser are shown in Figure 17.

**Figure 17:** Process diagram of alkaline electrolysis.

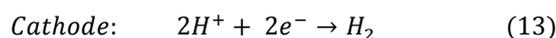
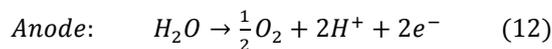


Source: IEA. [13]



### PEM electrolysis:

Polymer electrolyte membrane (PEM) electrolyzers use an acidic polymer membrane as electrolyte. Since it does not have a liquid electrolyte, the design is much simpler. The reactions that take place to produce  $H_2$  (in the cathode) and  $O_2$  (in the anode) are shown below.

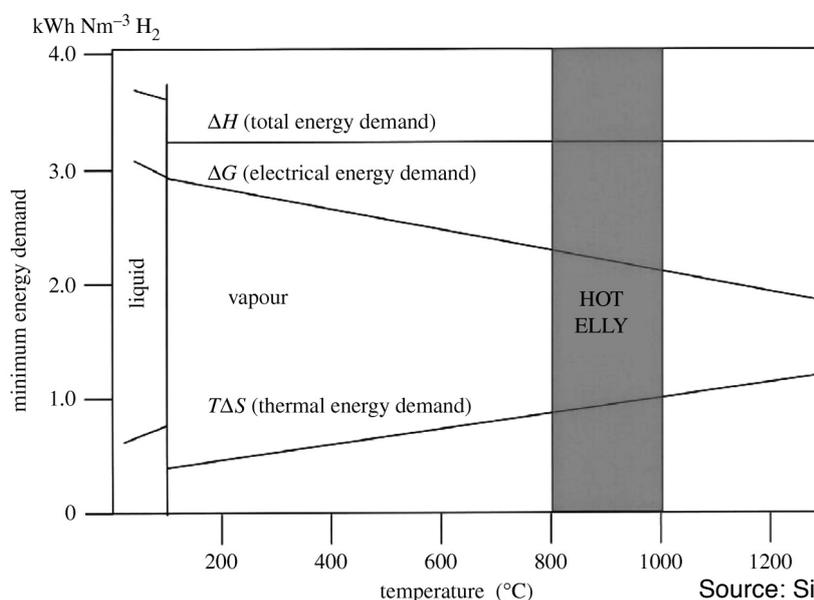


Even when this is a relatively new technology, it is taking advantage of the strong development of PEM fuel cells, which goes in parallel with the development of electrolyzers. They present several advantages over alkaline electrolyzers, such as a higher theoretical efficiency (predicted to achieve 94%), a good performance in small applications, higher operation pressure (up to several hundred bar) and higher densities that enables a compact design. It also has a great performance with fluctuating current, which is typical when using renewable sources to generate electricity. Despite that, their cost is relatively high and some technological improvements still have to be done.

### High temperature electrolysis (HTE):

High temperature electrolyzers also take advantage of development of fuel cells, specifically on solid oxide fuel cells (SOFC). Solid oxide electrolyser cells (SOEC) operate in a temperature range of 800-1000 °C for HTE, in a process nicknamed Hot Elly. As it can be seen in Figure 18, at these temperatures total energy demand ( $\Delta H$ ) grows slightly, but the demand for electricity is reduced by 25% over low-temperature electrolysis. This makes HTE ideal for reducing electrical demand when combining it with the waste heat of other processes, such as the heat in new generation nuclear reactors.

**Figure 18:** *Thermodynamics of hydrogen electrolysis.*



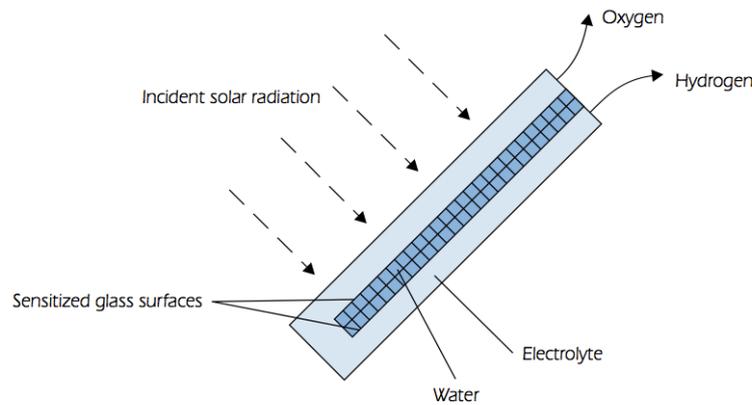
Source: Sigfusson T. I. [29]



### 2.2.2. PHOTO-ELECTROLYSIS (PHOTOLYSIS).

Solar energy can be used for electrolysis through photovoltaic systems that produce electricity. Instead of that, direct photo-electrolysis goes beyond, putting both processes together in one single device called photo-electrochemical cells (PEC). In PEC, sunlight is used to split water, as shown in Figure 19. Actually in a state of research and development, this process presents great expectations for the future. Several countries are running different R&D programs, a significant part of them coordinated by IEA-HIA.

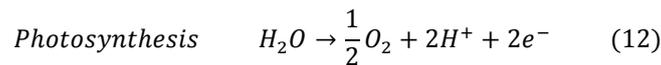
**Figure 19:** Principle of photo-electrolytic hydrogen production.



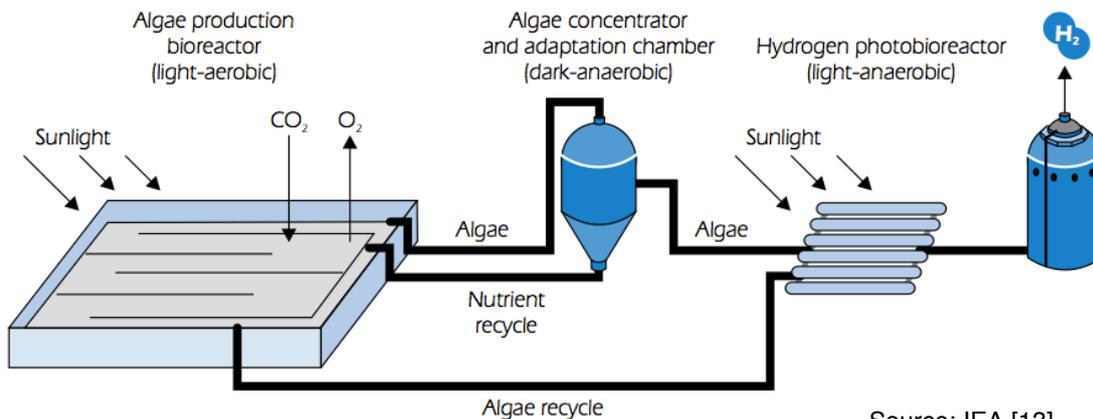
Source: IEA [13]

### 2.2.3. PHOTO-BIOLOGICAL PRODUCTION (BIOPHOTOLYSIS).

Biophotolysis is a two-step hydrogen production process. First step (12), photosynthesis, is followed by hydrogen production (13) catalysed by hydrogenases in green algae or cyanobacteria. It also needs, as photolysis, an important labour in research and development, but it could be a great long-term renewable solution to produce hydrogen.



**Figure 20:** Principle of photo-biological hydrogen production.



Source: IEA [13]



## 2.3. SOLAR THERMAL WATER SPLITTING.

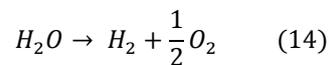
This work focuses on production through a process with a renewable energy source and zero, or nearly-zero, greenhouse gas emissions. Fossil fuels have been discarded from the beginning, even when, as we have seen, they may be a good solution in the middle term, in a transition to a renewable hydrogen energy. Instead of that, the chosen option has been:

- **Water** as a carbon-free feedstock
- Solar as a renewable energy source, focusing on **solar thermal** due to its great potential in hydrogen production

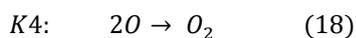
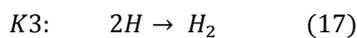
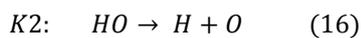
The chosen process to study it in more detail is thermal water splitting, a chemical reaction in which water is separated into oxygen and hydrogen when heated. This could be done in a single step, in a process called Thermal Dissociation or **Thermolysis**, or in two or more steps, in a process called **Thermochemical cycles**.

### 2.3.1. THERMAL DISSOCIATION (THERMOLYSIS).

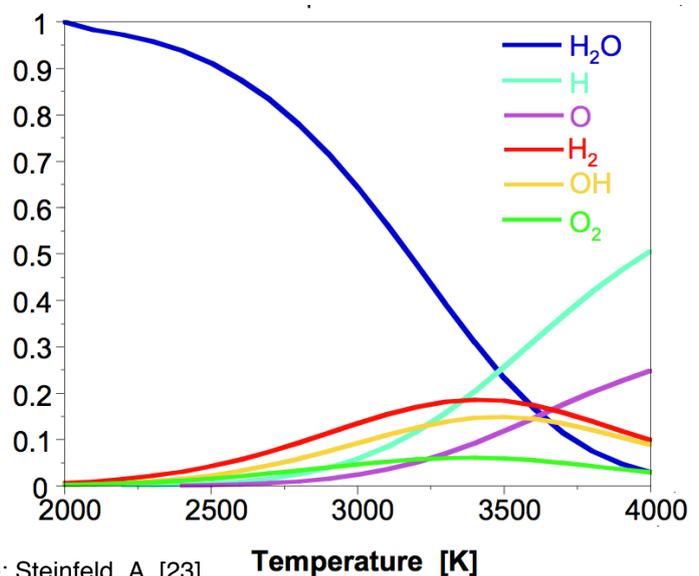
Water thermolysis is the dissociation of water vapour in a single step reaction 14.



This is a conceptually simple reaction, but it needs very high temperatures above 2500-3000 K to obtain an acceptable dissociation degree, as can be seen in Figure 21. As an example, at 3000 K and 1 bar, 64% of water is dissociated [24]. It is also important to consider that not only H<sub>2</sub> and O<sub>2</sub> are produced, but also H, O and HO following reactions (15) to (18) [16]:



**Figure 21:** Equilibrium mole fraction (1 bar).



Source: Steinfeld, A. [23]



The pressure equilibrium constants for this reaction are shown in Table 6.

**Table 6:** *The pressure equilibrium constants of the water dissociation reaction.*

constants	Temperature [K]		
	2500	3000	3500
K1	$1,34 \cdot 10^{-4}$	$8,56 \cdot 10^{-3}$	$1,68 \cdot 10^{-1}$
K2	$4,22 \cdot 10^{-4}$	$1,57 \cdot 10^{-2}$	$2,10 \cdot 10^{-1}$
K3	$1,52 \cdot 10^3$	$3,79 \cdot 10^1$	$2,67 \cdot 10^0$
K4	$4,72 \cdot 10^3$	$7,68 \cdot 10^1$	$4,01 \cdot 10^0$

Source: Rajeshwar, K.; McConnell, R.; Licht, S.; Rajeshwar, K. [16]

Obtaining the high temperatures required for the process supposes a problem by itself, and also pose other obstacles:

- Gaseous products can recombine and generate an explosive mixture. To avoid that, effective methods for separating hydrogen from the other products have to be developed.
- There are severe material problems to construct a reactor that supports those high temperatures. The lack of suitable materials can also lead to significant re-radiation, lowering the efficiency.

While those obstacles are solved, research has been pushed on the direction of thermochemical cycles.

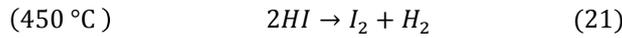
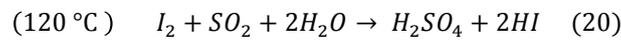
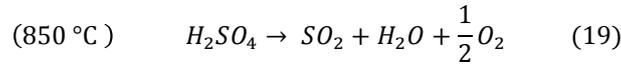
### 2.3.2. THERMOCHEMICAL CYCLES.

Water-splitting thermochemical cycles also follow equation XX in a global balance, but in an indirect way through various reaction sequences in a closed cycle that, ideally, only have H<sub>2</sub> and O<sub>2</sub> as net products. This configuration solves the problems raised by direct water dissociation, as they require lower temperatures and avoid high-temperature gas separation through producing H<sub>2</sub> and O<sub>2</sub> in different steps. There are lots of possible cycles that can be classified into **multi-step cycles** (more than two) and **two-step cycles** (using metal oxide redox reactions).

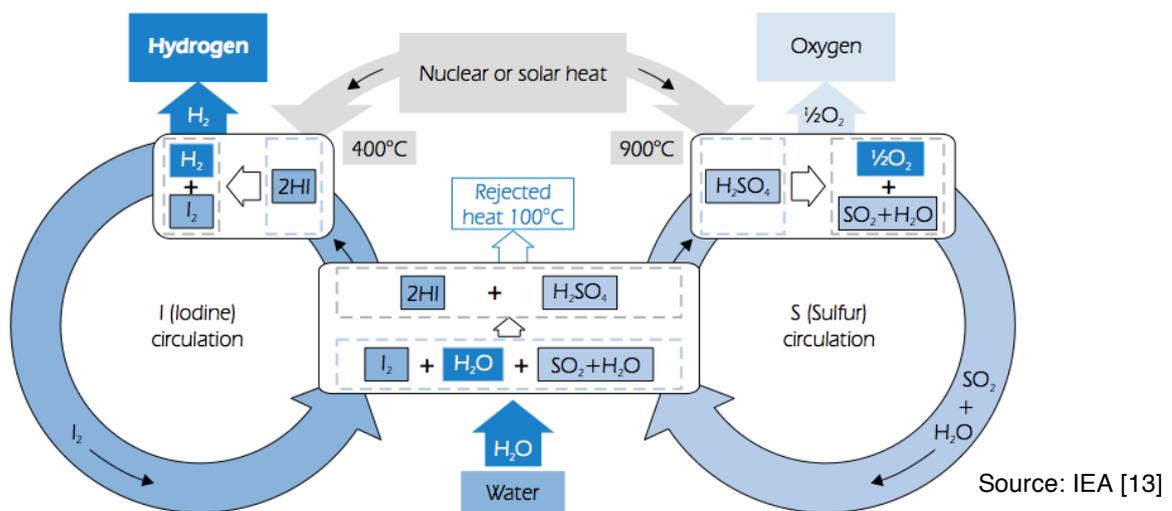
The first ones, **multi-step thermochemical cycles**, have the advantage of requiring lower temperatures than the second ones. Most of them are characterized to work with temperatures below 1200 K, so they are feasible to be implemented with both nuclear and solar heat sources. The disadvantage of these processes is the low efficiency achieved, as there are losses in each step during heat transfer and product separation.



An example is given by iodine/sulphur cycle, characterized by equations (19) to (21) and shown in Figure 22.



**Figure 22:** Schematic of iodine/sulphur thermochemical process.



This concrete cycle is one of the most favourable options for multi-step thermochemical hydrogen generation in the future. It is currently being investigated and evaluated, and seems to be a good candidate for new IV generation nuclear plants, as it is included in the Gen IV Program in collaboration between CEA (French Alternative Energies and Atomic Energy Commission) and U.S. Department of Energy. [30]

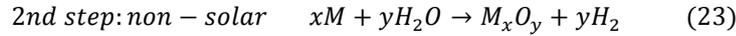
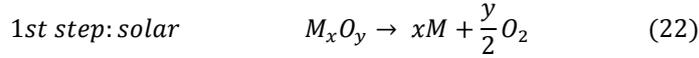
### Two-step thermochemical cycles:

To solve the low-efficiency issue, an interesting alternative is to use a more efficiently **two-step thermochemical cycle**: by reducing the number of steps, higher efficiency rates are obtained. This also implies the need of higher temperatures, between direct water splitting and multi-step cycles, but still feasible for current solar thermal plants and material technologies. However, nuclear heat source should be discarded in this case, as temperatures above 1000 °C are not recommended for security reasons.

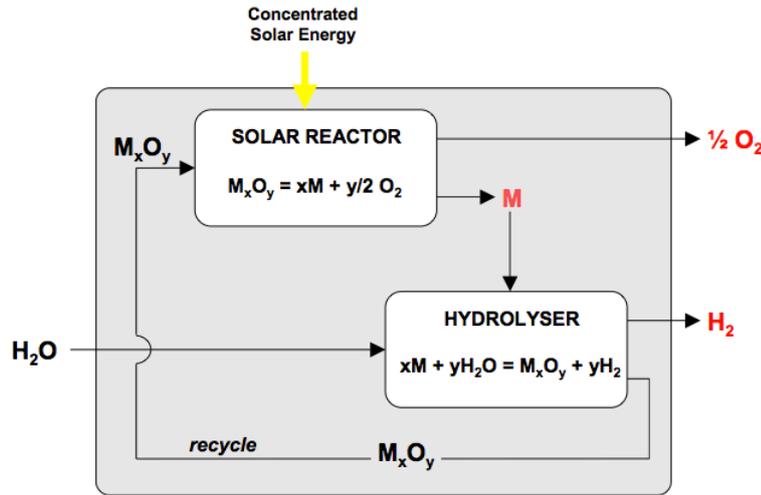
The cycles are based on metal oxide redox systems, following the general equations (22) and (23). The first step, endothermic, consists of separating metal oxide using solar thermal energy. The second



step, exothermic, consists of the hydrolysis of the metal obtained before to form again the metal oxide and produce hydrogen [25]. A schematic of the process is shown in Figure 23.



**Figure 23:** Schematic of two-step thermochemical cycles.

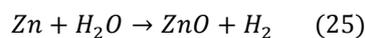
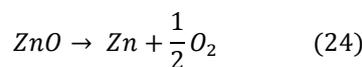


There are several redox pair candidates, such as ZnO/Zn, Fe<sub>3</sub>O<sub>4</sub>/FeO, TiO<sub>2</sub>/TiO<sub>x</sub>, Mn<sub>3</sub>O<sub>4</sub>/MnO or Co<sub>3</sub>O<sub>4</sub>/CoO. The problem with most of them is that they require again very high temperatures above actual material capabilities, or that their efficiency is too low. Finding the appropriate two-step cycle would be critical to the success of large-scale commercial hydrogen production.

### 2.3.3. ZnO/Zn TWO-STEP THERMOCHEMICAL CYCLE.

We have seen that two-step thermochemical cycles are the most appropriate to combine with solar thermal energy. To be more specific in this study, it is interesting to select a concrete one.

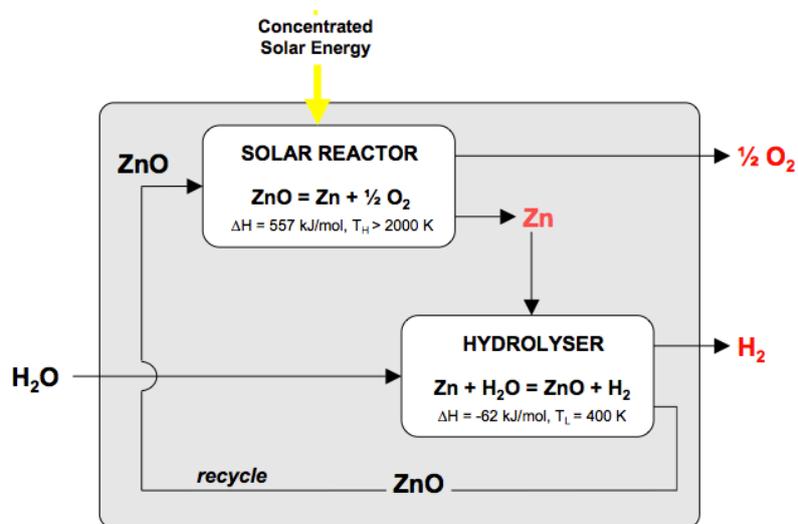
Among this cycles, metal oxide redox pair zinc oxide/zinc cycle is presumably the most suitable for solar thermal implementations. It has been studied by several authors (Palumbo 1998, Steinfeld 2002 and others [24] [25] [43]) and has great expectations for a middle term future. Although the required temperature is high (> 2000 K), it is still acceptable with actual technology, and has a good global efficiency. The particular reactions for zinc, (24) and (25), are shown below.





A schematic of the cycle is shown in Figure 24.

**Figure 24:** Schematic of ZnO/Zn thermochemical cycle.



Source: Steinfeld, A [23]



### **3. LARGE-SCALE IMPLEMENTATION STUDY USING SOLAR THERMAL ENERGY.**

---

After getting a view of the main hydrogen production processes, it is time to study the viability of a large-scale commercial implementation using renewable energy sources, specifically solar thermal energy.

In chapter 2 we have seen the main characteristics of solar thermal hydrogen production processes. On this basis it is decided that thermolysis requires to high temperatures to be commercially implemented nowadays, so instead of it, thermochemical cycles will be used. Among them, **ZnO/Zn two-step thermochemical cycle will be the selected process**. We have seen that two-step cycles have good features for a large-scale implementation with solar thermal energy, and ZnO/Zn is one of the best studied and known nowadays.

To analyse the viability, this study is divided into three parts:

- Concentrated solar thermal technology** required for the process.
- Energetic study**, comparing our process with electrolysis, the main “renewable” hydrogen production process nowadays.
- Other determining factors in viability**, like finding a suitable location (limiting the study to Europe) or the economical perspectives for this technology in next years.



### 3.1 CONCENTRATED SOLAR THERMAL TECHNOLOGY.

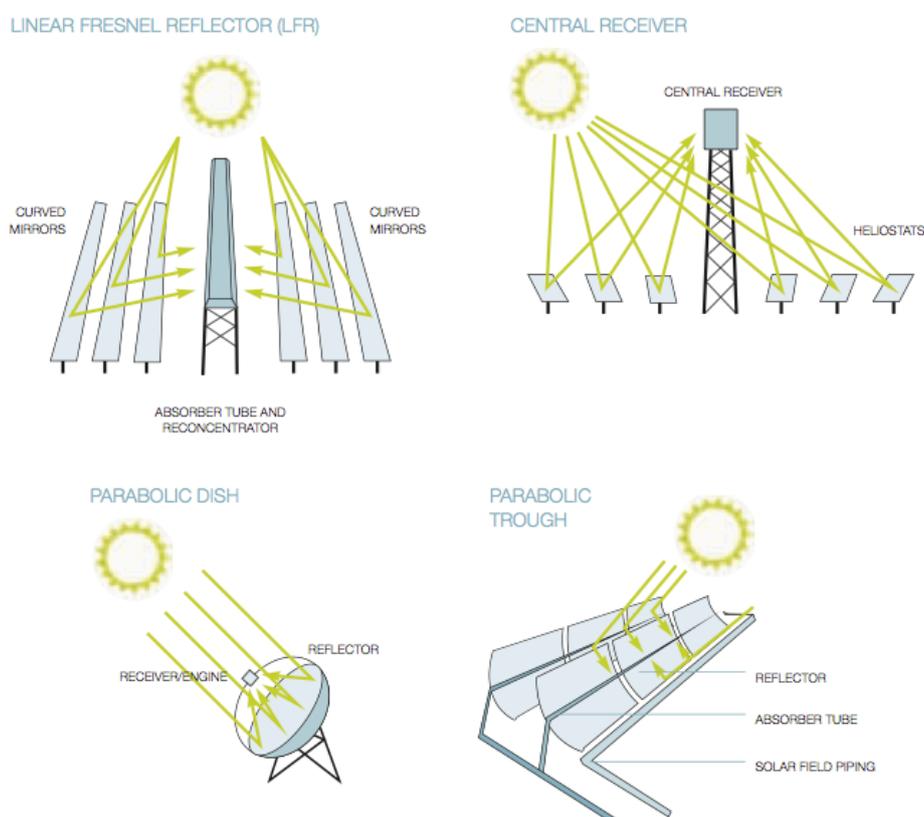
The first thing to be analysed is the current situation of concentrated solar thermal technologies, which are necessary for the implementation of the thermochemical cycle. In this paragraph main solar thermal plants will be briefly presented, pointing out the elements required for the ZnO/Zn cycle in the selected one.

#### 3.1.2. CONCENTRATING SOLAR POWER (CSP) PLANTS.

With the ZnO/Zn cycle in mind, it is important to decide the solar technology to be used. For large-scale solar thermal implementations, this technology is known as Concentrating Solar Power (CSP). Even when there are a lot of variants, all CSP systems are based on the same principle: the use hundreds of mirrors to concentrate direct sunlight and transform it into heat or electricity. The main requirement for this purpose is a good solar irradiation. To consider that a place is suitable for this kind of plants, it should be around 2000 kWh/m<sup>2</sup> annually [31] [32]. This is a reference value that should be taken in consideration when deciding the geographic location of this study.

CSP plants can be classified into 4 types, according to Figure 25: Linear Fresnel Reflector (LFR), Central receiver, parabolic dish and parabolic trough. Among them, the only one that can reach temperatures of 2000 K is Central Receiver (or solar tower) CSP, so that will be the one used in our thermochemical cycle.

Figure 25: CSP technologies.



Source: Greenpeace International, SolarPACES and ESTELA [31]



Solar Tower CSP plants use a field of heliostats, large mirrors with sun tracking motion, to concentrate sunlight in a central receiver located at the top of a tower. There, a working fluid is heated, reaching temperatures typically between 800 °C to 1000 °C in electricity production [31]. But this is not the limit, as it can reach temperatures well over 1000 °C, even over 2000 °C [32][33], depending on the concentrating ratio of the heliostat field.

This technology has been already proved, and nowadays is starting his commercial phase. As an example, first commercial solar tower power plants, PS10 with 11 MWe and PS20 with 20 MWe, have been operative since 2007 and 2009 respectively (Figures 26 and 27).

**Figure 26:** *PS10 (right) and PS20 (left), first commercial solar tower CSP plants located in Sevilla (Spain).*



Source: Abengoa solar [34]

**Figure 27:** *Central tower of PS10 (right) and PS20 (left) CSP plants.*



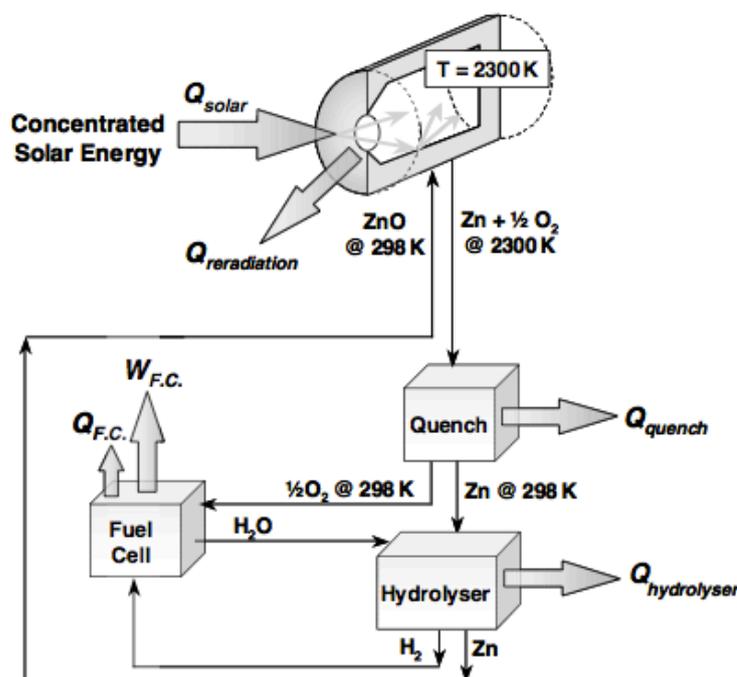
Source: Abengoa solar [34]



### 3.1.2. ELEMENTS FOR ZnO/Zn CYCLE IN A CSP PLANT.

As commented before, ZnO/Zn thermochemical cycle using thermal solar energy has already been studied in the last decade, including the use of solar tower CSP technology. One example is the research of A. Steinfeld [33], which would be a reference work for this chapter. Based on this, the elements required to implement the cycle using this particular CSP plant are shown in Figure 28, where the ZnO/Zn cycle is represented.

**Figure 28:** Model flow diagram of ZnO/Zn thermochemical cycle in a central tower CSP plant.



Source: Steinfeld, A [33]

On one side we can find the elements of a CSP plant that are used to generate electricity: the heliostat field, the central tower, a tower reflector and the solar reactor.

On the other side, some new elements are needed to adapt the plant for hydrogen production: a Quench, where oxygen is separated after the first step of the cycle, and an electrolyser, where hydrogen is obtained by adding water to the zinc. In the figure there is also a fuel cell represented, that can be used to transform hydrogen into electricity.

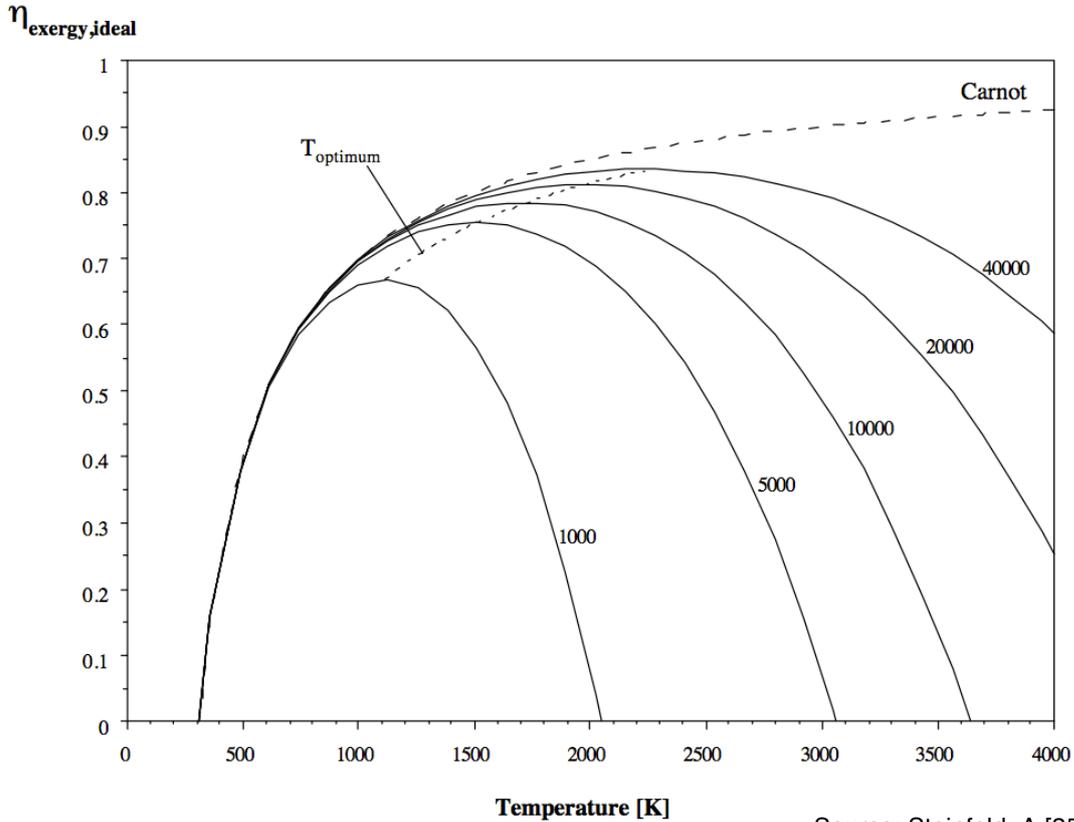
It is also important to note that solar tower plants for electricity generation usually have solar flux concentration ratios<sup>1</sup> between 1000 and 1500 suns, which are not enough to achieve the high

<sup>1</sup> Solar flux concentration ratio can be defined as “the ratio of the solar flux intensity achieved after concentration to the incident beam normal insolation. It is a dimensionless number, sometimes reported in units of “suns” [32]



temperatures required for ZnO/Zn thermochemical cycle. As it can be seen in Figure 29, the concentration ratio defines the optimum temperature and the efficiency of the process.

**Figure 29:** For a blackbody cavity-receiver, ideal efficiency is a function of the operating temperature and the mean solar flux concentration ratio (1000, 5000, ... 40000).



Source: Steinfeld, A [25]

The ratio required for ZnO/Zn cycle should be of 5000 suns or higher [32]. To achieve this ratio, it is necessary to add secondary concentrators in tandem with the heliostat field, which are usually parabolic concentrators (or CPC's). Increasing the concentration ratio represents an increase of cost, but also improves the efficiency of the process.

In conclusion, we have seen that CSP technology is developed enough to successfully combine with our cycle. In technological terms, the large-scale implementation is viable.



## 3.2. ENERGY COMPARISON BETWEEN ZnO/Zn CYCLE AND ELECTROLYSIS.

As commented before, the reason to compare ZnO/Zn cycle with electrolysis is that it is the main “renewable” hydrogen production process nowadays. To compare both processes, the focus will be on the energy required to obtain the hydrogen. In addition, to take into account the whole process, the energy consumption will be measured from primary energy until the hydrogen is obtained as an energy carrier.

### 3.2.1. PRELIMINARY COMMENTS.

The first thing to point out about the comparison with electrolysis is that the process itself is not necessary renewable, as it uses electricity. Depending on the feedstock used to obtain this electricity, the global balance will be (or not) environmental friendly. That shows again, as it has being seen in chapter 1, the strong relation between different phases of hydrogen production, and the importance of studding the process in a holistic way from primary energy to the final use. However, it is true that the characteristics of electrolysis allow the use of renewable energy sources and the achievement of a carbon-free global process.

Another important thing to comment are the production characteristics of the compared processes. Electrolysis is going to be compared not only with ZnO/Zn thermochemical cycle, but also with High Temperature Electrolysis (HTE), as it also represents a good alternative to de conventional process. Due to their characteristics, both of them require a centralized production, which involves a posterior distribution of the obtained hydrogen that implies losses.

In the case of conventional electrolysis, it is suitable for both centralized and distributed production. Distributed production has the great advantage of avoiding losses and costs of distribution, since hydrogen is generated in the same place of consumption. Despite that, both cases will be considered, as it is necessary to calculate centralized production energy consumption in order to compare it with ZnO/Zn cycle and with HTE.

Finally, to perform the energy calculations the efficiency values in generation and distribution are needed, so it is necessary to define a specific geographic location. The chosen country for that will be Spain, as it is the European country leading CSP technologies nowadays. This election will be discussed later, in section 3.3, but it will be already taken into account in this paragraph.

Considering this, I am going to calculate the primary energy needed to obtain 1 Nm<sup>3</sup> of hydrogen, that initially will be in normal conditions of temperature and pressure: 20 °C and 1 atm.



### 3.2.2. ELECTROLYSIS.

An electrolyser only requires an electricity supply to produce hydrogen. To calculate the necessary amount we just need to know the efficiency of the device, which will be assumed of 80% according to precedent chapters. However, to calculate the primary energy required it would also be necessary to consider loses in generation and distribution of electricity.

$$\text{Electricity consumption} = 1 \text{ Nm}^3 \text{ H}_2 \cdot \frac{3 \text{ kWh}}{1 \text{ Nm}^3 \text{ H}_2} \cdot \frac{1}{0,80} = 3,75 \text{ kWh} \quad (26)$$

Then, considering the electricity generation efficiency in Spain, which is around 40% [35], we can obtain the primary energy consumption for centralized production.

$$\text{Primary energy consumption (CENTRALIZED)} = 3,75 \text{ kWh} \cdot \frac{1}{0,40} = 9,38 \text{ kWh} \quad (27)$$

Finally, to consider distributed production we should also consider the efficiency of electricity distribution infrastructures in Spain, which is 44% [35]. That way, we obtain the primary energy consumption for distributed production.

$$\text{Primary energy consumption (DISTRIBUTED)} = 3,75 \text{ kWh} \cdot \frac{1}{0,40} \cdot \frac{1}{0,44} = 21,3 \text{ kWh} \quad (28)$$

### 3.2.3. HIGH TEMPERATURE ELECTROLYSIS (HTE).

In chapter 2 we have seen that high temperature electrolysis is an alternative to the conventional process that allows a reduction of the electricity consumption. In Figure 18 (chapter 2.2.1) it has being shown how total energy grows slightly, while electricity is reduced by 25% at temperatures around 1000 °C. Knowing that, we can calculate the electricity consumption and the thermal energy required to heat water from 20 °C up to that temperature.

$$\text{Electricity consumption} = 1 \text{ Nm}^3 \text{ H}_2 \cdot \frac{3 \text{ kWh}}{1 \text{ Nm}^3 \text{ H}_2} \cdot \frac{1}{0,80} \cdot (1 - 0,25) = 2,81 \text{ kWh} \quad (29)$$

$$\text{Primary energy consumption for electricity} = 2,81 \text{ kWh} \cdot \frac{1}{0,40} = 7,03 \text{ kWh} \quad (30)$$

Before calculating the thermal energy needed to heat the water, it is necessary to determinate the amount of it required to produce 1 Nm<sup>3</sup> of H<sub>2</sub>.

$$\text{Water consump.} = 1 \text{ Nm}^3 \text{ H}_2 \cdot \frac{0,0838 \text{ kg H}_2}{1 \text{ Nm}^3 \text{ H}_2} \cdot \frac{1 \text{ kmol H}_2}{2 \text{ kg H}_2} \cdot \frac{1 \text{ kmol H}_2\text{O}}{1 \text{ kmol H}_2} \cdot \frac{18 \text{ kg H}_2\text{O}}{1 \text{ kmol H}_2\text{O}} = 0,754 \text{ kg H}_2\text{O} \quad (31)$$



Finally, to calculate the energy requirement we will use the efficiency of a standard boiler, which is around 90% [35]. The enthalpy of vaporization of water is also needed ( $40,7 \text{ kJ/mol} \cdot 1000\text{mol}/18\text{kg} = 2261 \text{ KJ/Kg}$ ) [36], to calculate the energy required for vaporization, and its specific heat capacity as a liquid ( $4,18 \text{ kJ/kg}\cdot\text{K}$ ) and as vapour ( $1,97 \text{ kJ/kg}\cdot\text{K}$ ) [36], to calculate the energy for heating water up to  $1000 \text{ }^\circ\text{C}$ .

*Energy for heating 1kg of water*

$$\begin{aligned} &= \frac{2261 \text{ kJ}}{1 \text{ kg } H_2O} + \frac{4,18 \text{ kJ}}{1 \text{ kg } H_2O \cdot ^\circ\text{C}} \cdot (100 \text{ }^\circ\text{C} - 20 \text{ }^\circ\text{C}) + \frac{1,97 \text{ kJ}}{1 \text{ kg } H_2O \cdot ^\circ\text{C}} \cdot (1000 \text{ }^\circ\text{C} - 100 \text{ }^\circ\text{C}) \\ &= \frac{4368,4 \text{ kJ}}{1 \text{ kg } H_2O} \end{aligned} \quad (32)$$

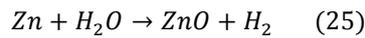
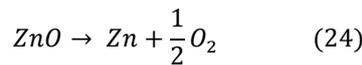
$$\text{Thermal energy consumption} = 0,754 \text{ kg}H_2O \cdot \frac{4368,4 \text{ kJ}}{1 \text{ kg } H_2O} \cdot \frac{1 \text{ kWh}}{3600 \text{ kJ}} \cdot \frac{1}{0,90} = 1,02 \text{ kWh} \quad (33)$$

With that, the total amount of primary energy is:

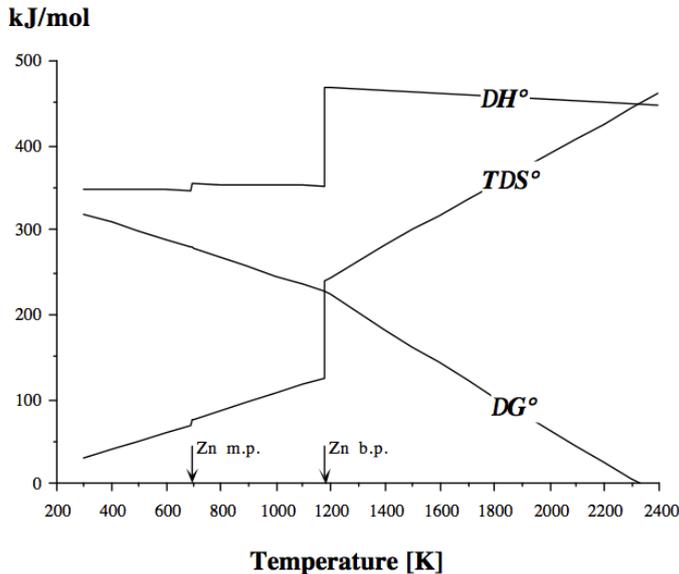
$$\text{Primary energy consumption} = 7,03 + 1,02 = 8,05 \text{ kWh} \quad (34)$$

### 3.2.4. ZNO/ZN THERMOCHEMICAL CYCLE.

For the analysis on ZnO/Zn thermochemical cycle, zinc oxide should be heated up to  $2300 \text{ K}$  to dissociate it. Then the resultant zinc should be mixed with water in the hydrolyser, but a much lower temperatures. In this case, it is appropriate to recall reactions (24) and (25) of the cycle:



In Figure 30 the energy required for ZnO dissociation reaction (24) can be seen.



**Figure 30:** Energy for ZnO dissociation reaction (24).

Source: Steinfeld, A [25]



In case of a theoretical analysis, we would have to calculate the energy necessary to heat zinc oxide and to overcome to phase transitions. The energy for reaction (24), endothermic, could be not considered, because at this temperatures Gibbs energy is nearly zero (Figure 30), and the reaction will be almost spontaneous. Finally, we should calculate the energy required to heat water to the temperature of reaction (25), exothermic.

This theoretical study would be too complex for the aspirations of this work, as it should be based on too many assumptions. Luckily, it is already included in Steinfeld work. As it depends on the solar flux concentration ratio (C), two case were considered: C=5.000 and C=10.000. In Table 7 the results of this study can be seen.

**Table 7:** Exergy analysis of the solar thermal dissociation of ZnO using the process represented in figure 28. The ZnO molar rate is assumed 1 mol/s.

C	5000	10,000
$Q_{\text{solar}}$	815 kW	662 kW
$Q_{\text{reradiation}}$	258 kW	105 kW
$Q_{\text{reactor,net}}$		557 kW
$Irr_{\text{reactor}}$		0.81 kW K <sup>-1</sup>
$Q_{\text{quench}}$		209 kW
$Irr_{\text{quench}}$		0.52 kW K <sup>-1</sup>
$Q_{\text{hydrolyser}}$		64 kW
$Irr_{\text{hydrolyser}}$		0.27 kW K <sup>-1</sup>
$Q_{\text{FC}}$		49 kW
$W_{\text{FC}}$		237 kW
$\eta_{\text{absorption}}$	68%	84%
$\eta_{\text{exergy}}$	29%	36%
$\eta_{\text{exergy}} (\eta_{\text{FC}} = 0.7)$	20%	25%

Source: Steinfeld, A [33]

To compare these results with the electrolysis ones, we should refer them to 1 Nm<sup>3</sup> of H<sub>2</sub>. This is almost a direct process, as 1 mol of ZnO produces 1 mol of H<sub>2</sub>.

$$H_2 \text{ consump.} = 1 \text{ Nm}^3 H_2 \frac{0,0838 \text{ kg } H_2}{1 \text{ Nm}^3 H_2} \cdot \frac{1 \text{ kmol } H_2}{2 \text{ kg } H_2} \cdot \frac{1000 \text{ mol } H_2}{1 \text{ kmol } H_2} = 41,9 \text{ mol } H_2 = 41,9 \text{ mol } ZnO \quad (35)$$

The, power [kW] also has to be converted into energy [kWh] dividing by 3600. That way, the primary energy (thermal) is:

$$\text{Primary energy consump. } (C = 5000) = \frac{815 \text{ kW}}{1 \text{ mol } ZnO/s} \cdot 41,9 \text{ mol } ZnO \cdot \frac{1h}{3600 \text{ s}} = 9,49 \text{ kWh} \quad (36)$$

$$\text{Primary energy consump. } (C = 10000) = \frac{662 \text{ kW}}{1 \text{ mol } ZnO/s} \cdot 41,9 \text{ mol } ZnO \cdot \frac{1h}{3600 \text{ s}} = 7,70 \text{ kWh} \quad (37)$$



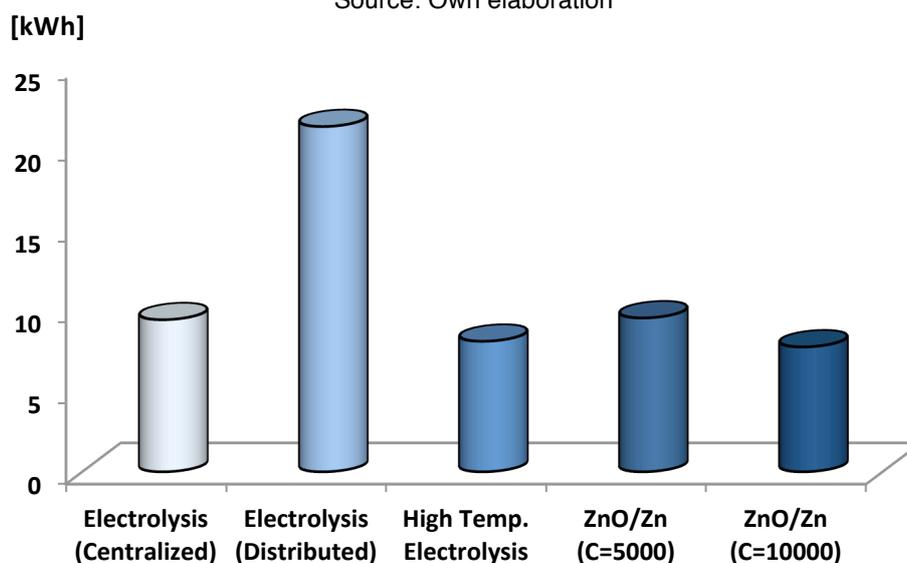
### 3.2.5. ANALYSIS OF RESULTS.

The results obtained in this energy analysis are summarized in Table 8 and represented in Figure 31.

**Table 8 and Figure 31:** Energy consumption to produce 1 Nm<sup>3</sup> of H<sub>2</sub>. Comparison between ZnO/Zn cycle and electrolysis.

		Production characteristics	Energy consumption [kWh]			Increase [%] referred to conventional electrolysis
			Electricity	Thermal energy	[TOTAL] Primary energy	
<b>Electrolysis</b>		Centralized	9,38	-	9,38	reference
		Distributed	21,3	-	21,3	127 %
<b>H.T. Electrolysis (HTE)</b>		Centralized	7,03	1,02	8,05	-14,2 %
<b>ZnO/Zn cycle</b>	C=5.000	Centralized	-	9,49	9,49	1,17 %
	C=10.000		-	7,70	7,70	-17,9 %

Source: Own elaboration



When comparing energy consumption, if we only use the efficiency of electrolysers, electrolysis would be considered much better than the other ones. Despite that, when electricity production efficiency (40%) is taken into account, ZnO/Zn thermochemical cycle is as good as electrolysis, or even better depending on the concentration ratio (C). This is a more realistic calculation, as it considers the whole process from primary energy form of the feedstocks until hydrogen is obtained as an energy carrier.

About HTE, the total energy requirement is lower than conventional electrolysis. That differs with the theory in chapter 2, where we have seen that it should grow slightly even when electric consumption is reduced. This miscalculation can be attributed to thermal energy, which has been calculated



supposing an ideal process. Even when boiler efficiency has been considered, other factors like combustion efficiency or waste heat after electrolysis should increase this value.

Finally, about distributed production through electrolysis, it can be seen how when distribution efficiency is considered (44%) the energy requirement grows considerably. Despite that, we should not forget that losses and costs of hydrogen distribution are being avoided. Considering that, it is still a very interesting option.

In conclusion, in energetic terms ZnO/Zn thermochemical cycle is not only viable, but also a very interesting hydrogen production alternative to electrolysis.



### 3.3. OTHER DETERMINING FACTORS IN VIABILITY.

Once seen that a large-scale hydrogen production implementation is feasible in technological and energetic terms, there are some other factors that can affect viability remaining to be analysed.

#### 3.3.1. LOCATION.

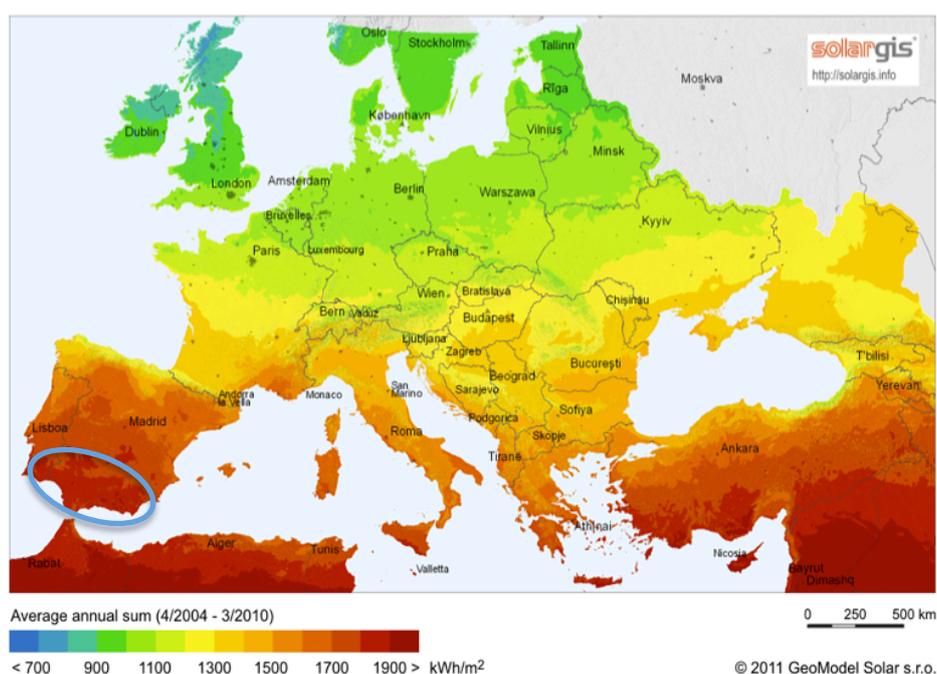
It is also necessary to place the CSP plant in a specific geographic scenario. As commented before, the best candidate country is Spain, one of the European countries with better conditions for solar thermal energy, and the one leading development of CSP technologies worldwide [31]. Not only that, it wants to maintain this leadership in the future, as we can see from the data below.

In first place, the installed capacity has increased quickly during last years: in 2010 there was a total capacity of 682 MW (representing an increase of 141,6% over 2009) [37], and at the end of 2011 949 MW were reached (an increase of 78,3% over 2010) [38]. There are also many other projects proposed or even in development [31] that presumably will maintain this tendency.

Secondly, during last years the government of Spain has had the clear objective of increasing renewable energy production, that at present represents the 22% of the electric demand generation [38]. It has an important 'feed-in tariff' funding system for renewable energy sources. In the case of CSP, it has been the first southern European country to introduce them.

To be more specific about the solar resources of the country, in Figure 32 a map of solar irradiance in Europe is shown. It can be seen how Southern Spain is a suitable location, with an irradiance value

**Figure 32:** Annual irradiance in Europe [ $kWh/m^2$ ].



Source: SolarGis [39]



that almost reaches 2000 kWh/m<sup>2</sup> annually, the reference value mentioned before. This region of Spain, marked on the map, will be the final location of the CSP plant.

Finally, a last issue related with location is the easy availability of raw materials. For ZnO/Zn cycle, those are zinc oxide and water. In this case, none of them represents a problem, as both can be easily found in this region.

In conclusion, this experience in the sector and the interest of the country for CSP, added to its good solar conditions, makes it a really good scenario for our large-scale implementation.

### 3.3.2. ECONOMIC PERSPECTIVES

The last factor to consider in viability is the economic perspectives for the next years. It would be interesting to know not only the estimated production cost for thermochemical cycles, but also for other production processes. In this field, the most accurate studies are the ones from the United States Department of Energy (DOE), realized through the Office of Energy Efficiency and Renewable Energy (EERE). We will take them as a reference.

To analyse cost, the first thing needed is a reference in which hydrogen could be competitive. Last year studies have established this value **between 2 and 4 dollars per gallon<sup>1</sup> gasoline equivalent** (gge) [40]. This can be considered the objective for the different hydrogen production processes, and a reference to know if they are close to competitiveness.

It is also interesting to note that 1 gge and 1 kg of hydrogen are almost equivalent: both have an energy content around 120 MJ. As it is not a precise value, depending on the fuel composition, both can be considered equivalent without an important error.

With that in mind, in Figure XX and Table XX we can see the results of different studies about hydrogen production cost for several processes. That will be useful to contextualize the cost of our process and to determine if it is economically viable. In the first study of the EERE [41], seven pathways were considered to produce, deliver and distribute hydrogen. The cost for each pathway, referred to 2005 U.S. dollars, is shown in Figure 33. The second study also comes from the EERE, but in this case it is a recompilation of different independent reviews. Once again, they report the cost of several hydrogen production pathways, but in this case delivering and distribution are not included. The costs are referred to 2005 U.S. dollars, with the exception of solar thermochemical, where 2007 dollars are used. The results are summarized in Table 9.

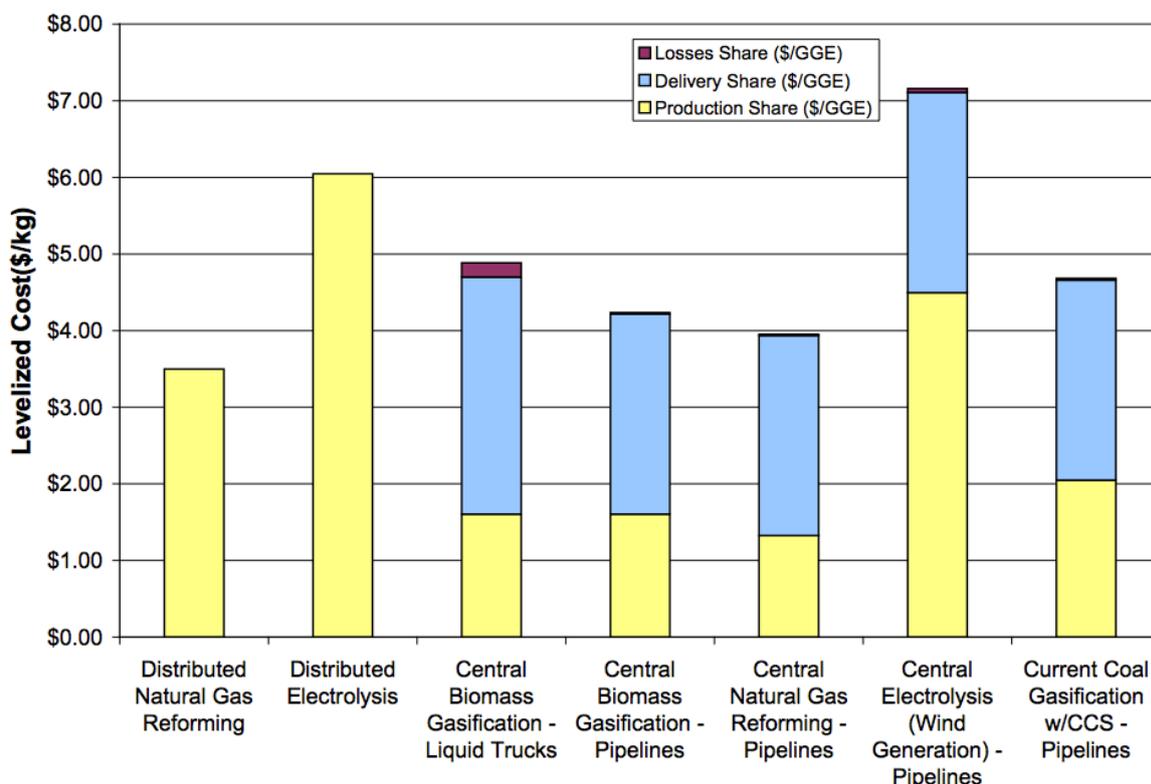
There are some interesting things to point out about these results. The first one is that even when they are independent analysis, the cost for the common pathways are quite similar, confirming the consistence of both studies. It is also remarkable that some production options are already competitive (considering the reference of 2 - 4 \$ per gge), and several others are not really far away

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<sup>1</sup> 1 gallon = 3,785 liters.



**Figure 33: Cost of hydrogen for seven pathways**



Source: Ruth, M.; Laffen, M.; Timbario, T. A [41]

**Table 9: Targets and projected costs informed by independent analysis**

Production pathway		Status [ \$ / gge ]	Observations	Report
Steam Methane Reforming (SMR)		2,75 – 3,05		<i>Distributed Hydrogen Production from Natural Gas</i> , NREL, October 2006
Electrolysis	Distributed	4,90 – 5,70	~ 75% membrane efficiency (PEM)	<i>Current (2009) State -of-the-Art Hydrogen Production Cost Estimate Using Water Electrolysis</i> , NREL, September 2009.
	Centralized (wind)	2,70 – 3,50	~ 75% membrane efficiency (PEM)	
Photoelectro-chemical (PEC)		4 – 10	Projected cost assuming technology reaches technology readiness. Promising PEC materials identified, but durability issues remain.	<i>Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production</i> , Directed Technologies Inc., December, 2009.
Biological		3 – 12	Projected cost assuming technology reaches technology readiness. 15% solar-to-chemical energy efficiency by microalgae.	<i>Technoeconomic Boundary Analysis of Biological Pathways to Hydrogen Production</i> , Directed Technologies Inc., September, 2009.
Biomass Gasification		Preliminary results: feedstock costs, capital costs, and financing structure are primary influences on cost.		<i>Hydrogen Production Cost Estimate Using Biomass Gasification</i> , Independent Panel Review, NREL, Draft, April, 2011
Solar Thermochem.	Hybrid Cycles	3,9 – 5,4	Cost predicted for 2025	<i>Cost Analyses on Solar-Driven High Temperature Thermochemical Water-Splitting Cycles</i> , TIAX, February, 2011
	Hi Temp. Cycles	2,4 – 4,7	Cost predicted for 2025	

Source: U.S. DOE. EERE [40]



from it. Nowadays the cheapest way to produce hydrogen is natural gas reforming, which confirms what was seen in chapter 2. However, there are renewable options that can already represent a good alternative. This is really important to achieve the objective of carbon-free hydrogen for the middle and long term.

For thermochemical cycles, the cost is a prediction for 2025, with a value between 2,4 and 4,7. That means this technology is predicted to be competitive in 12-13 years. But if we look at other DOE's reports, predictions for the short term are not so good. Even when established targets are very encouraging, predictions based on the current project status are far from achieving the objective of 2-4 \$ per gge in next years (see Table 10).

**Table 10: Progress towards Meeting Technical Targets for Solar-Driven High-Temperature Thermo-chemical Hydrogen Production.**

Characteristics	Units	U.S. DOE Targets			Project Status
		2008	2012	2017	
Solar-Driven High-Temperature Thermo-chemical Water Splitting Cycle Hydrogen Production Cost	\$/gasoline gallon equivalent H <sub>2</sub>	10.00	6.00	3.00	\$7.74 (2015) \$4.65 (2025)
Heliostat Capital Cost (installed cost)	\$/m <sup>2</sup>	180	140	80	97 <sup>b</sup>
Process Energy Efficiency <sup>c</sup>	%	25	30	>35	19.3

<sup>a</sup> Electrolytic system projected costs based on latest H2A analysis.

<sup>b</sup> Based on SAIC glass-reinforced concrete structure with 10 sq.m. area and low production quantity.

<sup>c</sup> Plant energy efficiency is defined as the energy of the hydrogen produced (lower heating value) divided by the sum of the energy delivered by the solar concentrator system plus any other net energy imports (electricity or heat) required for the process.

Source: U.S. DOE. EERE [42]

If finally we focus in the ZnO/Zn cycle, to keep the same example than before, predictions are similar to the general process case. A 2011 report by TIAX LLC for the DOE [43] includes an economical analysis of the cycle. The CSP plant elements are the same that the ones presented in chapter 3.1 for a central tower receiver plant, and the results are summarized in table 11.

**Table 11: Zinc Oxide Cycle Hydrogen Cost Breakdown.**

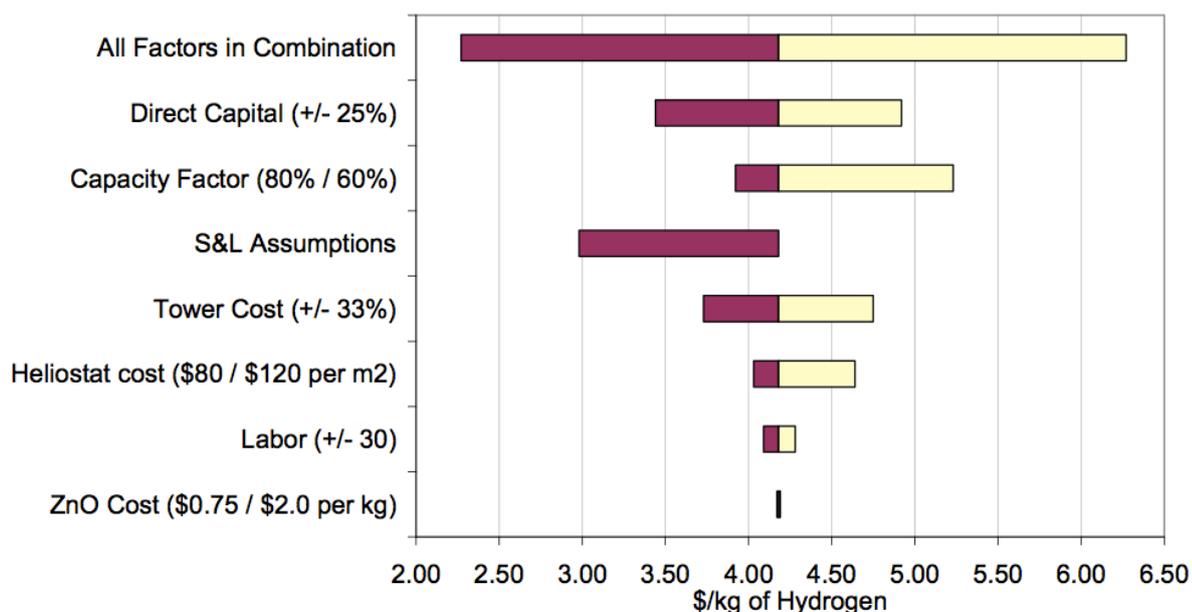
Analysis Year	Cost [ \$ / gge ]				Critical Assumptions
	Capital	Fixed O&M	Var. O&M	TOTAL	
2015	4.83	0.96	0.28	6.07	70% Zn/ZnO Conversion (no back reactions) - Reactor durability - \$127/m2 heliostat cost
2025	3.50	0.67	0.01	4.18	85% Zn/ZnO Conversion (no back reactions and improved yields) - Reactor durability - Reactor modifications (reduces argon supply, VSA cost, electricity use) - \$90/m2 heliostat cost

Source: Kromer, M [43]



Once again, according to these results, the cycle is far from being competitive in the short term. Even that being true, in the sensitivity analysis shown in Figure 34 we can see how these costs may vary significantly. Apart from the economic assumptions (S&L Assumptions), the most significant variable, there are other aspects to work on to reduce the total cost. That way, it could be possible to reach the economic goal in 2025.

**Figure 34:** ZnO Single variable sensitivity analysis, 2025 Case.



Source: Kromer, M [43]

From all the data shown above, the main conclusion is that solar thermal water splitting is not economically competitive nowadays. However, it is predicted to reach competitiveness in 15 years approximately. Meanwhile, economical support will be necessary to enable the incorporation of this technology to the energy market.



## 4. CONCLUSIONS.

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After an overview about world energy situation, classifying the main hydrogen production processes and analysing viability of a large-scale hydrogen production implementation using solar thermal energy, the main conclusions of this Master Thesis are summarized below:

- The current energy model has to be redefined, as we can observe from its ecological footprint, the world's energy consumption and the limited lifetime of fossil fuels. Hydrogen economy is a good alternative.
- There are many hydrogen production pathways. Nowadays, 96% of production is based on fossil fuels, but renewable production processes can change this tendency.
- Solar thermal water splitting has great perspectives to achieve carbon-free hydrogen production.
- Thermolysis is not enough developed. Two-step thermochemical cycles, like ZnO/Zn, are the best solution to combine with solar thermal energy.
- The solar technology for that are solar tower CSP plants, with high concentrating ratios to achieve higher temperatures (sometimes over 2000 °C).
- An energy analysis confirms that ZnO/Zn cycle is a good alternative to other production pathways. It has a energy consumption similar to centralized electrolysis.
- There are many appropriate locations with good solar resources. Southern Spain is an example.
- This technology will not be economically competitive for the next years. Meanwhile, it will need financial support.

Summarizing, large-scale hydrogen production using solar thermal water splitting is feasible nowadays. It will need support in its first commercial phases, like many other developing technologies, but even though it represents a great renewable carbon-free alternative to produce hydrogen.



## 5. REFERENCES

- [1] Fuel Cell and Hydrogen Energy Association (FCHEA). *Hydrogen Production Overview. Fact sheet*. FCHEA. Consulted in October 2011 in: [http://www.fchea.org/core/import/PDFs/factsheets/Hydrogen%20Production%20Overview\\_NEW.pdf](http://www.fchea.org/core/import/PDFs/factsheets/Hydrogen%20Production%20Overview_NEW.pdf)
- [2] ISO. *International Standard. ISO 13600. Technical energy systems – Basic concepts*. ISO, Switzerland, 1997.
- [3] U.S. Department of the Interior. Definitions for mineral resources and reserves. U.S. Geological Survey. Mineral Commodity Summaries 2001. Appendix C. Washington, D.C.: GPO, 2001.
- [4] Rifkin, J. *La economía del hidrógeno. La creación de la red energética mundial y la redistribución del poder en la tierra (The hydrogen economy: the creation of the worldwide energy web and the redistribution of power on earth)* Editorial Paidós, Barcelona, 2002.
- [5] Flavin, C. *Construir una economía baixa en carboni (Building a Low-Carbon Economy)*. Article from *L'estat del món. Innovacions per a una economía sostenible (State of the world. Innovations for a Sustainable Economy)*. Worldwatch Institute. Barcelona, UNESCOCAT, 2008. (93-111).
- [6] Collins, J. *Is 'Peak Oil' Behind Us?*. The New York Times, 14 Nov. 2010. Consulted in September 2011 in: <http://green.blogs.nytimes.com/2010/11/14/is-peak-oil-behind-us/?partner=rss&emc=rss>
- [7] Energy Watch Group (EWG) *Coal: Resources and future production. March 2007*. Consulted in October 2011 in: [http://www.energywatchgroup.org/fileadmin/global/pdf/EWG\\_Report\\_Coal\\_10-07-2007ms.pdf](http://www.energywatchgroup.org/fileadmin/global/pdf/EWG_Report_Coal_10-07-2007ms.pdf)
- [8] OECD. International Energy Agency (IEA). *World Energy Outlook 2009*. IEA Publications, France, 2009.
- [9] BP. *BP Energy Outlook 2030 booklet*. BP p.l.c, London, 2011.
- [10] BP. *BP Statistical Review of World Energy June 2011*, BP p.l.c, London, 2011.
- [11] Nobuo Tanaka. OECD. International Energy Agency (IEA). *World Energy Outlook 2010*. IEA Publications, France, 2009.
- [12] EU. Eurostat. *Energy, transport and environment indicators. 2010 edition*. Publications Office of the European Union, Luxembourg, 2011.
- [13] International Energy Agency (IEA), Hydrogen Implementing Agreement (HIA). *Hydrogen Production and Storage. R&D Priorities and Gaps*. IEA Publications, France, 2006.
- [14] U.S. Department of Energy (DOE). *The Department of Energy Hydrogen and Fuel Cells Programme Plan*. Consulted in November 2011 in: [http://www.hydrogen.energy.gov/pdfs/program\\_plan2011.pdf](http://www.hydrogen.energy.gov/pdfs/program_plan2011.pdf)
- [15] McGraw Hill. *Tabla periódica de los elementos (Periodic table of the elements)*. Consulted in November 2011 in: [http://www.mcgraw-hill.es/bcv/tabla\\_periodica/element/elemento1.html](http://www.mcgraw-hill.es/bcv/tabla_periodica/element/elemento1.html)
- [16] Rajeshwar, K.; McConnell, R.; Licht, S.; Rajeshwar, K.; *Solar Hydrogen Generation. Towards a Renewable Energy Future*. Springer, Chapter 1, pp. 1-18, Chapter 5, pp. 87-121, 2008.



- [17] U.S. DOE. Hydrogen Analysis Resource Centre. *Basic Hydrogen Properties*. Consulted in November 2011 in: [http://hydrogen.pnl.gov/filedownloads/hydrogen/datasheets/hydrogen\\_properties.xls](http://hydrogen.pnl.gov/filedownloads/hydrogen/datasheets/hydrogen_properties.xls)
- [18] U.S. DOE. Hydrogen Analysis Resource Centre. *Lower and Higher Heating Values of Hydrogen and Fuels*. Consulted in November 2011 in: [http://hydrogen.pnl.gov/cocoon/morf/projects/hydrogen/datasheets/lower\\_and\\_higher\\_heating\\_values.xls](http://hydrogen.pnl.gov/cocoon/morf/projects/hydrogen/datasheets/lower_and_higher_heating_values.xls)
- [19] U.S. DOE. Hydrogen Analysis Resource Centre. *Comparative Properties of Hydrogen and Fuels*. Consulted in November 2011 in: [http://hydrogen.pnl.gov/filedownloads/hydrogen/datasheets/comparative\\_properties.xls](http://hydrogen.pnl.gov/filedownloads/hydrogen/datasheets/comparative_properties.xls)
- [20] IUPAC. *Glossary of atmospheric chemistry*. Pure Appl. Chem., Vol. 62, No. 11, pp. 2167-2219, 1990.
- [21] Suresh B.; Yoneyama M.; Schlag S. CEH Marketing Research Report Abstract. Hydrogen. Chemical Industries Newsletter October 2007, pp 7-8, SRI Consulting. Consulted in November 2011 in: <http://www.sriconsulting.com/nl/Public/2007Oct.pdf>
- [22] International Energy Agency (IEA). *IEA Energy Technology Essentials. Hydrogen Production & Distribution. April 2007*. AECD/IEA, 2007. Consulted in: <http://www.iea.org/techno/essentials5.pdf>
- [23] Steinfeld, A. *Concentrated solar energy: Power-Fuels-Storage*. Department of Mechanical and Process Engineering, ETH (Swiss Federal Institute of Technology). Consulted in October 2011 in: <http://www.weizmann.ac.il/conferences/ASEO/Steinfeld.pdf>
- [24] Steinfeld, A. *Solar thermochemical production of hydrogen – a review*. Solar Energy 78, pp 603-615, Elsevier Ltd., 2005
- [25] Steinfeld, A.; Palumbo R. *Solar thermochemical process technology*. Encyclopedia of Physical Science & Technology. R.A Meyers Ed., Academic Press, Vol. 15, pp. 237-256, 2001.
- [26] Bellona. *Bellona Report 6:02: Hydrogen. Status and possibilities*. The Bellona Foundation, Belgium, 2002.
- [27] Abengoa. *SET-TE: Producción hidrógeno*. Consultado en Abril de 2011 en: [http://www.energiaycambioclimatico.com/colab/export/sites/foro/resources/pdf/programa\\_investigacion/investigacion/101126\\_SET-TE\\_H2.pdf](http://www.energiaycambioclimatico.com/colab/export/sites/foro/resources/pdf/programa_investigacion/investigacion/101126_SET-TE_H2.pdf)
- [28] Ulleberg, O. *Modelling of advanced alkaline electrolyser; a system simulation approach*. International Journal of Hydrogen Energy 28, 1, 21-33, Elsevier, 2003.
- [29] Sigfusson T. I. *Philosophical Transactions of the Royal Society A*. 2007, 365:1025-1042 Consulted in January 2012 in: <http://rsta.royalsocietypublishing.org/content/365/1853/1025.full>
- [30] Gallet, D.; Grastien, R. (CEA). *Thermochemical water splitting cycles*. CLEFS CEA, n° 50/51, winter 2004-2005.
- [31] Greenpeace International; SolarPACES; ESTELA. *Concentrated Solar Power. Global Outlook 09*. Consulted in December 2011 in: [http://www.pre.ethz.ch/publications/0\\_pdf/various/CSPbyGreenpeace\\_Solapaces.pdf](http://www.pre.ethz.ch/publications/0_pdf/various/CSPbyGreenpeace_Solapaces.pdf)



- [32] Steinfeld, A. *Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn=ZnO redox reactions*. International Journal of Hydrogen Energy 27, 611–619, Elsevier, 2002
- [33] SolarPACES. *Solar Fuels from Concentrated Sunlight*. Burger Druck GmbH, Germany, 2009.
- [34] Arbegoa solar. *Plantas en operacion*. Consulted in January 2012 in: [http://www.abengoasolar.com/corp/web/es/nuestras\\_plantas/plantas\\_en\\_operacion/espana/index.html](http://www.abengoasolar.com/corp/web/es/nuestras_plantas/plantas_en_operacion/espana/index.html)
- [35] Sancho Torrent, A.; Mechanical engineering and worker of ENDESA. Private communication in January 2012
- [36] Housecroft, E.; Constable, E. *Chemistry*. 3<sup>rd</sup> Edition. Pearson Education Limited, England, 2006.
- [37] Red Eléctrica de España (REE). *El sistema eléctrico español 2010. (The Spanish electric system 2010)*. Red Eléctrica de España, S.A.U., Madrid, 2011.
- [38] Red Eléctrica de España (REE). *El sistema eléctrico español. Avance del informe 2011. (The Spanish electric system. Progress report 2011)*. Red Eléctrica de España, S.A.U., Madrid, 2012.
- [39] SolarGis. SolarGIS © 2012 GeoModel Solar s.r.o. Consulted in January 2011 in: [http://solargis.info/doc/\\_pics/freemaps/1000px/ghi/SolarGIS-Solar-map-Europe-en.png](http://solargis.info/doc/_pics/freemaps/1000px/ghi/SolarGIS-Solar-map-Europe-en.png)
- [40] U.S. DOE. *DOE Hydrogen and Fuel Cells Programe. Annual Progress Report 2011: II.0 Hydrogen Production Sub-Program Overview*. U.S. Department of Energy, Washington, 2011.
- [41] Ruth, M.; Laffen, M.; Timbario, T. A. *Hydrogen Pathways: Cost, Well-to-Wheels Energy Use, and Emissions for the Current Technology Status of Seven Hydrogen Preproduction, Delivery and Distribution Scenarios*. National Renewable Energy Laboratory (NREL), Colorado, 2009.
- [42] U.S. DOE. *DOE Hydrogen and Fuel Cells Programe. Annual Progress Report 2011: II.F.1 Solar High-Temperature Water Splitting Cycle with Quantum Boost*. U.S. Department of Energy, Washington, 2011.
- [43] Kromer, M. *Support for Cost Analyses on Solar-Driven High Temperature Thermochemical Water-Splitting Cycles*. TIAX LLC, 2011.
- [44] AEH2: Asociación Española del Hidrógeno (Spanish Hydrogen Association). *Los números del hidrógeno (Hydrogen numbers)*. Consulted in November 2011 in: <http://aeh2.org/datos2.htm>
- [45] U.S. DOE. Hydrogen Analysis Resource Center. *Hydrogen Compressibility (Z) at Different Temperatures (oC) and Pressures (MPa)*. Consulted in November 2011 in: [http://hydrogen.pnl.gov/filedownloads/hydrogen/datasheets/Compressibility%20\(SI\).xls](http://hydrogen.pnl.gov/filedownloads/hydrogen/datasheets/Compressibility%20(SI).xls)



## 6. APPENDIX

### APPENDIX 1: ENERGY CONTENT OF HYDROGEN.

A feature of interest in the use of hydrogen is its equivalent in energy terms. Table 12 shows some reference values, calculated based on low heating value (LHV).

**Table 12:** *Hydrogen-Energy equivalence.*

Source: Adapted from AEH2 [44]

Hydrogen-Energy equivalence				
H <sub>2</sub> [kg]	H <sub>2</sub> (gas) [Nm <sup>3</sup> ]	H <sub>2</sub> (liquid) [liter]	Energy [MJ]	Energy [kW·h]
1	11,12	14,12	120	33,33
0,0899	1	1,27	10,8	3
0,0708	0,788	1	8,495	2,359
0,00833	0,0926	0,1177	1	0,278
0,03	0,333	0,424	3,6	1

It is also interesting to know the electrical power supplied by a determinate flow of hydrogen. Table 13 shows some power values based on LHV. It is a tool that can be useful for performing calculations of consumption in both ways: hydrogen produce by an electrolyzers and the opposite process, in which energy is extracted by an hydrogen fuel cell.

**Table 13:** *Equivalence between hydrogen flow and electrical power.*

Source: Adapted from AEH2 [44]

Equivalence between hydrogen flow and electrical power			
[kg/h] de H <sub>2</sub>	[Nm <sup>3</sup> /h] de H <sub>2</sub> gas	[liter/h] de H <sub>2</sub> líquido <sup>1</sup>	Potencia [kW]
1	11,12	14,12	33,33
0,0899	1	1,270	3,00
0,0708	0,788	1	2,359
0,00833	0,0926	0,1177	0,278
0,0300	0,333	0,424	1

<sup>1</sup>El Hydrogen is liquid at atmospheric pressure below 20.39 K



## APPENDIX 2: RELATION BETWEEN VOLUME AND PRESSURE.

One important characteristics when working with hydrogen as a gas is the strong relation between pressure, temperature and volume, especially when talking about its storage. To unify measures it is usual to work with  $Nm^3$  instead of  $m^3$ . It means the volume occupied by the gas in normal conditions of temperature and pressure (NTP): 20 °C and 1 atmosphere.

With that in mind, it is important to know the compressibility factor ( $Z$ ) at different temperatures and pressures, in order to being able to work with hydrogen in various ambient conditions. Values for  $Z$  are can be consulted in appendix 3.

To understand the use of this table is relevant to recall that the compressibility factor ( $Z$ ) is the ratio between the real volume occupied by a gas and the volume that it would occupy if it were an ideal gas, according to equation 38.

$$Z = \frac{V_{real}}{V_{ideal}} \quad (38)$$

If Ideal Gas Law is considered (equation 39), substituting (38) in (39) equation 40 is obtained.

$$P \cdot V_{ideal} = n \cdot R \cdot T \quad (39) \quad \rightarrow \quad P \cdot V_{real} = Z \cdot n \cdot R \cdot T \quad (40)$$

Where:

$P$ = Absolute pressure [ $Pa$ ]

$V$ = Volume [ $m^3$ ]

$R$ = Universal ideal gas constant = 8,314472[( $Pa \cdot m^3$ )/( $mol \cdot K$ )]

$T$ = Absolute temperature [ $K$ ]

$Z$ = Factor de compresibilidad [-]

$n$ = Moles of gas [ $mol$ ]

Then, considering two different states and using (40), equation 41 is obtained:

$$\frac{P_1 \cdot V_1}{T_1 \cdot Z_1} = \frac{P_2 \cdot V_2}{T_2 \cdot Z_2} \quad (41)$$

A practical application of 41 is calculate the amount of compressed hydrogen in a storage system in  $Nm^3$ , using for that two different states. The first one will have atmospheric pressure ( $P_1 = 1 \text{ atm} = 1,01325 \cdot 10^5 \text{ Pa}$ ) and  $T_1 = 20 \text{ °C} = 293,15 \text{ K}$ , corresponding to normal conditions, so  $V_1$  will have units of  $Nm^3$ . With that,  $Z_1 = 1,0006$  is obtained from Table 14. The second state will have pressure, volume and temperature of the storage system:  $P_2$ ,  $V_2$  and  $T_2$ , obtaining equation 42:

$$V_1(Nm^3) = \frac{T_1 \cdot Z_1}{P_1} \cdot \frac{P_2 \cdot V_2}{T_2 \cdot Z_2} = \frac{293,15 \cdot 1,0006}{1,01325 \cdot 10^5} \cdot \frac{P_2 \cdot V_2}{T_2 \cdot Z_2} = 2,89490 \cdot 10^{-3} \frac{P_2 \cdot V_2}{T_2 \cdot Z_2} \quad (42)$$



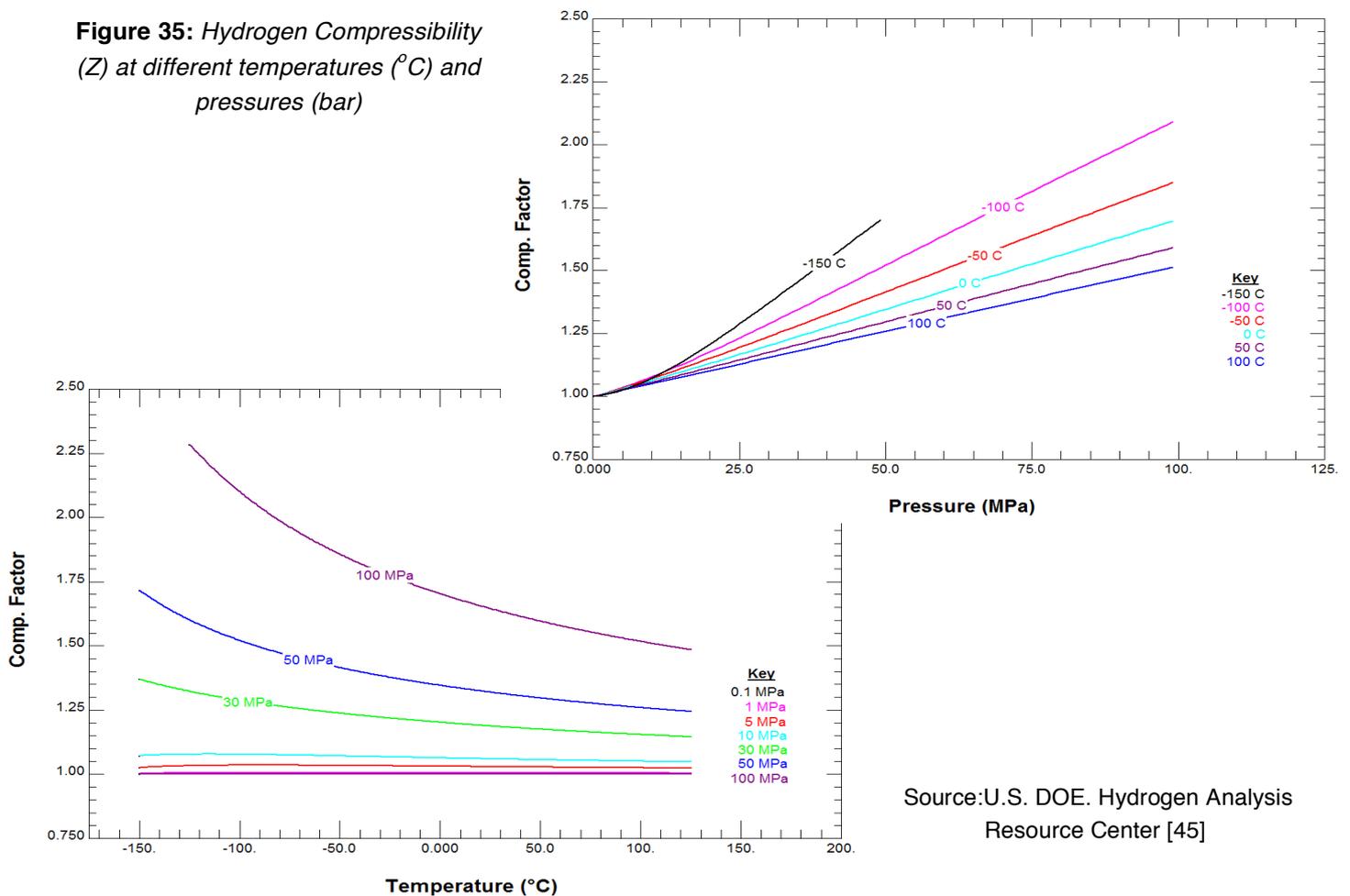
### APPENDIX 3: HYDROGEN COMPRESSIBILITY FACTOR (Z)

**Table 14:** Hydrogen Compressibility Factor (Z) at different temperatures (°C) and pressures (MPa)

		PRESSURE [MPa]						
		0,1	1	5	10	30	50	100
TEMPERATURE [°C]	-150	1,0003	1,0036	1,0259	1,0726	1,3711	1,7167	
	-125	1,0006	1,0058	1,0335	1,0782	1,3231	1,6017	2,2856
	-100	1,0007	1,0066	1,0356	1,0778	1,2880	1,5216	2,1006
	-75	1,0007	1,0068	1,0355	1,0751	1,2604	1,4620	1,9634
	-50	1,0007	1,0067	1,0344	1,0714	1,2377	1,4153	1,8572
	-25	1,0006	1,0065	1,0329	1,0675	1,2186	1,3776	1,7725
	0	1,0006	1,0062	1,0313	1,0637	1,2022	1,3462	1,7032
	25	1,0006	1,0059	1,0297	1,0601	1,1879	1,3197	1,6454
	50	1,0006	1,0056	1,0281	1,0567	1,1755	1,2969	1,5964
	75	1,0005	1,0053	1,0266	1,0536	1,1644	1,2770	1,5542
	100	1,0005	1,0050	1,0252	1,0507	1,1546	1,2596	1,5175
	125	1,0005	1,0048	1,0240	1,0481	1,1458	1,2441	1,4852

Source: Adapted from: U.S. DOE. Hydrogen Analysis Resource Center [45]

**Figure 35:** Hydrogen Compressibility (Z) at different temperatures (°C) and pressures (bar)



Source: U.S. DOE. Hydrogen Analysis Resource Center [45]

Renewable hydrogen production.

The role of Solar Thermal Water Splitting.

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