CRANFIELD UNIVERSITY

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THERMOCHEMICAL HYDROGEN PRODUCTION

SCHOOL OF ENERGY & POWER
MSc Energy Systems and Thermal Processes

MSc THESIS
Academic Year: 2017 - 2018

Supervisor: Dr Dawid Hanak
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This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science
(NB. This section can be removed if the award of the degree is based solely on examination of the thesis)

ABSTRACT

The world population is continually increasing and so does the energy consumption. Moreover, a huge percentage of this energy comes from fossil fuels. To solve this issue, one of the streams of research is focused on hydrogen as a fuel. Hydrogen has three times more calorific power than any other common fuels such as gasoline. However, the most common way of producing hydrogen is using non-renewable. On the other hand, the water molecule can be split by increasing the temperature of this component. However, the temperature needed to split it is incredibly large.

The aim of this project, is to research about different ways of making water splitting feasible. Specifically, a deep research on the different thermochemical cycles that have been studied will be done, getting focused on one of them. Concretely, the UT-3 cycle will be developed using ASPEN PLUS. Additionally, some parts will be suggested to make the process more efficient, changing its efficiency from 21% to 32%.

Keywords:

Hydrogen, fuel, chemical engineering, ASPEN PLUS, UT-3, chemistry.

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CSP	Concentrating Solar Power
LHV	Low Heating Value
PEM	Proton Exchange Membrane
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell

1 INTRODUCTION

Currently, the world is under huge issues that might affect the development of the glove for future generations. The world population is continually increasing and so does the energy consumption all over the planet (Enerdata, 2016). Moreover, a huge percentage of this energy comes from fossil fuels combustion, which involves millions of tonnes of CO_2 delivered to the environment each year. A lot of pollution restrictions are set for combustion processes. In addition, some carbon capture technologies are being more and more developed each year with the aim of mitigate this global warming. Although a lot of effort is invested in solving this issue, it seems that the problem will persist if some drastic changes are not applied.
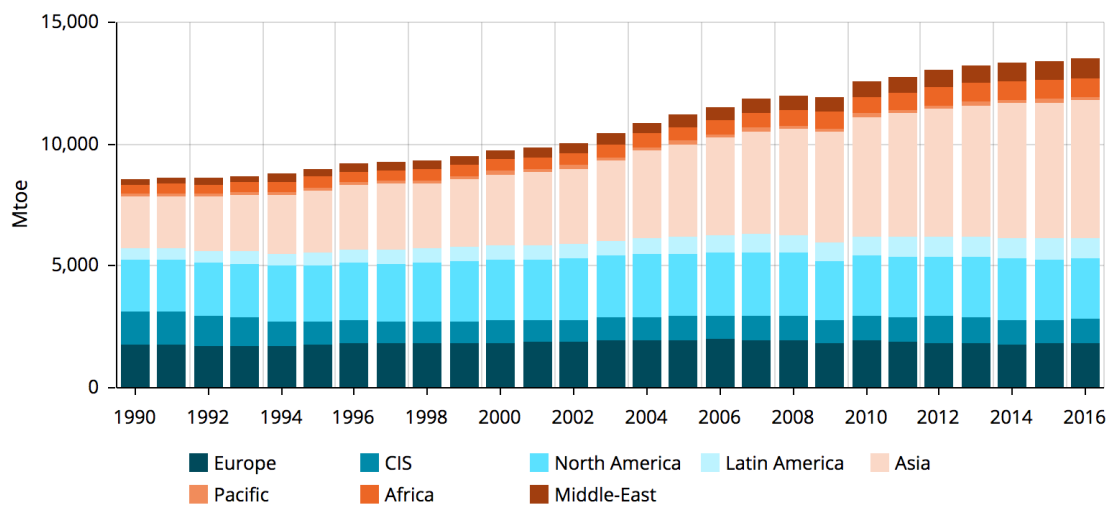
Figure 1-1. World energy consumption progression (Enerdata, 2016).

Another stream of research is developing alternative fuels that after combustion release non-toxic products. Specifically, hydrogen technologies have been highly developed in the last decades being known as the fuel of the future. Investments in hydrogen by the Hydrogen Council are at least 1.9 billion euros per year (Hydrogen Council EU, 2017). Hydrogen, which can be obtained from water splitting, can be used as an energy carrier to solve the sustainability problem that the glove is living currently. As it will be shown along this document, hydrogen can be produced using sustainable processes which not only allows using a green fuel, but also do not produce any carbon emissions while being produced.

Hence, this process helps building a sustainable energy ecosystem which might be helpful for future generations (Hydrogen Council EU, 2017).
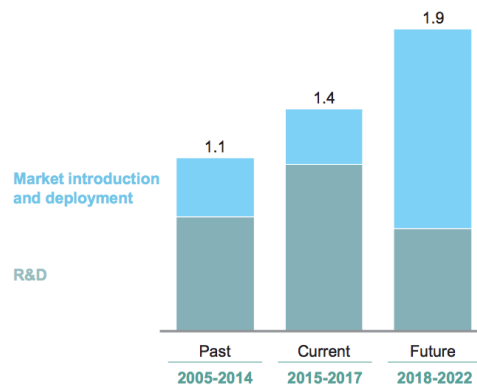
Figure 1-2. Hydrogen Council members plan to orient their increasing annual investments in hydrogen (Hydrogen Council EU, 2017).

Hydrogen is the most abundant compost in the world. Besides, it does not produce any pollutant after combustion, rather than water and has the highest energy density of all the used fuels. For these reasons, it is considered the most suitable green fuel to substitute the fossil fuels (Blagojević et al., 2012). Although being the most abundant component on earth, it cannot be obtained freely. Normally, hydrogen is obtained from components such as water, which include hydrogen in its molecular composition. However, the main issue is how to split this component from the whole molecule, since sometimes it is required more energy to separate the component; than energy is obtained from the hydrogen energy generation.

Obviously, the importance of this component is huge and its properties are critical to understand more its behaviour. On the one hand, hydrogen is the lightest component on earth, having a density of 0.084 kg/m3 in gaseous phase. However, the most interesting part of this component is its calorific power, which compared with other commonly used fuels is huge. This comparison is displayed in **¡Error! No se encuentra el origen de la referencia.**.

Table 1-1. Calorific power comparison.

Fuel	Calorific power (MJ/kg)
Gasoil	43.20
Gasoline	43.47
Natural gas	48.10
Hydrogen	120

As it has been shown, hydrogen has three times more energy per mass unit than any other conventional fuels. This fact is a huge motivation to continue the research of this component, and more in particular its main issue, the production.

Finally, it is important to have an overview of the hydrogen industry. Although the main researches are talking about hydrogen as an energy carrier, this is not the only usage that this component has in industry. Rather than its physical properties, hydrogen is mainly used because its reactivity. The main uses of hydrogen are (Ramachandran, 1998):

- Hydrogen as a reactant: in this case, the properties of different components are change due to the properties of hydrogen. Specifically, lower molecular weight is achieved for these components. Petroleum and fertilizer production and processing are the main streams inside this group.
- As a "O2 scavenger": prevent oxidation by removing O2 waste from materials.
- As an energy carrier.
- As a refrigerant for electrical generators.

Along this document, it will be explained the importance of hydrogen, focusing on its production. Specifically, several ways of thermochemical hydrogen production will be displayed. Additionally, one of the most promising techniques will be developed using a chemical engineering software to study its performance, improving its efficiency.

2 LITERATURE REVIEW

2.1 Hydrogen production

As it is already known, hydrogen is the most abundant component on earth. Hence, there must be a way where nature produces hydrogen directly, without the humankind help. First studies about hydrogen started at the beginning of the 20th century (Hallenbeck and Benemann, 2002). In these studies, the first biological hydrogen production methods were developed, being bacterial and microalgal hydrogen production. Roughly, the way nature produces hydrogen is using enzymes which catalyse, taking place a very common reaction:

$$2H^+ + e^- \rightarrow H_2$$
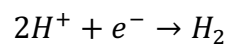
The composition of the enzymes and the complex process taking place in order to catalyse them makes incredibly difficult to apply this process to industry.

Currently, the main idea to produce hydrogen is to decompose a component that contains hydrogen in its molecular structure, for instance H_2O. However, there are other feasible methods that consist on fuel treatments to obtain hydrogen as a product, this technology is called hydrocarbon reforming. After the endothermic reforming process, there is a stream composed mainly of hydrogen, carbon dioxide and carbon monoxide. Therefore, this process has several disadvantages which make the technology unfeasible currently. Firstly, the hydrocarbon reforming mainly consists on burning hydrocarbons with oxygen, producing hydrogen and other components. Besides, some of the components produce are extremely poisonous for the environment, for instance carbon monoxide or different kinds of sulphur-based components, which make compulsory the use of desulfurization processes (Holladay *et al.*, 2009). Due to the fact of being a really pollutant technology, several derivatives have been developed. Aqueous phase reforming, plasma reforming or ammonia reforming are some of the most used. Another hydrogen production process with significantly less carbon emissions is the pyrolysis. Although it still uses hydrocarbons as the main source to produce hydrogen, water or air are not needed.

Currently, new hydrogen production technologies independent from fossil fuels are being developed, hence there are some hydrogen production methods that do not need fossil fuels. It is noteworthy to describe the way hydrogen is produced from biomass where a reforming process is used and the main technology used to subtract the hydrogen is gasification.

As it has been said, the main way of producing hydrogen currently, and the most developed is obtaining hydrogen from water. The most studied technology inside this group is electrolysis, where water is split by means of an electric current and to electrodes (anode and cathode). Currently it has achieved an efficiency of up to 73% (water conversion).

$$Anode: 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$Cathode: 4H^+ + 4e^- \rightarrow 2H_2$$
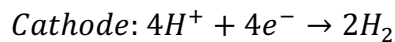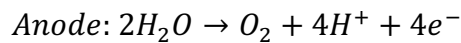
Alkaline electrolysers are the most used, however Proton Exchange Membranes (PEM) and Solid Oxide Electrolysis Cells (SOEC) are also used. Although being a non-emission hydrogen producer with high purity, it is a really expensive technology (Holladay *et al.*, 2009).

Finally, the thermochemical hydrogen production (thermolysis) also produces hydrogen from water, but in this case using thermal energy. This is a really interesting technology, as the overall efficiency is approximately 50% (Holladay *et al.*, 2009).

2.2 Thermochemical Hydrogen Production

Thermochemical hydrogen production is not a new technology, since it was first published in the 1960s (Funk and Reinstrom, 1966) and some years later, in the 1970s was studied in laboratories (Beghi, 1981).

It is one of the ways of producing hydrogen currently. However, doing it in one step is not feasible since high temperatures have to be achieved. Specifically, to separate hydrogen from a water molecule the thermal decomposition temperature of water must be achieved, which is over 2,800 K. Even at this temperature, the water electrolysis efficiency is only around 10% (Abanades *et*

al., 2006). Hence, there is a necessity of looking for thermochemical cycles that decrease this temperature and make feasible the hydrogen production. These cycles combine endothermic and exothermic reactions with the aim of reducing the operation temperature and increase the efficiency of the process. Furthermore, one of the main advantages of this cycles is that oxygen and hydrogen are produced in different reactions

Several hundreds of cycles have been researched currently. However, not all the processes are equally developed and, even more, some of the are not even feasible. For this reason, a selection process will take place according to the criteria displayed in the following lines (Abanades *et al.*, 2006):

- Maximum cycle temperature. This is one of the most important factor, as depending on this temperature the selection of material will be different. Then, the cost of the installation is directly proportional to this factor. Moreover, these technologies are usually run either by portable nuclear reactors or by thermo-solar panels, which cannot achieve infinite temperature.
- Number of reactions per cycle, which will directly affect the complexity and cost of the system.
- Number of elements used in the cycle, which generally affects the complexity and cost of the technology.
- Type of cycle. Cycles can be purely thermal or hybrid, which combines thermal and electrical reactions.
- Feasibility of the cycle. Obviously, if the technology is not feasible will be automatically discarded.

According to the following criteria, some thermochemical cycles have been discarded (Abanades *et al.*, 2006). For instance, regarding the temperature criteria, cycles such as Mo/MoO_2 cycle (3,986 K max. temperature), SiO_2/SiO cycle (3,250 K max. temperature) or $W/WO3$ cycle (4,183 ºC max. temperature).

Finally, after getting rid of the worse cycles, a list with most promising one has been done. These cycles are listed in Table 2-1

Table 2-1. Best feasible cycles for hydrogen production (Abanades et al., 2006).

Cycle	Max. Temperature (ºC)	Number of steps
MnO/MnSO4	1,100	2
FeO/FeSO$_4$	1,100	2
CoO/CoSO$_4$	1,100	2
Fe$_3$O$_4$/FeCl$_2$	1,500	2
FeSO$_4$ Julich	1,800	3
C7 IGT	1,000	3
Shell Process	1,750	3
CuSO$_4$	1,500	3
LASL BaSO$_4$	1,300	3
Euratom 1972	1,000	3
Cr, Cl Julich	1,600	3
Euratom JRC Ispra	1,000	3
Bi, Cl	1,700	3
Fe, Cl Julich	1,800	3
Fe, Cl Cologne	1,800	3
Li, Mn LASL	1,000	3
Mn PSI	1,500	3
Fe, M ORNL	1,300	3
Sn Sourian	1,700	3
Co ORNL	1,000	3
Ce, Ti ORNL	1,300	3
Ce, Cl GA	1,000	3

As it has been displayed in Table 2, even at feasible temperatures there are a lot of possible cycles to use. To reduce this number, it is important to define a thermochemical process, which can be described as cycles where water is split using heat energy from temperatures under 1,500 K (1,227 ºC) giving hydrogen and oxygen as outputs (Beghi, 1981). According to this description, only 9 cycles included in Table 2-1 can be seen as thermochemical cycles, as the maximum temperature is under 1,500 K.

According to thermochemical cycles, it is noteworthy that there are three main types of cycles: two-step water splitting cycles, multi-step water splitting cycles and hybrid cycles (Petrasch and Klausner, 2012). From each type, there are several cycles that have been more studied than the others. The review of its research will be shown in the following pages.

2.2.1 Two-step water splitting cycles

It was the first option studied to decrease the temperature of direct water splitting. Specially, two step metal oxide cycles have the highest efficiency in the group. It consists of an endothermic step, which needs the biggest temperature, followed by an exothermic reaction which has a lower temperature (Petrasch and Klausner, 2012). The hydrogen is produced in the exothermic reaction, as it can be seen in the following expression.

$$MO_{ox} \xrightarrow{heat} MO_{red} + \frac{x}{2}O_2$$

$$MO_{red} + xH_2O \rightarrow MO_{red} + xH_2$$
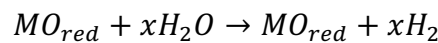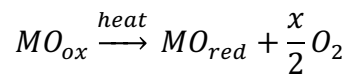
Although there are a lot of cycles available, the most promising ones are Zn/ZnO (Bilgen *et al.*, 1977), Fe_3O_4/FeO (Nakamura, 1977) and other mixed iron cycles, which can reduce thermal reduction temperature.

2.2.2 Multi-step water splitting

Several three and four steps thermochemical cycles are proposed for hydrogen production. Although these cycles were firstly thought to take advantage of the residual heat of nuclear reactors, it can also be use concentrated solar power, since the temperature needed is lower than the two-step cycles (Petrasch and Klausner, 2012). The most researched cycles inside this group are: the S-I cycle developed by General Atomic Company, which can be run with temperatures of approximately 1,073 K (O'Keefe *et al.*, 1982); the UT-3 cycle, developed by the University of Tokyo that is a four-step cycle with a maximum temperature of 1,025 K (Aochi *et al.*, 1989). However, these cycles are the ones with less kinetic and thermodynamic problems than other multi-step water splitting cycles (Petrasch and Klausner, 2012).

2.2.3 Hybrid cycles

This kind of cycles combine electric and heat energy in order to produce hydrogen. The main advantage is to produce hydrogen at a lower voltage than pure electrolysis, which needs (-1.73 V). The Westinghouse cycle (Ispra Mark 12)

decompose sulfuric acid and then produces hydrogen from electrolysis (Carty and Conger, 1980). A similar cycle is the Ispra Mark 13, which thermally decompose sulfuric acid using a two-step cycle (Beghi, 1986).

2.3 Thermochemical hydrogen production cycles

2.3.1 Zn/ZnO cycle

This cycle consists on a two-step thermochemical cycle based on a thermal dissociation of ZnO (Oxidation) and a hydrolysis reaction. The two-step reaction is as follows:

$$First\ step: \quad ZnO(s) \rightarrow Zn(g) + 0.5O_2$$

$$Second\ step: Zn(l) + H_2O \rightarrow H_2 + ZnO$$
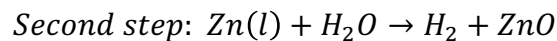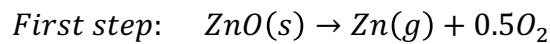
An endothermic oxidation occurs in the first step. In other words, ZnO is dissociated at 2,300 K. To make the Gibbs free energy minimized and hence reach the chemical equilibrium of the reaction, the minimum temperature that has to be achieved is 2,235 K. Operating at greater temperatures will ensure that the products of the reaction are fully separated. Normally, this thermal energy is supplied by either a nuclear reactor or a concentrated solar energy system.

As it is shown in the reaction, in the first step gaseous Zinc is obtained. However, the second step requires liquid Zinc. Thus, to make this process feasible, a condensation process will take place. Some studies have affirmed that fractional crystallization in a temperature-gradient tube furnace is a feasible option (Steinfeld, 2002).

The second reaction is exothermic and the heat released can be used to produce steam or melted Zinc. However, the reactants of this reaction have to be at 700 K to make the reaction feasible.

Finally, the maximum conversion efficiency is around 30% and the equipment needed to satisfy it contains: solar/nuclear reactor, quenching device, hydrolyser reactor and H_2/O_2 fuel cell (Steinfeld, 2002). An overall scheme of the cycle is displayed in Figure 2-1.
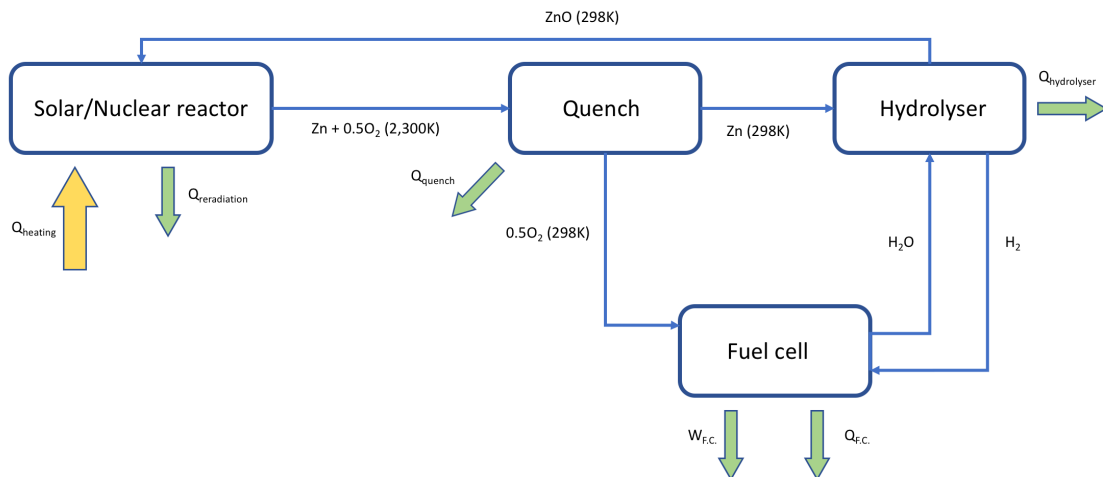
Figure 2-1. ZnO/Zn thermochemical cycle scheme

As it can be shown in the scheme, although there is an energy input to make the cycle run, there are several energy outputs that can be used. Besides, the scheme includes a fuel cell where hydrogen and oxygen, both outputs of the cycle, are used to obtain water and work, which makes the cycle more efficient.

2.3.2 Fe3O4/FeO cycle

As the previous cycle, it consists of two steps: an endothermic reduction and an exothermic water splitting process. In the previous cycle, it was also shown that the maximum temperature in the cycle was huge, as there are only two cycles, and it occurs the same in this cycle. Specifically, the maximum temperature achieved in the cycle is above 2,000 K (Nakamura, 1977). The reactions taking place in this cycle are as follows (Steinfeld, Sanders and Palumbo, 1999):

$$First\ step: Fe_3O_4(l) \rightarrow 3FeO(l) + 0.5O_2$$

$$Second\ step: 3FeO + H_2O \rightarrow H_2 + Fe_3O_4$$
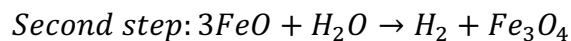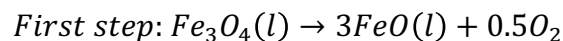
The first step of the cycle takes place in a reactor, and the thermal energy needed is normally obtained either from solar or nuclear sources. The reactants enter the reactor at ambient temperature and are heated inside until a temperature above 2,000 K is achieved. Once the reaction has finished, the products exit the reactor having an equilibrium composition.

As the products of the first step suffer huge temperatures, there is a need of cooling them down. This process takes place in the Quench. Besides, the products are separated, obtaining oxygen on one stream and FeO in other, as there are use in different processes. This product separation can be done naturally, as the phase of these ones is different.

The last part of the cycle is the water splitting, where the main output, the hydrogen, is obtained. This is an exothermic reaction that can take place at temperature values around 650 K (Steinfeld, Sanders and Palumbo, 1999). It has as reactants FeO, which was first created in the first step, and water. Besides the hydrogen production, in this step Fe_3O_4 is produced, and send it again to the first reactor.

To have an overview of the whole cycle, Figure 2-1 can be used, as this cycle is behaving in the exactly same way, although maximum temperature values are slightly bigger in the ZnO/Zn cycle.

2.3.3 S-I cycle

The sulfur-iodine cycle has been the most studied cycle to date (Giaconia *et al.*, 2007). It combines three different reactions, being the maximum temperature of 1,123 K. These reactions are (Kane and Revankar, 2008):

- Bunsen reaction (exothermic):

$$I_2(l) + SO_2(aq) + 2H_2O(l) \rightarrow 2HI(l) + H_2SO_4(aq)$$
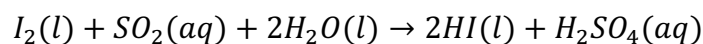
- Sulfuric acid decomposition (endothermic):

$$H_2SO_4(g) \rightarrow H_2O(g) + SO_2(g) + \frac{1}{2}O_2(g)$$
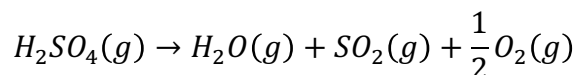
- Hydrogen iodide decomposition (endothermic):

$$2HI(l) \rightarrow H_2(g) + I_2(l)$$
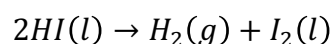
As it can be seen, the cycle is composed of two endothermic reactions, being the sulfuric decomposition the most critical one, according to the temperature. Besides, there is an exothermic reaction which follows a Bunsen reaction.

The Bunsen reaction can take place at mid temperatures (372 K) and hydriodic and sulfuric acid are obtained as products. These two acids are the main inputs for the following reactions, which produce oxygen and hydrogen (Giaconia *et al.*, 2007). Besides, this reaction is the most studied part of the cycle, being known that the overall efficiency of the process depends on the H_2SO_4 decomposition (Huang and T-Raissi, 2005). The most efficient cycle was developed in the University of Montreal, being 75.6% (Ozturk, Hammache and Bilgen, 1995). Comparing this efficiency with the one achieved by the two-step water splitting cycles, is obvious that adding steps to the cycles not only decrease the maximum temperature, but also increase the efficiency of the process. The whole process is summarised in Figure 2-2.
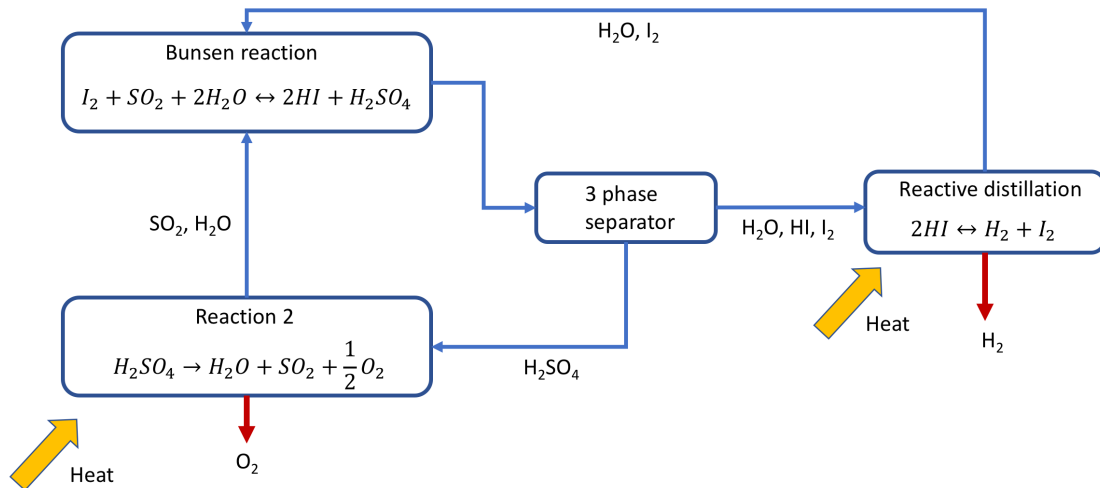
Figure 2-2. Sulfur - Iodine cycle scheme

Although it is a very promising cycle, some improvements are in further research. The main problem of this cycle is the reliability of thermodynamic models.

2.3.4 UT-3 cycle

The UT-3 cycle was developed in the University of Tokyo a few decades ago and it is also known as one of the most promising cycles for hydrogen production (Aochi *et al.*, 1989). It consists on 4 reactions, being the maximum temperature 1033 K, necessary to ensure a complete conversion of all the reactants into

products. Besides, all reactants are in either solid or gaseous phase. The reactions taking place inside the cycle are (Sakurai *et al.*, 1996):

$$(1)\ CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$$

$$(2)\ CaO(s) + Br_2 \rightarrow CaBr_2(s) + 0.5O_2(g)$$

$$(3)\ Fe_3O_4(s) + 8HBr(g) \rightarrow 3FeBr_2(s) + 4H_2O(g) + Br_2(g)$$

$$(4)\ 3FeBr_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HBr(g) + H_2(g)$$
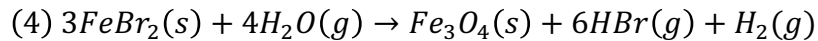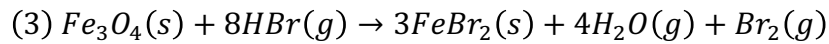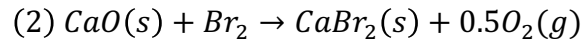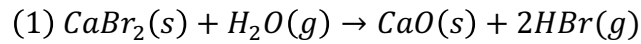
The temperatures inside each reaction are 1033 K, 845 K, 493 K and 833 K, respectively. The way this cycle works is by passing only the gaseous products through the different reactors, while the solid reactants are maintained inside each reactor, as it is displayed in Figure 2-3.

When developing this cycle, it was assumed that the reactors were adiabatic. Hence, some heat exchanger are needed to either supply or absorb the heat needed in each stream (Sakurai *et al.*, 1996).
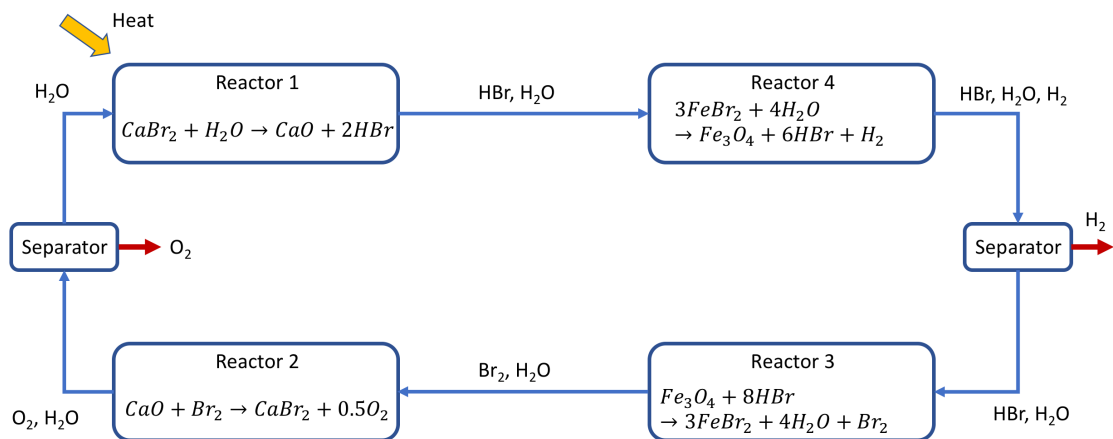
Figure 2-3. UT-3 cycle scheme

2.3.5 Westinghouse cycle (Ispra Mark 12)

The Westinghouse cycle is a hybrid thermochemical/electrochemical cycle for hydrogen production. The process consists of two chemical reactions, which are run by either thermal or electrical energy. The reactions are the following (Farbman and Corporation, 1979):

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- Oxygen production by means of a thermal reduction of sulfuric acid:

$$H_2SO_4 \rightarrow H_2O + SO_3 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$$
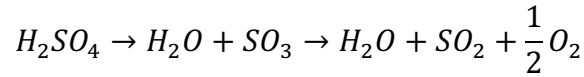
- Depolarization of the electrolyzer's anode:

$$2H_2O + SO_2 \rightarrow H_2 + H_2SO_4$$
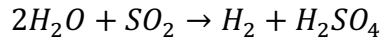
Besides, the reactions of the electrolyzer are (Brecher, Spewock and Warde, 1977):

$$Cathode: 2H^+ + 2e^- \rightarrow H_2 \quad [0\ Volts]$$

$$Anode: H_2SO_3 + H_2O \rightarrow 2H^+ + H_2SO_4 + 2e^- \quad [-0.17\ Volts]$$
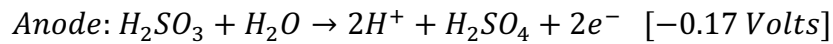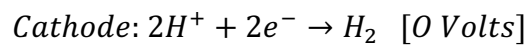
While the sulfuric acid reduction needs a heat source to run (complete reaction occurs at 1,123 K), the depolarization needs electric power. However, as it is a hybrid cycle, the power required is a 15% of that required for conventional electrolyzers, giving an overall efficiency of nearly 50% (Farbman and Corporation, 1979). The process of the cycle is displayed in Figure 2-4.
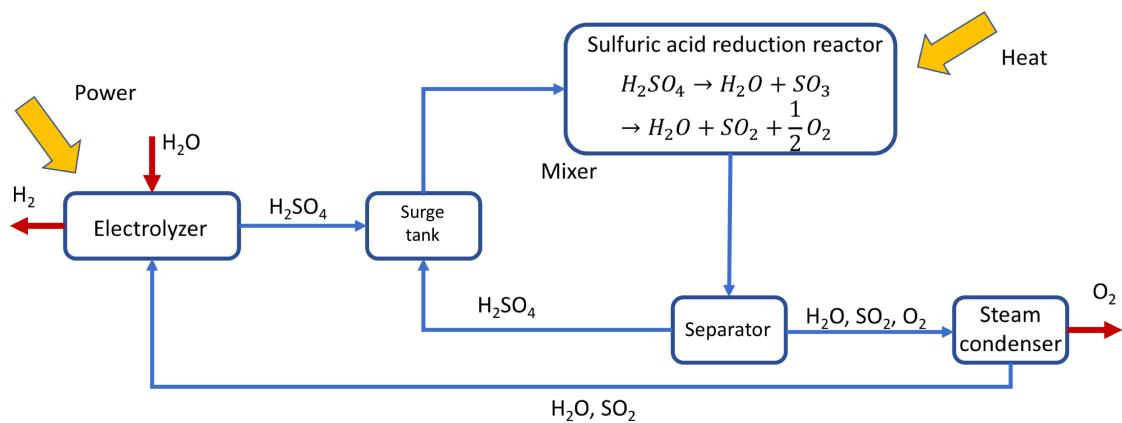
Figure 2-4. Westinghouse cycle scheme

2.4 **Cycles comparison**

In the following project, some of the most promising cycles are going to be analysed. In Table 2-2, a summary of some of the best and more studied cycles

are listed. Therefore, this table will be useful to decide which cycles are more suitable to be analysed deeply.

Table 2-2. Cycles comparison

Cycle	Reactions	Nº reac	Max. temp. (K)	η (%)	Type
Zn/ZnO	$ZnO(s) \rightarrow Zn(g) + 0.5O_2$ $Zn(l) + H_2O \rightarrow H_2 + ZnO$	2	2,300	30	Two-step
Fe₃O₄/FeO	$Fe_3O_4(l) \rightarrow 3FeO(l) + 0.5O_2$ $3FeO + H_2O \rightarrow H_2 + Fe_3O_4$	2	2,000	-	Two-step
S-I	$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ $H_2SO_4 \rightarrow H_2O + SO_2 + 0.5O_2$ $2HI \rightarrow H_2 + I_2$	3	1,023	75.6	Multi-step
UT-3	$CaBr_2 + H_2O \rightarrow CaO + 2HBr$ $CaO + Br_2 \rightarrow CaBr_2 + 0.5O_2$ $Fe_3O_4 + 8HBr \rightarrow 3FeBr_2 + 4H_2O + Br_2$ $3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2$	4	1,033	50	Multi-step
Westing-house cycle	$H_2SO_4 \rightarrow H_2O + SO_3 \rightarrow H_2O + SO_2 + 0.5O_2$ $2H_2O + SO_2 \rightarrow H_2 + H_2SO_4$	2	1,023	50	Hybrid

2.5 **Solar energy for thermochemical hydrogen production**

As it is known, the energy sector in general is moving to a renewable energy environment, trying to avoid the use of fossil fuels. The hydrogen production sector has also studied the possibility of producing hydrogen uniquely by using renewable energy sources, specially the solar energy (Nakamura, 1977; Steinfeld, Sanders and Palumbo, 1999; Abanades *et al.*, 2006; Petrasch and Klausner, 2012).

As it has been shown in previous chapters, the thermochemical hydrogen production needs a thermal energy source in order to make some of the reactions run in the process. Normally, this heat was obtained from a nuclear reactor. Although nuclear reactors do not contaminate as fossil fuel combustion processes, it is true that is not a renewable source, as the uranium required has limited availability. Furthermore, its wastes have to be properly treated and stored for ages in order to prevent radiation contamination.

On the other hand, solar energy is the most abundant renewable energy in the world (Petrasch and Klausner, 2012). Besides, the technology has been deeply developed in the last decades and can achieve huge temperatures. Specifically, the technology available for hydrogen production is the concentrated solar energy, which obtains directly thermal energy from the panels. This technology can achieve temperatures of up to 2,000 K available in reservoirs (Steinfeld, 2005). Of course, this number change with the climate conditions, but according to the literature review of previous chapters, the temperature should be enough to run a thermochemical hydrogen production plant.

A Concentrating Solar Power (CSP) technology, consists on a number of panels reflecting the solar energy to a reservoir, which will exchange heat with the solar reactor, where the required reactions of the cycle are taking place. The technology has been used for decades and, surely, will improve the efficiency of the hydrogen production, as well as being an eco-friendly way of producing hydrogen.

Figure 2-5. Gemasolar 20MW CSP plant, Spain.

3 MATERIAL AND METHODS

In the previous section, the different types of thermochemical hydrogen production cycles were explained. The aim of this project is now to make a model of one of the cycles to discuss its performance and make an economic analysis.

3.1 ASPEN PLUS

To study the cycles, a powerful software is needed. Hence, the first step is to find the appropriate software to make the calculations and describe the main parts that are going to be used. The most used software in chemical engineering are HYSYS, ASPEN PLUS and PRO/II. All of them can work under steady-state or dynamic simulations and are more than enough powerful to run the simulations that this project needs.

In particular, ASPEN PLUS is one of the most used software, as a lot of research have been done using it (Sakurai *et al.*, 1996; Huang and T-Raissi, 2005; Chukwu, 2008; Kane and Revankar, 2008). Although all of the software named are suitable for this project, it seems that ASPEN PLUS is used a lot for this kind of applications, according to past papers. Thus, it will be the software used.

However, ASPEN has a huge number of libraries that can be used and hence, the parts that are going to be used in the project need to be explained.

Firstly, one of the most important parts of the model will be the reactors. The software includes seven different reactors. There are really complex ones, but, as the reactions of the process are known, the stoichiometric reactor will be used (RStoic). Besides, it allows to introduce the extent of reaction or conversion to make the model more actual (Aspen Technology, 2000).
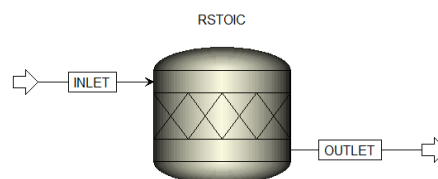
Figure 3-1. RStoic reactor block

Another important part inside the model will be the separators. As reactors, ASPEN includes a few options to separate mixtures. In particular, as the complexity of the cycle is not really high, the ideal separator will be used (Sep). With this block, only the splits have to be added, so the mixture can be separated ideally ({Aspen Technology, 2000). However, there are some mixtures that need to be treated in order to split them into different components. This block does not do this, and it will have to be taken into account for the correct performance of the cycle.
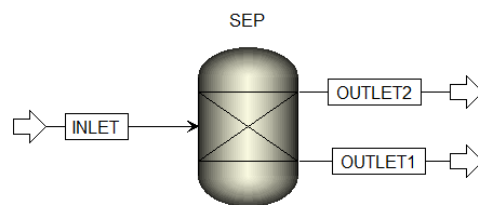
Figure 3-2. Dep separator block

Besides, as it was explained in the literature review, these cycles require a huge temperature to be run. Hence, a block to add and subtract heat from the different reactors and pipes must be add. Of course, these blocks are heat exchangers and, as it has happened with the other blocks, there are also different options. On the one hand we have the heater, which only adds or subtracts the heat duty specified by the user. On the other hand, the HeatX block allows the user to make calculations with two-stream heat exchangers, being able to change the kind of heat exchanger (Aspen Technology, 2000).
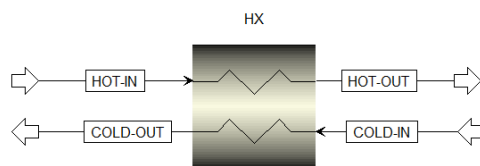
Figure 3-3. Heat exchanger block

Finally, it will also be use a combination of systems to increase/decrease the pressure of the system depending on the specific requirements in each section.

3.2 **Building the cycle**

In the following chapter, it will be explained how the cycle is built. However, firstly one of the cycles described in the literature review has to be choose. According to the literature review, there were three different type of cycles: two-step, multi-step and hybrid cycles. As it was said, the two-step water splitting cycles require an incredibly big temperature to be run, and for this reason will be discarded. On the other hand, although seems a really interesting option, hybrid cycles need electric power to be run. This means that they are slightly out of the scope of the project, as the main idea is to study pure thermochemical cycles.

Hence, seems fair to choose between one of the multi-step thermochemical cycles described on previous chapters (S-I or UT-3). On the one hand, the Sulphur-Iodine cycle has a good efficiency and one reaction less than UT-3 cycle, which seems a good reason to choose this as the cycle to study. However, once inside each of the cycles, it appears that the complexity of the Sulphur-Iodine cycle is much bigger than UT-3 one, although it has one more reaction. For this reason, it will be the UT-3 cycle the one studied in the following chapters.

According to Figure 2-3, the main components of this cycle are four reactors where the four reactions will take place, some heat exchangers and two main separators where oxygen and hydrogen are obtained, which are the main outputs of the cycle.

The flowsheet of the model is displayed in Figure 3-4. As it is shown, the cycle starts with an inlet stream where water is feed in the cycle. This water is pumped (PUMP1) to achieve the pressure required for the process, which is 20 bar (Sakurai *et al.*, 1996). Then, the water is mixed firstly with the water excess from the cycle (MIXER1) and then with the reactants (MIXER2) which are totally recycled.

The whole mixture enters inside REACTOR1, being heated before by HEATER1 until the temperature required, which is around 700ºC (Kameyama *et al.*, 1992). As it is shown in Table 3-1, after this first reaction there is a mixture of vapour and solid phase. Before feeding this mixture into REACTOR4, it has to be cooled,

since the temperature required for the second reaction is 570ºC (Kameyama *et al.*, 1992).

Once this reaction is completed, hydrogen is produced and needs to be separated from the whole mixture. The problem with this separation is that HBr and hydrogen are mixed in the vapour phase. Both components have low fusion point (-250ºC for hydrogen and -67ºC for HBr) which means that is not feasible to condensate HBr to separate it. Hence, although to simplify the model it has not been added, the best way of separating this mixture would be a membrane. After this separation, it can be affirmed that nine kilograms of water are needed to produce one kilogram of hydrogen.

After this separation, the mixture arrives to the exothermic reactors. Hence, the temperature needs to be decreased again by means of HEATER2 until 200ºC, which is the temperature needed to run the third reaction, taking place at REACTOR3 (Kameyama *et al.*, 1992).

For REACTOR2, the last one of the cycle and where the oxygen is produced, the temperature needs to be increased again until 823 K (Kameyama *et al.*, 1992). After it, the oxygen produced needs to be separated from the whole mixture, as it happened before with the hydrogen. In this case, it is a mixture containing water, oxygen and some solid reactants. In this case, is totally feasible to condensate water before the separation in order to have three different phases in stream 11A. HEATER 3 is in charge of decreasing cooling down the mixture to obtain an additional liquid phase, as it is shown in Table 3-1. After this separation, it can be demonstrated that for each kilogram of hydrogen produced 8 additional kilograms of oxygen are also formed.

Finally, the last steps are mixture treatments in order to recycle the water excess and the reactants, which are totally recycled as it is displayed in the flowsheet.
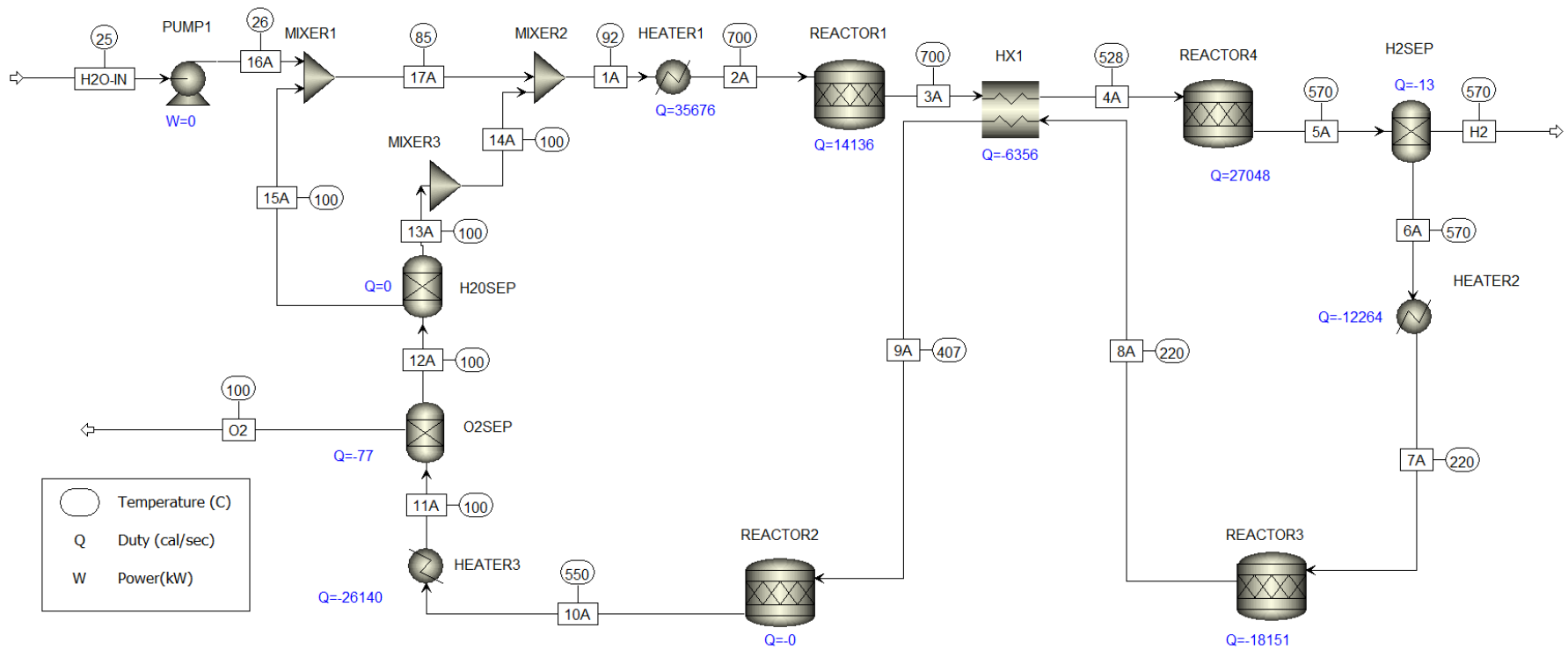
Figure 3-4. UT-3 cycle flowsheet

Table 3-1. Data from the flowsheet from Figure 3-4

Stream Name	Units	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	H2	H2O-IN	O2
Pressure	bar	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	1	20
Mass Vapor Fraction		0,0	0,1	0,2	0,2	0,7	0,7	0,7	0,2	0,2	0,09	0,02	0,0	0,0	0,0	0,0	0,0	0,0	1,0	0,0	1,0
Mass Liquid Fraction		0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,08	0,08	0,0	0,0	1,0	1,0	1,0	0,0	1,0	0,0
Mass Solid Fraction		0,9	0,9	0,8	0,8	0,3	0,3	0,3	0,8	0,8	0,91	0,9	0,92	1,0	1,0	0,0	0,0	0,0	0,0	0,0	0,0
Mole Flows	kmol/hr	9	9	10	10	11	10	10	9	9	8,5	8,5	8	4	4	4	1	5	1	1	0,5
CaBr2	kmol/hr	1	1	0	0	0	0	0	0	0	1	1	1	1	1	0	0	0	0	0	0
H2O	kmol/hr	5	5	4	4	0	0	0	4	4	4	4	4	0	0	4	1	5	0	1	0
CaO	kmol/hr	0	0	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0
HBr	kmol/hr	0	0	2	2	8	8	8	0	0	0	0	0	0	0	0	0	0	0	0	0
FeBr2	kmol/hr	3	3	3	3	0	0	0	3	3	3	3	3	3	3	0	0	0	0	0	0
Fe3O4	kmol/hr	0	0	0	0	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0
H2	kmol/hr	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
Br2	kmol/hr	0	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0
O2	kmol/hr	0	0	0	0	0	0	0	0	0	0,5	0,5	0	0	0	0	0	0	0	0	0,5
Mass Flows	kg/hr	936,9	936,9	936,9	936,9	936,9	934,9	934,9	934,9	934,9	934,9	934,9	918,9	846,9	846,9	72,1	18,0	90,1	2,0	18,0	16,0
CaBr2	kg/hr	199,9	199,9	0,0	0,0	0,0	0,0	0,0	0,0	0,0	199,9	199,9	199,9	199,9	199,9	0,0	0,0	0,0	0,0	0,0	0,0
H2O	kg/hr	90,1	90,1	72,1	72,1	0,0	0,0	0,0	72,1	72,1	72,1	72,1	72,1	0,0	0,0	72,1	18,0	90,1	0,0	18,0	0,0
CaO	kg/hr	0,0	0,0	56,1	56,1	56,1	56,1	56,1	56,1	56,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
HBr	kg/hr	0,0	0,0	161,8	161,8	647,3	647,3	647,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
FeBr2	kg/hr	647,0	647,0	647,0	647,0	0,0	0,0	0,0	647,0	647,0	647,0	647,0	647,0	647,0	647,0	0,0	0,0	0,0	0,0	0,0	0,0
Fe3O4	kg/hr	0,0	0,0	0,0	0,0	231,5	231,5	231,5	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
H2	kg/hr	0,0	0,0	0,0	0,0	2,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	2,0	0,0	0,0
Br2	kg/hr	0,0	0,0	0,0	0,0	0,0	0,0	0,0	159,8	159,8	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
O2	kg/hr	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	16,0	16,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	16,0

3.3 **Heat recovery system**

In the previous chapter, it was explained how the main part of the project, the UT-3 cycle, was developed. However, the cycle can afford some changes that will improve its performance.

Firstly, it is important to understand the importance of the heat exchanger HX1. According to Figure 2-3, there were two different heat exchangers between the reactors. However, as one of the streams needs to be heated and the other one cooled, it makes sense to use the heat released from one to heat the other one. This aspect will increase the efficiency of the system, as it will be explained in following chapters.

Moreover, as it is shown in Figure 3-4. UT-3 cycle flowsheet, there are some components of the systems that release some heat, making the overall system's efficiency lower. The idea of this chapter, is to develop a heat recovery system using ASPEN PLUS, where that heat can be used, improving the efficiency of the system.

It has been chosen a combined cycle generation system as the best option for this project. This technology consists of a heating chamber where a fluid is transformed into gas at high pressure, getting this gas inside a gas turbine where some electricity is obtained. As it can be imagined, this complementary cycle is really simple and is totally adaptable to the thermochemical hydrogen production system.

Before analysing the cycle, the heat release by each of the components is displayed in Table 3-2. As it can be seen, the heat released by these components is not negligible.

Table 3-2. Heat released per kmol of hydrogen produced

Component	Q (kW)
HEATER2	51.35
REACTOR3	76
HEATER3	109.44
TOTAL	236.79

The proposed combined cycle, which is displayed in Figure 3-5 is run by CO2 as working fluid and it consists of a single step turbine process. However, the energy required and the work released by this system depends in huge quantity of the mass flow of CO2 that flows through the cycle. The aim of this model is to improve the efficiency of the hydrogen production model; hence, the exact mass flow of CO2 needs to be calculated in order to feed the heat recovery model with the same amount of heat released by the UT-3 cycle.

A relationship between CO2 mass flow and the heat needed by the cycle has to be found. To do so, some simulations will be run with different mass flows and then these results will be plotted in Figure 3-6.
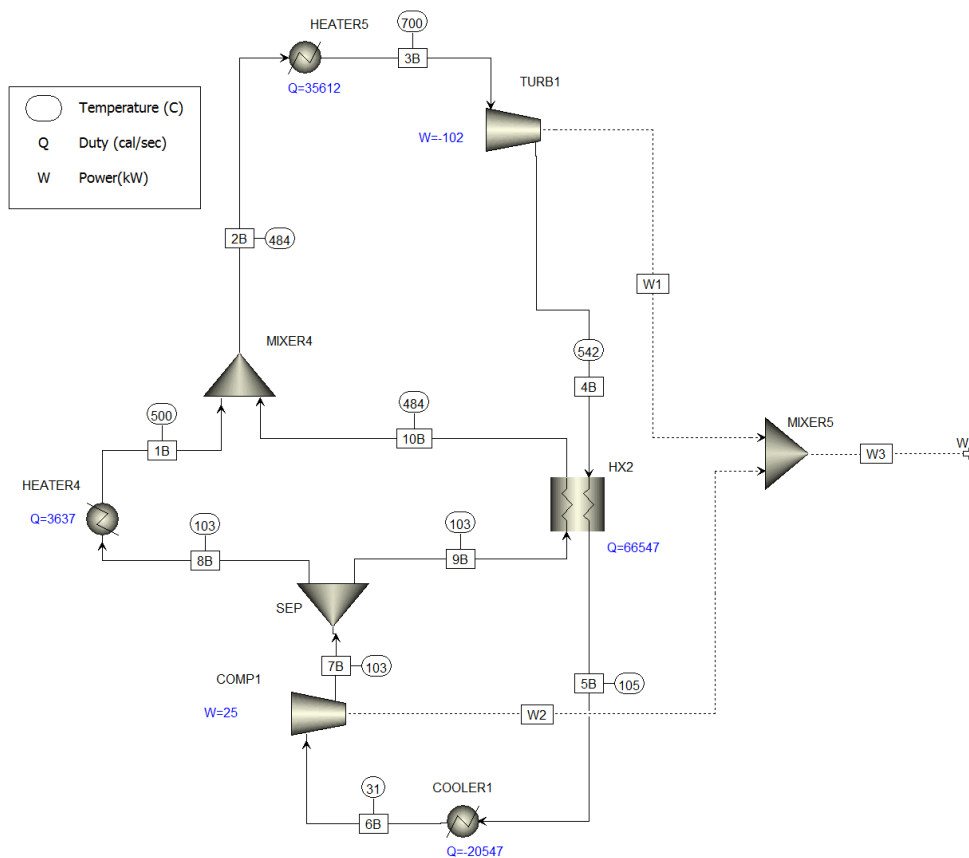

Figure 3-5. Heat recovery system for the UT-3 cycle

Table 3-3. Data from flowsheet shown in Figure 3-5

Stream Name	Units	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B
Pressure	bar	250	250	250	77,31	77,31	74	250	250	250	250
Mass Flows	kg/hr	98,01	1960,2	1960,2	1960,2	1960,2	1960,2	1960,2	98,01	1862,19	1862,19

As it can be seen in Figure 3-6, the relationship between the heat needed by the heaters and the CO_2 mass flow needed is directly proportional, drawing a straight line. Hence, it is easy to calculate the mass flow required to "connect" both heats. Hence, the CO_2 mass flow that will go through the cycle will be 32.67 kg/minute, or 1960.2 kg/hr, as it is shown in Table 3-3.
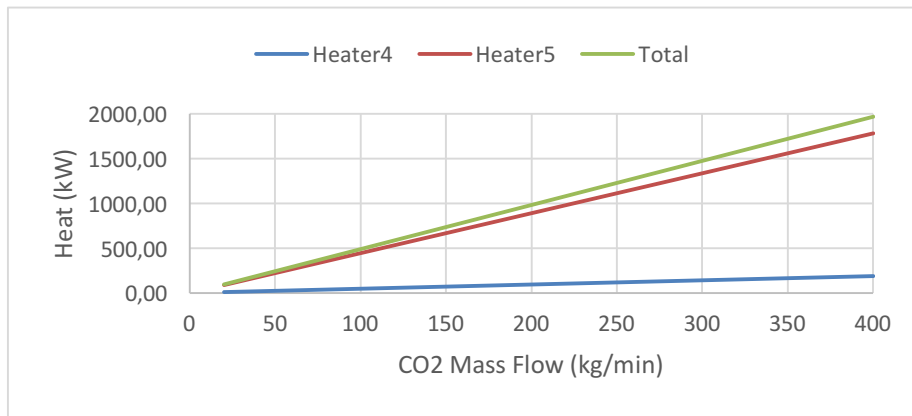
Figure 3-6. Heat variation with CO2 mass flow changes for the heat recovery model

On the other hand, as it can be seen in Figure 3-5, the cycle is quite simple. The heat released from the UT-3 cycle will be feed into HEATER4 and HEATER5, needing more heat duty the second one, as the target temperature is bigger. After these temperatures increasing, the working fluid is at large pressure and temperature. This energy contained in the fluid is recovery in a turbine, which gives around 100 kW. As the fluid still has some thermal energy, HX2 is installed to exchange this heat to the high-pressure stream. Then, a compressor COMP1 is needed to increase the pressure again and restart the cycle. Of course, this compressor needs some work to be run, which is taken from the turbine, having a final work of 77 kW.

As it is shown in the flowsheet, there are several temperature changes along the cycle. It is worth to note that these temperatures can be different. The criteria used to choose these temperatures is, on the one hand, to increase the temperature in two more or less equal steps. On the other hand, the maximum temperature achievable by the turbine blades has also been respected, being this one 1300 K (Culham, 2012).

3.4 UT-3 cycle + Heat Recovery System

In previous sections, it was explained the thermochemical hydrogen production cycle and a way of recovering the heat released by the system. However, joining both systems to form a whole one is not easy. In this section, it will be explained the way to take advantage of the heat released in the most efficient way, which is the Pinch Point technology.

From both systems (UT-3 and Heat Recovery System) there are some streams that have to be either heated or cooled. The main parameters of each stream are displayed in Table 3-4.

Table 3-4. Streams to be joint

Stream	Type	T_s (ºC)	T_t (ºC)	C_p (kJ/kgK)	Mass-Flow (kg/s)	CP (kW/K)
HEATER2	Hot	570	220	0.64	0.26	0.1664
HEATER3	Hot	550	100	0.57	0.26	0.1482
HEATER4	Cold	103	500	2.13	0.027	0.0575
HEATER5	Cold	490	700	1.26	0.54	0.6804

Firstly, in the table it can be seen that hot streams are the ones that temperature is decreasing, while cold ones is increasing. It is also worth to explain the way the value CP has been calculated:

$$CP = C_p \cdot MassFlow \tag{3-1}$$

The method chosen to join these streams is the pinch technology, which is based on getting a pinch temperature that makes the system as efficient as possible. Firstly, a minimum temperature difference has to be set, in this case will be 283 ºK Knowing this value, it is obtained that the "pinch point" is 768 K being 124.4

36

kW the minimum heat supplied by hot utilities, and 83.6 kW the minimum heat removed by cold utilities.
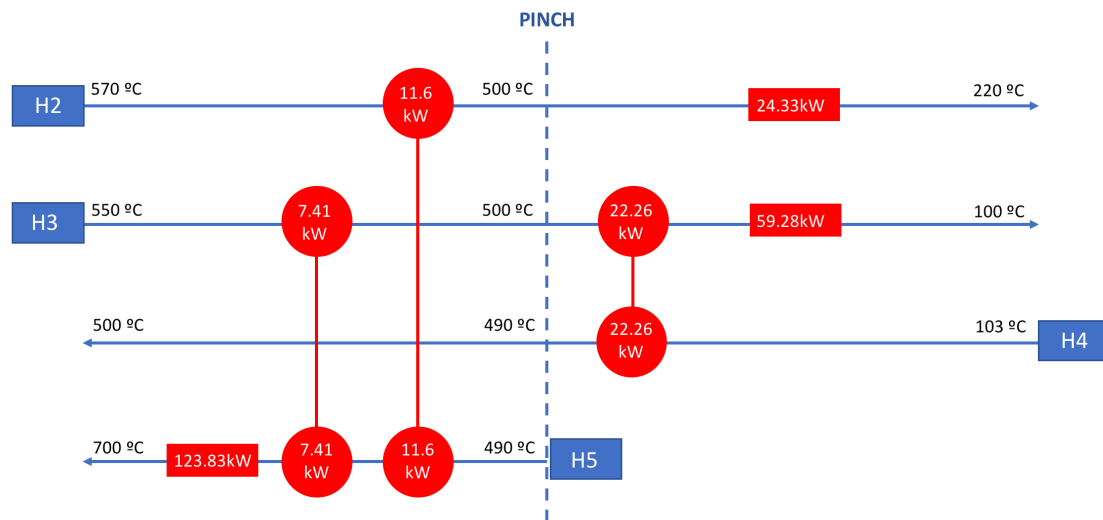
Figure 3-7. Grid diagram

In Figure 3-7 it is displayed the most efficient way of merging the streams in order to supply the minimum heat by coolers and heaters. As it is shown, stream H5 needs 123.83 kW to achieve the target temperature of 973 K. On the other hand, streams H2 and H3 need 24.33 kW and 59.28 kW respectively to be cooled until their target temperatures.

The way of implementing this in the model is by means of heat exchangers, where the outlet temperature of one of the streams is specified and ASPEN PLUS makes the remaining calculation. Specifically, as it is displayed in Figure 3-8, heat exchangers HX2, HX3 and HX4 are in charge of achieving the target temperatures shown in Figure 3-7.
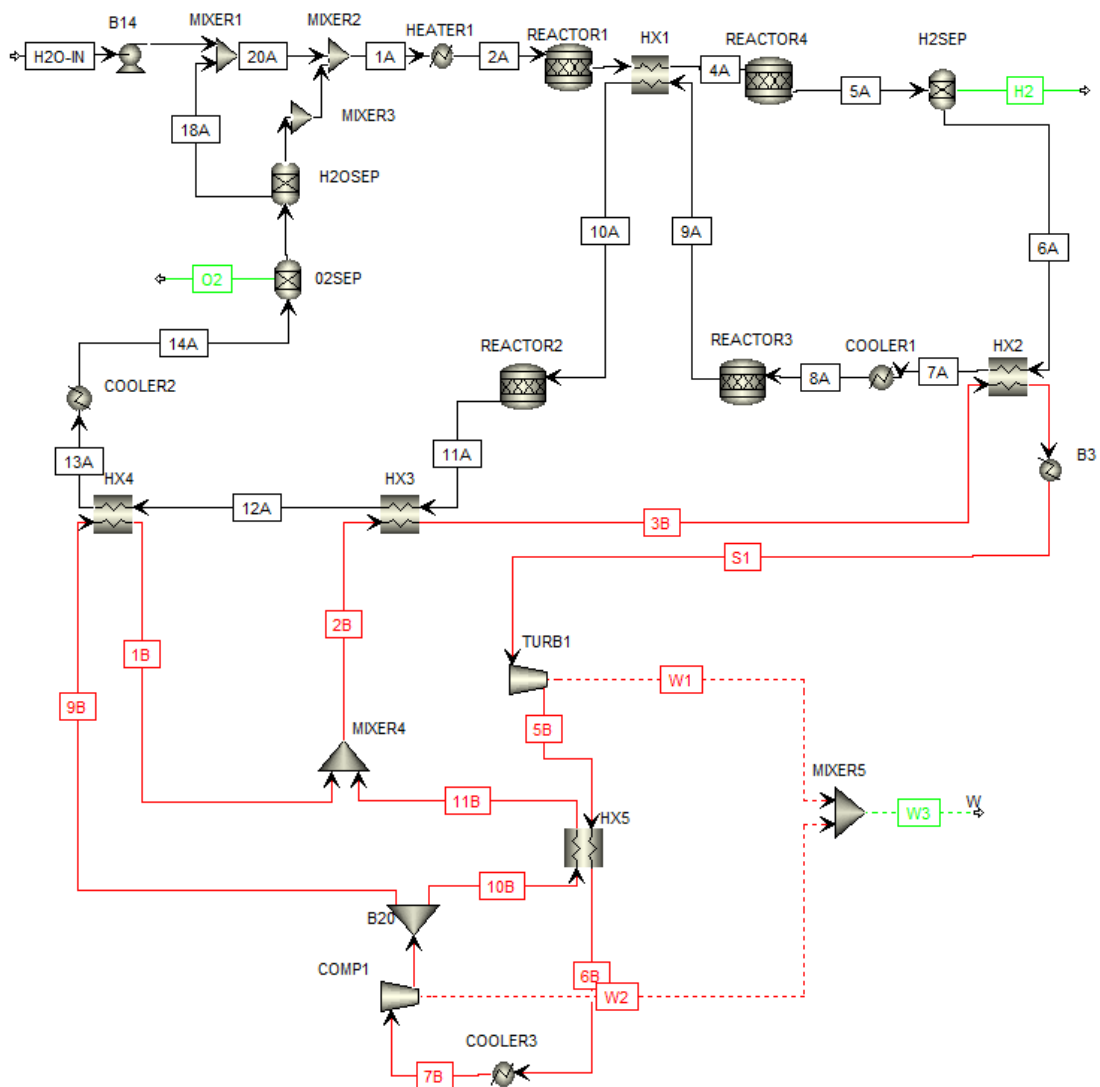
Figure 3-8. Hydrogen production + Heat Recovery System Flowsheet

3.5 Power from hydrogen

In the previous chapter, it was displayed an option to join the hydrogen production cycle with the heat recovery system. Then, the last step to make the overall cycle complete is design a system to obtain power from hydrogen. The possible options are:

- Solid Oxide Fuel Cells (SOFC): this system consists of joining oxygen and hydrogen to produce electricity. However, it is a really complex model to develop in ASPEN PLUS, as cathode and anode blocks have to be designed separately, which makes the model really complex. Hence, as it

is not the main objective of the project to obtain power from the hydrogen, but to produce hydrogen; this method is discarded.

- Gas turbine cycle with hydrogen as a fuel: this method is much simpler and based on the commercially-available technology. It consists of a combustion chamber where hydrogen is burned in the presence of air at high pressure. The flue gasses pass through a turbine, obtaining work. As this method is also quite efficient and the flue gasses are mainly water vapour, it is the system that it is going to be design.
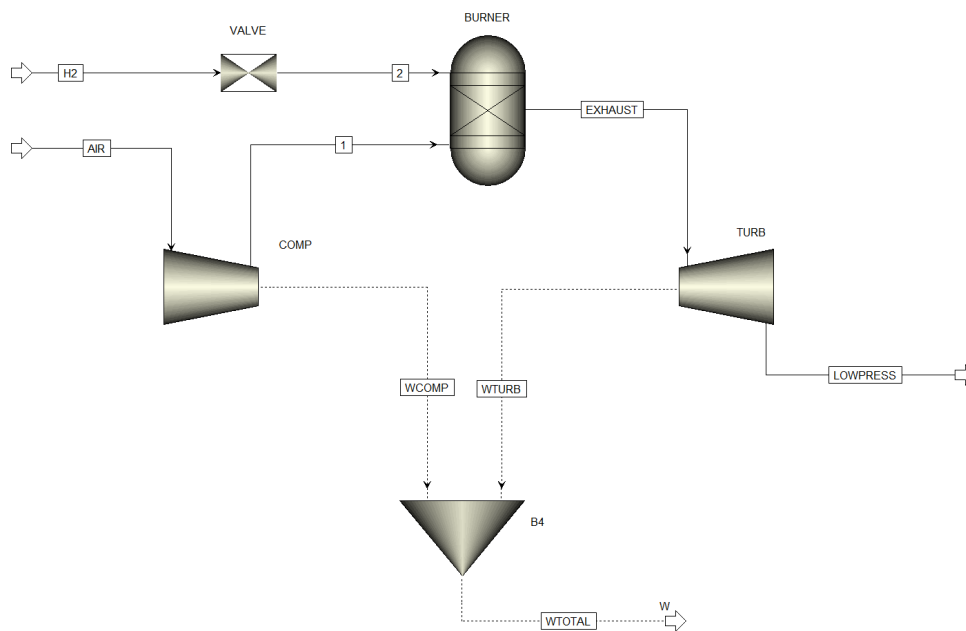
Figure 3-9. Open gas turbine cycle flowsheet

In Figure 3-9 it is displayed the model designed. As it can be seen, there are two inlets in the system: the hydrogen produced in the UT-3 cycle and air at atmospheric conditions. This air is compressed before entering in the combustion chamber, where hydrogen is burned. Then, in the exhaust stream there will be water and nitrogen, as it is not burned. This stream, at high pressure, is then pass through a turbine, obtaining some work.

However, there are some parameters that have to be obtained to make the cycle perform as efficient as possible. On the one hand, the pressure ratio (r_p) has to

be design, knowing that this value affects directly to the efficiency of the cycle. The maximum pressure ratio achievable is (Culham, 2012):

$$r_p = \left(\frac{T_{max}}{T_{min}}\right)^{\frac{k}{2k-2}}$$

(3-2)

Being k the isentropic coefficient of air, which will be assume as 1.4 at any temperature. The minimum temperature is the atmospheric temperature at which air enters the system, and the maximum temperature is given by the resistance of turbine blades, which is around 1300K for common blades (Culham, 2012). Then, it is obtained that the maximum pressure ratio is:

$$r_p = \left(\frac{1300}{298}\right)^{\frac{1.4}{2 \cdot 1.4 - 2}} = 13.17$$

(3-3)

Another parameter that has to be obtained is the air/fuel ratio for the hydrogen combustion. This ratio is around 34:1 for stoichiometric conditions (Walter, 2001). However, this ratio is the minimum air needed to run the combustion process. To control the temperature of the exhaust gasses, a specification will be installed in the model to make the air flow vary, being always greater than the stoichiometric ratio. Hence, some oxygen excess will happen in the combustion process.

Table 3-5. Hydrogen gas turbine data

Stream Name	Units	1	2	AIR	EXHAUST	H2	LOWPRESS
Temperature	C	375,4	570,0	25,0	1026,9	570,0	443,8
Pressure	bar	13,17	13,17	1	13.17	20	1
Mass Enthalpy	cal/gm	86,74	1892,88	0,00	2718,45	3815,81	-1976,89
Mass Entropy	cal/gm-K	0,05	1,08	0,03	0,23	0,67	0,25
Mass Flows	kg/hr	313,98	2	313,98	315,98	2	315,98
H2	kg/hr	0,00	2,00	0,00	0,00	2,00	0,00
N2	kg/hr	248,04	0,00	248,04	248,04	0,00	248,04
O2	kg/hr	65,94	0,00	65,94	50,06	0,00	50,06
H2O	kg/hr	0,00	0,00	0,00	17,87	0,00	17,87

4 RESULTS

In the previous chapter, the main parts of the hydrogen production process were presented. Firstly, an UT-3 cycle was developed and then, some improvements were suggested to improve the efficiency and the realism of the project. In the following chapter, the results of the main parts of the project will be analysed independently and as a whole model.

4.1 **UT-3 cycle**

This thermochemical method of hydrogen production was presented in the previous chapter, and the main flowsheet of the model is displayed in Figure 3-4. The process followed by the cycle was also explained in another chapter, however, when studying these kind of models, some parameters such as the efficiency of the hydrogen production or the hydrogen production capacity must be evaluated.

On the one hand, the efficiency of the system is one of the most important parameters to consider. As it was shown in the flowsheet of the model, there are some heat inputs and outputs that might vary the efficiency of the process. Besides, it has to be remind that this cycle has been deeply studied, being the maximum efficiency 50%.

To calculate the efficiency of the system, the following formula will be used:

$$EFF(\%) = \frac{H_2 \, Energy}{Thermal \, energy \, input} x100 \qquad \textbf{(4-1)}$$

Firstly, to calculate the energy supplied by the hydrogen produced, it needs to be obtained the Lower Heating Value (LHV) for hydrogen, which is 119,909 kJ/kg; and the mass flow of hydrogen (0.00056 kg/sec):

$$H_2 \, Energy = LCV \cdot \dot{m} = 119,909 \cdot 0.00056 = 67.145 \, kW \qquad \textbf{(4-2)}$$

On the other hand, according to the flowsheet, the components that need heat are:

Table 4-1. Heat inputs per kmol of hydrogen produced

Component	Heat input (kW)
HEATER1	149.37
REACTOR1	59.18
REACTOR2	113.24
TOTAL	321.79

Hence, the efficiency of the system is:

$$EFF = \frac{67.145kW}{321.79kW} x100 = 20.87\%$$

(4-3)

As it is shown, this first efficiency is extremely low compared with the maximum efficiency achieved for this process. However, it is worth highlighting that there is also some heat released (236.79 kW), as it shows Table 3-2. Moreover, in previous chapters a way of recovering this heat was explained, and it will also be shown how this recovery system increases the efficiency of the process.

It is also worth to say that the heat released per kmol/hour of hydrogen is the sum of the heat released by HEATER2, HEATER3 and REACTOR3. As it is displayed in Figure 3-4, there are other blocks that release some heat, such as H2SEP or O2SEP. However, this heat is negligible compared with the one discharged by the other blocks. Then, this heat released is 236.78 kW/kmol H_2 produced. It has also been proved that the heat released and heat needed to run the cycle are directly proportional to the amount of hydrogen produced. Hence, the efficiency of the model stays the same whatever quantity of hydrogen is produced.

4.2 Heat Recovery System

In this chapter, it will be shown how applying this technology to the hydrogen production cycle, the efficiency is increased. Firstly, the behaviour of the cycle has to be studied. To do so, a chart plotting temperature and entropy will be study. With this chart, it will be possible to know if the model describes a correct performance, and also associate it with a known cycle.

Some of the most important data for this cycle is displayed in Table 4-2.

Table 4-2. Main data from heat recovery system (streams from Figure 3-5)

Stream	Pressure (bar)	Temperature (ºC)	Entropy (kJ/kgK)	Enthalpy (kJ/kg)
7B	250	103.94	-1.1	-9037.04
3B	250	700	0.23	-8223.54
4B	77.31	542.48	0.25	-8412.27
6B	74	31.25	-1.12	-9081.95
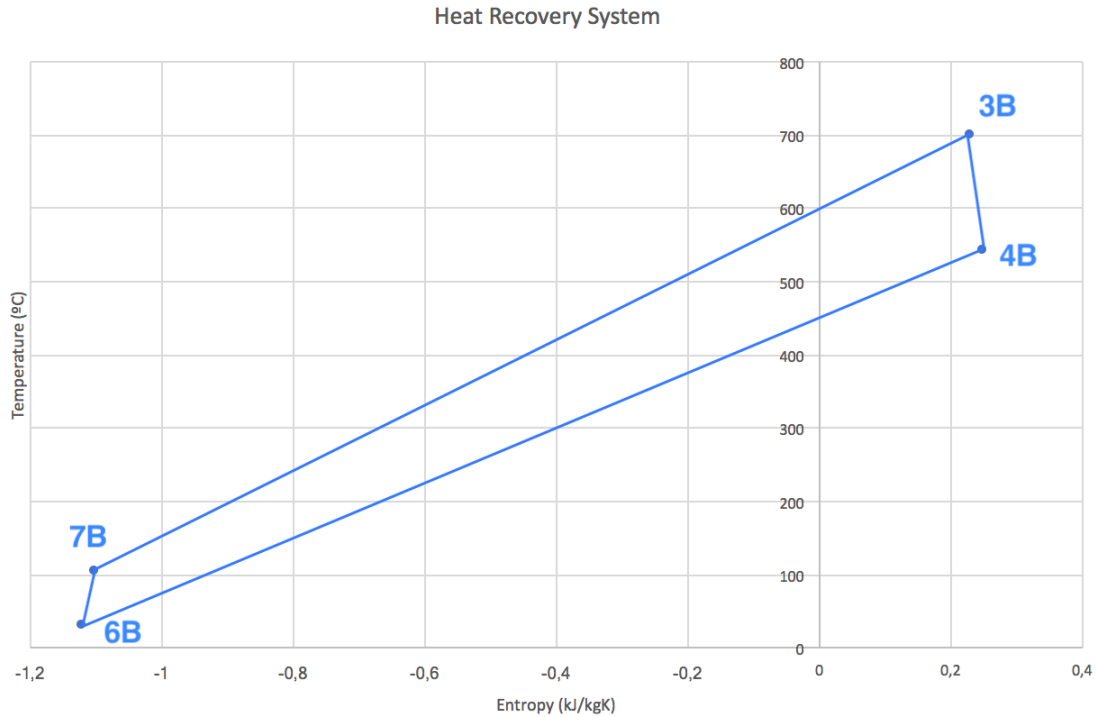
Figure 4-1. Heat recovery system diagram of performance

Regarding Figure 4-1, it is totally clear that it is a closed-circuit gas turbine, as the T-S diagram is quite similar (Horlock and Bathie, 2004). Moreover, this diagram displays what is called a Brayton cycle.

Besides, regarding the formula used to obtain the maximum pressure ratio; it can be proved that the pressure ratio used for this cycle is below the maximum:

$$r_p = \left(\frac{T_{max}}{T_{min}}\right)^{\frac{k}{2k-2}} = \left(\frac{700 + 273}{31.25 + 273}\right)^{\frac{1.4}{2 \cdot 1.4 - 2}} = 7.65 \qquad \textbf{(4-4)}$$

As it is shown, the maximum pressure ratio is 7.65, while the pressure ratio used for this model is 3.38.

On the other hand, calculate the efficiency of this cycle is extremely simple, as the power output only needs to be divided by the heat input, as it is shown in the following expression:

$$EFF = \frac{W}{Q}x100 = \frac{77kW}{164.33kW}x100 = 47\%$$

(4-5)

However, in the previous calculation different kinds of energy have been mixed, which might develop in not really actual results. Knowing the kind of cycle that is being used, the expression to get the actual efficiency is as follows (Culham, 2012):

$$EFF(\%) = \left(1 - (r_p)^{\frac{1-k}{k}}\right)x100$$

(4-6)

To calculate this new efficiency, the parameter "k" has to be firstly calculated. This parameter is the ratio between the heat capacity at constant pressure and at constant volume ($k=C_p/C_v$). These values can be exported from ASPEN, obtaining $k=2.37$. Hence, the efficiency is:

$$EFF(\%) = \left(1 - (3.38)^{\frac{1-2.37}{2.37}}\right)x100 = 50.54\%$$

(4-7)

After calculating the efficiency of the isolated system, it is time to prove that it actually improves the efficiency of the hydrogen production model. To calculate this efficiency:

$$EFF = \frac{P_H + P_{HRS}}{Q_{UT-3} + Q_{HRS}}x100 = \frac{66.62kW + 77kW}{321.8kW + 130.88kW}x100 = 31.73\%$$

(4-8)

Hence, the production of hydrogen using the heat recovery system is now more than 10% greater.

4.3 Power from Hydrogen

After analysing the results from the hydrogen production and the heat recovery system proposed; it is time to evaluate the performance of the power generation using the hydrogen obtained. It is worth to note that the cycle used to generate this power is similar to the one used for recovering the heat, although it has some

differences. As in the previous chapter, a table summarizing the main data from the cycle will be shown, which will be helpful to plot a Temperature – Entropy diagram to evaluate the correct performance of the model.

Table 4-3. Main data from heat recovery system (streams from Figure 3-9)

Stream	Pressure (bar)	Temperature (ºC)	Entropy (Kj/kgK)	Enthalpy (Kj/kg)
AIR	1	25	0.1424	0
1	13.17	375.83	0.201	363.16
EXHAUST	13.17	1027	0.976	11381.61
LOW-PRESS	1	443.84	1.03	3104.76
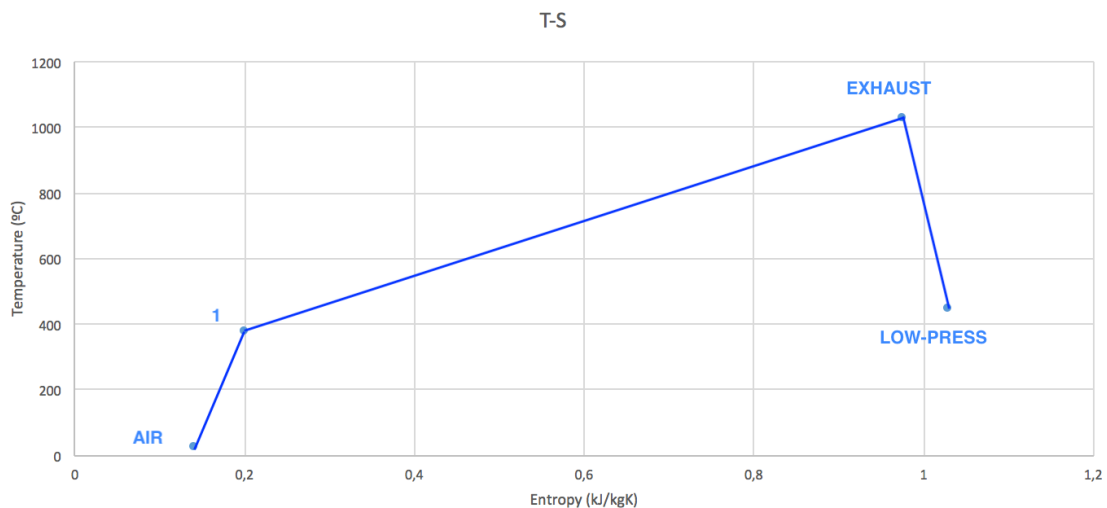
Figure 4-2. Power generation diagram of performance

As it is shown, the diagram corresponds to an open-loop gas turbine cycle (Horlock and Bathie, 2004). Here it is displayed the first difference between the heat recovery system and the power generation system, since this one operates in open loop. The main reason of this performance, is the fluid used for the cycle. In this case, the working fluid is air, which is obtained directly from the atmosphere, so it can be delivered again after one cycle. On the other hand, the heat recovery system uses as working fluid CO_2, which cannot be obtained from the atmosphere directly. Then, closing the cycle avoids obtaining the component from the air a lot of times.

On the other hand, as it was said before, the air entering the system is that to make the temperature of the stream EXHAUST exactly 1300K. As there is a

combustion taking place in this system, it will be analysed the quality of this combustion by getting the amount of oxygen used to burn the fuel (hydrogen) and the remaining oxygen. Regarding Table 3-5, the oxygen entering the system is 65.94 kg/hr. If the combustion is stoichiometric, all the oxygen should have been burned, however, it is shown that 50.06 kg/hr of oxygen have not been burned during the combustion, in other words, there is a 75.92% oxygen excess. This means that only 15.88 kg/hr are burned.

It is clear that the excess of oxygen is slightly big, however, the main reason to introduce this amount of air to the system is to refrigerate the exhaust gasses and obtain a temperature below 1300K, which is the maximum temperature that turbine blades can achieve.

Regarding the energy inputs and outputs, this system does not receive any heat sources. The main energy input is in the form of power and it is introduced to the compressor. The power needed is 33.34 kW to increase the pressure of the fluid. On the other hand, the system is giving some power as an output, in this case 59.2 kW, which are produce by the turbine.

Table 4-4. Power inputs and outputs from gas turbine cycle

POWER (kW)	
COMPRESSOR	33.34
TURBINE	-59.2
NET POWER	-25.86

As it is shown in Table 4-4, the net power output is 25.86 kW delivered (negative). There are several ways of calculating the efficiency of this cycle. On the one hand, it can be calculated the energy that the hydrogen had before entering the cycle, which can be calculated obtaining the low heating value (LHV) of hydrogen times the mass-flow of hydrogen produced. Then, knowing the power output obtained, the efficiency can be easily calculated:

$$EFF(\%) = \frac{Power\ Output}{LHV \cdot \dot{m}} x100 = \frac{25.86 kW}{(119,909 \cdot 0.00056)kW} x100 = 38.51\% \qquad \textbf{(4-9)}$$

This means that more than a third of the energy contained in the hydrogen is transformed into power. However, this is not the only way of calculating the

efficiency of the cycle. A disadvantage of this first efficiency, is that different types of energy are mixed during the calculation (power and thermal energy). The best way to calculate the actual efficiency of the cycle, is by calculating the Brayton's cycle efficiency, which can be obtained following the next expression (Culham, 2012):

$$EFF(\%) = \left(1 - \left(r_p\right)^{\frac{1-k}{k}}\right) x100 = 52.12\%$$ **(4-10)**

As it is displayed, this efficiency is greater than the one calculated above, but is also better calculated, since the only inputs in the expressions are parameters from the cycle and any kind of energy is taken into account.

4.4 **Overall system**

In previous chapters, each of the small parts of the system has been analysed in an isolated way. In this chapter, the overall system coming from joining all these small parts is going to be presented and evaluated.

Firstly, the flowsheet of this model is displayed in Figure 4-3. As it is shown, the complexity of this model is greater, however, it is worth to note that the properties and values of each stream or block are exactly the same as the ones displayed in each isolated system. Hence, these values can be analysed in Table 3-1 (hydrogen production system), Table 3-3 (heat recovery system) and Table 3-5 (power from hydrogen system).

As it has been done with each of the parts of the system, to measure the performance of this model, the efficiency must be calculated. However, this time the model has to be evaluated as a power production system, either than a hydrogen production system. The main reason is the addition of the "power from hydrogen" model, which transform the hydrogen into power. Hence, there is not anymore hydrogen as an output of the system. The expression used to calculate this efficiency is as follows:

$$EFF(\%) = \frac{Total\ Work\ Output}{Total\ heat\ input} x100 = \frac{102.615 kW}{(149.4 + 59.18 + 113.24 + 130.88) kW} x100$$ **(4-11)**
$$= 22.67\%$$
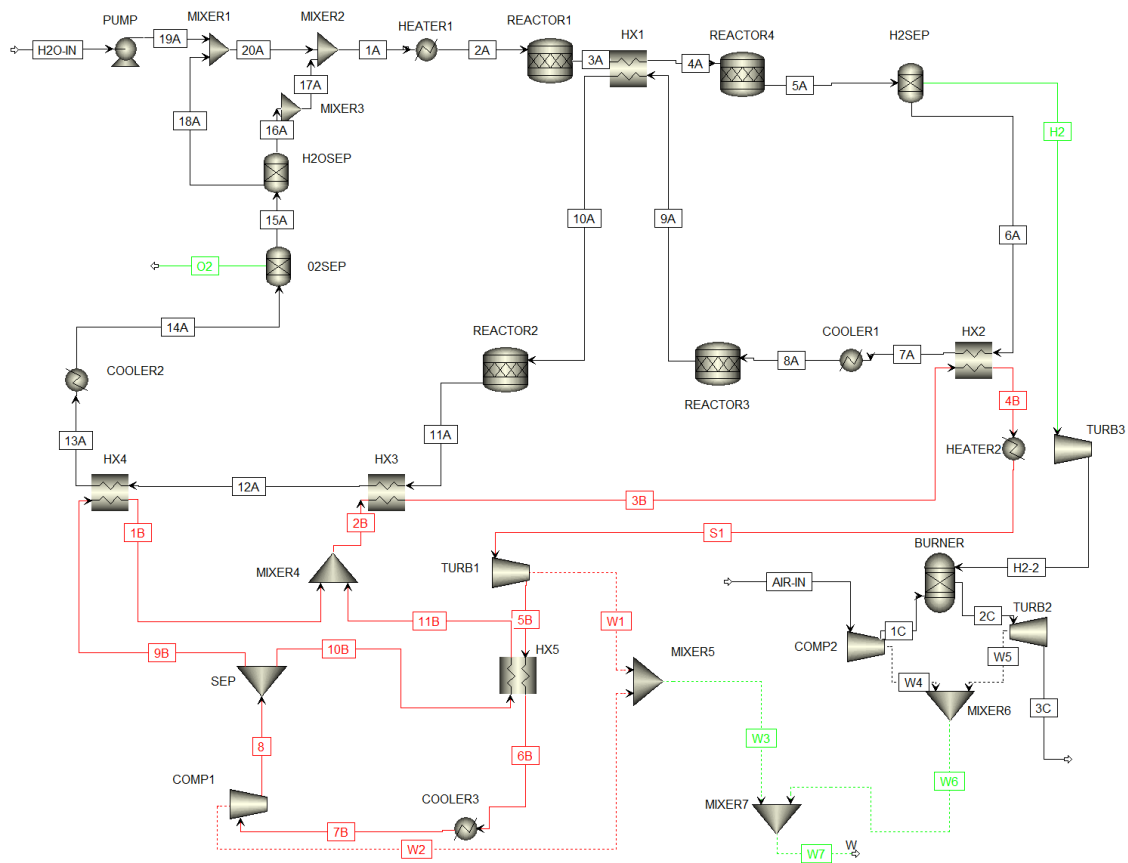
Figure 4-3. Overall system flowsheet

4.5 **Economic analysis**

In this chapter, the investment needed for this plant is going to be calculated. It is worth to note that the prices for the equipment needed for this system are not clear in the market. Hence, the main data for these calculations has been obtained from the paper written by Aochi *et al.* in 1989.

Moreover, during the whole project, some systems have been suggested to improve the performance of the system. Specifically, the last system proposed (power from hydrogen system), makes the system work as a power generation plant rather than a hydrogen production plant. Hence, the investment will be calculated as a hydrogen production plant and as a power generation plant in separate ways.

The investment costs have been calculated according to the general way of calculating costs for engineering processes. Firstly, there are some important assumptions, which are displayed in Table 4-5, and then production, capital and variable costs can be calculated.

Table 4-5. Economic analysis assumptions (Aochi et al. 1989)

Economic assumptions		
Project Life	30	years
Plant capacity (hydrogen production)	2	kg/hr
Plant availability	7200	hr/year

Knowing the previous assumptions, an estimation of the capital cost of the plant can be done. To do so, it has been taken as a reference the economic analysis studied by Aochi *et al.* in 1989. However, the plant capacity of their plant is larger than the one studied in this project. Hence, to know the proportional cost for this plant, the price per unit of hydrogen produced will be done. Regarding their paper, they were running a plant that produce 20,000 m^3/hr, which is approximately 1,420,000 kg/hr (density of hydrogen in standard conditions is 71 kg/m^3). Knowing also that the capital cost for this plant is 81,600,000 £, the capital cost per kg/hr of hydrogen produced is:

$$Unitary\ Capital\ Cost = \frac{81,600,000\ £}{1,420,000\ kg\ of\ H_2/hr} = 57.46\ \frac{£}{kg\ of\ H_2/hr} \qquad \textbf{(4-12)}$$

Hence, the capital cost for the plant studied in this project is:

$$Capital\ Cost = 57.46\ \frac{£}{kg\ of\ H_2/hr} \cdot 2\ \frac{kg}{hr} = 114.92\ £ \qquad \textbf{(4-13)}$$

Moreover, it has been shown the materials needed to run the system, such as water, heat or solid reactants. The cost associated to these materials are:

Table 4-6. Raw materials and Utility Cost (Aochi et al. 1989)

Raw Materials and Utility Cost	Cost		Unit price	
Heat	603,30	£	6,17E-06	£/kJ
Solid Reactants	13887,50	£	12,24	£/kg
Pure Water	6609,6	£	1,7	£/ton

Finally, to calculate the variable cost, which includes maintenance, labour, depreciation, etc; a similar process to the one used for the capital cost has to be done. Regarding the same paper, the variable cost for an average year was 32,544,800 £/year for a plant that produces 1,420,000 kg/hr of hydrogen. Hence, to obtain the unitary variable cost:

$$Unitary\ Variable\ Cost\ (per\ year) = \frac{32,544,800\ £}{1,420,000\ kg\ of\ H_2/hr} \tag{4-14}$$

$$= 22.92\ \frac{£}{kg\ of\ H_2/hr}$$

Thus, the variable cost for the plant studied in this project is:

$$Variable\ Cost = 22.92\ \frac{£}{kg\ of\ H_2/hr} \cdot 2\ \frac{kg}{hr} \cdot 30\ years = 1375.2\ £ \tag{4-15}$$

Summarising, the overall cost of the plant is displayed in Table 4-7:

Table 4-7. Cost Analysis Summary

COST		
Capital Cost	126,41	£
Raw Materials and Utility Cost	21,100.40	£
Variable Cost	1,375.2	£
TOTAL	22,602.01	£

Once the cost for the plant life is calculated, it can be obtained the revenues that can be obtained from the different outputs that the system has: oxygen, hydrogen and power. As it was explained before, this plant can be treated as a hydrogen production plant or as a power generation plant. Hence, it will be study both possibilities to analyse which of them is more profitable (selling hydrogen or selling power).

Firstly, the price of hydrogen can vary depending on the step in which is being sold. However, knowing that the hydrogen will be sold to another company, the price will be around 4.4 £ per kilogram of hydrogen (Hidrógeno, 2015).

Table 4-8. Hydrogen revenues summary

Hydrogen revenues calculation		
Plant capacity (hydrogen production)	2	kg/hr
Hydrogen produced	432,000	kg
Hydrogen price	4,4	£/kg
Revenues from hydrogen	1,900,800	£

On the other hand, to calculate the revenue of selling the energy produced, the energy obtained during the life of the plant has to be calculated. As it has been shown during the document, the software gives power, in this case in kW. Hence, multiplying this power times the number of hours that the plant will be available in 30 years of plant life will give the energy that has been obtained. Besides, knowing that the price per kWh in United Kingdom is 0.15 £/kWh, the revenues are displayed in Table 4-9.

Table 4-9. Energy revenues summary

Energy revenues calculation		
KW available (without h2 conversion)	77	kW
kWh available (without h2 conversion)	16,632,000	kWh
kW available (with h2 conversion)	102,86	kW
kWh available (with h2 conversion)	22,217,760	kWh
Price energy	0.153208	£/kWh
Revenue without h2 conversion	2,548,155.45	£
Revenue with h2 conversion	3,403,938.57	£

5 DISCUSSION

5.1 **Hydrogen production and power generation**

In the previous chapter, it was exposed the efficiency with which hydrogen was obtained using the UT-3 method. It has been found that the efficiency is around 21%. It is low number compared with the highest efficiency achieved for this method, which is around 50% according to the last researches done. However, there are some interesting points to consider about this model.

On the one hand, regarding the efficiency, it has been calculated as an energy balance. As it has been shown, there is plenty of heat released from the system without use. Using this heat will increase the efficiency of the overall system significantly. Moreover, as it is displayed in the literature review, the last studies done for this topic have included in their systems solar panels to provide the heat duty required. This makes the hydrogen production environmentally friendly and puts this project under the current stream of research.

Then, to increase the efficiency of the process a closed-loop gas turbine cycle has been suggested. The working fluid is CO_2, as its thermodynamic properties match really well with the purpose of this secondary system. Its efficiency, calculated as an isolated system, is around 50%; which confirms that the performance of this cycle is on average with other gas turbine cycles studied. After matching this system with the main system of the project, the efficiency of the overall system is 31.73%. Comparing both efficiencies, it is shown that using some techniques to match streams with different temperatures, the efficiency of the cycle has been increased by more than 10%.

Hence, this is one of the main strengths of this cycles, as most of the cycles studied by different authors have not include a way of recovering the heat except for simple heat exchangers. Opposite to this, in this project it is suggested a methodology (the pinch point technique) to match streams with different temperatures in order to satisfy the outlet temperatures needed in the most efficient way possible. This part of the project could be further research by increasing the efficiency of this isolated system or by studying the feasibility of

different systems that might help the hydrogen production to be even more efficient.

It is also worth to note, that a power generation system has been included to the main system. This turns the overall system in a power generation plant, rather than a hydrogen production plant. As well as in the heat recovery system, a gas turbine system has been selected. However, in this case the working fluid will be common air and it will be an open loop. It has been calculated that the efficiency of producing the power was around 52%.

This is also a strength of this project, as it is the point where hydrogen production and power generation are joint. It is then quite important, as the tendency of hydrogen is to be used as a fuel in the future, since the exhaust gases are free of pollutants.

Once all the different parts of the system are joint, the efficiency of power production is 22.67%. Although being a low value, it has to be highlighted that the way of obtaining this power is totally free of pollutants, and the efficiency is not very far away from other ways of obtaining power. For instance, a combined cycle plant produces electricity with an efficiency of around 55%. It is true that this efficiency is double the one obtained in this project, but it delivers dangerous components for the environment.

This last system has also been an improvement in the stream of research, as there are not a lot of papers joining hydrogen production and power generation, which might be a "green" power generation technology to consider.

In short, this project continues the research done by different authors, like Aochi *et al.,* (1989); and suggests a new stream of research consisting on analysing new sub-systems that, added to the UT-3 cycle can improve the performance of the overall cycle.

5.2 **Economic analysis**

An economic analysis has also been done for this project. As it has been shown, the total cost to produce a kilo mole of hydrogen per hour is around 22,500

pounds, assuming the plant has a life of 30 years. This cost has been calculated based on the economic analysis done by Aochi et. al. (1989), obtaining the cost to produce one kilogram of hydrogen, and then obtaining the proportional value for this project. However, this way of calculating the cost of a project is not totally realistic, since this cost is not totally directly proportional to the quantity of hydrogen produced. Hence, the cost of the project might be larger than it actually is.

On the other hand, it has also been show that there are some outputs from the system which make some incomes. In other words, selling oxygen, hydrogen and nitrogen makes the project be totally feasible and profitable, although being the cost low accurate.

6 CONCLUSIONS

The project exposed in this document has deeply analysed the different ways of hydrogen production through thermochemical processes. It has been found that there are three main types: two-step, multi-step and hybrid water splitting cycles. It has also been discovered that the two-step cycles need a bigger temperature to be run, while the hybrid cycles also need a source of electricity.

After this small analysis, multi-step water splitting cycle has been the topic chosen, which means that a model of one of the several cycles available has been developed. Specifically, after comparing the different multi-step cycles developed along the last decades, the UT-3 cycle has been chosen. The main reason has been the simplicity compared with other cycles that achieve the same results.

The UT-3 cycle has been developed using ASPEN PLUS, achieving some interesting results. On the one hand, it is worth to note that the model has been focused on values to obtain one kilo mole of hydrogen per hour. Hence, the thermal efficiency for these parameters was at the beginning 20.87%. Although this efficiency is low compared, it was found that there was a huge quantity of heat delivered by the model. Hence, a heat recovery model has also been included, increasing the efficiency to 31.73%. To do so, a closed-loop gas turbine cycle has been developed, having an isolated efficiency of 50.54% and being run by CO_2.

Finally, a model to obtain power from the hydrogen produced has been suggested. This model also consists of a gas turbine cycle, but in this case in open loop, being atmospheric air the fluid used. Having a similar efficiency to the one obtained in the heat recovery system, the efficiency achieved to produce power is 22.67%. This performance seems to be a bit small, however, all the heat used to produce the power is obtained from solar energy. Besides, this last model is one of the main strengths of this project, as it is not common to find a power generation system added to this kind of models in the literature.

In conclusion, a new and green way of producing hydrogen and energy has been suggested. However, it has been developed to produce one kilo mole per hour. Hence, it would be really interesting to focus further research in study the capacity of this models, to see the actual quantity of hydrogen that can be produced. Besides, the addition of solar panels to supply the heat duty has been suggested, but not implemented, which could be another stream for further research.

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