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THEME

Thermodynamic study of a new thermochemical cycle for the hydrogen production powered by different thermal sources

Defended on 21/09/2023, before the jury composed of:

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ABSTRACT

The present study aims to investigating and simulating a hydrogen cycle production at low temperatures using thermochemical reactions. The cycle used in this work is based on the dissociation of water molecules depending on a copper-chlorine couple (Cu-Cl). Furthermore, the proposed method uses mainly thermal energy provided by a turbine exhaust. This proposed cycle differs from what is found in the literature. However, most of the thermochemical cycles for hydrogen production work at quite high temperature which is a technical challenge. Therefore, the maximum temperature used in the present cycle is limited to 500 °C. A thermodynamic analysis based on both first and second laws is performed to evaluate the energy, exergy, and efficiency of each reaction and the overall exergetic efficiency of the system. Furthermore, a parametric study is conducted to figure out the impact of the surrounding temperatures on the overall exergetic efficiency using the energy simulation software EES. The results show that the cycle can achieve an exergy efficiency of 30.5%. the quantity of hydrogen and oxygen produced from this cycle was calculated for this cycle after connecting the hydrogen production unit with a thermal power plant producing electricity with gas turbines at Hassi R'mel.

Keywords

Hydrogen production; thermochemical process; Copper-Chlorine cycle; water dissociate; exergy and energy analyses.

Résumé

La présente étude vise à étudier et simuler la production d'un cycle d'hydrogène à basse température à l'aide de réactions thermochimiques. Le cycle utilisé dans ce travail est basé sur la dissociation des molécules d'eau en fonction d'un couple cuivre-chlore (Cu-Cl). De plus, le procédé proposé utilise principalement l'énergie thermique fournie par un échappement de turbine. Ce cycle proposé diffère de ce que l'on trouve dans la littérature. Cependant, la plupart des cycles thermochimiques pour la production d'hydrogène fonctionnent à des températures assez élevées, ce qui représente un défi technique. Par conséquent, la température maximale utilisée dans le présent cycle est limitée à 500 °C. Une analyse thermodynamique basée sur les première et deuxième lois est effectuée pour évaluer l'énergie, l'exergie et l'efficacité de chaque réaction et l'efficacité exergétique globale du système. De plus, une étude paramétrique est menée pour déterminer l'impact des températures environnantes sur l'efficacité exergétique globale à l'aide du logiciel de simulation énergétique EES. Les résultats montrent que le cycle peut atteindre un rendement exergétique de 30,5 %. la quantité d'hydrogène et d'oxygène produite a été calculée pour ce cycle après raccordement de l'unité de production d'hydrogène à une centrale thermique produisant de l'électricité à turbines gaz à Hassi R'mel.

Mots clés

Production d'hydrogène; processus thermochimique; Cycle cuivre-chlore; dissocier de l'eau; Analyses exergétiques et énergétiques.

ملخص

تهدف الدراسة الحالية إلى فحص ومحاكاة إنتاج دورة الهيدروجين في درجات حرارة منخفضة باستخدام التفاعلات الكيميائية الحرارية. تعتمد الدورة المستخدمة في هذا العمل على تفكك جزيئات الماء اعتمادًا على زوج من النحاس والكلور (Cu-Cl). علاوة على ذلك، تستخدم الطريقة المقترحة بشكل أساسي الطاقة الحرارية التي يوفرها عادم التوربينات. تختلف هذه الدورة المقترحة عما هو موجود في الأدبيات. ومع ذلك، فإن معظم الدورات الحرارية الكيميائية لإنتاج الهيدروجين تعمل في درجات حرارة عالية جدًا وهو ما يمثل تحديًا تقنيًا. لذلك، فإن درجة الحرارة القصوى المستخدمة في الدورة الحالية تقتصر على 500 درجة مئوية. يتم إجراء تحليل ديناميكي حراري يعتمد على كل من القانونين الأول والثاني لتقييم الطاقة، وكفاءة كل تفاعل والكفاءة الإجمالية للنظام. علاوة على ذلك، يتم إجراء دراسة بارا مترية لمعرفة تأثير درجات الحرارة المحيطة على الكفاءة الشاملة للطاقة باستخدام برنامج محاكاة الطاقة EES. أظهرت النتائج أن الدورة يمكن أن تحقق كفاءة طاقة بنسبة 30.5٪. تم حساب كمية الهيدروجين والأكسجين المنتجة لهذه الدورة بعد ربط وحدة إنتاج الهيدروجين بمحطة طاقة حرارية تنتج الكهرباء بتوربينات غازية في حاسي الرمل.

الكلمات المفتاحية

إنتاج الهيدروجين؛ عملية كيميائية حرارية؛ دورة النحاس والكلور؛ ينفصل الماء؛ تحليلات الطاقة.

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I cordially pay tribute to all the members of my very dear family, sisters, and especially to my mother and my father, who have guided me throughout my life. Their love and support gave me the motivation and courage to continue my graduate studies. Without their moral support and sincere prayers, I would be unable to accomplish a single task in my life.

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List of abbreviations and symbols

$\dot{m}$	Mass flow rate
N	Mole number, kmol
n_R	Number of moles of reactants, kmol
n_P	Number of moles of products, kmol
T	Temperature, ^{O}C
T_0	Environment Temperature, ^{O}C
T_{rxn}	Reaction Temperature, ^{O}C
$\dot{Q}$	Heat transfer
$\dot{H}$	Total enthalpy (kJ)
$\bar{h}_f^0$	Specific molar enthalpy of formation, kJ/mol
$\bar{h}$	Specific molar enthalpy, kJ/mol
$\bar{h}^{\,0}$	Specific molar enthalpy, kJ/mol
$\bar{s}$	Molar Entropy, kJ/ kmol. K
$\bar{s}^0$	Standard specific entropy J/mol. k
g_f^0	Specific Gibbs free energy of formation (kJ kmol^{-1})
$\overline{ex}$	Specific exergy
$\overline{ex}^{ph}$	Physical exergy
$\overline{ex}^{ch}$	Chemical exergy kJ/mol
G	Gibbs function (kJ)
W	Work (kJ)

Greek letters

η_{ex}	Exergy efficiency
$\eta_{ex\ overall}$	Overall exergy efficiency
η_{R1}, η_{R2}, η_{R2}	Exergetic efficiency of different stages

Acronyms

EES	Engineering Equation Solver
TWSCs	Thermochemical Water Splitting cycles
SMR	Steam Methane Reforming
OECD	Organization for Economic Co-operation and Development
UT-3	University of Tokyo-3
SOFC	Solid Oxide Fuel Cell
MCFC	Molten Carbonate Fuel Cell
AFC	Alkaline Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
DMFC	Direct Methanol Fuel Cell
SONALGAZ	Société Nationale de Gaz et Electricité
MTEP	Million Ton Metric

Abbreviations

$Cucl_2$	Copper bichloride
Cu	Copper
Cl_2	Chlorine
Hcl	Hydrochloric acid
H_2O	Water
H_2	Hydrogen
O_2	Oxygen
S-I	Sulfur Iodine

Subscripts

out	Output
in	Input
dest	Destraction
R	Reactant
P	Product
f	Formation

GENERAL INTRODUCTION

1. ENERGY STATUS

The world has a voracious appetite for energy, we cannot imagine existence without it. This energy, derived from resources that are not sustainable, has ensured technological advancement from the Industrial revolution to the present day. Energy is essential for humans, it represents a major challenge in the economic, political, scientific and environmental fields. Even if the man knew several sources of energies which helped him to develop and to discover his universe, he seized fossil sources such as coal to ensure his industrial development and improve his comfort. Then he went in search of new sources such as oil and natural gas. Today, technology makes it possible to produce them in large quantities, using all the know-how acquired. At the dawn of the 21st century, energy remains a major issue, the world has experienced unprecedented demographic growth (more than 7000 million people on earth) which requires the continuous overconsumption of energy, in all its forms. to ensure the desired comfort. In 2022 the sources of energy in the world are represented in figure 1.1 [1].

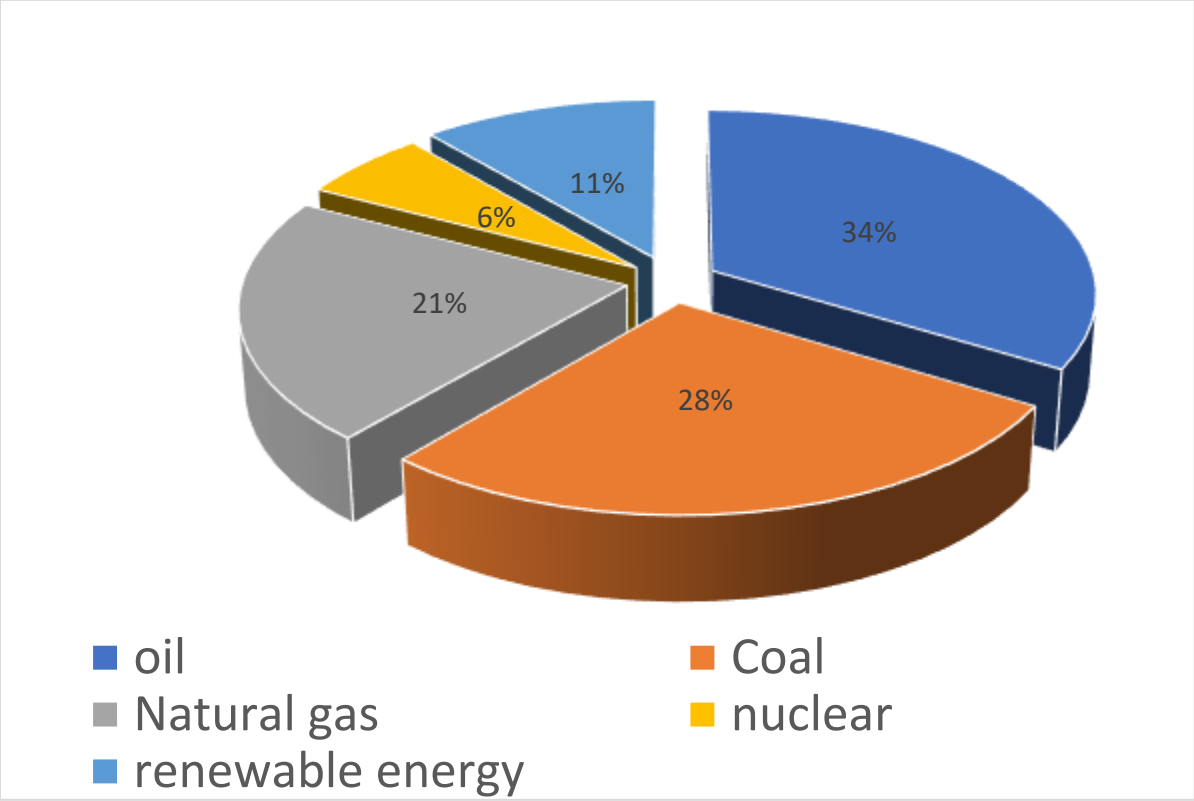

Figure 1 Sources of energy in the world in 2022 [1]

Fossil fuels, including oil, natural gas and coal, remain the primary source of energy for electricity, transportation and residential services. Formed from organic matter over millions of years, fossil fuels have contributed significantly to global development over the past century. According to recent figures released by the US Department of Energy and Energy Information, global energy consumption is expected to increase from 524 Exa Joule [1 Exa Joule = 10^{18} J] in 2010 to 820 Exa Joule d by 2040 [2]. In other words, global energy demand will increase by 56% between 2010 and 2040. Due to economic growth and expanding population, global consumption mainly in developing countries that do not belong at the Organization for Economic Co-operation and Development (Non-OECD) has increased considerably, figure 2.

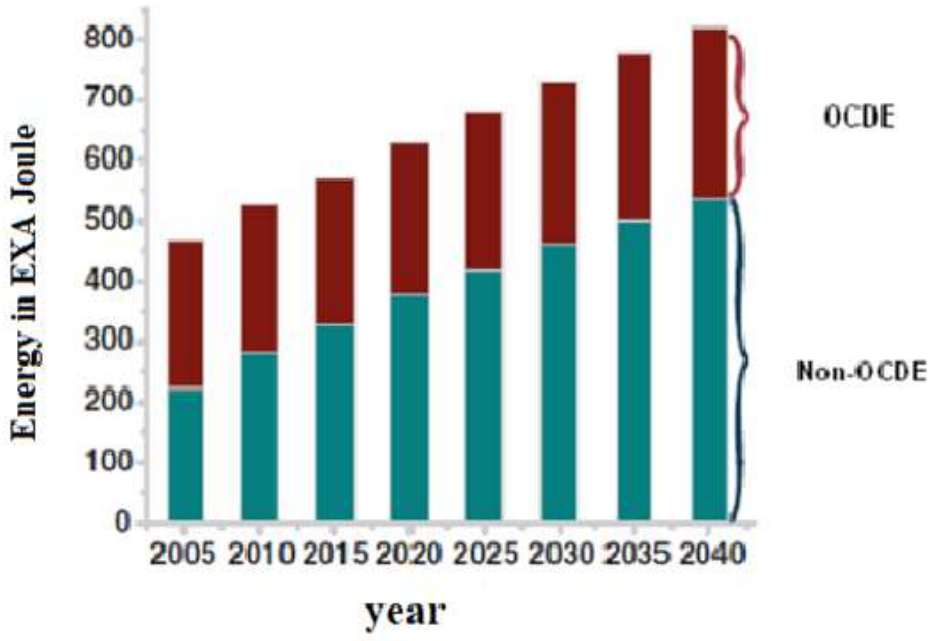

Figure 2 World energy consumption in developed countries (OECD) and developing countries (non-OECD) [2]

Energy use will increase by 90% in non-OECD countries while in OECD countries, this increase is estimated at 17% [2]. Although renewable energy (pink curve in Figure 3) is growing faster worldwide, fossil fuels are expected to provide nearly 80% of global energy consumption. Natural gas is the fastest growing fossil fuel. An increase of 1.7% per year. The growth in the contribution of natural gas is due to the growing supply of shale gas. Coal use is assumed to grow faster than oil and other liquid fuels. Until 2040, demand is growing in developing countries, see Figure 3.

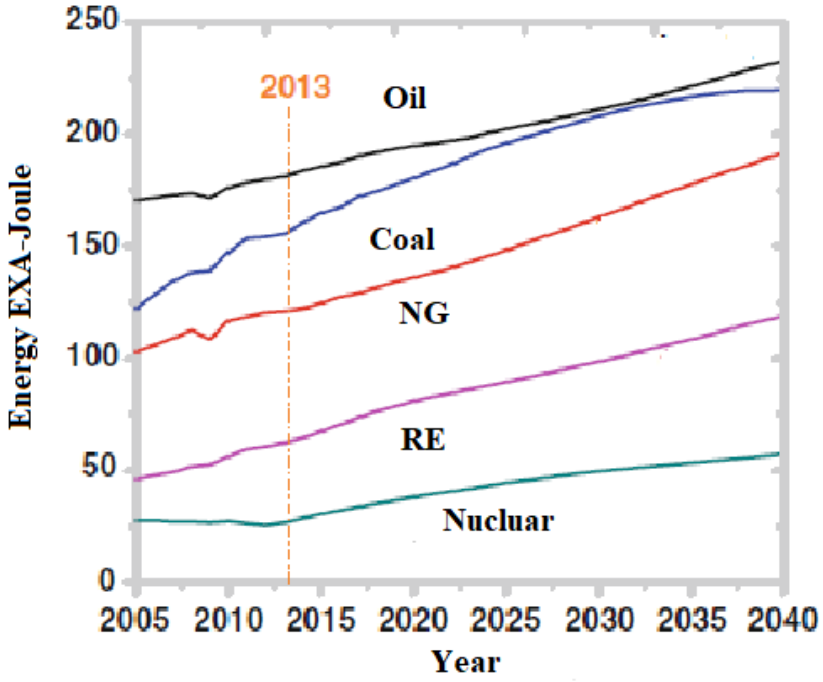

Figure 3 World energy consumption by fuel type [3]

Fossil fuels are attractive due to their relatively low cost compared to renewable sources such as biomass, wind, geothermal and solar energy. As fossil fuels have limited reserves, the crucial question is; how much time is left for these resources to run out. Fossil fuel production for Turkey will be exhausted in 2038 [3]. Similarly, India, China, Russia and the United States, their coal reserves run out in 315, 83, 1034 and 305 years respectively [4]. Countries like the United States and India are already seeking new coal reserves and investing in clean coal technology innovation [5, 6]. Research predicts that oil and gas will run out sooner than coal. The exhaustion times for oil, gas and coal are calculated at around 35, 37 and 107 years, respectively. Therefore, coal reserves will be the only remaining fossil fuel after 2042 and will most likely be exhausted by the year 2112 [7].

Another major concern in the use of fossil fuels is the emission of greenhouse gases such as: CO_2, CH4, N_2O, CFCs, HFCs, PFCs, SF6, etc. These elements absorb a considerable fraction of thermal solar radiation. In addition, these gases reflect solar radiation back to the earth's surface as visible light and thus prevent heat from escaping outside the earth's atmosphere. The concentration of these gases in the atmosphere has increased considerably since the industrial revolution [8]. CO_2 is considered the main element causing global warming and accounts for 64% of the increase in greenhouse gases [9].

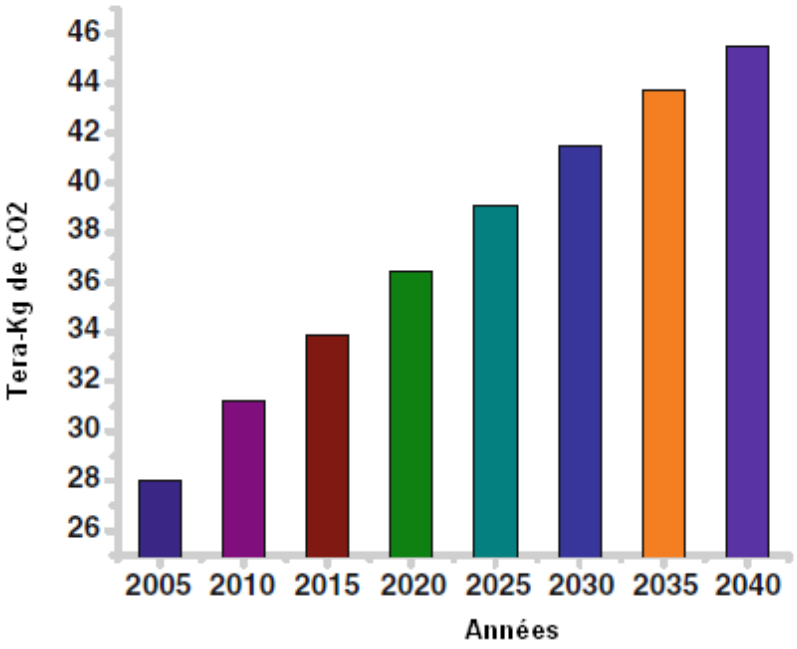

Figure 4 Global carbon dioxide emissions in tera-kilograms of CO_2 [9]

It is increasingly certain that if the use of fuels continues for the next 50 years, the current rate of CO_2 concentration will increase to 580 ppm, which would cause serious climate change [10]. At the beginning of 2014, the atmospheric concentration of CO_2 was 397.8 ppm, about 42% higher compared to that of the year 1800 [10]. Figure 4 represents global CO_2 emissions related to energy consumption. According to the International Energy Agency (2022), emissions are projected to increase from 36.28 billion metric tons in 2022 to 45.5 billion metric tons in 2040 [1]. Non-OECD countries rely on fossil fuels to meet their energy needs and therefore emit huge amounts of CO_2. Figure 5 illustrates the annual CO_2 emissions resulting from the use of coal, liquid fuels and natural gas. Among fossil fuels, the use of coal alone contributed 44% of global CO_2 emissions in 2010 and is expected to rise to 47% between 2020 and 2030, before dropping slightly to 45% in 2040. Liquid fuels are growing more slowly, resulting in a decrease of 3.5 billion tons of CO_2 from 2010 to 2040. As shown in Figure 5, natural gas consumption is growing faster than coal or oil. The current global energy needs for transport and heating are estimated at 2/3 of the primary energy demand, these two sectors are mainly fueled by oil and natural gas.

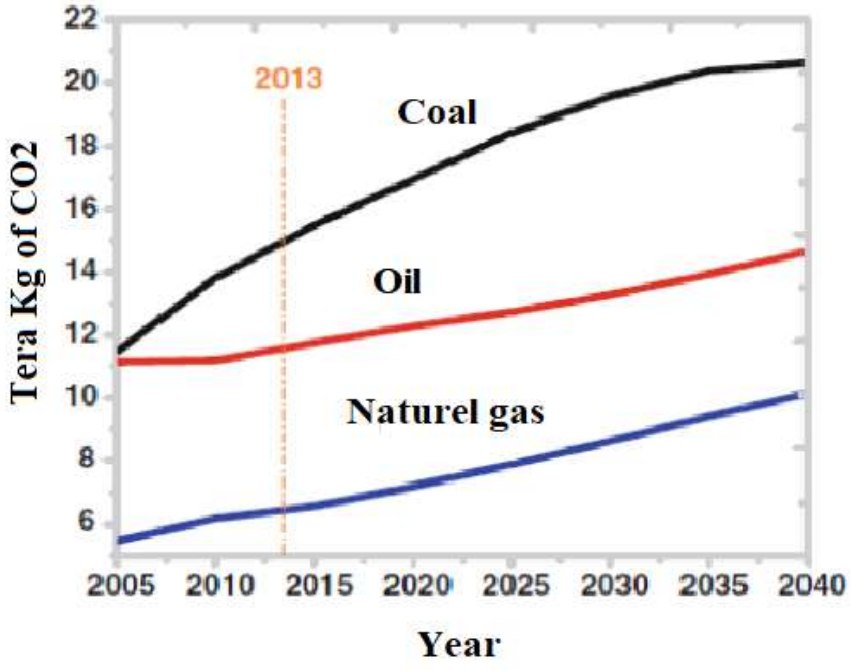

Figure 5 Global carbon dioxide emissions in Tera kilograms of CO2 according to the type of fuel [11]

Both of these types of fuels are preferred because of their ease of transportation in liquid or gas forms. It should be noted that the combustion of hydrocarbon fuels for the transport and housing sector accounts for more than half of greenhouse gas emissions and emissions of atmospheric pollutants [11]. Most of the populations in the world, especially in the regions of Africa and Central Asia, are increasingly exposed to the risks of famine, desertification, reduced water quantities and floods. Other environmental pollution is responsible for more than 150,000 deaths per year. Oil and natural gas prices will rise over the next 15 years from 105 $/barrel in 2022 to 215 $/barrel in 2035 [1]. The world is currently facing two huge problems which are the depletion of oil, and the need to reduce greenhouse gas emissions, which are the main causes of climate change. Man is now trying to reduce his consumption of fossil fuels and is looking to replace them with renewable energies.

Use of these energies represents a sustainable solution to ensure the protection of the environment and the global energy supply. Renewable energies are the engine of sustainable development and will be available as long as the earth exists. The new progressive establishments of power plants worldwide indicate that renewable energies are ahead of fossil fuels. Among the advantages of exploiting renewable energies is its existence in various forms distributed in an equitable manner throughout the planet earth. Their development becomes imperative for the authorities in order to ensure energy security and meet the growing energy needs of the world population, especially in terms of electrical energy.

Electricity production in Algeria is based on fossil fuels, in particular natural gas. Current thermal power plants in production use the power of gas turbines for the conversion of thermal energy supplied from the combustion of natural gas into mechanical energy which will drive an electricity generator. The latest statistics and annual records of electricity consumption on the national territory indicate that the demand for electrical energy is growing, especially in regions and hot seasons.

Algeria is a gas producing country more than oil, the national economy is based mainly on the export of hydrocarbons. In 2020, Algeria produced 175.9 MTEP of hydrocarbons divided into 80.7 MTEP of oil and 95.2 MTEP of natural gas. With an increase of 7.5% compared to that of 2010 (162.6, 81.7 and 80.8). National energy consumption rises gradually from 43.8MTEP in 2010 to 50.2MTEP in 2020. If the situation continues in this way (12.7% increase in consumption), in the future, Algeria will not have more hydrocarbons to export after the year 2028 [12]. Algeria must reduce the rate of energy consumption, and invest in the field of renewable energies, especially solar energy, whether photovoltaic or thermal.

1.1 ISSUE

Modern society requires many types of services to maintain a good standard of living; such as electricity, hot water, space heating and air conditioning, transportation fuels, various chemicals and materials, etc. Traditional methods of producing these products are mostly fueled by the burning of fossil fuels, which contributes to air, water and soil pollution.

The rapidly increasing global energy demand and the climatic upheavals causing disasters such as earthquakes, tsunamis, abnormal rainfall rates, the melting of polar glaciers, etc., due to greenhouse gas emissions have motivated the governments of the majority of countries, especially industrialized ones, to seek another alternative to conventional energies and thus limit planetary threats. The solution to these problems is undoubtedly the use of renewable energies such as solar energy, wind energy, geothermal energy, hydrogen energy, hydroelectricity, biomass, wave energy, etc. Although much of the available natural energy resources such as solar, geothermal, hydroelectric and wind energy are limited due to their reliability, qualities, quantities and densities.

Currently, hydrogen is an important energy carrier to meet future energy needs. However, hydrogen production, either direct or indirect, should meet certain sustainability criteria such as low or zero emissions, including CO_2 and wide availability with a competitive cost price. Hydrogen is abundant on Earth, but only in a form chemically bound with other chemical elements. For hydrogen to be useful as an energy carrier, its chemical bond must be broken to obtain it as a pure element. However, a substantial energy input is required to obtain hydrogen bound to the chemical reactions involved.

The production of hydrogen from the decomposition of water constitutes an interesting technique of producing clean energy which has the potential to be a sustainable development par excellence.

Currently, industrial-scale production technologies are focused primarily on steam methane reforming. However, factories using this technology emit considerable amounts of carbon dioxide, considered to be the main culprit of the phenomenon of the global greenhouse effect. Hydrogen production techniques deemed to be ecological and sustainable are the decomposition of the water molecule by thermochemical means as well as electrolysis. Thermochemical cycles are more cost effective than electrolysis in terms of hydrogen production since they avoid the intermediate process of consuming electricity before producing hydrogen.

Since the beginning of the development of thermochemical cycles, now four decades ago, a very long list of thermochemical cycles which counts about 280 cycles of water decomposition have been discovered, but few of them which have given promising results. In this work, a new thermochemical cycle based on copper and chlorine discovered and proposed by the author of this thesis will be studied exhaustively from a thermodynamic point of view.

1.2 OBJECTIVES

In this thesis, an in-depth study of a new original thermochemical cycle based on copper-chloride is conducted, and various evaluations are carried out using several thermodynamic modeling and thermochemistry tools. The results are transferred to the energy simulation software Engineering Equations Solver (EES) for thermodynamic evaluation and parametric studies.

The main objective of this thesis is to study the proposed thermochemical cycle based on copper and chlorine (Cu-Cl) by conducting research on the individual reactions of the cycle and specify the advantages and disadvantages in order to improve these performances.

Most thermochemical cycles require thermal processes at very high temperatures, something that restricts the feasibility of the junction between hydrogen production units and thermal, nuclear and solar power plants. Recently, thermochemical cycles producing hydrogen at low temperatures (below 600°C) have been developed in order to be compatible with the temperature ranges produced by the majority of available and accessible thermal sources.

The copper-chloride thermochemical cycle, in particular, is very promising. This cycle consists of a series of chemical reactions in which the water is decomposed into hydrogen and oxygen via the copper and chloride components which will be recycled. The chosen thermochemical cycle was developed jointly by Japanese, American and Canadian laboratories. Several studies have shown that this cycle is very promising because its yield is relatively high compared to most other cycles.

This cycle with have not been previously considered in the literature. This cycle may use solar energy or any thermal source, such as the heat released by the exhaust gases of the means of transport or gas turbines for its operation.

The Hassi Rmel thermal power plant was chosen to supply this power plant. The method chosen for the analysis of these systems is the exergy method. This method is very robust because it is a very effective tool for the analysis, feasibility and optimization of energy systems.

1.3 THESIS PLAN

The organization of this thesis is presented in five main sections. Firstly, a complete introduction presenting the different aspects of this work, which are the current global energy situation and the major energy issues. The latter represents the main pillar on which today's civilization is built. Over time, this overconsumption of energy of fossil origin because of innumerable problems of a planetary scale, the one and only way out of this critical situation is undoubtedly the use of renewable energies on a large scale. as well as the energy situation in Algeria presenting the thermal potential that our country has. Finally, we presented the problem and the motivations that led us to start this work, as well as the objectives traced at the beginning of this study and the results obtained and then the structure of this manuscript including a summary view of the different chapters.

The first chapter is devoted to the identification of the element hydrogen, it begins with a brief history starting with the discovery of this element and up to its use as an alternative energy to conventional energies. A detailed list of the physico-chemical characteristics of hydrogen is exposed. There follows a brief overview of the techniques for producing hydrogen, its use in the different sectors of life as well as the possible storage methods.

The second chapter talks about most of the hydrogen production methods, since about 97% of the hydrogen produced worldwide comes from the transformation of hydrocarbons, so the first part of this chapter deals with the different processes used to extract from hydrogen from fossil fuels. Other renewable hydrogen production techniques are mentioned such as electrolysis, biomass, photolysis, etc. an important part in this section exposes the thermochemical cycles of hydrogen production. This technique is starting to gain momentum since its efficiency is relatively high in addition to its renewable nature. Finally, the most widespread and most used thermochemical cycles are cited.

Chapter three of this thesis is undoubtedly the main pillar of this work, a lot of effort has been invested in this direction in order to find the most adequate thermochemical cycle in the context of this work. In this chapter we propose a thermochemical cycle based on copper and chlorine, new and original. Although there are several cycles based on Cu-Cl in multiple configurations, the course proposed in this thesis is completely different from what is found in the literature. An in-depth thermodynamic study based on the balance of mass, energy, entropy, exergy and chemically reactive systems is applied to the different chemical reactions of this cycle. A parametric study of

the different quantities and especially the destroyed exergy or the generated entropy is carried out in order to optimize the cycle as much as possible from a performance point of view.

In the four chapter, the results were obtained regarding the amount of molar heat required for each reaction with the appropriate temperature, in addition to the destroyed exergy and the exergy efficiency of the three steps and the overall exergetic yield of the thermochemical cycle.

In the chapter five, a proposal was presented for a thermal power plant for turbines in order to supply the Cu-Cl based hydrogen production cycle unit with the heat necessary for the operation of this unit. After that, the amount of hydrogen and oxygen produced was calculated for this unit.

lastly, the results are drawn from the studies conducted in this manuscript. Many useful conclusions and recommendations are cited in this section.

CHAPTER 1

1. GENERAL INFORMATION ON HYDROGEN

1.1 HYDROGEN HISTORY

Hydrogen is the first element in the periodic table with atomic number 1, it is first in class. It is the lightest of all, it is the most abundant element in the universe representing 75% by mass or 90% by volume of all matter. It is present in large quantities in stars and gaseous planets; it is also the main component of nebulae and interstellar gas. On earth, it is present in practically all compounds with almost all other chemical elements. In the earth's crust, hydrogen represents only 0.22% of the atoms, far behind oxygen (47%) and silicon (27%) [13]. It is also rare in the Earth's atmosphere, since dihydrogen represents only 0.55 ppm of atmospheric gases by volume. The largest and most common source of hydrogen is water.

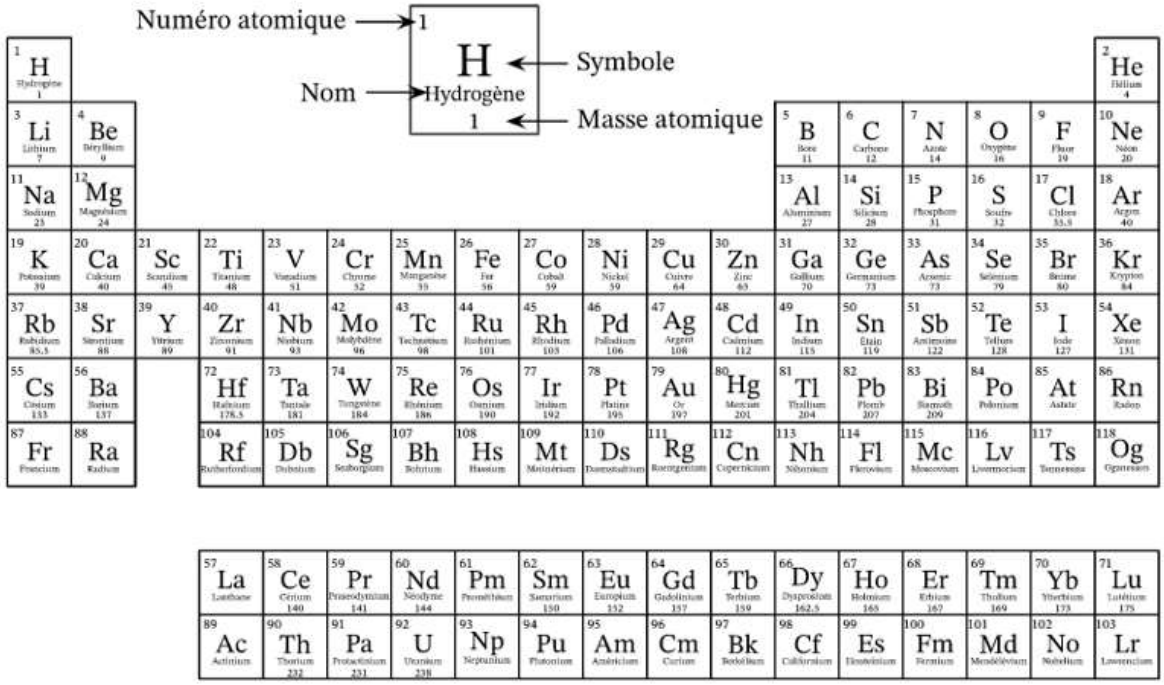

Figure 1.1 Periodic Table of Chemical Elements

In 1776, Henry Cavendish identified hydrogen as a separate species. Seven years later, Antoine Lavoisier proved that water was composed of hydrogen and oxygen [14].

The most common isotope of hydrogen is pretium (H-1, H) its atomic mass is 1.007822. The second isotope is stable deuterium (H-2, D) or heavy hydrogen discovered in 1932 by H. C. Urey and his colleagues. Deuterium has a natural fraction of 0.014% with slightly different physical and chemical properties from (H-1). Almost all of the deutrium in natural hydrogen is in combination with hydrogen atoms. The third hydrogen isotope is radioactive tritium (H-3, T) with a half-life of 12.3 years, discovered in 1934 by E. Rutherford. But also the short-lived isotopes H-4, H-5, and H-7 have been synthesized recently [15-16].

The few important dates in the history of hydrogen are as follows [17]:

- 1671: Robert Boyle dissolves iron turnings in dilute hydrochloric acid and

reports that the 'vapours' released are highly flammable.

- 1766: British chemist Henry Cavendish manages to isolate a strange substance

gas which when burned in the air, gives water: "Hydrogen".

- 1781: Until then called "flammable gas", this gas was named "Hydrogen"
- 1782: The Montgolfier brothers inflated small balloons with hydrogen to see them fly away.
- 1783: French chemist Antoine Lavoisier synthesized water.
- On December 1, 1783, Jacques Charles continued this work and took off with a balloon inflated with hydrogen and traveled 35 km.
- 1804: The Frenchman Louis Joseph Gay-Lussac and the German Alexander Von Humboldt jointly demonstrate that water is composed of one volume of oxygen for two volumes of hydrogen.
- 1839: the operating principle of fuel cell technology is discovered by the Swiss Christian Friedrich Schönbein who, by electrolysis of water, managed to obtain hydrogen and oxygen by passing a current electricity in two electrodes immersed in a U-shaped tube filled with water and who observed that by cutting off this current, the gases gave rise to an electric current in the opposite direction in the circuit outside the tube. The first laboratory model of a fuel cell was made by an English lawyer, Sir William R. Grove, an amateur researcher in electrochemistry in the period 1839-1842. This model works with hydrogen and oxygen, at low temperature, with porous platinum electrodes and sulfuric acid as electrolyte.
- 1883: Professor Wroblewski liquefies hydrogen.
- 1899: James Dewar recovers hydrogen in a stable static bath and produces solid hydrogen for the first time.
- 1900: The Germans, Fritz Haber and Carl Bosch invent the process of synthesis of

ammonia.

- 1900: The first "Zeppelin" makes its maiden flight, filled with hydrogen.
- 1931: Harold Urey discovers deuterium.

- 1939 – 1953: Englishman Francis T. Bacon advances the chemical generators of electricity which allow the realization of the first industrial prototype of power.
- 1950: the idea of using hydrogen in a reactor for aircraft propulsion.
- 1960: From this date, NASA uses the fuel cell to supply electricity to its space vehicles (Apollo and Gemini capsules)
- 1970: the electro chemist John O'M. Bockris coined the term "hydrogen economy" during a discussion at the General Motors (GM) Technical Center in Warren, Michigan. He subsequently published in the journal "Energy" The SolarHydrogen Alternative, describing his envisioned hydrogen economy in which he explains how cities in the United States are powered by energy derived from the sun.
- 1973: The oil shock and OPEC's stance that cheap oil prices had ended prompted the western world to develop hydrogen fuel cells. Commercial applications have begun.
- 1976: The International Journal of Hydrogen Energy (IJHE) was established by Prof. T. Nejat Veziroglu as Editor-in-Chief, and published by Pergamon Press, to provide a platform for scientific papers related to Hydrogen Energy. hydrogen energy.
- 1977: The International Energy Agency (IEA) was created in response to disruptions in the oil market. IEA activities included research and development of hydrogen technologies.
- 1989: The National Hydrogen Association (NHA) was created in the United States with 10 members. Today, the NHL has nearly 100 members.
- 1990: The United Nations International Organization for Standardization (ISO), to Prepare international standards for hydrogen technologies.
- 1990: The world's first solar hydrogen production plant was established at Solar-Wasserstoff-Bayern, a research and test laboratory in southern Germany.
- 1994: Daimler Benz demonstrated its first NECAR I fuel cell vehicle at a press conference in Ulm, Germany.
- 1998: Iceland unveiled a plan to create the world's first hydrogen economy, made by Daimlere-Benz and Ballard Power Systems.
- 1999: Royal DutchShell committed to the future of hydrogen. The first hydrogen refueling stations in Europe

were in the German cities of Hamburg and Munich.

- 2000: the Canadian company "Ballard Power Systems" introduced the world's first PEM-type fuel cell, ready for production for applications in the automotive sector.
- 2004: The world's first fuel cell submarine undergoes deep water trials by the German Navy.
- 2013: Honda unveiled its new fuel cell vehicle hydrogen-powered FCEV concept in Los Angeles, promising to market the car initially in Japan and the United States.
- 2015: The Japanese company Chiyoda Corp, plans to build the world's first large-scale power plant Fueled mainly by hydrogen (70%) and natural gas (30%).

1.2 PHYSICO-CHEMICAL CHARACTERISTICS OF HYDROGEN

Hydrogen is considered an ideal gas over a wide temperature range and even at high pressures. At normal conditions of temperature and pressure, it is colorless, odorless, tasteless, non-toxic, non-corrosive, a diatomic gas, which is in principle physiologically non-hazardous. One of its most important characteristics is its low density, which makes it necessary for all applications either to compress hydrogen or to liquefy it. Hydrogen is the simplest chemical element; its most common isotope consists of just one proton and one electron. Hydrogen is thus the lightest existing atom. As it has only one electron, it can only form a covalent bond: it is a univalent atom. However, solid hydrogen can be metallic when under very high pressure. It then crystallizes with a metallic bond. In the periodic table of elements, it is in the column of alkali metals. Not being present in this state on earth, it is however not considered a metal in chemistry. It is positively buoyant above a temperature of 22 K, i.e., over almost the entire temperature range of its gaseous state [18].

When it is released, hydrogen gas mixes rapidly with the ambient air, it is very diffusive and very buoyant. The diffusion rate is proportional to the diffusion coefficient and varies with temperature according to the relation T^n with n lying in the range from 1.72 to 1.8. Diffusion in multi-component mixtures is usually described by the Stefan-Maxwell equation. The positive buoyancy of hydrogen is a favorable safety feature in unconfined areas, but it can cause a dangerous situation in partially confined spaces, where hydrogen can accumulate, for example under the fireplace roof. Diffusion and buoyancy determine the rate at which the gas mixes with ambient air.

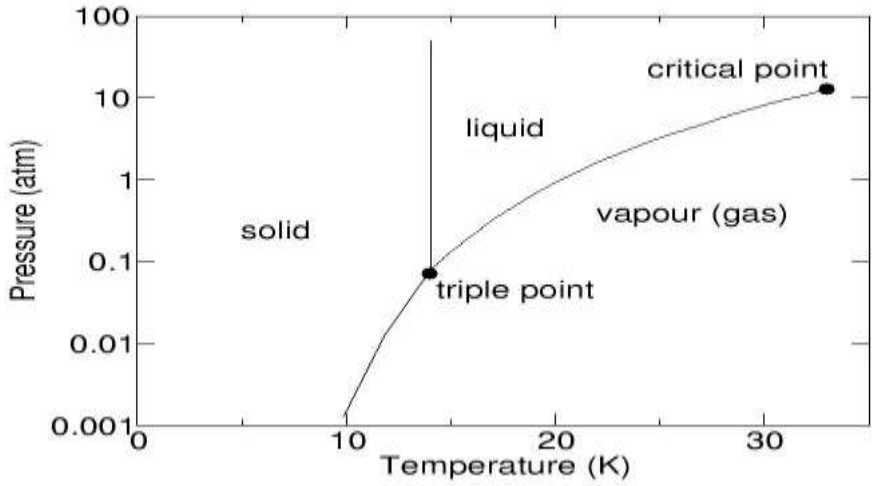

Figure1.2 Hydrogen phase diagram

The rapid mixing of hydrogen and air is a safety problem, because it very soon leads to flammable mixtures which, on the other hand for the same reason, also quickly dilute. Therefore, it is

estimated that in a typical unconfined hydrogen explosion, the fraction of the mixed gas cloud (air – hydrogen) releases very low energy compared to the amount of energy of hydrogen available [19].

Hydrogen reacts with elements whose electronegativity is high such as non-metals and with metals whose electronegativity is low, to form ionic or covalent hybrids (e.g. HCl, H_2O) the electronegativity of hydrogen is 2.20 on the Pauling scale. Table 1.1 brings together some physico-chemical characteristics of hydrogen, while Figure 1.3 illustrates the temperature-entropy diagram of hydrogen.

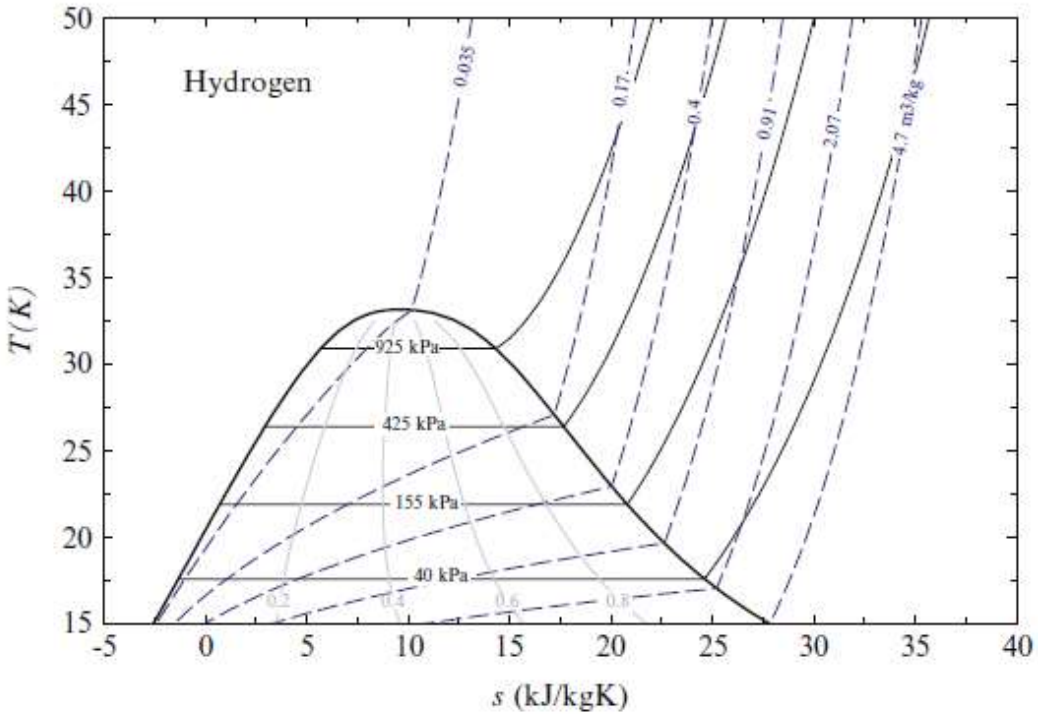

Figure 1.3 Hydrogen [T S] diagram.

Hydrogen is above all the main constituent (in number of atoms) of all living matter, associated with carbon in all organic compounds. For example, hydrogen represents 63% of the atoms in the human body [20].

Under very low pressures, such as exist in space, hydrogen tends to exist as individual atoms, simply because then they are unlikely to collide to combine. Hydrogen clouds are the basis of the star formation process.

The hydrogen present in large quantities in the core of stars is a source of energy via nuclear fusion reactions, which combine 4 nuclei of hydrogen atoms (4 protons) to form a nucleus of helium atom. [21].

Table 1.1: Physico-chemical characteristics of hydrogen [21,22]

Physico-chemical characteristics of hydrogen	Values
Molar mass	2,016 gr
Volumic mass	0,085 Kg/m^3
Gas density at 20.3K	1,34 Kg/Nm^3
Gas density at 273K	0,08988 Kg/m^3
Melting temperature (1 atm)	14.01K
Boiling temperature (1 atm)	20.45K
Critical point	32.97K à 12.9Bar
Evaporation energy	445 KJ/Kg
Theoretical liquefaction energy	14112 KJ/Kg
Ignition energy	0,020 MJ
Specific heat Cp	14,3 KJ/Kg K
Specific heat Cv	10,3 KJ/Kg K
Autoignition temperature in air	858 K
Electronegativity (Pauling)	2,1
Air diffusion coefficient	0,61 cm/s
Flame speed in air**	260 cm/s
Detonation velocity in air	2,0 Km/s
Average distance between H2 nucleons	0,074nm
Thermal conductivity	0.177W/m.K
Water solubility at 101.33Kpa and 298K	0,019 m3/m3
Lower calorific value	119930 kJ/kg
Higher calorific value	141860 kJ/kg

** six times faster than gasoline under the same conditions.

Solid hydrogen is obtained by lowering the temperature below the melting point of hydrogen, which is 14.01 K (-259.14°C). The solid state was obtained for the first time in 1899 by James Dewar. The latter published his work under the title "On the solidification of hydrogen" [22].

By mass, the amount of energy produced during the combustion of hydrogen is higher than that released by any other fuel. Hydrogen easily reacts with oxygen in the atmosphere strongly exothermic producing a huge enthalpy variation of the order of -286000 kJ. $kmol^{-1}$.

$2H_2\ (g) + O_2\ (g) \rightarrow \quad 2H_2O(l) \qquad \Delta H = -286000 kJ.kmol^{-1}$

According to the graph in Figure 1.4, the lower and higher calorific value of hydrogen, under standard conditions, is 2.4, 2.8 and 7 times higher than that of methane, gasoline and methanol, respectively. Hydrogen has a wide flammability range (4%-75%). Its auto-ignition temperature is 858K.

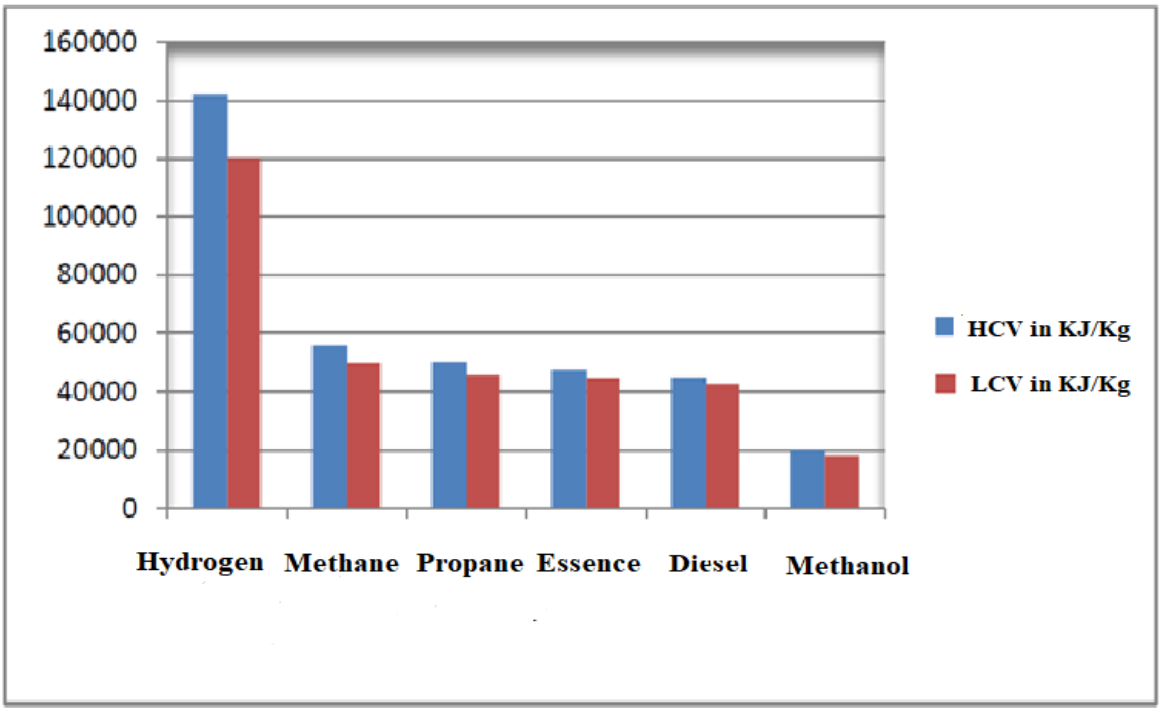

Figure 1.4 Lower and higher calorific value of some fuels

The flame of the combustion of hydrogen in the air is almost invisible and very hot, its temperature is estimated at 2000°C. Table 1.2 shows the different ignition characteristics of hydrogen and a typical hydrocarbon, propane.

Table 1.2 Ignition characteristics of hydrogen and propane.

Properties	**Hydrogen**	**Propane**	**Units**
Flammability Limit in Air	4-75	2,1-9,5	%vol
Minimum ignition energy	0,02	0,26	MJ
Auto-ignition temperature	858	760	k
Burning rate in air at atm pressure	265-325	30-40	cm/s

Table 1.3 Comparison of H_2 with traditional fuels

Properties	**Units**	**H2**	**CH_4**	**C_3H_8**	**Essence**
Molecular weight	g/mol	2, 016	16,043	44,10	
Flammability Limit in Air	vol%	4,0-75,0	5,3-15,0	2,1-9,5	1-7,8
Minimum ignition energy	MJ	0,02	0,29	0,26	0,24
Air diffusion coefficient	cm2/s	0,61	0,16	0,12	0,12
Diffusion rate in the air	cm/s	<2,0	<0,51	N.A.	
Burning rate in air	cm/s	265-325	37-45	N.A.	0,42

1.3 HYDROGEN PRODUCTION

There are three types of energy sources used, namely, coal energy, that of fossil hydrocarbons such as oil, natural gas, shale gas, oil sands, etc.… and renewable sources and sustainable energy sources that are zero carbon. Renewable and sustainable energies are those that do not release greenhouse gases. Typical examples of zero carbon energies are biomass, hydroelectricity, wind energy, solar energy, hydrogen energy, nuclear and others. Figure 1.5 illustrates the trend of zero carbon, coal and fossil fuel consumption around the world from 1800 to the present day. The graph is extrapolated to 2100 based on a prediction model [23].

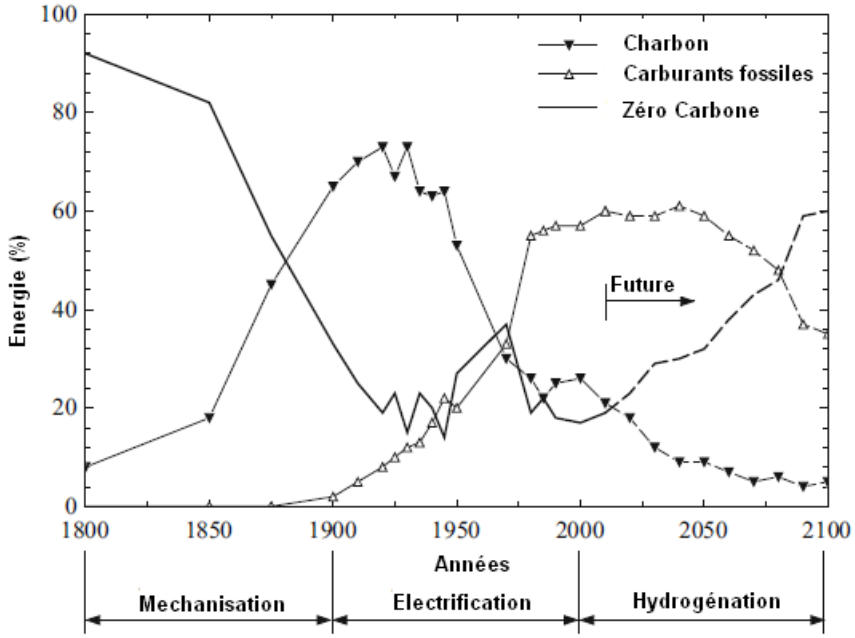

Figure 1.5 Global energy supply from the industrial revolution until the year 2100

Interestingly, before the Industrial Revolution, the global energy supply included only zero-carbon energy sources such as wood, wind, and animal power. From the industrial revolution and the introduction of the steam engine, the consumption of coal increased sharply. We can call this era of "mechanization" of about 100 years during which Western society, particularly in Europe, experienced remarkable technical and scientific progress. Around 1900, another source of energy began to proliferate in the West, namely oil.

At the same time, advances in electrical generation propelled a second industrial revolution of about 100 years. This stage is called the electrification period. With the help of electricity, almost all mechanized equipment has become more efficient, which has encouraged the strong development of the chemical and process industries. Germany was at the beginning of the twentieth century a world leader in inventions, especially in the chemical and process industries. One of the most important processes invented is the Haber-Bosch ammonia synthesis process in

1913. The manufacture of ammonia by this process has become a major consumer of hydrogen in the world. In the Ruhr region of Germany, a strong development of coal mining and metallurgy took place at the beginning of the twentieth century. Hydrogen was in high demand to ensure the start-up of this sector. As a result, in 1938, a 240 km hydrogen pipeline transported 250*106 Nm^3 per year of hydrogen, obtained from coal. Currently in Europe, there are approximately 1,500 km of hydrogen pipelines, while in the United States there are approximately 900 km of hydrogen pipelines [24].

The geopolitical context of the first half of the 20th century encouraged the development of engines and fuels for transport. Gasoline gained in proportion due to its highoctane rating, high energy density and easy extraction from crude oil. Currently, the road transport sector mainly uses gasoline and diesel and the maritime transport industry uses heavy oil and/or diesel. Liquefied hydrogen has found uses in space transportation as rocket fuel.

It can be seen that at the end of the twentieth century, science has increasingly become the dominant driving force influencing the development of society. A self-awareness has been developed which sensitizes humans to possible catastrophic scenarios related to the careless use of fossil energy resources [25]. The activity of the scientific community has channeled people's thinking towards the beginning of a new 100-year era that will follow the eras of mechanization and electrification. This has often been cited as the period of hydrogenation [26]. The rise of a hydrogen civilization is predicted to be driven by preventive actions based on scientific analyzes of the negative impact of greenhouse gas emissions on the climate and the depletion of fossil fuel resources.

The world demand for primary energy was 595 Exa-Joule in 2021, dominated mainly by oil and coal followed by natural gas, which means that the current production of hydrogen would only cover 1.5% of the demand. There are therefore many efforts to be made in the field of mass production of hydrogen for it to reach a significant share, especially if a growing global energy demand is considered [27]. Figure 1.6 shows that the massive hydrogen production comes mainly from hydrocarbon-based fuels, 96%, while only 4% of this production comes from water.

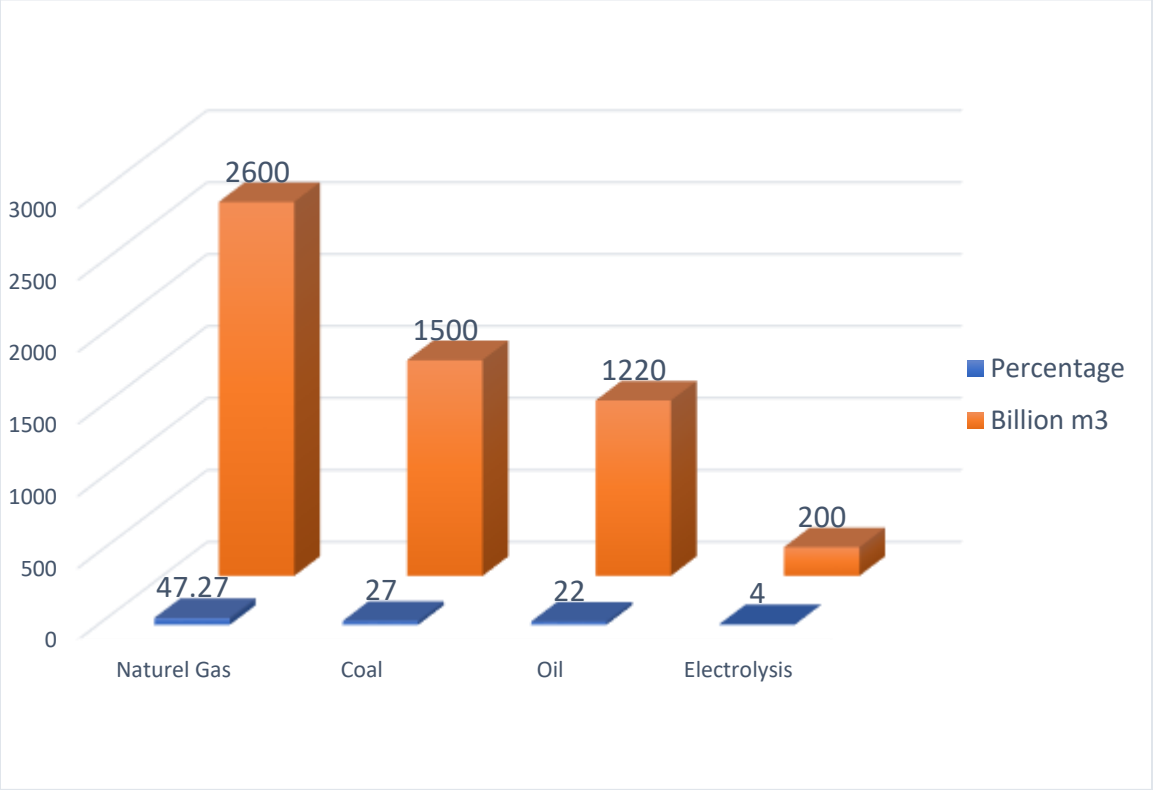

Figure 1.6 Annual global production of hydrogen different energies 2021.

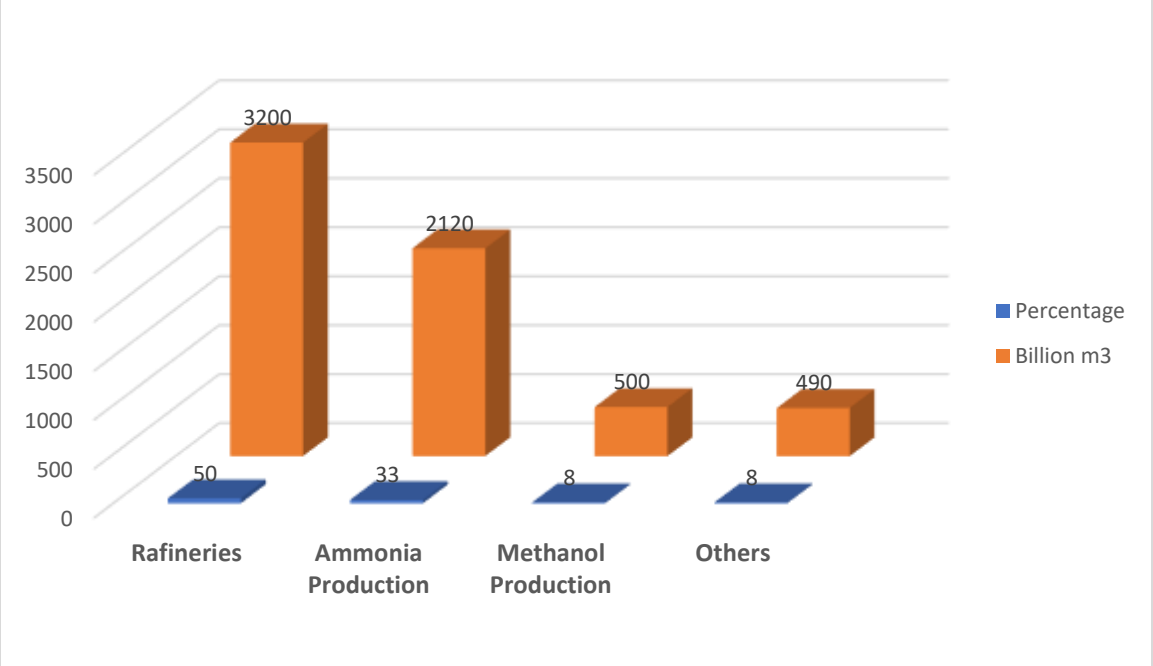

Figure 1.7 Annual global consumption of hydrogen

1.4 USE OF HYDROGEN

Hydrogen can be converted into electricity, heat or motive power depending on the end use. It has the advantage of having a storage capacity and being able to be produced without CO_2 emissions. As an energy vector, it thus has a very wide field of application compared to all other forms of energy.

1.4.1 PETROCHEMICAL SECTOR

The two main applications of hydrogen are the operation of refining oil into lighter fractions that can be used as fuel and the production of ammonia NH_3, via the Haber-Bosch process, which is used directly or indirectly as fertilizer, see Figure 1.8. H_2 is also used in the manufacture of methanol and hydrochloric acid. As a hydrogenating agent, it is used in particular to increase the level of saturation of unsaturated fats and oils in the oleochemical industry.

1.4.2 AEROSPACE SECTOR

Hydrogen has the highest energy-to-mass ratio of fuels, because hydrogen is the lightest element that can exist, therefore, for a given charge, the mass of hydrogen required is only about one-third of the mass of hydrocarbon fuel required. It is for this reason that hydrogen has been widely used in the space program, where weight is crucial. For decades, for example, NASA has used liquid hydrogen to power space vehicles, see figure 1.9.

1.4.3 TRANSPORT SECTOR

Electricity can be produced by fueling an internal combustion engine or a gas turbine with hydrogen or a hydrogen/fossil fuel mixture in order to reduce the CO_2 emissions of this type of energy machine. This use of hydrogen will allow a smooth transition towards the generalization of fuel cells for automotive and stationary applications. There are still a number of technological constraints related to the use of hydrogen (physico-chemical properties) before generalizing its use in such devices. Low-cost renewable electricity is increasingly used to produce hydrogen electrolytically, for example the German hydrogen vessel "Challenger" figure 1.10, this vessel is equipped with a vertical axis of wind turbines that harness the strong winds of the outer seas and use them to create the electricity used to electrolyze it to produce the hydrogen that will later be fuel for the ship's internal combustion engine.

Figure 1.8 Hydrogen is co -produced with carbon monoxide from natural gas vaporeformation.

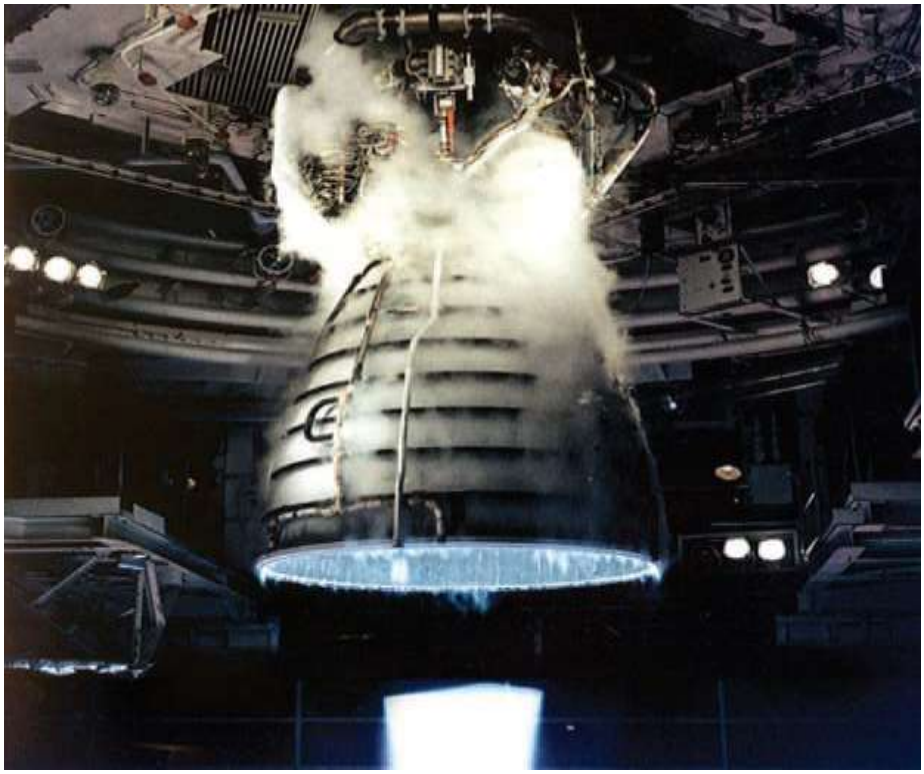

Figure 1.9 The space shuttle's main thruster burns hydrogen with oxygen, the flame is almost invisible at full thrust.

Figure 1.10 The Challenger ship, based in Germany, powered by a hydrogen engine produced by electrolysis powered by wind electricity.

1.4.4 FUEL CELL

The principle of the fuel cell was stated in 1839 by Sir William GROVE [28]. A fuel cell converts chemical energy directly into electrical energy. Typically, a battery is made up of an assembly of elementary cells, the number of which depends on the desired voltage and current. each of these cells comprises an anode compartment supplied with fuel and a cathode compartment supplied with oxidizer separated by two electrodes loaded with catalyst and an intermediate electrolyte ensuring the ionic bond. Since their discovery, enormous scientific and technological progress has been made.

A fuel cell is a cell in which the production of electricity is done through the oxidation on one electrode of a reducing fuel, for example dihydrogen, coupled with the reduction on the other electrode of an oxidant, such as than the oxygen in the air. The hydrogen oxidation reaction is accelerated by a catalyst which is generally platinum. While other combinations are possible, the most commonly studied and used fuel cell is the dihydrogen-dioxygen or dihydrogen-air fuel cell, this being explained in particular by the abundance of hydrogen resources on earth and the ease of production of dihydrogen.

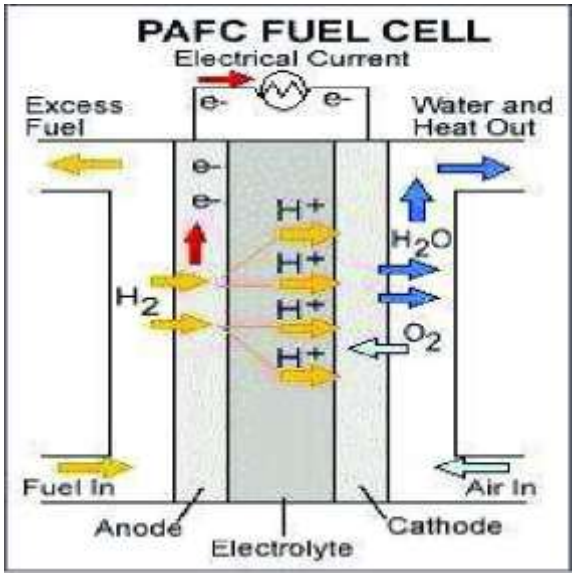

Figure 1.11 Diagram of the operating principle of a PEMFC fuel cell.

Since 1977, certain batteries (used on satellites) contain polymer membranes (solid acid or alkaline electrolyte) made conductive, taking the form of a thin membrane separating the two electrodes. These polymers contain platinum. The operation of a dihydrogen-dioxygen fuel cell is particularly clean since it only produces water and only consumes gases. But until 2010 the manufacture of these batteries was very expensive, in particular because of the non-negligible quantity of platinum required and the cost of the ion exchange membranes. The principle of the fuel cell is the reverse of electrolysis. The chemical reaction produced by the oxidation and the meeting of gases produces electricity, water and heat. The operation of the fuel cell requires a supply of fuel, the most used being hydrogen. A fuel cell produces an electrical voltage of approximately 0.7 to 0.8 volts, depending on the load (current density) and produces heat. Their operating temperature varies from 60 to 200°C depending on the model. The water is generally evacuated in the form of vapor with the excess of oxygen. There are several types of fuel cells, the best known of which are the proton exchange membrane cell and the solid oxide cell [29].

1.4.4.1 PROTON EXCHANGE MEMBRANE CELL

Proton exchange membrane fuel cells, also known as polymer electrolyte membrane fuel cells (or PEMFC according to the acronym of the English expressions proton exchange membrane fuel cells or polymer electrolyte membrane fuel cells) are a type of fuel cells developed for applications in transport as well as for applications for portable computers. Their specific characteristics include operation at low pressure and temperature ranges and a specific DMFC (Direct Methanol Fuel Cell) polymer electrolyte membrane [30]. Hydrogen (from electrolysis or hydrocarbon reforming) enters through the bipolar plate on the left in Figure 1.11. Arriving at the anode, the dihydrogen (H_2) dissociates (oxidation) into H^+ ions and electrons according to: $2H_2 = 4H^+ + 4e^-$. The ions

then cross the membrane, but the electrons, blocked, are forced to borrow an external circuit, which will generate an electric current at the cathode, the hydrogen ions, the electrons, and oxygen (pure or coming from the air) meet to form water according to the reaction: $4H^+ + 4e^- + O_2 = 2H_2O$. Water and oxygen pass through the right bipolar plate. This reaction will also produce heat that can be recovered.

1.4.4.2 SOLID OXIDE BATTERY

The principle is similar with proton exchange membrane fuel cells. The only difference is that the proton exchange membrane is replaced by another membrane called "solid oxide membrane". The molecules in the fuel cell will then not react in the same way, but this type of cell is not more efficient than the proton exchange membrane cell, it only works at "very high" temperature (around 600 to 800°C) and it is more expensive to manufacture for low-power batteries. They are therefore reserved for specific applications requiring high power. In addition, each cell has different fuel requirements.

1.4.4.3 APPLICATIONS AND PROSPECTS

The main fields of application for fuel cells are:

- **TRANSPORT**

Hydrogen-powered fuel cells are being used to power several prototype electric cars and electric buses. It is also planned that trains for non-electrified railway lines will enter service by 2018 in Germany [31].

- **ELECTRICITY PRODUCTION**

In the United States, the US Department of Energy (DOE) supports the deployment of power generation systems, whether for electrical backup, powering sites or buildings, or electric forklifts.

- **COGENERATION**

Low-power cogeneration systems (mini-cogeneration) are being developed, particularly in Europe, and are at a demonstration stage.

- **DOMESTIC COGENERATION OR MICRO-COGENERATION**

Household heaters incorporating a 750 W fuel cell, called ENE-FARM, have been on the market in Japan since 2009. Several European fuel cell micro-CHP manufacturers have field-tested pre-commercial prototypes in 12 European countries. The European ENE.FIELD project aims to install fuel cells in homes. Some brands have joined this project to develop and install these systems [32].

Table 1.4: Different types of fuel Cell and their characteristics

Battery type	Low temperature batteries				High temperature batteries	
	AFC	PEMFC	DMFC	PAFC	MCFC	SOFC
Electrolyte	Solution KOH	Membrane polymer driver of protons	Proton Conducting Polymer Membrane	Phosphoric acid	Li2CO3 and KCO3 molten in a LiAlO2 matrix	ZrO2 and Y2O3
Temperature level	60-80°C	60-100°C	60-100°C	180-220°C	600-660°C	700-1000°C
Combustible	H2	H2 (pure or reformed)	Methanol	H2 (pure or reformed)	H2 (pure or reformed)	H2 (pure or reformed)
Application areas	Spatial	automobiles, Portable, Cogeneration, Maritime	Portable	Cogeneration	Cogeneration Production centralized electricity, Maritime	Cogeneration Production centralized electricity, Automotive (COULD), Maritime

PAFC (Phosphoric Acid Fuel Cell).

AFC (Alkaline Fuel Cell).

MCFC (Molten Carbonate Fuel Cell).

SOFC (Solid Oxid Fuel Cell).

PEMFC (Proton Exchange Membrane Fuel Cell).

DMFC (Direct Methanol Fuel Cell)

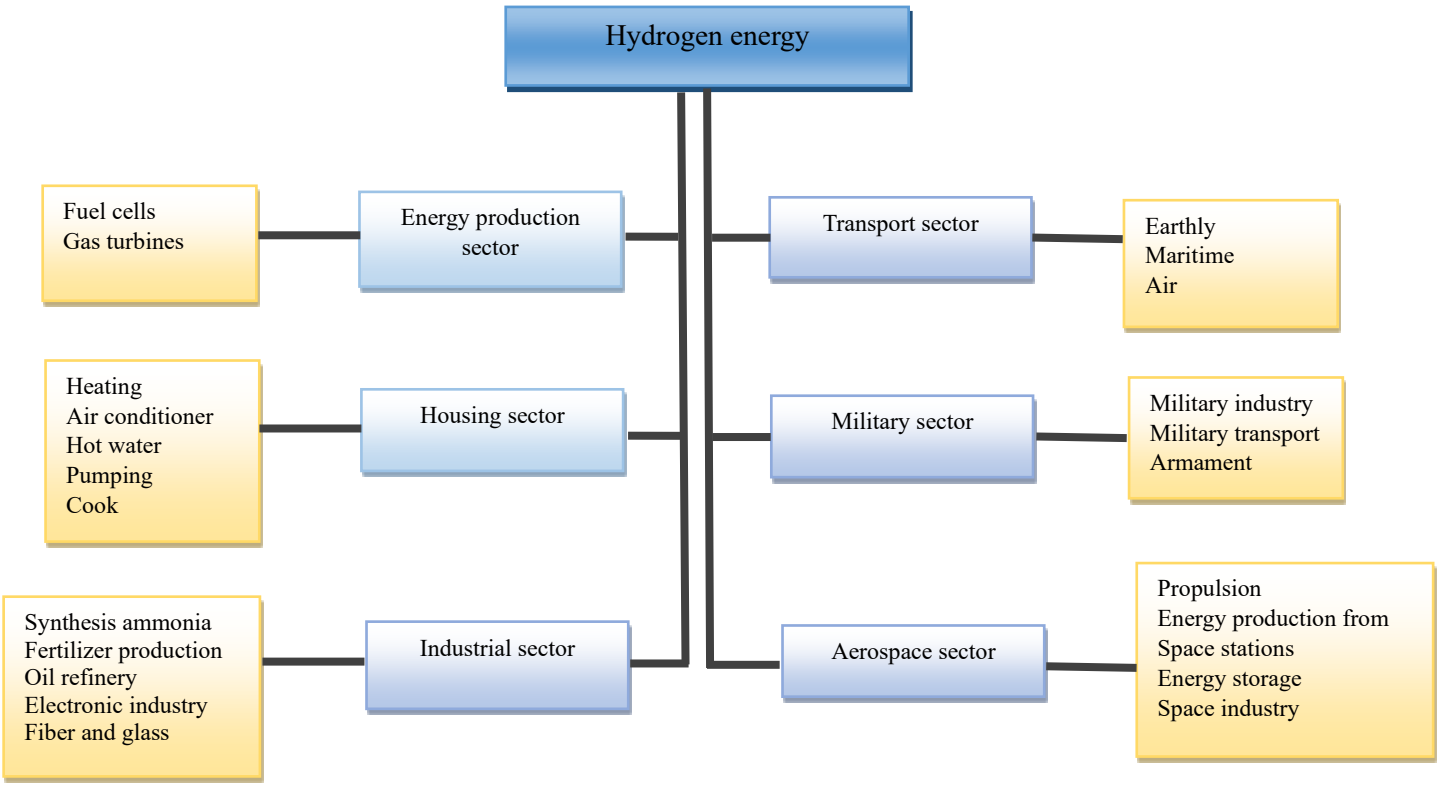

Figure 1.12 Summary of Hydrogen Energy Scope

1.5 METALLIC HYDROGEN PRODUCTION

It might be possible to produce considerable amounts of metallic hydrogen for profit. As diamond is a transformation of graphite by compression which retransforms only with difficulty by decompression, because the retransformation would require a lot of energy, a theory predicts the existence of a form of hydrogen, called metastable metallic hydrogen, which would return only with difficulty to its normal hydrogen state when decompressed. This form of hydrogen could be used to make very light automobiles with high fuel efficiency. Moreover, it could be used as fuel itself. Clean enough, it would only have water and nitrogen oxide as combustion products. It is nine times denser than normal hydrogen and would produce considerable energy when it resumes this form. It would be a fuel five times more efficient than the combination of liquid hydrogen and liquid oxygen used by the space shuttle [33].

1.5.1 SUPERCONDUCTIVITY

One theory is that metallic hydrogen is a superconductor at temperatures as high as room temperature. This is much higher than for any other candidate for superconductivity, but it is doubtful whether industrial applications can be derived from it, the pressure necessary to maintain hydrogen in metallic form at room temperature being very difficult to maintain, much more than to maintain the low temperature necessary for the other superconductors.

In 2016, the scientific research center based in Washington in the United States of America (Carnegie Institution for Science, 2016) seems to have made new discoveries relating to a sodium-hydrogen compound which would present the characteristics of a metal and unique structures as well as superconducting properties [34].

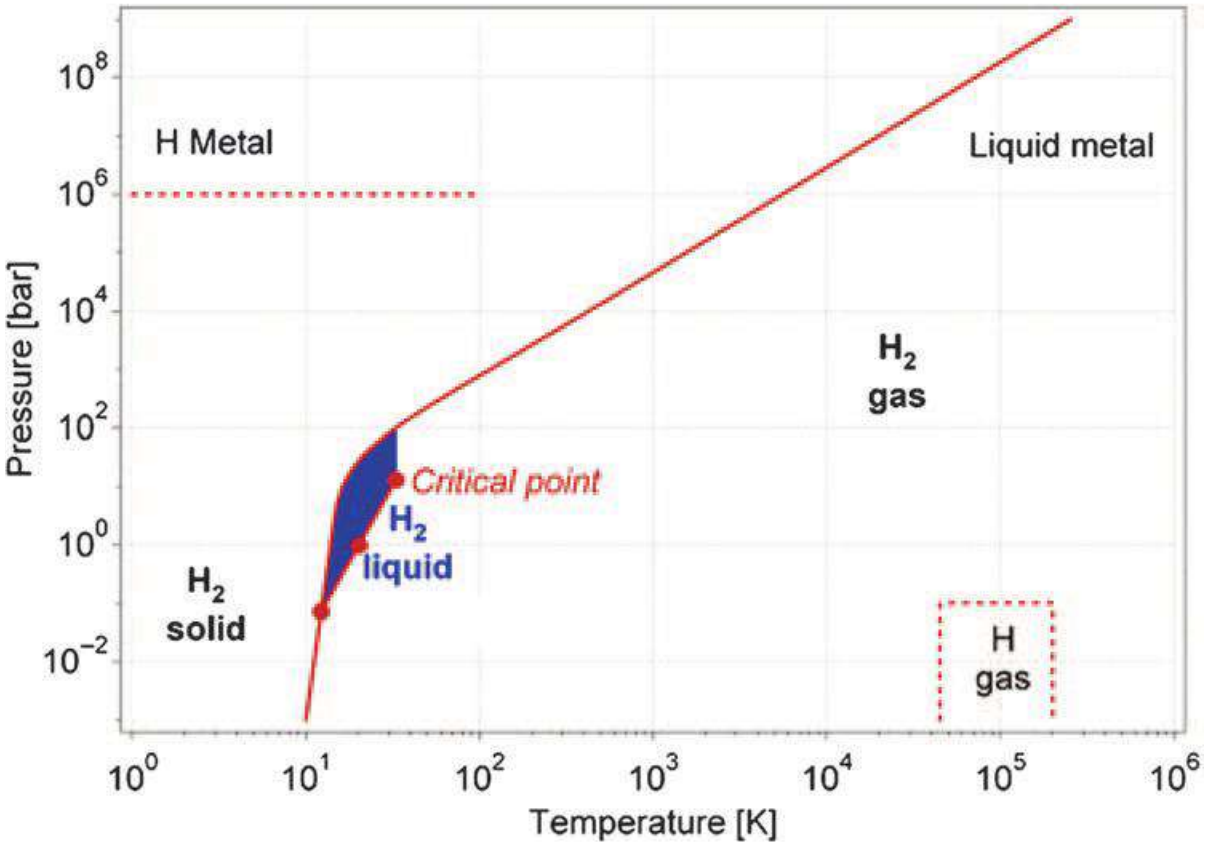

Figure 1.13 Extended hydrogen phase diagram

1.6 HYDROGEN STORAGE

Storage in general involves a number of technologies, ancient and modern, which are based on a daily store-retrieve cycle and which can extend to seasonal energy storage. The storage and reinjection of the stored energy into the network, as well as the conditions for the distribution of hydrogen to the end consumer, are hard points for enabling hydrogen technology to break through and meet major future challenges. The terms of the problem are of course posed differently, depending on whether one seeks to value a storage capacity, the available power, the storage duration, the reactivity or the number of acceptable cycles. Hydrogen energy storage is one of the solutions for managing future electricity production surpluses.

Any energy storage via hydrogen has three components:

- A conversion system that receives energy from the distribution network as input and converts it into a storable form,
- A proper storage system for the energy thus converted,
- An energy conversion system that restores stored energy to diffuse applications,

Hydrogen offers the ability to choose each of the components independently of the other two:

- ENR, nuclear, fossil energy input,
- Massive storage or not, long term or not,
- Electricity, CH_4 injected into the gas network, heat, hydrogen output,

The types of storage most often cited are the physical and chemical types, also called solid storage. Indeed, the types of storage can be divided into three main categories: physical storage, reversible chemical storage and irreversible chemical storage figure 1.14.

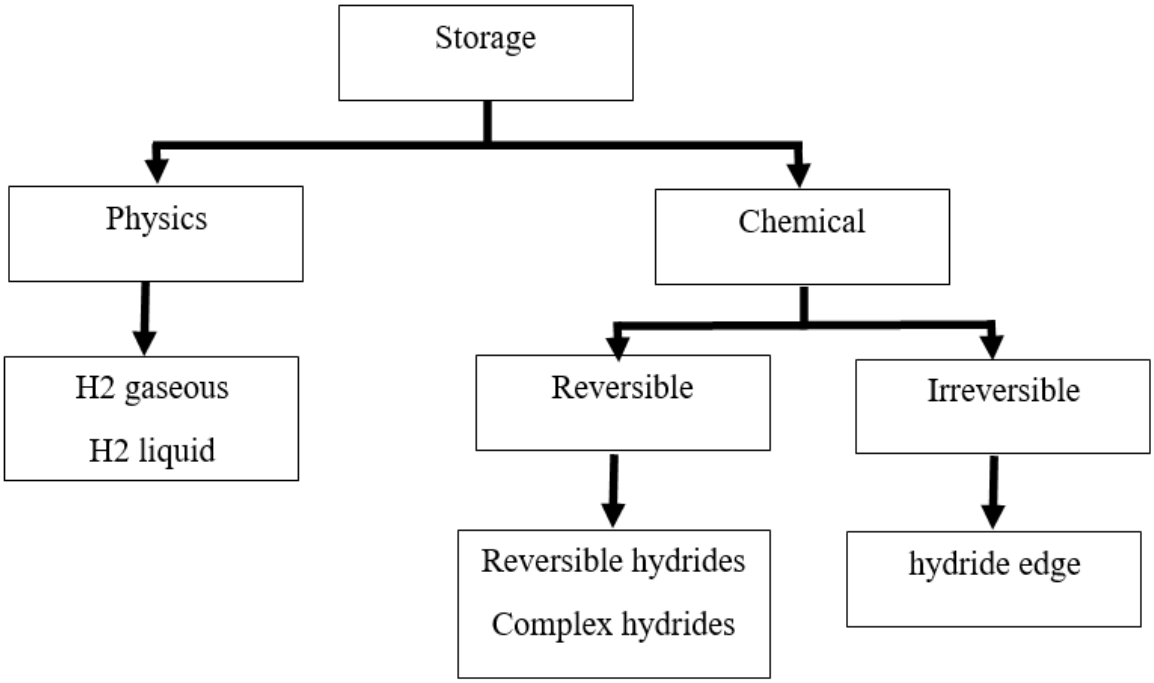

Figure 1.14 Classification of the different hydrogen storage methods.

Physical storage corresponds to direct or primary hydrogen storage. Either it is not bound to another element and is directly available (gaseous or liquid hydrogen), or bound by physical forces to a solid material. In the case of reversible chemical storage, the hydrogen is this time reversibly bound to another material: we speak of absorption in the form of metal hydride for metal compounds. Finally, in the case of irreversible chemical storage, the hydrogen is bound to the compound by a chemical reaction. It is then released under conditions of pressure and temperature close to ambient. Once all of the hydrogen has been released, the reaction by-products must be evacuated and are replaced by new reagents [35].

Table 1.5: Advantages and disadvantages of hydrogen storage under pressure, liquid and solid.

	Gaseous 	Liquid 	Solid 
Benefits	• commercial	• commercial • Volume capacity	• Safeties (low pressures) • Volume capacity
Disadvantages	• Safeties (700 bar) • Volume capacity • Compression energy expenditure	• Boil-off (release of H_2 into the atmosphere) • Energy expenditure for liquefaction	• Mass capacity • Heat exchanges

1.6.1 GAS STORAGE

The gaseous route is the simplest and most widespread storage technology. The hydrogen is contained in pressurized tanks. The higher the pressure, the greater the amount of hydrogen stored. The reservoirs currently developed operate with maximum pressures around 300-350 bar (30-35 MPa) or even 480 bar.

The current work consists of creating gaseous reservoirs under 700 bar in order to improve the volume capacity, the main shortcoming of this technology. For design, gas tanks are grouped into 4 types:

Type I: Cylindrical metal tank.

Type II: Reservoir containing a metal casing for mechanical strength, hooped with continuous fibers impregnated with resin.

Type III: Tank made up of a metal casing to contain the hydrogen and a casing of continuous fibers impregnated with resin for mechanical strength.

Type IV: tank consisting of a non-metallic envelope to contain the hydrogen and an envelope of continuous fibers impregnated with resin for mechanical strength.

1.6.2 LIQUID STORAGE

To store hydrogen in the liquid state, it is cooled down to 20K (-235°C). The technology is mastered, in particular for space applications or stationary storage. The volume capacity is certainly important but the very low temperature remains the major problem of this technology. In addition, the liquefaction energy is high. This technology lends itself more to stationary storage for which large means of thermal insulation can be implemented. On the other hand, in the case of mobile applications where the thermal insulation is limited, the heating of the tank conducts. The evaporation of the hydrogen which must then be released limits the internal pressure in the tank.

1.6.3 SOLID STORAGE

Methods for storing hydrogen in solid form are techniques involving mechanisms of absorption or absorption of hydrogen by a material. An example is the formation of solid metal hydride by reacting hydrogen with certain metal alloys. Since the studies on the solid storage of hydrogen in palladium, various families of materials have required the attention of scientists to find the most suitable support for the storage of hydrogen Figure I.15.

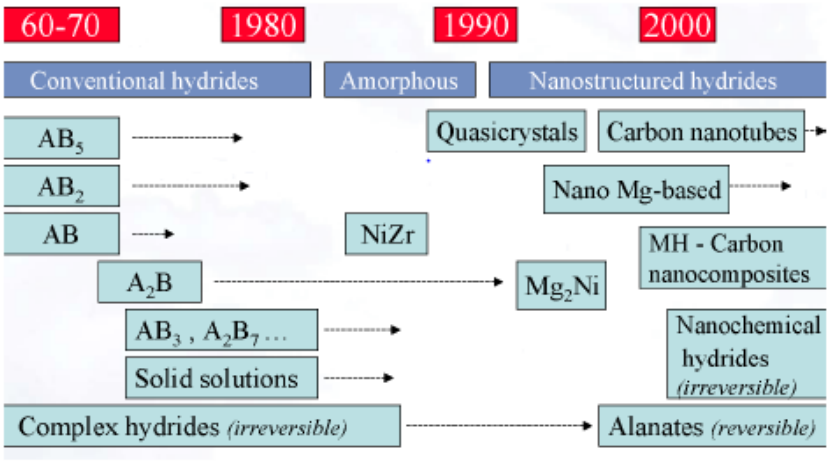

Figure 1.15 Development of solid storage over 50 years

Table 1.6 The different groups of solid storage.

Adsorption storage	Chemical hydrides
- Activated carbon - Nanotubes - Graphite nanofiber - MoFs, Zeolites,…	-NaH encapsulated - LiH and MgH_2 - CaH_2

Solid storage seems to be the most promising way forward. The volume capacities are very interesting, higher than those of liquid storage.

1.6.3.1 STORAGE BY HYDRIDE:

It is the storage in atomic form of hydrogen in compounds known as hydrides. During the process of the latter, the following reaction takes place:

$$M + x/2\ H_2 \leftrightarrow MHx + \Delta Q\ (heat) \qquad (1\text{-}1)$$

M: metal or alloy.

x: coefficient (integer or not) corresponding to the hydrogen content of the hydride.

We can distinguish 2 main families: metal alloys where hydrogen is found in the interstitial sites formed by metals and the hydride of metals other than transition, such as alanates or borohydrides. Additional information on alanates and borohydrides can be found in the state of the art of compounds used for hydrogen storage. From these families of compounds, 2 categories are distinguished:

- "Reversible" hydrides which are most often classified according to their operating temperature and their capacity (intermetallic compounds, solid solutions, complex hydrides, etc.).
- "Irreversible" hydrides from which hydrogen is generated either by thermal decomposition or by chemical reaction. (This category is also referred to as "chemical hydrides".

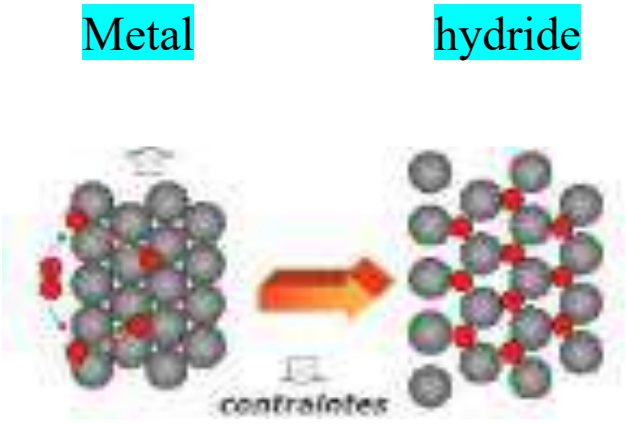

Figure 1.16 Hydrogen phenomenon that generates stresses.

Hydrogen is difficult to store and transport, due to its low energy density per unit volume, there are different levels of maturity for its distribution. Among the mature technologies are gaseous hydrogen networks or in pipelines, as well as the storage of hydrogen in cylinders in gaseous or liquid form [36].

1.7 MAIN ADVANTAGES OF HYDROGEN

- It does not exist in the natural state but it is very abundant on earth in atomic form (water, hydrocarbons, etc.);
- Hydrogen has a high calorific value compared to oil, methanol and natural gas. Its combustion generates a large amount of energy (about 3 times more than gasoline at constant weight);
- Its combustion is carbon-free (no CO_2 emissions when it comes from renewable sources); the use of hydrogen as an energy carrier allows to obtain energy without the production of greenhouse gases, which makes it possible to achieve a clean energy supply chain.
- Hydrogen reacts with oxygen, releasing water and heat, no formation carbon, sulfur or nitrogen oxide derivatives
- Hydrogen is storable, and hydrogen storage can be carried out in several forms: gaseous hydrogen storage, liquid hydrogen storage and storage in solid form, etc.
- Hydrogen is capable of producing and storing electricity using fuel cells.
- Hydrogen can be used in engines instead of gasoline, such as LPG or methane (natural gas)
- Hydrogen is transportable compared to other types of renewable energy (solar, wind, geothermal) which are nearly impossible to transport

Finally, hydrogen is already a basic material in the chemical and petrochemical industry. It can be manufactured specifically to meet the needs of an industry or be a by-product in another manufacture (manufacture of ethylene or chlorine for example).

1.8 RISKS AND PHENOMENA ASSOCIATED WITH HYDROGEN

Hydrogen is a colorless, odorless, non-toxic and non-corrosive gas likely to generate, in particular, a risk of asphyxia (anoxia), a thermal risk and an explosive risk [37].

1.8.1 RISK OF ASPHYXIATION

The risk of asphyxiation will mainly occur in confined environments. Hydrogen is a very light gas (density: 0.066); it will therefore tend to rise and dilute very quickly in the air in an open environment. It should however be noted that if the conditions are conducive to the appearance of the risk of asphyxia (anoxia), the appearance of the risk of explosion will still be

1.8.2 THERMAL RISK

The combustion reaction of hydrogen in air corresponds to the following balance equation:

$$H_2 + 12\ O_2 + 2N_2 \rightarrow H_2O + 2N_2 \qquad (I.2)$$

Hydrogen is an extremely flammable gas under normal conditions of temperature and pressure. It is characterized by the following data:

Table 1.7: Flammability characteristics of hydrogen

Proprieties	Related data
Lower flammability limit	4%
Upper flammability limit	75%

The essential characteristics of hydrogen are a very wide flammability range and a very low ignition energy.

1.8.3 EXPLOSIVE RISK PRESENTED BY HYDROGEN

The explosive range of hydrogen is very wide, considering that the flammability limits are similar to the explosive limits. The speed of propagation of the flame makes it possible to determine the nature of the energy regime of the explosion:

• Either the deflagration: the flame front moves at a subsonic speed, the fresh gases are then compressed by the expansion of the volume, a continuous increase in pressure is observed in the gaseous cloud;

• Either detonation: the speed of propagation of the flame is supersonic, we observe the formation of a shock wave.

1.8.4 CRYOGENIC AND VAPORIZATION HAZARDS

The liquid state being more favorable for storage and transport, hydrogen is maintained at -252.8°C (i.e., 20.35°K), under a pressure of between 1 and 10 arms. In this state, it is comparable to a cryogenic liquid.

There are three dangers associated with hydrogen in its cryogenic liquid state. It's about:

• the ability to be extremely cold (cryogenic risk);

• the propensity of small quantities of liquid to occupy very large volumes by passing into the gaseous state.

• its temperature below the condensation points of the air, leading to oxygen enrichment of the non-insulated areas in contact with the liquid hydrogen.

Cryogenic Hazard: Cryogenic liquids may cause skin effects similar to thermal burns.

CHAPTER 2

2. HYDROGEN PRODUCTION PROCESSES

2.1 HYDROGEN PRODUCTION FROM FOSSIL FUELS

Given their availability, their price, their integration in refining or petrochemicals and their good chemical reactivity, hydrocarbons ensure a percentage of 90% of the traditional production of hydrogen. The different techniques developed to date for the production of hydrogen from fossil fuels, also called synthetic methods, give rise to different by-products, like CO, CO_2, CH_4, H_2O.

2.1.1 STEAM REFORMING

Steam reforming consists of reacting methane with water vapor over a nickel-based catalyst on alumina rings impregnated with 10 to 16% by mass of nickel. This transformation takes place at high temperature of 840 to 950°C, at high pressure of 20 to 30 bars. The nature of the reaction is endothermic:

$$CH_4 + H_2O + \Delta H° \rightarrow CO + 3H_2 \quad (2.1)$$

With ΔH°: the standard enthalpy of formation at (298K) = 206.2 kJ/mol (H2O steam).

The carbon monoxide produced in the reaction also reacts with water according to the following reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 - \Delta H° \quad (2.2)$$

With ΔH°= -41.1kJ/mol, if all the reactants are in gas form at ambient pressure and temperature. ΔH°= -5.0 kJ/mol if the water is liquid.

The steam reforming process separates into two reactions: the first is the reaction of methane with water which produces CO and hydrogen, the second is the reaction of water and CO which produces CO_2 and H_2. The first reforming reaction takes place around 800-900°C for a pressure of 25 bars, this gives a gas rich in CO and H_2 also containing CO_2.

It is then necessary to eliminate the CO, for this we use a water vapor transformation reactor (Water Gas Shift) in order to treat the gases produced where a third reaction will take place under more appropriate temperature conditions at around 200°C. Finally, preferential oxidation allows the last traces of CO to be eliminated by oxidation of the latter into CO_2. We then obtain a gas with essentially H_2 and H_2O, a little CO and CH_4 [38].

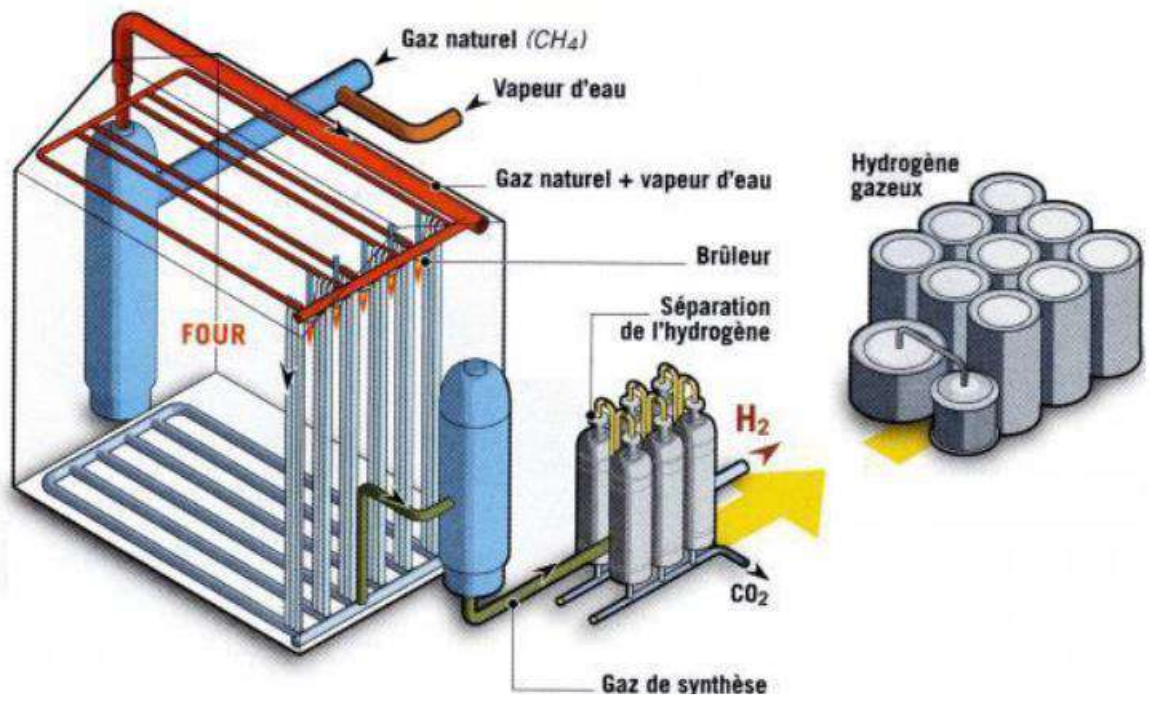

Figure 2.1 Steam reforming of natural gas

2.1.2 PARTIAL OXIDATION OF HYDROCARBONS

Hydrogen can be synthesized by the oxidation of hydrocarbons in the presence of air or pure oxygen, this procedure called partial oxidation which is also a master production process. In the case of methane, the partial oxidation of the latter can be described by the following reactions [39]:

$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$ $\Delta H°\ (298K) = -35.7$ kJ/mol (2.4)

$CH_4 + O_2 \rightarrow CO_2 + 2H_2$ $\Delta H°\ (298K) = -319$ kJ/mol (2.5)

These types of reactions are exothermic and usually proceed without a catalyst. But

the partial oxidation of natural gas, which is essentially composed of methane, undergoes the

transformations according to the following reactions:

$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$ $\Delta H°\ (298K) = -36$ kJ/mol (2.6)

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H°\ (298K) = -41$ kJ/mol (2.7)

The balance of the two reactions is:

$CH_4 + H_2O + 1/2\ O_2 \rightarrow CO_2 + 3H_2$ $\Delta H°\ (298K) = -77$ kJ/mol (2.8)

The first reaction is exothermic and is characterized by a H_2/CO mole ratio of the order of 2 and the second reaction is also exothermic and almost complete. For the balance of the two reactions,

the maximum yield of hydrogen relative to methane is: 6/16 = 0.375 or 37.5%. The two major technologies at the industrial level are the Shell and Texaco processes [40]. The production of hydrogen by partial oxidation of methane increases with process temperature, but reaches a maximum value at around 1000 K. Theoretical efficiency is similar to that of conventional steam reforming, but the process requires a lot of water to function.

2.1.3 AUTOTHERMAL REFORMING

Autothermal reforming is a combination of partial oxidation and steam reforming

featured in the following reactions:

$$CH_4 + H_2O \rightarrow CO+3H_2 \qquad \Delta H° (298K) = 206kJ/mol \qquad (2.9)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H° (298K) = -802kJ/mol \qquad (2.10)$$

This process is used to compensate for the heat of the endothermic reactions of steam reforming by the exothermic reactions of partial oxidation. In this process, natural gas and oxygen are mixed in parallel with steam before being preheated. They are then sent to the reactor (nickel-based catalyst, pressure of 20 to 60 bars and temperature of 900 to 1100°C) for the production of synthesis gas. The typical composition of the gas obtained is: 68% H2, 20% CO, 10% CO2, 5% CH4 and 5%. N2.

2.1.4 THE DISADVANTAGES OF HYDROGEN PRODUCTION BY FOSSIL FUELS

Currently, more than 90% of hydrogen production comes from fossil fuels (oil, gas, coal). This technique, which results in the release of CO_2, is therefore only environmentally valid if the CO_2 is stored. For this, certain conditions must be met, among these conditions high temperatures (1200-1500°C) and high pressures (20 to 90 bars or more). These difficult and costly technical conditions are justified by the very high price of the raw material. This technique has a big disadvantage of producing a lot of carbon dioxide which is a greenhouse gas. This method uses endangered fossil fuels.

2.2 COAL GASIFICATION

The general principle of gasification is to mix a charge of coal (either in solid state or as a slurry) with an oxidant (usually air or pure oxygen and water steam) to a temperature of 1000 to 1500°C and under high pressure, which makes it possible to obtain a gas containing mainly CO and hydrogen. The elimination of Carbon Monoxide is done through the Water Gas Shift reaction, the CO_2 formed then being dissolved. Indeed, the gasification of coal is a partial oxidation of solid compounds (biomass, coal, etc.). Overall, the main stages of coal gasification are similar to the

process of partial oxidation of petroleum residues. The first step is to gasify the coal in the presence of water and oxygen to produce a gas mixture containing CO and H_2. Product gas desulphurization can also be done before or after CO conversion. The purification of hydrogen (methanation or PSA) is generally carried out with prior separation of CO_2. Many reactions can take place in the gasifier. The main ones are given in Table 2.1:

Table 2.1 Reactions within the gasifier [41].

Heterogeneous reactions	Homogeneous reactions
$C + O_2 \rightarrow CO_2$	$CO + ½\ O_2 \rightarrow CO_2$
$C + ½\ O_2 \rightarrow CO$	$H_2 + ½\ O_2 \rightarrow H_2O$
$C + H_2O \rightarrow CO + H_2$	$CO_2 + H_2 \rightarrow CO + H_2O$
$C + 2H_2 \rightarrow CH_4$	$CO + 3H_2 \rightarrow CH_4 + H_2O$

Given the heterogeneous reactions involved, a judicious choice of gasifiers is very important for the smooth running of the process. Gasifiers are therefore solid-gas reactors, the choice of which depends in particular on the quality of the coal used. There are three main types of gasifiers which vary according to their operating conditions (temperature, pressure), the mode of contact between the oxidant and the carbon, the mode of introduction of the reagents and the mode of extraction of the ashes:

- The fixed bed gasifier: the gases circulate through a fixed bed of carbon particles. The temperature is 800 to 1000°C and the pressure 10 to 100 bar.
- The fluidized bed gasifier: the coal particles are suspended in a gas stream. The temperature is 800 to 1000°C and the pressure 10 to 25 bar.
- The forced flow gasifier: the carbon particles and gases flow through Co-current at high speed. The temperature is 1500 to 1900°C and the pressure 25 to 40 bar

Currently, forced flow reactors are the most widely used. The cost of hydrogen production by gasification is equivalent to that of the partial oxidation of petroleum residues but the CO_2 emissions are even higher and are of the order of 19 tons of CO_2 per ton of hydrogen produced [42,43].

2.2.1 DISADVANTAGES OF HYDROGEN PRODUCTION BY COAL GASIFICATION

This technique has a negative impact on the environment because it produces a lot of carbon dioxide. The yield of hydrogen production by coal gasification remains low compared with other methods of hydrogen production.

2.3 HYDROGEN PRODUCTION BY WATER DECOMPOSITION

2.3.1 WATER ELECTROLYSIS

The electrolysis of water is an electrochemical reaction of decomposition of water into hydrogen and oxygen by the application of a potential difference between two electrodes immersed in an electrolytic bath which creates an oriented electric field in which the ions set in motion (the cations move towards the cathode and the anions towards the anode). This voltage essentially depends on the enthalpy and the entropy of the reaction, this theoretical potential of decomposition is 1.481 V at 298 K but the classic values of the potentials of industrial cells are of the order of 1.7 to 2 .1 V, which corresponds to efficiencies of 70 to 85% [44]. When the voltage applied is sufficient, reactions occur.

produce at the electrolyte-electrode interfaces:

At the anode: oxidation with emission of electrons:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \quad (2.11)$$

At the cathode: reduction with electron capture:

$$2\,H^+ + 2\,e^- \rightarrow H_2 \quad (2.12)$$

2.3.2 DIFFERENT TECHNOLOGIES OF ELECTROLYSERS

2.3.2.1 ALKALINE ELECTROLYSERS

Alkaline electrolysis is the most widespread technology for the production of electrolytic hydrogen but also for the production of many chemical compounds such as chlorine. It thus benefits from a very high industrial maturity. In an alkaline technology electrolyser, the electrolyte is an aqueous solution of potassium hydroxide (KOH). Ionic conduction is then provided by hydroxide (OH-) and potassium (K^+) ions. The anodic and cathodic reactions are described below:

At the anode: $2OH^- \rightarrow \frac{1}{2}O2 + H_2O + 2e^-$ (2.13)

At the cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2.14)

The figure below schematically illustrates alkaline electrolysis.

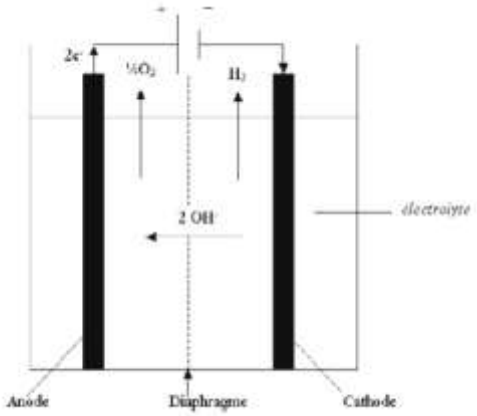

Figure 2.2 Principle of alkaline electrolysis.

2.3.2.2 PEM (Proton Exchange Membrane) ELECTROLYSERS

The operating principle of a PEM (Proton Exchange Membrane) electrolyser is based on the same concept as a PEM fuel cell. The main characteristic of the PEM electrolyser is its solid electrolyte, made up of a polymer membrane. It thus ensures the conduction of the hydronium ions (H_3O^+) produced at the anode and allows the separation of the gases produced (H_2 and O_2), according to the reactions below [44]

At the anode: $3H_2O \rightarrow \frac{1}{2}O_2 + 2H_3O^+ + 2e^-$ (2.15)

At the cathode: $2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$ (2.16)

The principle of PEM electrolysis is schematically described by the following figure:

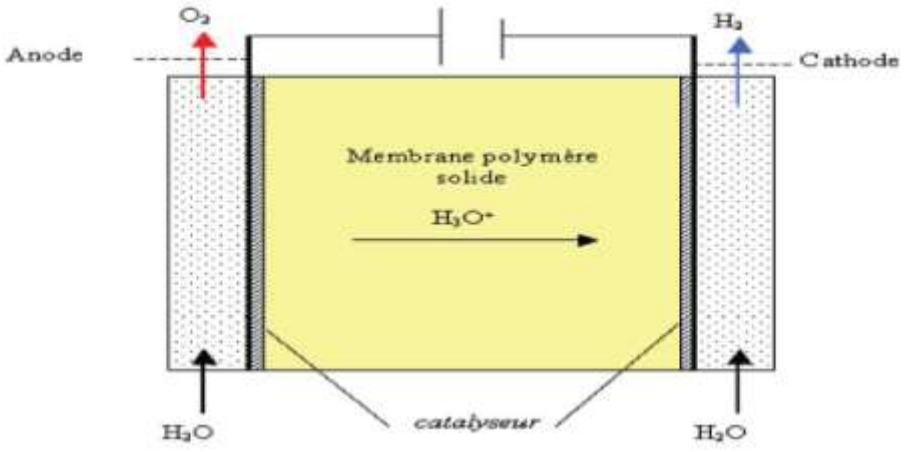

Figure 2.3 Schematic principle of the PEM electrolyser

2.3.2.3 HIGH TEMPERATURE ELECTROLYSERS

The principle of high temperature electrolysis is based on the decomposition of water molecules in the form of vapor at the cathode. This decomposition then depends on the nature of the electrolyte. This can provide either proton conduction or O_2 superoxide ion conduction. The reactions involved at the electrodes are described below according to the type of electrolyte:

- Superoxide ion conduction electrolyte:

At the anode: $2O_2 \rightarrow O_2 + 4e^-$ (2.17)

At the cathode: $2H2O + 4e^- \rightarrow 2O_2 + 2H_2$ (2.18)

- Proton conduction electrolyte:

At the anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ (2.19)

At the cathode: $4H^+ + 4e^- \rightarrow 2H_2$ (2.20)

From a thermodynamic point of view, the electrolysis of water at high temperature is more interesting because the electrolysis energy is provided by both heat and electricity. The main advantage of this type of electrolysis is that most of the electrolysis energy is provided by heat, which is much cheaper than electricity. From a kinetic point of view, the increase in temperature makes it possible to reduce all the electrode over voltages and therefore to reduce the consumption of electrical energy [45].

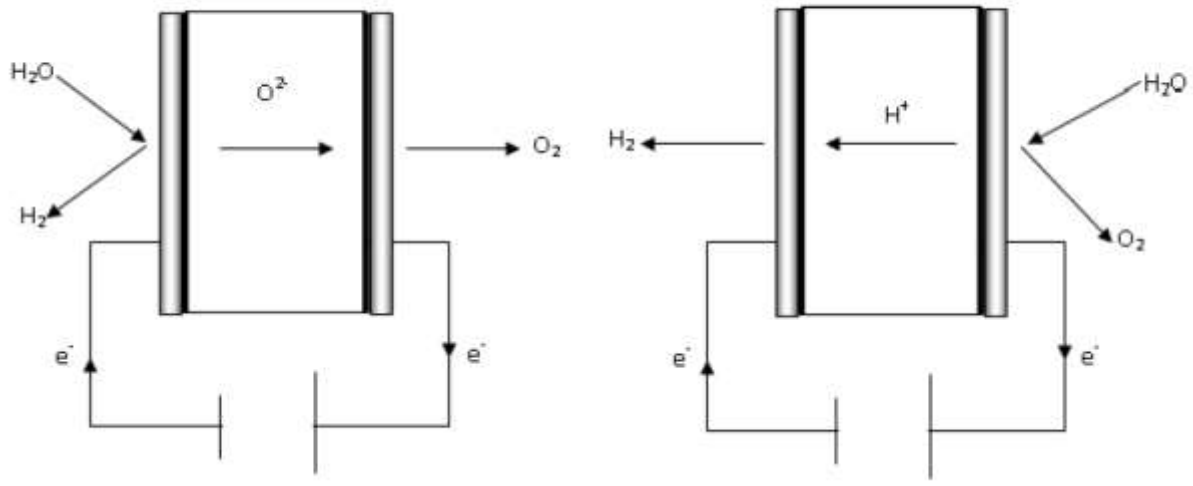

Figure 2.4 Principle of high temperature electrolysis according to the type of electrolyte.

2.3.3 WATER PHOTOLYSIS

The photolysis of water is the process of dissociating the water molecule into hydrogen and oxygen by the effect of light. It is implemented by lighting a semiconductor photocatalyst (such as titanium dioxide TiO_2 and Gallium arsenide AsGa), immersed in an aqueous electrolyte or in water [46]. These semiconductors provide sufficient voltage for the decomposition of water but they only absorb part of the light spectrum and the conversion efficiency remains low. It is therefore necessary to improve light absorption. This improvement can be obtained by modifying the structure of the semiconductor or by coupling with photosensitive structures such as coloring films which absorb a broader part of the light spectrum.

2.3.4 DISADVANTAGES OF HYDROGEN PRODUCTION BY DECOMPOSITION OF WATER

2.3.4.1 BY WATER ELECTROLYSIS

However, this technique has major drawbacks: the yield is low, its production cost is too high because of this technology which requires large quantities of electricity. The electricity consumed is more expensive than the hydrogen gas generated, so some materials used are polluting.

2.3.4.2 BY WATER PHOTOLYSIS

The efficiency of the photolysis of water remains low, because the semiconductors provide the sufficient voltage for the decomposition of water but they only absorb part of the light spectrum, It is therefore necessary to improve the light absorption.

2.4 GASIFICATION AND PYROLYSIS OF BIOMASS

The definition given to biomass by the agriculture sector indicates that it covers any product from agriculture, forestry and its industries, capable of degrading [47]. The production of hydrogen from Biomass is based primarily on the thermal gasification process by which organic compounds such as wood, agricultural products, municipal waste are primarily decomposed into hydrogen and carbon monoxide. Plant material processing techniques are similar to those used for fossil fuels. Using agricultural residues and losses, or biomass specifically developed for energy uses, hydrogen can be produced via pyrolysis or gasification. [48]

2.4.1 PYROLYSIS

Pyrolysis is a process of destruction of organic matter by heat in the absence of oxygen. Under the action of heat, biomass can be transformed into 3 states: "vegetable" charcoal also called charcoal (solid), condensable organic compounds (oils) and permanent gases, the main ones of which are CO_2, CO, H_2O, CH_4. production of one of these 3 products can be favored by adapting the reaction parameters Table 2.2 [49].

Table 2.2 Main products of biomass pyrolysis obtained at atmospheric pressure and according to temperature and heating rate conditions.

Features	**Gas**	**Oils**	**Vegetable coal**
Heating speed	High (>100°C/s)	High (>100°C/s)	Low (<50°C/s)
Temperature	High (>800°C)	Low (500°C)	Low (500°C)
type of reaction	Pyrogasification	Fast pyrolysis	Slow pyrolysis
Mass yield	70 to 80%	50 to 80%	25 to 35%
Energetic efficiency	80% 75% 60%	75%	60%

Mass yields can vary from 50 to 80% depending on the products obtained. The energy yields, meanwhile, can vary from 60% for vegetable charcoal to 80% for oils and pyrolysis gases. Different parameters make it possible to orient pyrolysis essentially towards one of the products of the reaction. These parameters are: reaction temperature, heating rate, residence time, pressure and intrinsic characteristics of the raw material (particle size and water content).

2.4.2 GASIFICATION

Gasification consists of the thermal and chemical transformation of a solid fuel into a gaseous mixture, called "syngas", in the presence of a gas (o_2, water steam, H_2, air, etc.). The proportion of syngas components varies according to the conversion process used, the latter depending on the raw material to be recovered and the type of use of the syngas (syngas) [49]. Table 2.3 presents the composition of the syngas produced during the gasification of biomass.

Table 2.3 composition of syngas from biomass gasification.

Gas	Content (%vol)
CO	28-36
H2	22-32
CO2	21-30
CH4	8-11
C2H4	2-4

Syngas can be used to produce:

• driving energy;

• electricity and heat (cogeneration);

• biofuels

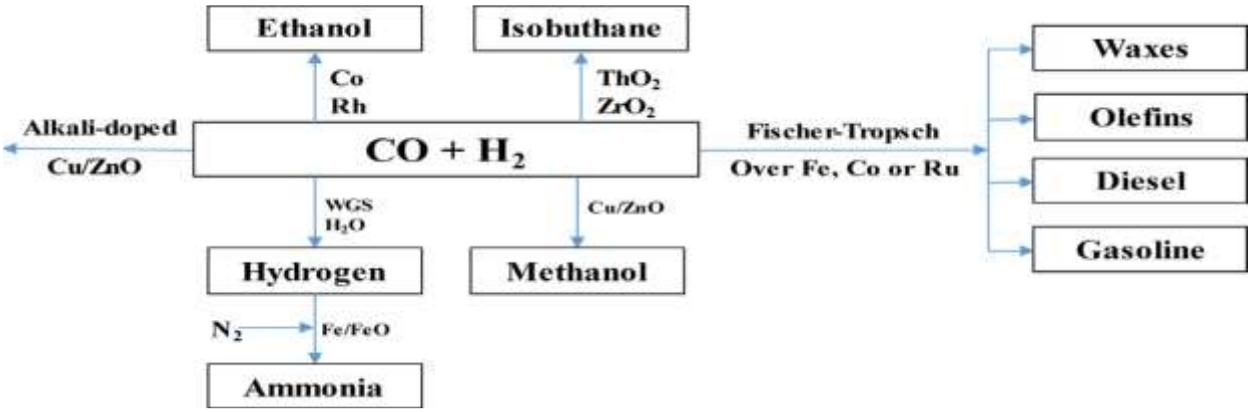

Figure 2.5 Process for the production of methanol, hydrogen, BTL (FT Diesel) via a biomass gasification process.

The main technical obstacles of the gasification of biomass reside at the level of:

- ✓ Raw material and fuel supply. The raw material can vary enormously, which causes feeding problems and requires various pre-treatments;
- ✓ the gasification reactor, which should preferably be able to accept different fuels and can be easily extended;
- ✓ gas purification, a critical step that must be effective.

2.4.3 DISADVANTAGES OF HYDROGEN PRODUCTION BY BIOMASS GASIFICATION AND PYROLYSIS

The yield of hydrogen production from biomass gasification and pyrolysis is rather low compared to other methods. This technique has a disadvantage for the environment and for CO_2 recycling methods.

2.5 BIOLOGICAL HYDROGEN PRODUCTION

Microorganisms mainly produce hydrogen by two methods: by photosynthesis and by fermentation. Besides the need for light, the big difference between the two processes is where the electrons come from for the reaction. Among these mechanisms, there are several specific methods [50]:

- photolysis of water by algae and photosynthetic cyanobacteria,
- photo fermentation of organic acids by photosynthetic bacteria,
- the anaerobic fermentation of organic compounds,
- a two-step hybrid process of anaerobic fermentation followed by photo fermentation

2.5.1 BIO PHOTOLYSIS

The photolysis of water by algae and photosynthetic cyanobacteria is also called direct biophotolysis. This process works through a photosynthetic apparatus of these organisms. This method of hydrogen production could be attractive for the industrial sector. This simplicity could make water biophotolysis more efficient than some alternatives in terms of energy efficiency.

2.5.2 PHOTO-FERMENTATION

Photo fermentation is a process that takes advantage of solar energy for the growth of the organism. Unlike photosynthesis which uses water as an electron donor, photo fermentation instead uses organic molecules to provide the electrons that are required for growth. A significant advantage for photo fermentation is the fact that a very wide variety of substrates can be used as electron donors. For example, butyric acid, succinic acid, lactic acid, malic acid, and acetic acid are all potential electron donors.

2.5.3 DISADVANTAGES OF BIOLOGICAL HYDROGEN PRODUCTION

The yield of biological processes remains low. Among the drawbacks of biological processes, we note the very long residence time (10 to 30 days), the culture and production conditions (composition of the medium, sensitivity, etc.) are difficult to control.

2.6 HYDROGEN PRODUCTION BY THERMOCHEMICAL CYCLES

Water-splitting thermochemical cycles are based on water decomposition through repetitive series of chemical reactions using intermediate reactions and substances which are all recycled during the process so that the overall reactions are equivalent to the dissociation of the water molecule into hydrogen and oxygen. Theoretically, thermal energy is the only requirement for this process.

Thermochemical water splitting cycle (TWSCs) are for hydrogen production using thermal energy and recycling of materials for reuse. TWSCs are not very catalyst dependent and the only consumed substance in the cycle is water, which is the source of hydrogen and all other material scan be recycled [51]. There are some advantages of TWSCs listed as follows:

• Membrane is not required for O_2-H_2 separation

• Temperature range of 500–1800 °C (in most cases)

• No input electricity in pure TWSCs, and low electricity requirement in hybrid TWSCs

The thermochemical cycles are driven either by only thermal energy (Figure 2.6a) which are called pure thermochemical cycles, or by thermal and another form of energy (e.g., electrical, photonic) which are called hybrid thermochemical cycles (Figure 2.6b). In hybrid TWSCs, water, high temperature heat from concentrated solar plants or nuclear reactors, and electricity or photonic energy are the inputs while hydrogen and oxygen are the outputs [52]. Water can be decomposed to H_2 and O_2 just in one step. However, due to the undesirable thermodynamics and the very high temperature required for the single-step, thermochemical cycles are proposed as a repeating set of reactions in which water is split using thermal energy at the temperatures below 2000 °C and usually in two or multi steps [53].

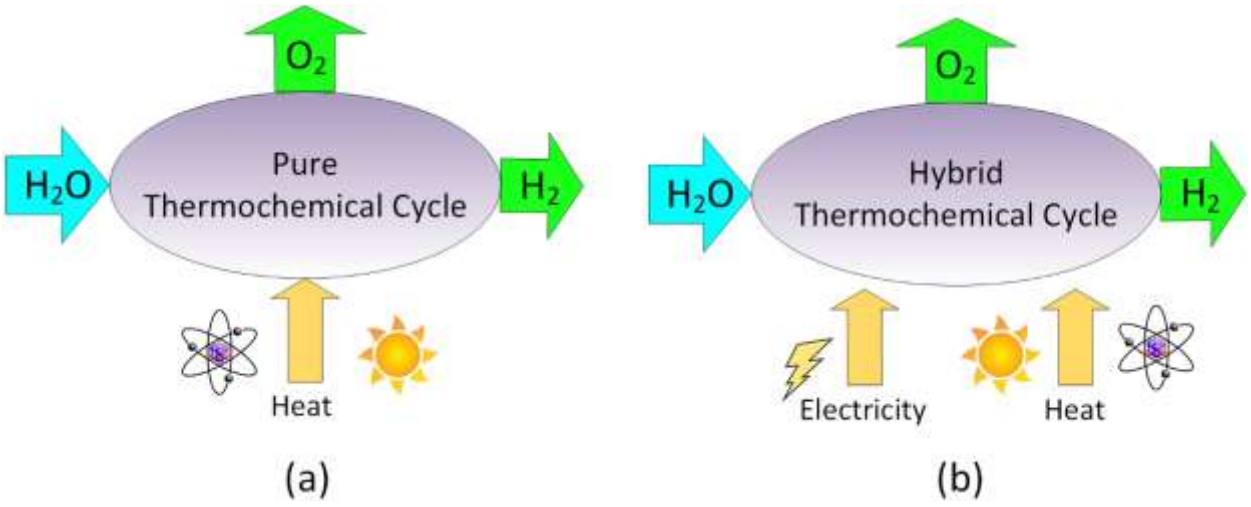

Figure 2.6 General schematic of pure and hybrid thermochemical cycles.

Research and development activities on thermochemical water splitting cycles was begun with some studies by Funk and Reinstrom [54] during 1960 s where thermochemical splitting of water was recommended for hydrogen production instead of conventional electrolysis. The first convention on hydrogen production through TWSCs was held in European Community Joint Research Center located in Ispra, Italy, in 1969 where 24 cycles (So-called Mark cycles) were identified to be investigated in the period of 1970 to 1983 [55]. Since then, many active studies have been carried out and number of different cycle shave been proposed in US, Japan and European countries in 1970s and1980s [56-57]. Even though more than 200 thermochemical cycles have been identified for the water splitting by General Atomic [58], very few of them are proved to have the ability for large-scale hydrogen production and proceed to experimental demonstrations. The Sulfur iodine(S-I) cycle is the most famous and well-studied version of the cycles which was proposed by General Atomics as a promising process regarding the utilization of nuclear heat sources which can supply heat at temperatures close to 900 °C [59]. In 1972, De Beniand Marchetti, proposed the first multi-step process so-calledMarc-1 based on calcium, bromine, and mercury with almost 50% efficiency [60].

By the end of 1976, University of Tokyo in Japan proposed a cycle so called UT-3 with 49% efficiency where Ca, Br and Fe were the main components [61]. After completion of Mark cycles investigations, JAEA research along with some other Japanese institutions continued within 1990 s [59,62]. As shown in Fig. 10, since 2003, research on TWSCs increased mainly by beginning of DOE's solar thermochemical hydrogen production research program (STCH) [63,64] which was followed by some other research projects in Canada [65], European union [66,67] and China [68,69] with continuation of Japanese research [70]. In 2006, Argonne national laboratory (ANL) published are port where more than 280 known thermochemical cycles were investigated for hydrogen production and some recommended for further investigation [71]. German aerospace research center (DLR) and Paul Scherrer institute in Switzerland have being developing solar reactor technologies in the last two decades for hydrogen production via high temperature two-step metal oxide redox pairs and sulfur based thermochemical cycles [72,73].

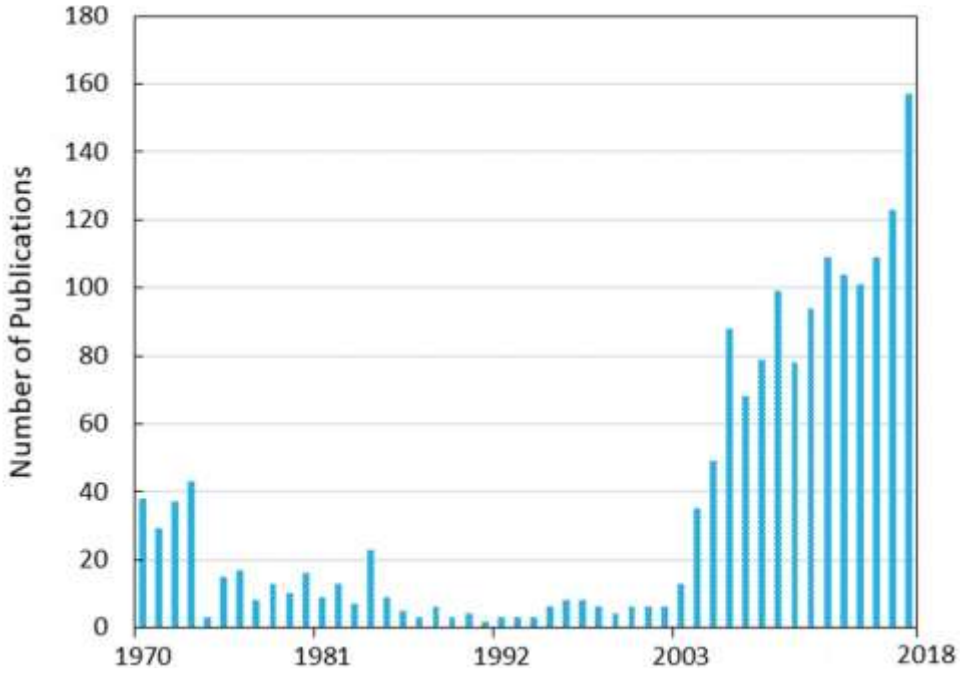

Figure 2.7 Publications statistics on thermochemical water splitting cycles between 1970 and 2018 (data from [74]).

In 2007, Canada's nuclear-based hydrogen production program begun by Atomic Energy of Canada Limited (AECL) and University of Ontario Institute of Technology (Ontario Tech) in partnership with ANL. They started a project for scaling up Cu-Cl thermochemical cycle as a suitable candidate for hydrogen production and integration with nuclear reactors [65,75,76]. Ontario Tech has also developed and enhanced magnesium-chlorine (Mg-Cl) thermochemical cycle in 2016, where Ozcan and Dincer [77,78] enhanced the efficiency of the process by adding a step to the cycle and investigating the hybrid type of the cycle. Numerous research on thermochemical water splitting technologies is performed in many research centers around the world with in the last 50 years.

2.7 SOME THERMOCHEMICAL CYCLES

The simplified representation of a thermochemical and electro-thermochemical water dissociation cycle is shown in Figure 2.8 and 2.9. In general, the cycle requires heat and water and generates two gases of hydrogen and oxygen. The simplest process of its kind consists of a direct water thermolysis reactor coupled with a separation system for the extraction of hydrogen and oxygen. Essentially, water thermolysis is the basic process for single-step thermochemical water separation with high temperature heat. The thermolysis of water is technically possible at temperatures above 3500 K, despite this temperature the products are difficult to obtain [79].

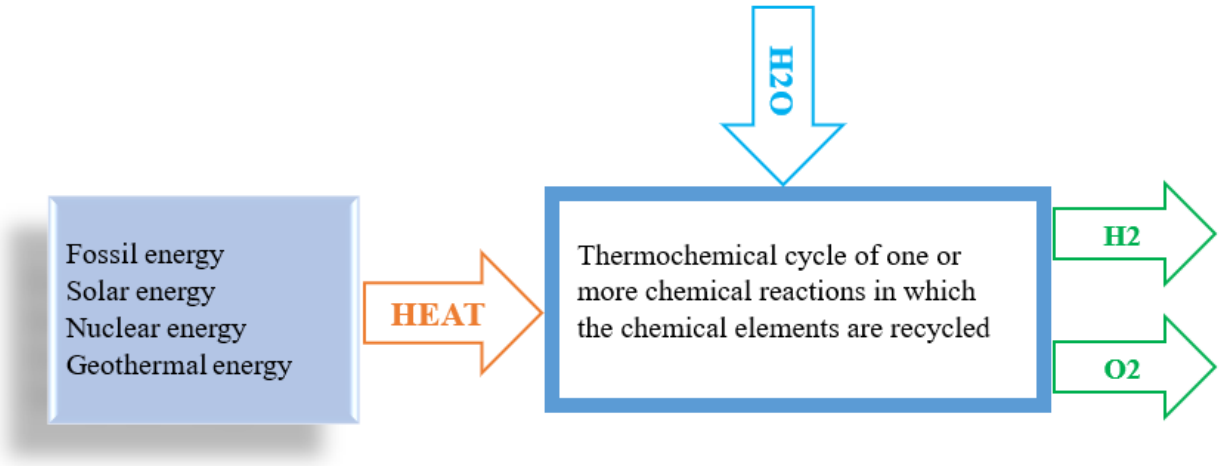

Figure 2.8 Simplified diagram of the thermochemical hydrogen production cycle

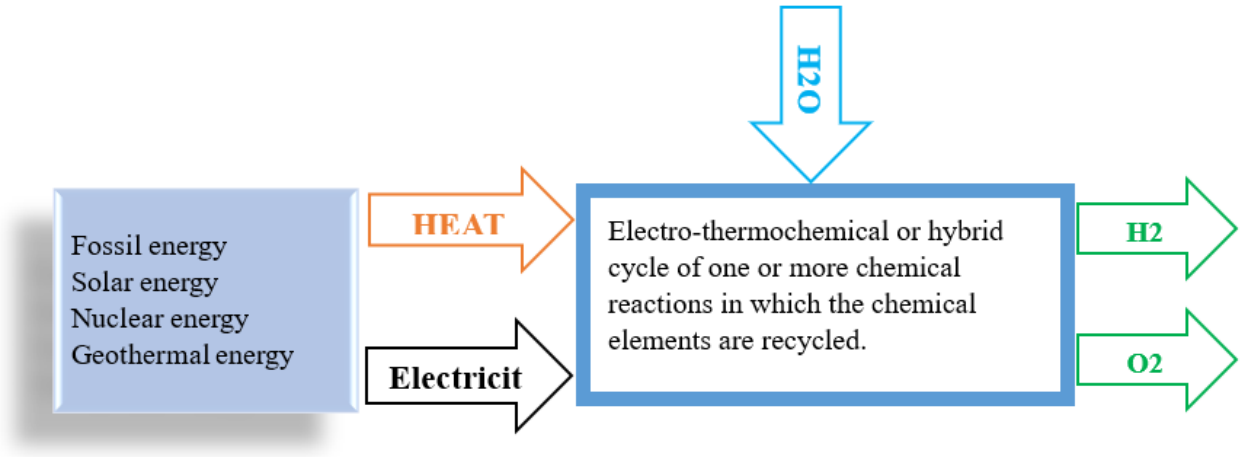

Figure 2.9 Simplified diagram of the electro-thermochemical hydrogen production cycle

Several multi-step processes involving recycled chemicals have been developed in two-step, three-step, four-step, five-step and even six-step. The step represents a chemical reaction or sometimes an important physical process such as electrolysis, hydrolysis, drying, extraction, crystallization…etc. Figure 2.9 illustrates the representation of electro-thermochemical or hybrid cycles, showing that in addition to heat, they also require electricity. In general, hybrid cycles work with medium and intermediate temperatures, while thermochemical cycles are designed for the highest range of temperature sources. Figure 2.10 shows the range of required temperatures correlated with the number of stages of chemical reactions [80]. As mentioned, direct thermolysis requires the highest temperatures. The temperature level decreases with the number of chemical steps involved in the cycle. There are both pure-thermochemical and hybrid processes with several stages. However, all cycles with temperatures below 1000 K are in general hybrid. The development of thermochemical cycles involves the identification of certain intermediate chemical compounds and chemical or electrochemical reactions that facilitate the processes of separation of water and products reacting during the cycle.

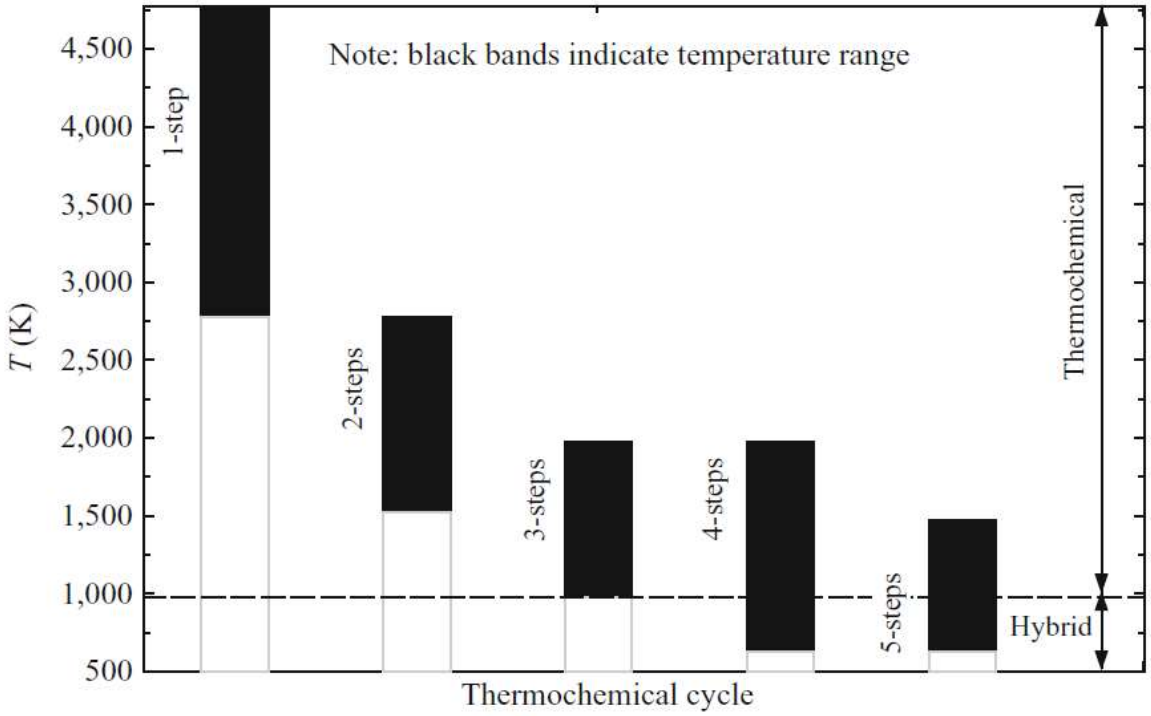

Figure 2.10 Temperature range of thermochemical and hybrid cycles according to the number of steps

The thermochemical decomposition of water through cyclic chemical reactions is considered to be one of the most promising methods for producing hydrogen from thermal energy due to its efficient use of thermal energy. The thermochemical cycle includes a series of looping endothermic and exothermic chemical reactions. The primary source of thermal energy for the production of hydrogen by thermochemistry can be fossil energy, renewable energy or nuclear energy. Although several hundred thermochemical cycles have been identified, research demonstrating technical and financial feasibility has only been reported for a few cycles. A selection of the most promising cycles has been made based on certain factors that influence the technical and commercial feasibility of hydrogen production. The three cycles that will be mentioned in the following paragraphs are; the Sulfur-Iodine cycle, the UT-3 cycle and the Copper-Chlorine cycle. These three cycles have several advantages, due to their simplicity, their technical and financial feasibility, their relatively low operating temperature and their relatively high efficiency.

Table 2.4 Main countries and institutions developing thermochemical cycles

Pays	Institution	Elements	T°C max	η %
Canada	University of Toronto	Cu-Cl	550	42
France	Gas de France	K	825	31
Germany	Rheinisch-Westfaelische Technische Hochschule Aachen	Fe, S	950	56
Italie	Joint Research Centre Ispra	Mark series I-S	900	45
Japan	Japan Atomic Energy Research Institute	I, Ni, S	850	26
	Mitsubishi Heavy Industry	Cl, Cu, Fe	750	27
	University of Osaka Osaka-75	Ba, C, I, N	800	48
	University of Tokyo UT-3	Br, Ca, Fe	750	50
USA	Argonne National Laboratory	Ag, Br, Na	1000	25
		Cu,Cl	550	42
	General Atomic Company GA (Mark 16)	I, S	850	47
	General Electric Agnes process	Cl, Fe, Mg	850	25
	General Electric Catherine process	I, K, Li, Ni	700	22
	Institute of Gas Technology (IGT) A-2	Cl, Fe	1000	51
	Lawrence Livermore Laboratory, University of California (LLLC)	Mg, Se	873	34
	Los Alamos Scientific Laboratory (LASL)	Li, Mn	1000	56
	University of Nevada Los Alamos 159		750	58
	University of Kentucky (UoK) UoK-8	Ba, Fe, S	1073	49
	Allison Laboratory of General Motors	Cl, Ta	973	30

2.7.1 SULFUR-IODINE BASED CYCLE

The sulfur-iodine cycle is proposed by the General Atomic Company of the United States of America, it consists of three stages in the form of chemical reactions:

$$H2SO4(aq) \rightarrow SO2(g) + H2O(g) + 0.5O2(g)\ 850°C \quad (2.21)$$

$$I2(g) + SO2(g) + H2O(g) \rightarrow 2HI(s) + H2SO4(aq)\ 120°C \quad (2.22)$$

$$2HI(s) \rightarrow I2(g) + H2(g)\ 400°C \quad (2.23)$$

The first stage of the cycle involves the decomposition of sulfuric acid at a temperature of 850°C. This step also generates oxygen gas. The second stage is used for the recycling of sulfuric acid and hydrogen iodide, also called the Bunsen reaction. This reaction is exothermic at about 120°C. The last step is the generation of hydrogen by decomposition of hydrogen iodide. This reaction step

occurs at about 400°C. This cycle has a thermal efficiency of about 47% and potentially reaches up to 60% efficiency with cogeneration of hydrogen and electricity [81].

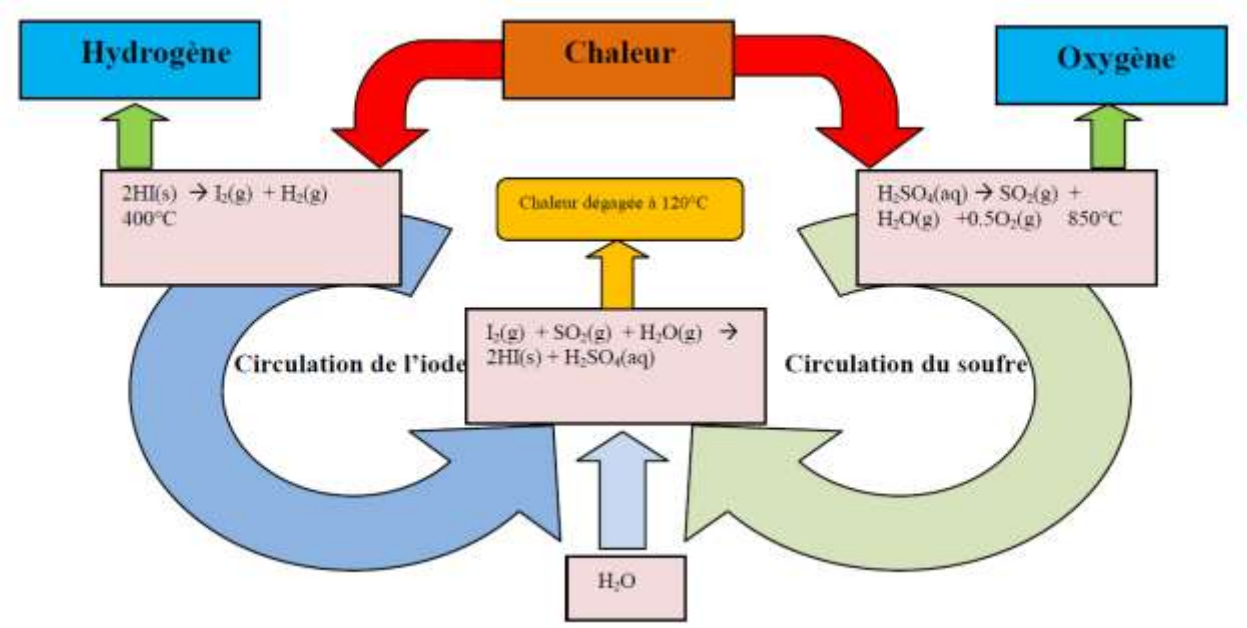

Figure 3.11 *Schematization of the Sulfur-Iodine thermochemical cycle*

2.7.2 CYCLE UT-3

UT-3 is a thermochemical hydrogen production cycle originally developed at the University of Tokyo -3. This cycle is essentially based on the chemical elements which are bromine, calcium and iron. The cycle is made up of four stages which include only solid and gaseous components, the maximum temperature being around 750°C. The stages of the UT-3 cycle are shown below.

$$CaO + Br_2 \rightarrow CaBr_2 + \tfrac{1}{2}O_2 \ 600°C \quad (2.24)$$

$$CaBr_2 + H_2O \rightarrow CaO + 2HBr \ 650°C \quad (2.25)$$

$$Fe_3O_4 + 8HBr \rightarrow 3FeBr_2 + Br_2 + 4H_2O \ 250°C \quad (2.26)$$

$$3FeBr_2 + 4\,H_2O \rightarrow Fe_3O_4 + 6HBr + H_2 \ 560°C \quad (2.27)$$

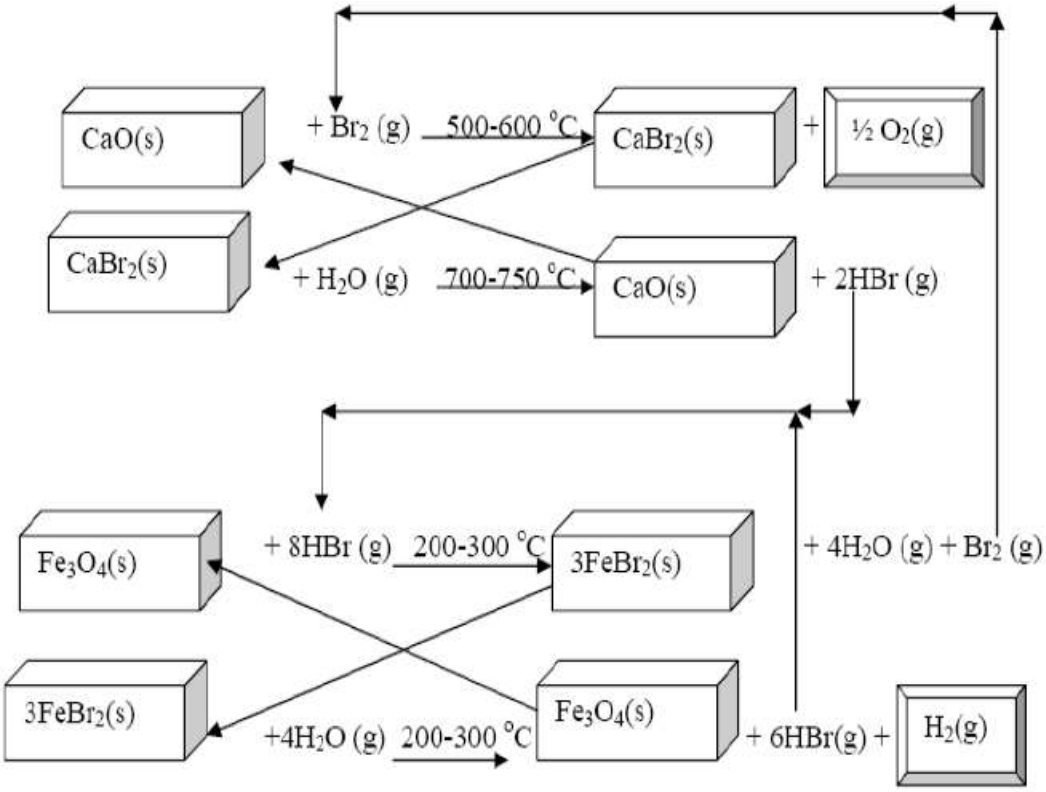

Figure 2.12 Schematization of the thermochemical cycle UT-3.

The predicted thermal efficiency of the adiabatic UT-3 cycle varies between 35% and 50%, depending on the efficiency of the membrane separators, and whether the electricity is co-generated with hydrogen or not. An increase in overall cycle efficiency of 10% is projected in the case of cogeneration. The UT-3 cycle has an advantage of changing the direction of flow of gaseous components, with solid components remaining attached, performing both endothermic and exothermic reactions intermittently in a reactor. This can eliminate the inconvenience of solids handling as the solids remain in the fixed bed reactor [82].

2.7.3 COPPER-CHLORINE BASED CYCLE

The copper-chlorine based thermochemical cycle, with its several variants under research and development in several institutions around the world. The United States Department of Energy DOE plans to use this cycle in conjunction with concentrated solar power to generate hydrogen. In Canada, Atomic Energy of Canada Limited (AECL) is interested in this development of the cycle for their nuclear power plants which generate heat at 800 to 900 K. In Japan and France, a lot of research is being carried out on this cycle for the coupling to existing nuclear power plants.

A comparative study of four hybrid cycles by Argonne National Laboratory in the United States of America concluded that the electro-thermochemical cycle based on copper-chlorine is retained as a potential candidate for further development for the following reasons:

- The cycle efficiency is relatively high,
- Chemical reactions are manageable and mature,
- The chemical elements involved are accessible and inexpensive and present no potential danger during handling,
- The operating temperature is the lowest compared to other cycles.

The main challenges identified for electro-chemicals are the generation of copper and developments related to the electrolyser membrane, the search for suitable electrode materials and the determination of the operating conditions to generate a well-concentrated cupric chloride solution. currently four different configurations of the electro-thermochemical cycle based on copper-chlorine are in research and development namely.

2.7.3.1 CONFIGURATION OF THE Cu-Cl CYCLE WITH THREE REACTIONS

The copper-chlorine cycle is shown in Figure 2.13 It consists of the three major reactions shown in Table 2.5. Reaction 1 is an electrolytic process in which copper chloride (Cu-Cl) is converted to copper dichloride ($CuCl_2$) at the anode and hydrogen ion is converted to H2 at the cathode. The $CuCl_2$ from reaction 1 is hydrolyzed with copper oxychloride (Cu_2OCl_2) at 400°C according to reaction 2. The Cu_2OCl_2 is then decomposed to give molten CuCl and oxygen at 550°C and 1 bar in reaction 3.

Table 2.5: Different steps and reactions and operating conditions of the three-way Cu-Cl cycle reactions [83]

steps	reactions	Terms
Electrolysis	$2CuCl(aq) + 2HCl(a) — 2CuCl_2(aq) + H_2(g)$	100°C, 24 Bar
Hydrolysis	$2CuCl_2(s) + H2O(g) — Cu_2OCl_2(s) + 2HCl(g)$	400°C, 1 Bar
Decomposition	$Cu_2OCl_2(s) — 1/2O_2(g) + 2CuCl(s)$	550°C, 1 Bar
S solid, l liquid, g gas, aq aqueous		

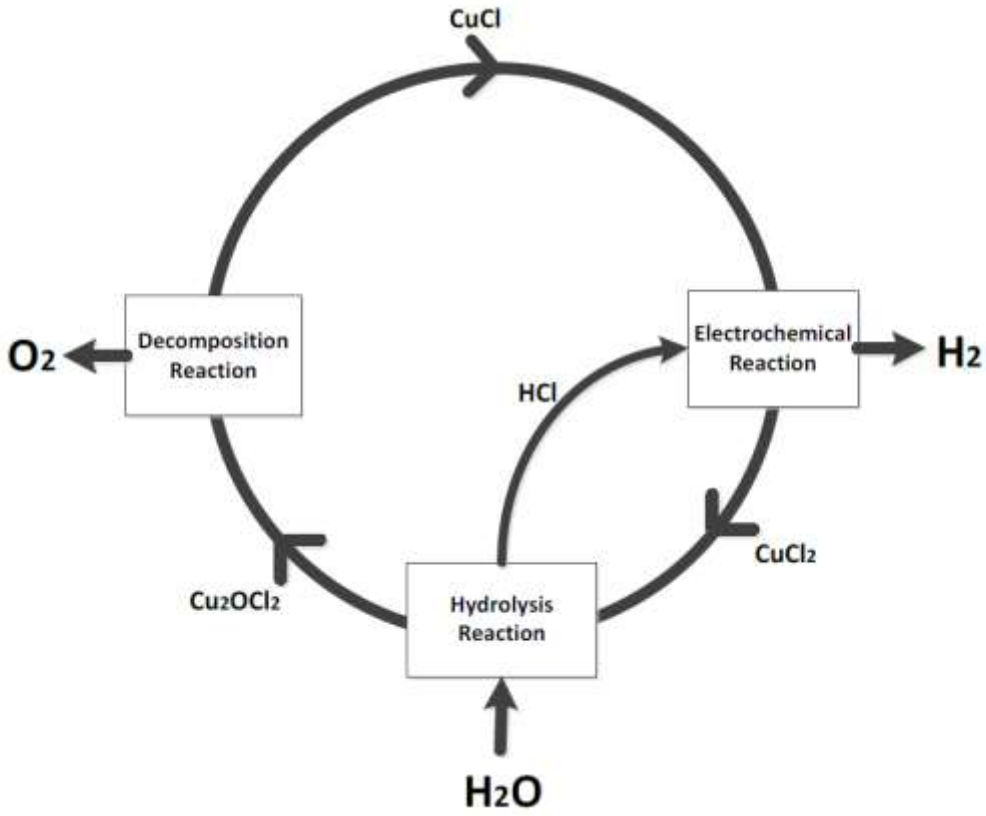

Figure 2.13 Flow diagram of the three-step Cu-Cl cycle

2.7.3.2 CONFIGURATION OF THE Cu-Cl CYCLE WITH FOUR REACTIONS

The four-step Cu-Cl cycle is shown with the main reactions described in Table 2.6. The first step is approximately equivalent to the combination of steps 1 and 4 in the five-step cycle. The aqueous cupric chloride is first dried to a solid product of cupric chloride particles; then introduced into the hydrolysis reactor to produce copper oxychloride. The 4-step cycle [84] combines these processes by supplying aqueous cupric chloride to the hydrolysis chamber, for example by vaporizing the solution with flowing steam to produce the same copper oxychloride product (see table 2.6). The 4-step process has the advantage of reducing complexity by eliminating solids handling and therefore less equipment. However, the 5-step process can be advantageous from an energy and energy efficiency standpoint, as low-grade heat can be used to remove water in the drying process, rather than high-temperature heat in the hydrolysis reactor for the unnecessary latent heat of water vaporization.

Table 2.6 Different steps and reactions and operating conditions of the four-reaction Cu-Cl cycle [85]

steps	reactions	Terms
Electrolysis	$2CuCl(aq) + 2HCl(a) \rightarrow 2CuCl_2(aq) + H_2(g)$	100°C 1Bar
Drying	$2CuCl_2(aq) \rightarrow 2CuCl_2(s)$	100°C 1Bar
Hydrolysis	$2CuCl_2(s) + H2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$	400°C, 1 Bar
Decomposition	$Cu_2OCl_2(s) \rightarrow 1/2O_2(g) + 2CuCl(s)$	500°C, 1 Bar

2.7.3.3 CONFIGURATION OF THE Cu-Cl CYCLE WITH FIVE REACTIONS

As shown in Figure 2.14, heat from nuclear power plants and water enter the process and only H_2 and O2 are produced. Liquid water at room temperature enters the cycle and passes through several heat exchangers where it evaporates and increases in temperature up to 400°C. The heat for this process is obtained from cooling the gases of hydrogen and oxygen before they leave the cycle.

Steam at 400°C and solid copper chloride ($CuCl_2$) at 400°C from the dryer enters the fluidized bed, where a chemical reaction takes place. The chemical formulation for this reaction is:

$$2CuCl_2(s) + H_2O(g) \rightarrow CuO*CuCl_2(s) + 2HCl(g)$$

This reaction is endothermic and produces hydrochloric acid (HCl) and Cu_2OCl_2 gases.

The hydrochloric acid gas is compressed and the $Cu2OCl_2$ is transferred to another process step after its temperature rises to the oxygen generation reaction temperature of 500°C. In the second stage (production of oxygen), an endothermic chemical reaction takes place:

$$CuO*CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$$

In which Cu_2OCl_2 is heated, and O_2 and copper monochloride (Cu-Cl) are produced. Liquid copper monochloride solidifies by cooling it to 20°C, after which it enters the third stage together with solid copper monochloride from the fifth stage. In this step the solid copper hydrochloride and water react successively at 20°C as follows:

$$4CuCl(s) + H_2O \rightarrow 2CuCl_2(aq) + 2Cu(s)$$

Table 2.7 Different steps and reactions and operating conditions of the five-reaction Cu-Cl cycle [85]

steps	reactions	Terms
HCI production	$2CuCl_2(s) + H2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$	400°C 1Bar
Decomposition	$Cu_2OCl_2(s) \rightarrow 1/2O_2(g) + 2CuCl(l)$	500°C 1Bar
Hydrolysis	$4CuCl(s) + H2O(l) \rightarrow 2CuCl_2(aq) + 2Cu(s)$	25-80°C, 1 Bar
Drying	$2CuCl_2(aq) \rightarrow 2CuCl_2(s)$	100°C, 1 Bar
Electrolysis	$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H2(g)$	430-475°C, 1 Bar

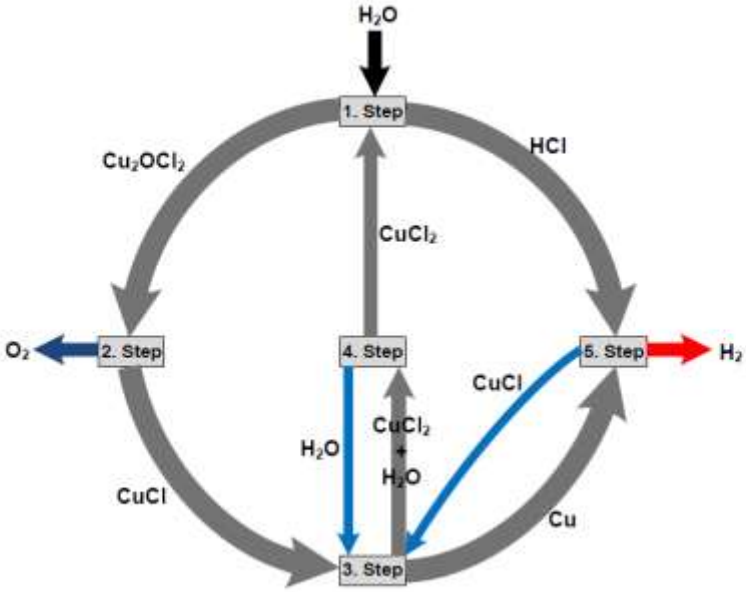

Figure 2.14 Functional diagram of the five-step Cu-Cl cycle

In this reaction, water acts as a catalyst and does not react with other elements or compounds. Another specification for this third reaction differentiates this step from the others and makes it more expensive, depending on the price of electricity. In this reaction, solid copper and a solution of copper chloride with water are produced. A mixture of copper chloride and water is transferred to the dryer in stage 4, and the solid copper enters the fifth stage after its temperature rises to the operating temperature of this stage. A physical reaction takes place in the dryer as follows:

$CuCl_2\ (aq) \rightarrow CuCl_2\ (s) + H_2O\ (l)$

In the fifth stage or hydrogen production stage, hydrogen chloride gas and copper enter, and are converted into gaseous hydrogen H2 and solid copper monochloride (Cu-Cl).

The reaction takes place at 450°C in steady state as follows:

$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$

An alternative arrangement of a five-step Cu-Cl cycle is given in Figure 2.15 This layout has been designed for efficient heat recovery. As explained above, there are five main stages in the cycle. A chemical reaction takes place at each step at varying and elevated temperatures. These chemical reactions form a closed internal loop that continuously recycles all chemicals. The product of one step is a reactant for another. However, since each stage is at a different temperature, the product from one stage must be cooled or heated to the temperature of the next stage before it enters. Thus,

there are many possibilities for heat recovery in the cycle. The recovered energy as well as the energy that is released from exothermic reactions could be reused in the cycle.

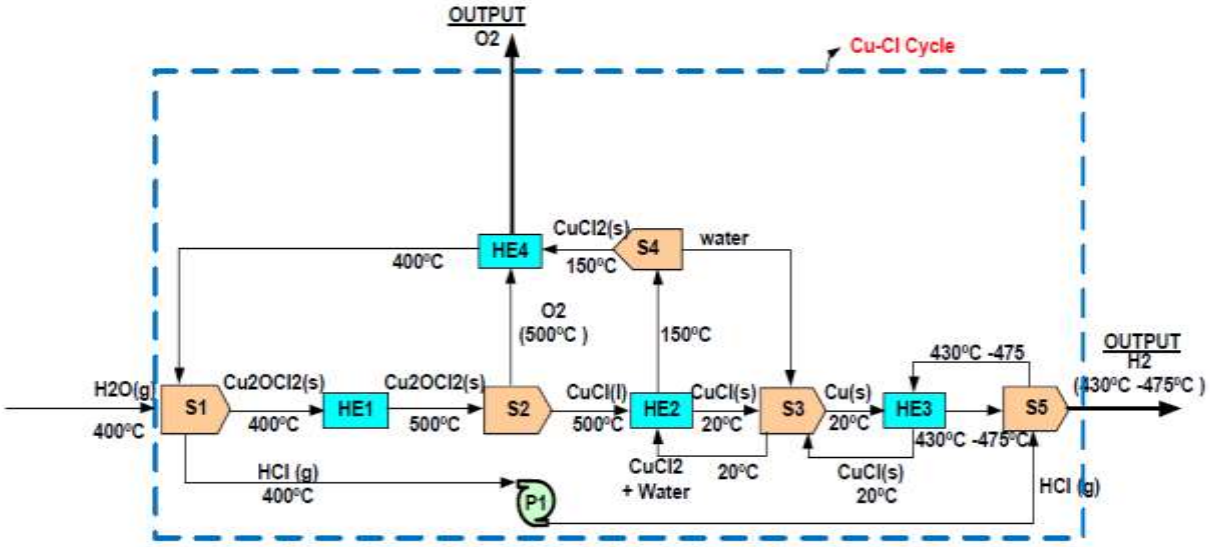

Figure 2.15 Operation of the five-step Cu-Cl cycle following energy saving mode

2.7.3.4 SIX REACTION Cu-Cl CYCLE CONFIGURATION

In this configuration, there are two electrochemical steps instead of just one as in the case of the five-step cycle. The reason for this additional reaction is to reduce the temperature for the dissociation of the Cu-Cl molecule whose purpose is to produce the gas of chlorine Cl_2 and solid copper for recycling purposes.

Table 2.8 Different Steps and Reactions and Operating Conditions of Five-Reaction Cu-Cl Cycle [85-86]

steps	reactions	Terms
Electrolysis	$2Cu(s)+ 2HCl(g) \rightarrow 2CuCl(l)+ H_2(g)$	400°C 1Bar
Electrolysis	$4CuCl(s) + 4Cl^-(aq) \rightarrow 4CuCl_2^-(aq)$	500°C 1Bar
Cu production	$4CuCl_2^-(aq) \rightarrow 2CuCl_2(aq) +2Cu(s)+ 4Cl^-(aq)$	25-80°C, 1 Bar
Drying	$2CuCl_2(aq) \rightarrow 2CuCl_2(s)$	100°C, 1 Bar
Hydrolysis	$2CuCl_2(s)+ H_2O(g) \rightarrow CuO(s)+CuCl_2(s)+2HCl(g)$	430-475°C, 1 Bar
Decomposition	$CuO(s)+CuCl_2(s) \rightarrow 1/2O_2(g)+2CuCl(l)$	

CHAPTER 3

3. ANALYSIS

In this chapter, a new cycle is studied thermodynamically. The proposed system is based on three chemical reactions. Analysis of energy and exergy enables assessment of the thermodynamic system. Different assessments are performed utilizing thermochemistry and thermodynamic tools [87]. Engineering Equation Solver (EES) software is used for simulations and thermodynamic modelling of the results. This research focuses on the proposed copper-chlorine (Cu-Cl) cycle to show the strengths, shortcomings, and gaps to create new techniques for producing cost-effective hydrogen.

3.1 DESCRIPTION OF THE CYCLE

This cycle including copper and chlorine proposed in this study is different from what is found in the literature, where decomposition of water is made by thermochemical means using heat as a driver to obtain oxygen and hydrogen. This cycle can have as a thermal source heat recovered from thermal power stations, gas turbines.

The cycle consists essentially of three stages, summarized in Table 3.1 and Figure 3.1. The three stages require thermal energy. Research and developments concerning the reactions of this cycle are relatively mature. The process consists of a closed internal loop that continuously recycles all copper-chlorine molecules. The principal reaction is that related to hydrogen production; the two remaining ones are used to recycle the chemical components for continuity of the process.

Table 3.1 Chemical reactions

Steps	Reaction	Temperature / Pressure
1. Production of Cu\Cl$_2$	$CuCl_2(s) \rightarrow Cu(s) + Cl_2(g)$	400°C-500°C/ 1atm
2. Production of HCl\O$_2$	$Cl_2(g) + H_2O(l) + Q \rightarrow 2HCl(g) + 1/2O_2(g)$	350-400°C/1atm
3. Production of H$_2$	$Cu(s) + 2HCl(g) \rightarrow CuCl_2(s) + H_2(g) + Q$	<50°C/1atm

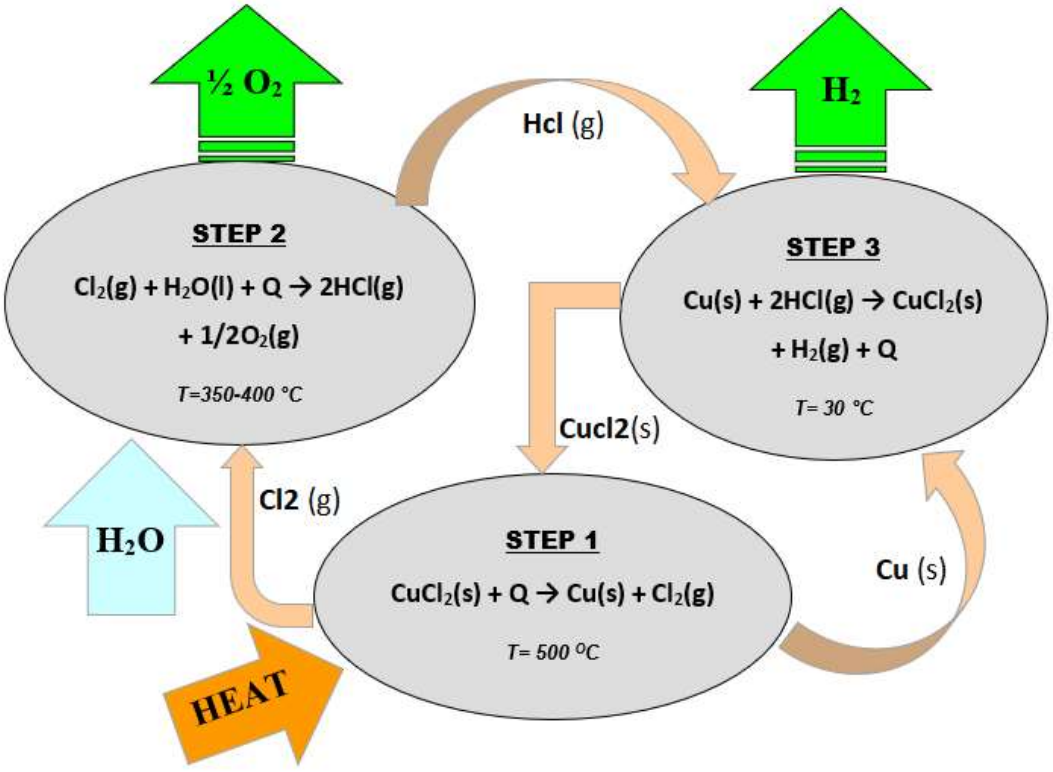

Figure 3.1 Diagram of the Cu-Cl thermochemical cycle.

The mechanism of this cycle is first started by a decomposition of Dichloro-copper in solid state to produce gas chlorine and copper in solid state within a temperature range of 400- 500 °C which is the highest of the cycle. In the second step water and chlorine gas are used to obtain half a mole of oxygen and two moles of hydrochloric acid, both products are in gaseous state. The reverse Deacon reaction is the name given to this reaction. In the third reaction the Cu with the hydrochloric acid HCl react to form solid Copper (II) chloride $CuCl_2$ to be reused in the first reaction in addition to one mole of hydrogen gas H_2, this reaction is exothermic. The Cu-Cl-based thermochemical cycle is one of the promising techniques for producing hydrogen at a temperature of 400-500 ° C and without releasing greenhouse gas emissions.

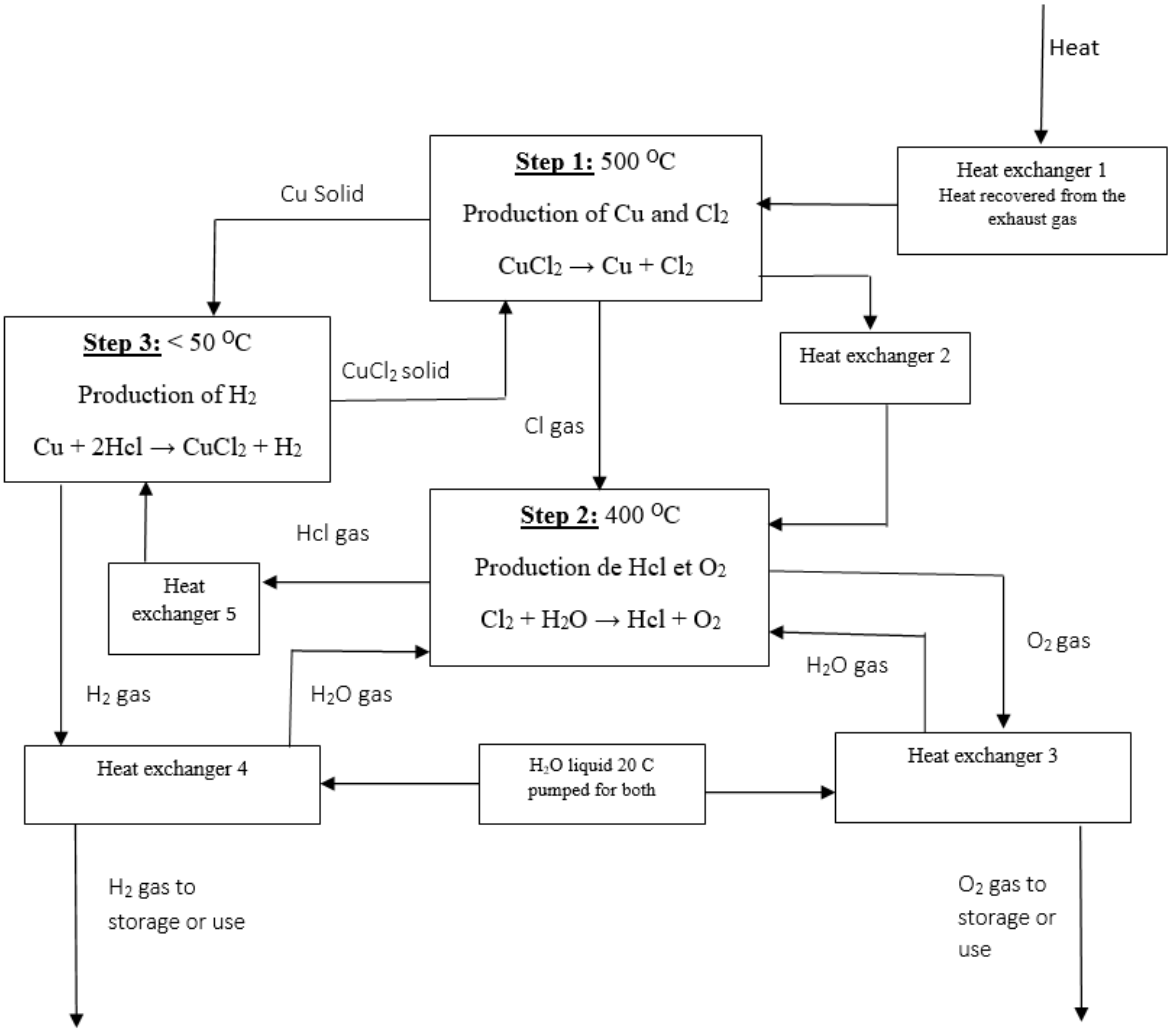

Figure 3.2 Proposed Cu-Cl Cycle Operation Diagram

Before starting the analysis of this cycle, the three chemical equations are checked up to ensure that the reactions are feasible by finding the values of the Gibbs function.

3.2 FEASIBILITY OF CHEMICAL REACTIONS

A chemical reaction is a transformation of matter in which the chemical species (atomic, ionic or molecular) that make up matter are modified. Species that are consumed are called reagents. Species formed during the reaction are called reaction products. Since the work of Lavoisier (1777), scientists know that the chemical reaction is done without measurable variation of the mass: «Nothing is lost, nothing is created, everything is transformed» this reflects the principle of mass conservation. Chemical reactions cause a change in the chemical nature of matter. Thermal

and mechanical transformations, such as state changes (melting, solidification, evaporation, boiling, etc.), wear and erosion, and rupture are therefore excluded. Generally speaking, a reaction can only take place if certain conditions are met (presence of all reagents, temperature, pressure, light conditions). Some reactions require or are facilitated by the presence of a chemical called catalyst. Traditionally, chemical reactions involve changes in electron movement, the formation and rupture of chemical bonds. However, the general concept of a chemical reaction, in particular the concept of a chemical equation, is also applicable to elementary transformations of particles and nuclear reactions. In organic chemistry, various chemical reactions are combined in chemical synthesis to obtain the desired product. The chemical reaction is the descriptive model of a chemical transformation; its symbolic writing, reflecting the transformation balance, is the chemical equation. The proportions of reagents consumed and products formed are given by stoichiometric numbers, obtained by applying the law of conservation of chemical elements and electric charges. In a general case where the species present are represented by the letters A, B, C and D with the respective stoichiometric coefficients a, b, c and d, the chemical equation is written

$$aA + bB \rightarrow cC + dD \quad (3\text{-}1)$$

In this equation, the species which do not undergo any transformation and do not take part in the chemical reaction, are not represented.

Stoichiometric numbers should be adjusted to meet

– the conservation of chemical elements,

– the conservation of the global electric charge.

Consider a closed chemical system whose composition varies due to the existence of the chemical reaction:

$$\sum_i V_i A_i \rightarrow \sum_k V_k A_k \quad (3\text{-}2)$$

When starting from any initial state, the system evolves irreversibly in direction 1 (left to right) or 2 (right to left) so as to reduce its free enthalpy. When the final state is reached, thermal and mechanical equilibrium is achieved (T and P are the same at all points in the system) and the composition no longer varies: state of chemical equilibrium of the system. Once equilibrium is reached, any change in one factor of the equilibrium causes a shift in one direction or the other towards a new state of equilibrium.

This function can predict the direction of the chemical reaction. It is the most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium state [88] which must be less than zero to be feasible and spontaneous. Gibbs free energy, denoted G, combines enthalpy and entropy (combines first law and second law of thermodynamics) into a single value. The change in free energy ΔG, is equal to the sum of the enthalpy change and the product of the temperature and entropy change of the system [89,90].

$$\Delta G = \Delta H - T\,\Delta S \quad (3.3)$$

G: Free enthalpy or Gibbs function with G considered as state function.

At constant temperature and pressure, the above derivation indicates that:

- $\Delta G < 0$; spontaneous reaction
- $\Delta G = 0$: the system is in balance
- $\Delta G > 0$: non-spontaneous reaction (not possible)

We have the following chemical reactions to check:

- $Cucl_2\,(s) + Q \rightarrow Cu(s) + Cl_2(g)$
- $Cl_2\,(g) + H_2O\,(l) \rightarrow Hcl(g) + O_2\,(g)$
- $Cu\,(s) + Hcl(g) \rightarrow Cucl_2(s) + H_2\,(g)$

Application of the Gibbs function on the first reaction;

Reaction 1; Cucl2 (s) → Cu(s) + Cl2(g)

$$\Delta G_{Reaction1} = \Delta G_{Cucl2} - (\Delta G_{Cu} + \Delta G_{Cl2}) \quad (3.4)$$

$$\Delta G_{Cucl2} = \Delta H_{Cucl2} - T\Delta S_{Cucl2} \quad \text{or} \quad \Delta G_{Cucl2} = (\bar{h} - \bar{h}^0)_{Cucl2} - T\,(\bar{s} - \bar{s}^0)_{Cucl2} \quad (3.5)$$

$$\Delta G_{Reaction1} = (\bar{h} - \bar{h}^0)_{Cucl2} - T\,(\bar{s} - \bar{s}^0)_{Cucl2} - [(\bar{h} - \bar{h}^0)_{Cu} - T\,(\bar{s} - \bar{s}^0)_{Cu} + (\bar{h} - \bar{h}^0)_{Cl2} - T\,(\bar{s} - \bar{s}^0)_{Cl2}] \quad (3.6)$$

We use the Shomate equations to develop the specific molar entropy $(\bar{s} - \bar{s}^0)$ and specific molar enthalpy $(\bar{h} - \bar{h}^0)$ values.

Using Equation (3.6), with the help of EES software, we get the following curve of reaction 1 in Figure 3.3. We follow the same steps to obtain the second and third curves of the chemical equations.

Figure 3.3 shows the change of free enthalpy with temperature. The results clearly illustrate that the three chemical reactions are all feasible because their Gibbs functions or free enthalpy is less than zero. One can observe that with the increase of the temperature the Gibbs function increases in the negative direction, which means all reactions are more profitable and spontaneous.

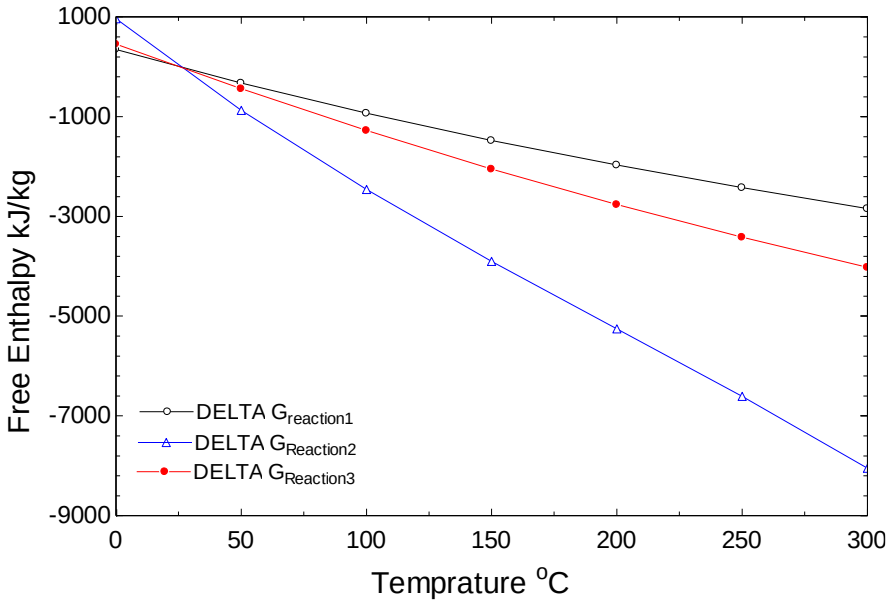

Figure 3.3 Variation of Gibbs function with temperature.

3.3 ENERGY ANALYSIS

When a chemical reaction takes place, the bonds of the reacting molecules between themselves will be broken, after which the atoms and electrons will be rearranged to form other molecules. During chemical reactions, mass will be conserved, so the mass of the products is equal to the mass of the reactants. However, the number of moles of the reaction products may be different from the number of moles of the reactants.

The principle of conservation of energy is applicable in cases where the chemical reaction will or will not take place, however the methods used for the evaluation of the properties differ somewhat between the systems which enter into reaction and the systems which remain inert. In the thermodynamic tables of the properties of systems which remain chemically inert, the values of the specific internal energy u, the enthalpy h and the entropy s correspond to a relative and arbitrary state where the enthalpy (or alternatively the internal energy) and the entropy are set equal to zero. This approach is very satisfactory for the evaluation involving the difference of the values of the thermodynamic properties between the states of the same composition in order to remove the arbitrary chronological state. However, when a chemical reaction takes place, the reactants change and the products are formed. for a reactive system, it is necessary to evaluate quantities such as mass internal energy, mass enthalpy, and mass entropy because there is no change in their properties. one can arbitrarily establish the zero enthalpy value for the chemically stable element at the standard reference state defined by $T_0 = 298.15$ K and $P_0 = 1$ atm.

The enthalpy of the element in the standard state is equal to its enthalpy of formation symbolized by h°. The enthalpy of formation is the energy released or absorbed when the chemical compound is formed from these elements. The specific enthalpy of the chemical compound in a state other than the standard state is calculated by adding the variation of the specific enthalpy between the standard state and the desired state in addition to the value of the enthalpy of training.

Several considerations come into play when the energy balance is established for a chemically reactive system. It is necessary in this case to determine the work and heat transfer. Other considerations are related to the combustion reaction, it is important to know the states and conditions of the reactants before the chemical reactions will take place. The condition of the products must also be assessed. According to the principle of conservation of mass for a system under a steady state, the mass in terms of flow rate remains constant at the inlet and at the outlet [91];

As a contribution to a sustainable plan to address the increasing energy requirements the Cu-Cl cycle can be a viable candidate for production of hydrogen for energy supply. The following quantities are given in terms of kilomole of hydrogen produced, where 1 kilomole of hydrogen is produced per cycle. In addition, the following assumptions are considered:

- Ambient temperature (T_0), and pressure (P_0) of the surroundings are considered.

-The temperature of the reactants and products are at the chemical reaction temperature.

-Steady-state with negligible kinetic energy and potential effects are assumed.

In the steady-state condition, the mass balance is expressed by the mass conservation law [92].

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \tag{3.7}$$

$\dot{m}$ represents the mass flow rate. The molar heat transfer can be extracted from the energy balance:

$\dot{E}_{in} - \dot{E}_{out} = \Delta\dot{E}_{sys}$, with $\Delta\dot{E}_{sys}$ is the rate of energy change of the system, it is assumed that the chemical reactions are done without work, W = 0.

With a steady state reaction, the energy balance can be written as:

$$\dot{Q} = \dot{H}_P - \dot{H}_R = \Sigma n_p(\bar{h}_f^0 + \bar{h} - \bar{h}^0)_p - \Sigma n_R(\bar{h}_f^0 + \bar{h} - \bar{h}^0)_R \tag{3.8}$$

3.4 EXERGY ANALYSIS

Exergy analysis can easily locate the degradation of energy quality in a transformation, something that can improve the operation or the technology of the equipment. The main objective of such an analysis is to identify the causes that affect the smooth running of the transformations and to calculate the value of the irreversibilities or even the destroyed exergy [93]. In thermodynamics, exergy is a quantity used to calculate the maximum work that a system can provide when it comes

into thermodynamic equilibrium with its environment. If energy can only be transformed without ever being destroyed, exergy can only decrease in real transformations. This phenomenon is related to the entropy of the system and its environment, which can only increase during a real, non-reversible transformation. The object of the present study is the energy and exergy analysis of the steps of the new Cu-Cl thermochemical cycle proposed.

For a process involving a chemical reaction, the exergy balance can be written as follows [94]:

$$\dot{E}x_{in} - \dot{E}x_{out} - \dot{E}x_{des} = \Delta\dot{E}x_{sys} \quad (3.9)$$

For steady-state process, $\Delta\dot{E}x_{sys}$ is equal to zero. Therefore, the exergy destroyed is the difference between the exergies entering the system minus the exergies leaving the system, and the specific exergy of flow can be written as follows:

$$\overline{ex} = \overline{ex}^{ph} + \overline{ex}^{ch} \quad (3.10)$$

With:

$$\overline{ex}^{ph} = (\bar{h} - \bar{h}^0) - T_0 (\bar{s} - \bar{s}^0) + \frac{V^2}{2} + gz \quad (4.11)$$

The specific kinetic exergy ($V^2/2$) and specific potential exergy (gz) terms of the physical exergies $\overline{ex}^{ph}$ are neglected in this analysis, $\overline{ex}^{ch}$ is the chemical exergy. Combining Eqs. (3.6) and (3.7) to obtain the term of destroyed exergy:

$$Ex_{dest} = \sum_{in} \dot{n} \left[\left(\bar{h} - \bar{h}^0\right) - T_0(\bar{s} - \bar{s}^0) + \overline{ex}^{ch}\right]_{in} - \sum_{out} \dot{n} \left[\left(\bar{h} - \bar{h}^0\right) - T_0(\bar{s} - \bar{s}^0) + \overline{ex}^{ch}\right]_{out} + \left(1 - \frac{T_0}{T_{rxn}}\right) \dot{Q} \quad (3.12)$$

$\dot{Q}$ is the heat flow into the system as given in Eq. (4.4), positive for endothermic reaction and negative for exothermic one.

After the development of the mass balance and energy as well as exergy analysis of the cycle, the National Institute of Standards and Technology (NIST) database [95] is used to obtain the specific entropy ($\bar{s} - \bar{s}^0$) and enthalpy ($\bar{h}$ -$\bar{h}^0$) values of all reactants through the Shomate equations

$$\bar{h} - \bar{h}^0 = At + B\frac{t^2}{2} + C\frac{t^3}{3} + D\frac{t^4}{4} + E\frac{1}{t} + F - H \quad (3.13)$$

And

$$\bar{s} = A*\ln(t) + Bt + C\frac{t^2}{2} + D\frac{t^3}{3} - E\frac{1}{2t^2} + G - R\ln\frac{P_{rea}}{P_0} \quad (3.14)$$

With: $t = \frac{T}{1000}$

The constant A, B, C, D, E, F, G, H are given in Table below for each chemical element involved in chemical interaction. with T is the temperature specified in Kelvin and values of the specific

enthalpies and entropies, Table 3.2, we calculate the value of the specific chemical exergy for each compound. Chemical exergy based on the value of typical reference exergy taken under standard conditions is called standard chemical exergy. To find the standard chemical exergy of an element not found in nature, one considers the interaction of this element with other compounds for which their standard chemical exergy is known.

Table 3.2 Shomate constants for the compounds [96]

Compounds	A	B	C	D	E	F	G	H
CuCl2(s)	70.21882	23.36132	-14.86876	4.053899	-0.366203	-228.9405	184.6378	-205.8532
Cu(s)	17.72891	28.0987	-31.25289	13.97243	0.068611	-6.056591	47.89592	0
Cl2 (g)	33.0506	12.2294	-12.0651	4.38533	-0.159494	-10.8348	259.029	0
H2O(l)	-203.606	1523.29	-3196.413	2474.455	3.855326	-256.5478	-488.7163	-285.8304
HCl(g)	32.12392	-13.45805	19.86852	-6.85393	-0.049672	-101.6206	228.6866	-92.31201
O2(g)	31.32234	-20.23531	57.86644	-36.5062	-0.007374	-8.903471	246.7945	0
H2(g)	33.066178	-11.363417	11.432816	-2.77287	-0.158558	-9.980797	172.707974	0

Table 3.3 Specific standard entropy and enthalpy of the compounds of the chemical reaction [97]

Compounds	Enthalpy of specific standard formation($\bar{h}_f^0$)kJ/kmol	Standard specific entropy($\bar{s}^0$)J/mol. k
H2(g)	0	130.68
Cu(s)	0	33.15
Hcl(g)	-92310	186.9
Cucl2(s)	-205850	108.06
Cl2(s)	0	223.08
H2O(l)	-285830	69.95
O2(g)	0	205.15

$$\overline{ex}^{ch} = -\Delta G + \sum_P n\overline{ex}^{ch} - \sum_R n\overline{ex}^{ch} \quad (3.15)$$

Where ΔG is the variation of free enthalpy at the standard temperature T_0 and pressure P_0 of the reactants and products. The constant n expresses the number of moles of the substances. in the present case, the chemical exergy of copper chloride $CuCl_2$ is obtained from the basic constituent elements of this molecule, for which the standard chemical exergy is already known, the formation reaction of this molecule is as follows:

$Cu + Cl_2 \rightarrow CuCl_2$

One can write Equation (3.15) as follows:

$$x_{Cucl2}^{ch} = [g_{Cucl2} - g_{Cu} - g_{Cl2}] (T_0, P_0) + x_{Cu}^{ch} + x_{cl2}^{ch} \quad (3.16)$$

The variation of the specific Gibbs function for this reaction is:

$$g_p - g_R = (h - Ts)_{Cucl2} - (h - Ts)_{Cu} - (h - Ts)_{cl2} \quad (3.17)$$

With $g_R = g_{cu} = g_{Cl2} = 0$ and $g_p = g_{fCucl2}^0 = h_{fCucl2}^0 - T_0(s_{Cucl2}^0 - s_{Cu}^0 - s_{cl2}^0)$ (3.18)

We can write the chemical exergy of copper chloride as follows:

$$x_{Cucl2}^{ch} = h_{fCucl2}^0 - T_0(s_{Cucl2}^0 - s_{Cu}^0 - s_{cl2}^0) + x_{Cu}^{ch} + x_{cl2}^{ch} \quad (3.19)$$

According to this procedure, one can obtain the other compounds of standard chemical exergy not found in nature. In addition, one can utilize the exergy balance for evaluating exergy efficiency of each chemical reaction and has a complete view of the Cu-Cl cycle and calculate its efficiency. Under steady-state condition, one can also neglect the exergy transfer to the external environment in the form of exergy losses.

Table 3.4 Standard chemical exergy and Gibbs free energy [97]

Compound	Specific Gibbs free energy of formation (kJ/kmol)	Specific standardchemical exergy $\overline{ex}^{ch}$ (kJ/mol)
$Cucl_2$(s)	-161689	82.1
H_2o(l)	-237 170	0.920
Hcl(g)	-95296	84.73
Cu(s)	0	134.200
O_2(g)	0	3.970
H_2(g)	0	236.1
Cl2(g)	0	123.6

4.5 REACTION ANALYSIS

4.5.1 FIRST REACTION ANALYSIS

Figure 3.4 presents the decomposition of the solid copper bichloride $CuCl_2$ to obtain Cu in the solid state and chlorine gas, where the reaction temperature can achieve 550 °C, the system is in a stable state and the transformation is adiabatic and endothermic.

The heat transfer for the first reaction is determined as follows:

$$\dot{Q} = [N(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{Cu} + [n_p(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{Cl2} - [N(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{CuCl2} \quad (3.20)$$

The destroyed energy is written as:

$$\overline{Ex}_{dest}= [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{CuCl2} - [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{Cu} - [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{Cl2} + \left(1-\frac{T_0}{T_{rxn}}\right)\dot{Q} \quad (3.21)$$

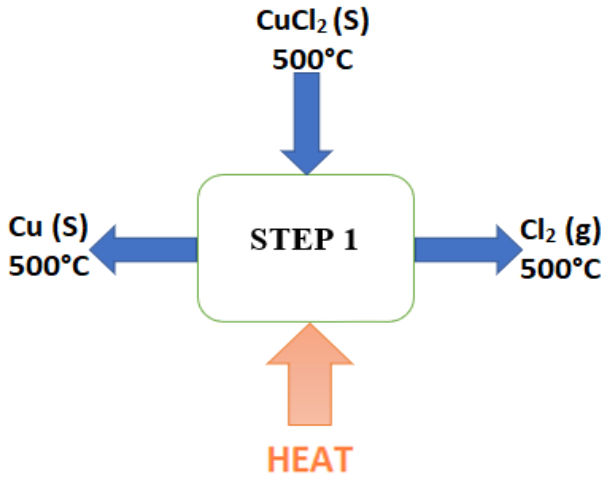

Figure 3.4 Step of Cu and Cl2 production.

3.5.2 SECOND REACTION ANALYSIS

In this step, the chlorine is heated with water until it produces oxygen O_2 and hydrochloric acid HCl in gaseous state as shown in Figure 4.5 The temperature of this reaction varies from 300 °C to 450 °C, the second reaction is considered as adiabatic transformation and endothermic in nature.

The molar heat transfer for the second step can be determined as follows:

$$\dot{Q} = [N(\bar{h}_f^0+\bar{h}-\bar{h}^0)]_{Hcl} + [N(\bar{h}_f^0+\bar{h}-\bar{h}^0)]_{O2} - [N(\bar{h}_f^0+\bar{h}-\bar{h}^0)]_{Cl2} - [N(\bar{h}_f^0+\bar{h}-\bar{h}^0)]_{h2o} \quad (3.22)$$

The destroyed energy is written:

$$\overline{Ex}_{dest}= [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{Cl2} + [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{H2O} - [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{Hcl} - [(\bar{h}-\bar{h}^0)-T_0(\bar{s}-\bar{s}^0)+\overline{ex}^{ch}]_{O2} + \left(1-\frac{T_0}{T_{rxn}}\right)\dot{Q} \quad (3.23)$$

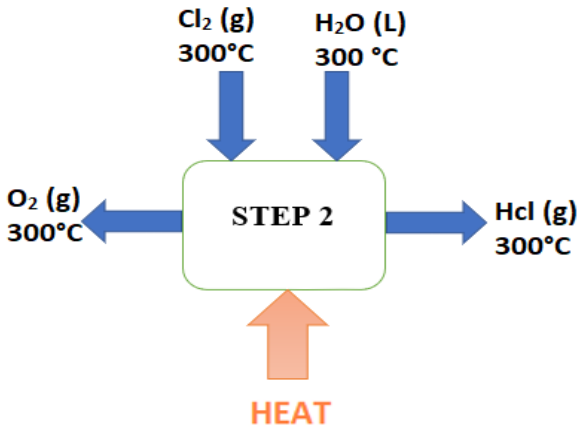

Figure 3.5 Step of Hcl and O2 production.

3.5.3 THIRD REACTION ANALYSIS

In the last step, both components Copper Cu and Hydrogen-chloride Hcl react to be Copper bichloride $CuCl_2$ and the gas of hydrogen, like in Figure 3.6 This interaction is below 50 °C. The third reaction is considered as adiabatic transformation and exothermic in nature.

The molar heat transfer for the third step can be determined as follows:

$$\dot{Q} = [N(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{CuCl2} + [N(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{H2} - [N(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{Cu} - [N(\bar{h}_f^0 + \bar{h} - \bar{h}^0)]_{Hcl} \quad (3.24)$$

The destroyed exergy is written:

$$\overline{Ex}_{dest} = [(\bar{h} - \bar{h}^0) - T_0(\bar{s} - \bar{s}^0) + \overline{ex}^{ch}]_{Cu} + [(\bar{h} - \bar{h}^0) - T_0(\bar{s} - \bar{s}^0) + \overline{ex}^{ch}]_{Hcl} - [(\bar{h} - \bar{h}^0) - T_0(\bar{s} - \bar{s}^0) + \overline{ex}^{ch}]_{CuCl2} - [(\bar{h} - \bar{h}^0) - T_0(\bar{s} - \bar{s}^0) + \overline{ex}^{ch}]_{H2} + \left(1 - \frac{T_0}{T_{rxn}}\right)\dot{Q} \quad (3.25)$$

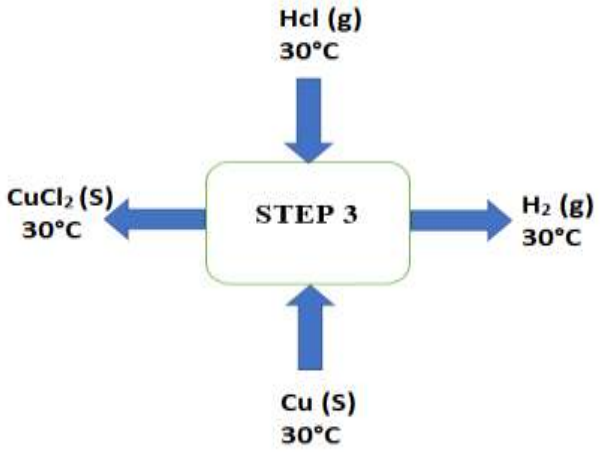

Figure 3.6 Step of H2 production.

3.6 YIELD ANALYSIS

An exergy analysis is imperative in order to identify the elements of the system whose irreversibility or destroyed exergy is the highest as well as the processes that cause these effects. Only part of the exergy destroyed can be avoided because this rate of exergy destroyed for all systems is imposed by physical, technological and economic constraints. There is an inevitable destroyed exergy rate and an avoidable destroyed exergy rate, this last rate is an opportunity to improve the thermodynamic efficiency of the system. Exergy efficiency can be evaluated as follows.

$$\eta_{ex}= \frac{\overline{ex}_{out}}{\overline{ex}_{in}} \tag{3.26}$$

Where $\overline{ex}_{out}$ is the exergy that exists the system, $\overline{ex}_{in}$ is the exergy that enters the system. The exergy efficiency is then:

$$\eta_{ex}= 1- \frac{\overline{ex}_{des}}{\overline{ex}_{in}} \tag{3.27}$$

Based on the assumptions mentioned at the beginning of this chapter and to facilitate the calculation of energy and exergy yields, we will only take the three main steps mentioned above, assuming that the heat losses are zero. The overall energy efficiency of the hydrogen production plant of the Cu-Cl cycle; η_{en} , can be expressed as the fraction of energy supplied Q_f by the useful energy based on the higher calorific value of hydrogen, PCS_{H2} [98].

$$\eta_{ex}= \frac{\mathrm{PCSH2}}{\mathrm{Qf}} \tag{3.28}$$

Where $PCSH2$ higher calorific value per kmole of hydrogen and Q_f the total energy supplied to produce one kmole of hydrogen. The higher calorific value of hydrogen is evaluated at: PCS_{H2} = $286030 kJ/kmole H2$.

The exergy balance can be formulated to determine the exergy yield for reacting systems. Since the steady state is established, the exergy flux at the entrance is equal to the exergy flux at the exit plus the exergy flux destroyed in the system. Suppose the hydrogen plant is well insulated, in which case there is no exergy transfer accompanying the heat transfer, and since there is no work, accordingly, the exergy comes out with the reaction products.

The energy and exergy analysis are done by using the 1st and 2nd law for the development of the heat transfer and the exergy destroyed as well as the exergy yield of each chemical reaction. Using EES software lead to the following results.

CHAPTER 4

4. RESULTS AND DISCUSSION

In this section we will compare some results of the work of references [99,100] with our results. For the variation of the quantity of heat of the first chemical reaction, a comparison between the quantities of heat calculated with that of the work of reference shows that the results of the two figures (4.1 and 4.2) have an identical pace. This will serve as a validation of our model. We can then continue our study by applying the method adopted in this case the exergy method.

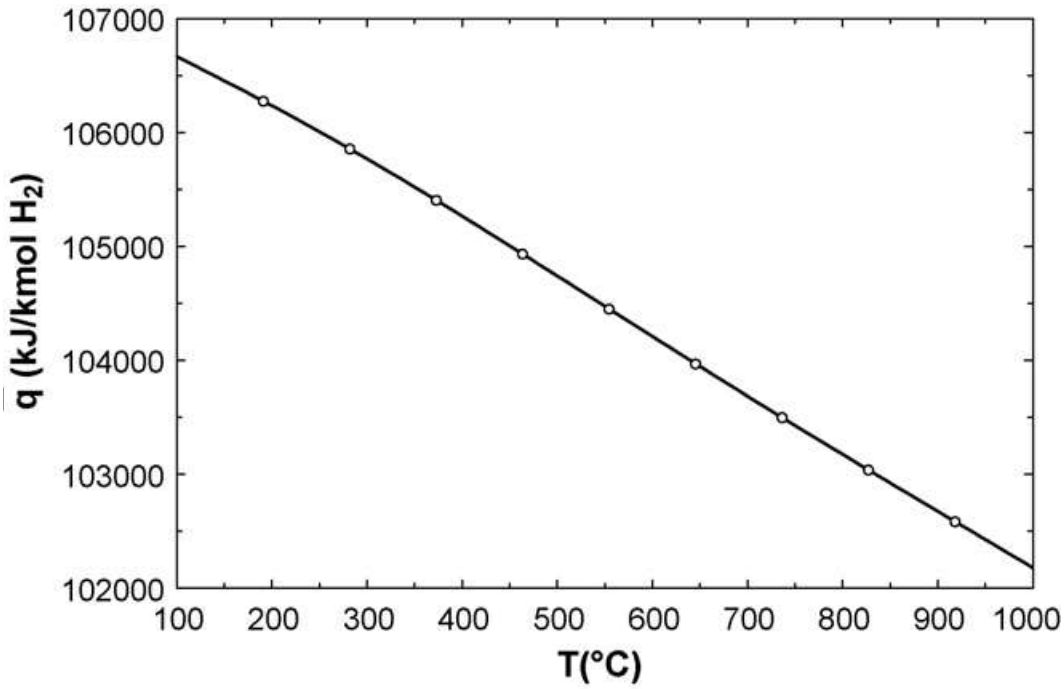

Figure 4.1 Variation of the heat of reaction as a function of temperature in the works of reference [99]

4.1 FIRST CHEMICAL REACTION

Figure 4.2 shows the variation of the quantities of heat in kJ/kmoles according to the variation of the temperatures of the chemical reaction produced during the process of the first stage [CuCl2(s)+ Q→Cu(s)+Cl2(g)]. The reaction temperatures vary in the range of 0°C to 500°C. This temperature range remains the same for the first and the second stage, it is chosen because the exhaust from the gas turbine of the thermal power plant cannot deliver more than 620°C to the hydrogen production plant. We note from this figure that the amount of heat produced is supplied to the

system by the external environment. As the reaction temperature increases, the amount of heat of reaction decreases. such as, the enthalpy of standard formation $\bar{h}_f^\circ$, sensible enthalpy $\bar{h}$, and reaction enthalpy $\bar{h}^\circ$. The enythalpy of copper chloride component is higher than the molar enthalpy of both copper and chlorine components. It is preferable to use high temperatures to save the thermal heat and improve thus the performance of the reaction. The chemical reaction is endothermic in nature in this step. The shape of the curve is almost linear. Results available in the literature show the same trends [101,102].

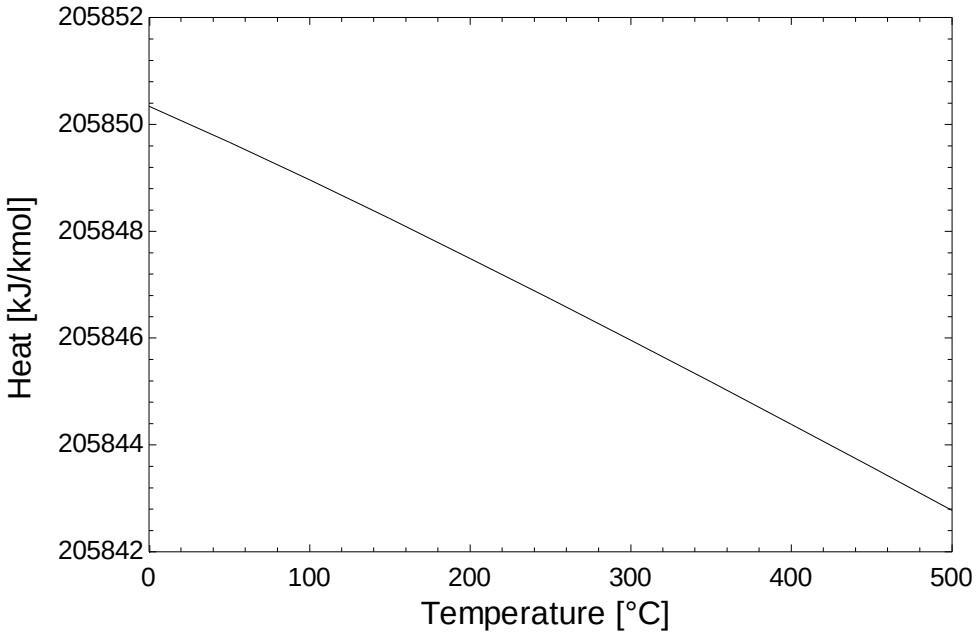

Figure 4.2 Variation of molar heat transfer with reaction temperature.

Figure 4.3 illustrates the variation of the specific exergy destroyed as a function of the reaction temperature for the first stage of the cycle, for several values of the ambient temperature. The destroyed exergy decreases in a nonlinear manner with increasing reaction temperature for different ambient temperatures. Unlike energy, the value of exergy depends at the same time on the state of the external environment as well as the state of the system. For this reason, we varied the ambient temperature for the case of destroyed exergy, since in the city of Laghouat, ambient temperatures can vary between -10°C in winter and 50°C in summer.

It is clear from the second law of thermodynamics that energy has a quality. The analysis of yields according to the first and second law of thermodynamics shows us that when the temperature is very high, the greater part of the thermal energy is converted into useful work and this is what coincides with the definition of Exergy. In other words, the higher the temperature, the better the quality of energy. And who says quality of energy says exergy. From these considerations the

curves of the destroyed exergy of figure 4.3 are in regression with the rise in temperature of reactions and the exergy destroyed increases with increasing ambient temperature. Irreversibilities, such as heat transfer and chemical reactions, always generate entropy and all transformations producing entropy cause the destruction of exergy. There does not exist in nature a reversible process and consequently the exergy is in the process of destruction, thus the exergy of the thermodynamic universe is in continuous decrease. The greater the irreversibility during a process, the greater the destruction of exergy.

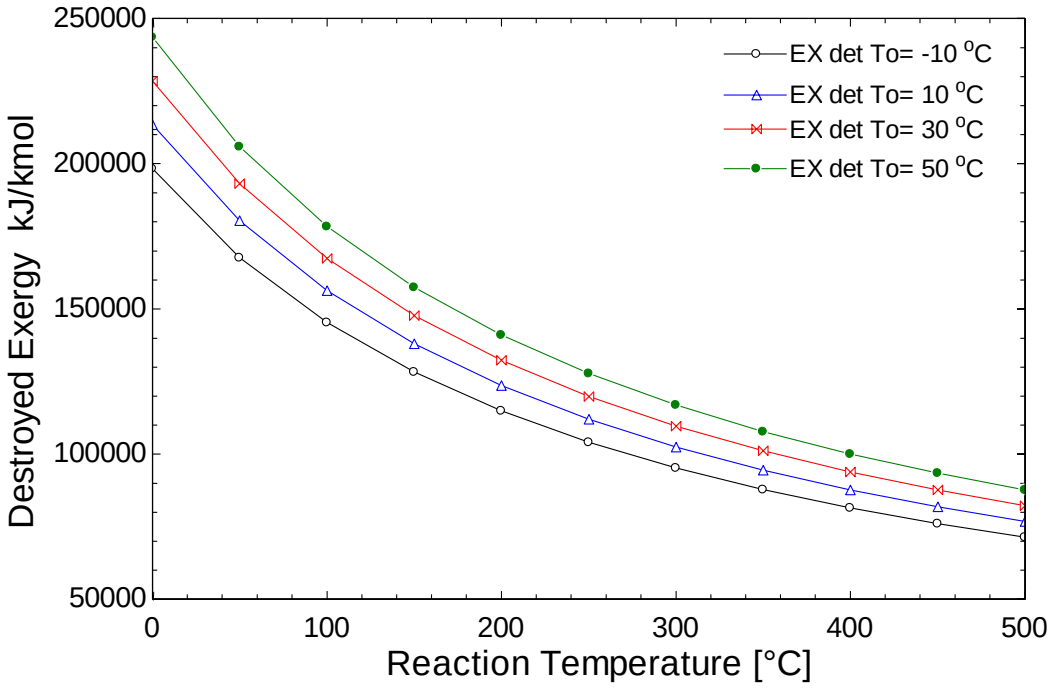

Figure 4.3 Variation of the destroyed exergy with the reaction temperature for several surrounding temperatures.

The exergy efficiency of the first stage, Figure 4.4, changes in the range of 0.14 to 0.74 and increases with increasing reaction temperature. This is due to the fact that the exergy of products such as copper Cu and chlorine Cl_2 is greater than the exergy of the reactants (copper chloride Cucl2), as well as at high temperatures the quality of energy increases and by then the exergy of the process will be better as the irreversibilities decrease and this is the main cause of the improvement in the exergy yield.

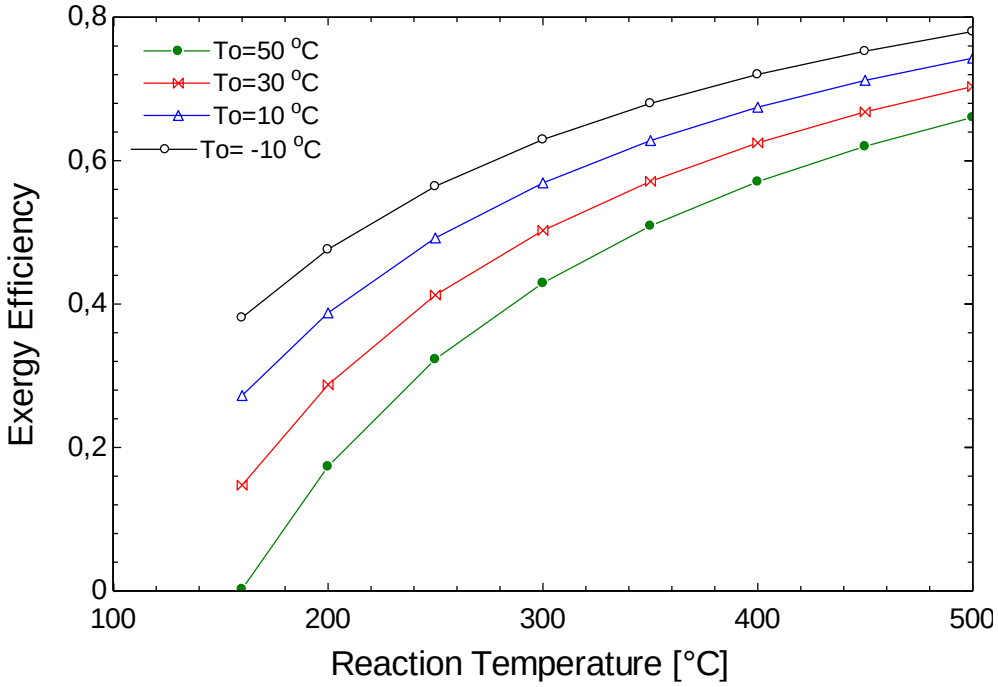

Figure 4.4 Variation of the exergy efficiency with the reaction temperature at several surrounding temperatures.

4.2 SECOND CHEMICAL REACTION

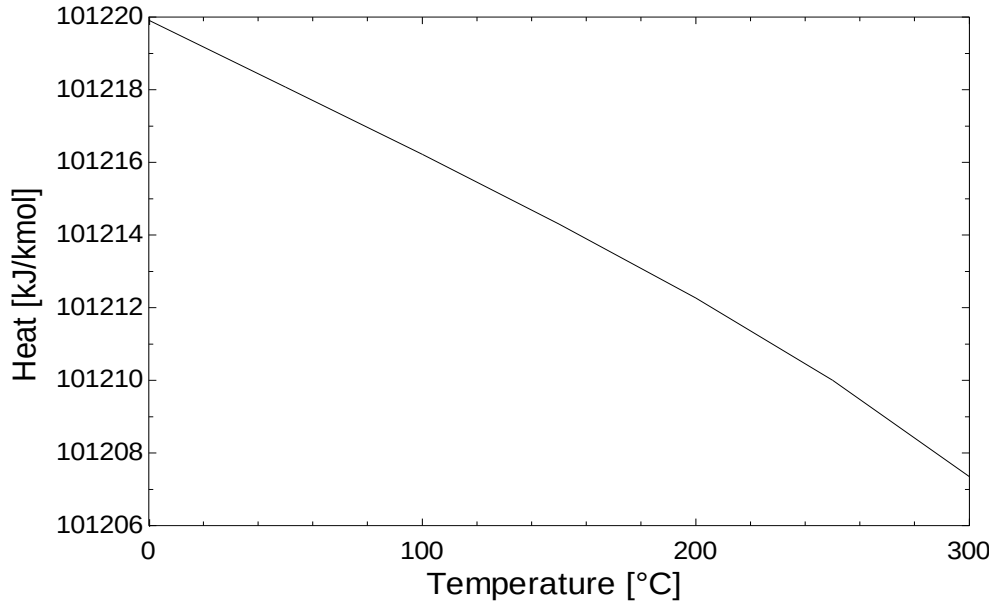

Figure 4.5 Variation of the molar heat transfer with reaction temperature.

Figure 4.5 shows the change in molar heat in kJ/kmoles with the change in chemical reaction temperature produced for the second reaction [Cl2 (g) +H2O(l/g)+ Q→2HCl(g)+1/2O2 (g)]. Reaction temperatures vary in the range of 0°C to 300°C. The chemical reaction is endothermic in nature in this step. The shape of the curve is nonlinear. In this reaction, the amount of molar heat transfer is provided by the environment to the system. As the reaction temperature increases, the amount of heat decreases due to the molar enthalpy of water and chlorine gas being higher than the molar enthalpy of hydrochloric acid and oxygen gas. It is preferable to work at high temperatures in order to save the amount of heat supplied and therefore increase the performance of the cycle.

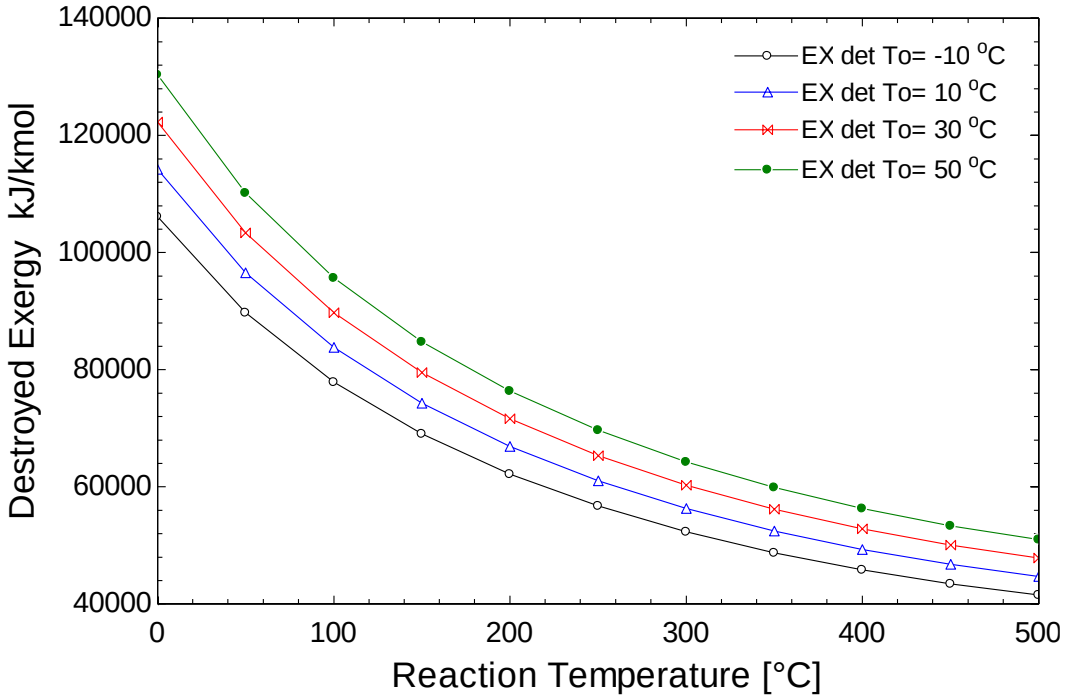

Figure 4.6 Variation of the destroyed exergy with the reaction temperature for several surrounding temperatures.

Figure 4.6 shows that the destroyed exergy declines in a non-linear manner with increasing reaction temperature and increases with increasing ambient temperature. This is because the exergy of the products (hydrochloric acid and Oxygen) is higher than the exergy of the reactants i.e., water and Chlorine. Therefore, more exergy in the form of heat is obtained. Irreversibilities, such as chemical reactions and heat transfer always generate entropy and any transformation

produced by entropy causes destruction of exergy. Greater irreversibility during the process causes greater the destruction of exergy.

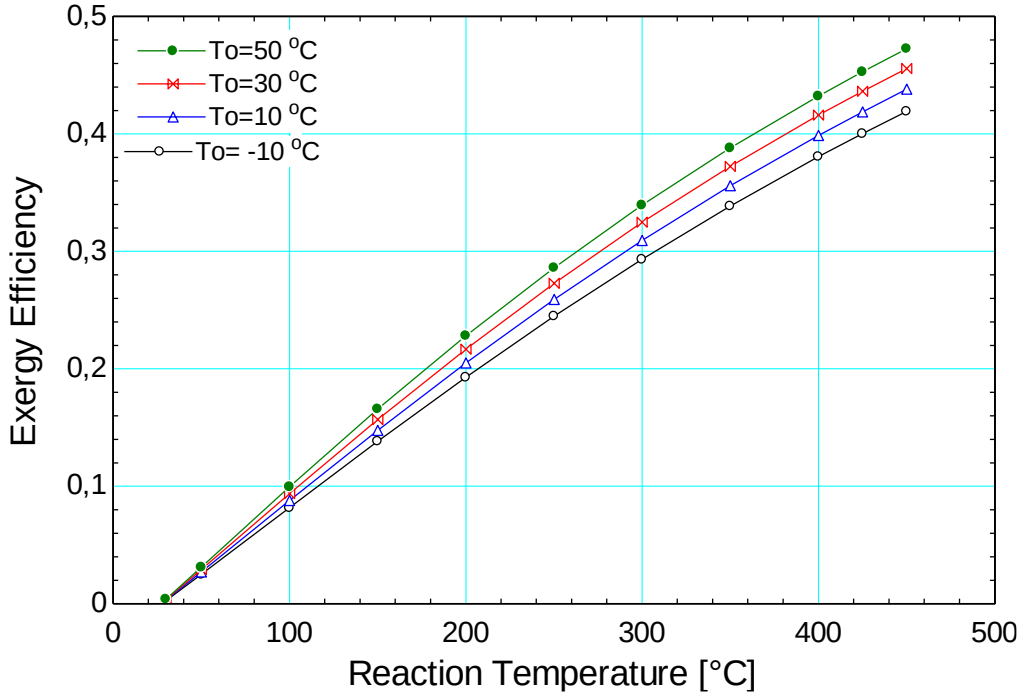

Figure 4.7 Variation of the exergy efficiency with the reaction temperature for different surrounding temperatures.

Figure 4.7 shows the exergy efficiency of the second step, varying in the range from 0.1 to 0.48. Increasing the temperatures of the reaction and surroundings increases the exergy efficiency. This is due to the exergy of products, that is hydrochloric acid and oxygen are higher than the exergy of reactants (water and chlorine). At high temperatures, the exergy increases and the irreversibilities decrease. This leads to enhancement of the economic performance. It is noticed that the yield is almost non-existent at low temperature whereas it grows rapidly at high temperature.

4.3 THIRD CHEMICAL REACTION

Figure 4.8 shows the variation of the quantities of heat in kJ/kmole of H_2 according to the variation of the temperatures of the chemical reaction produced during the process of the third stage. Reaction temperatures vary in the range of 0°C to 100°C. This temperature range is chosen in this way because, from experience, all the corrosion reactions in which a metal and an acid are reacted take place at atmospheric pressure and at ambient temperature. In an experimental study carried out in our laboratories, different metals such as copper, zinc and magnesium were mixed with

different acids, such as hydrochloric acid HCl and sulfuric acid H_2SO_4 for different concentrations. reacted completely and spontaneously at atmospheric pressure and room temperature 25°C. The rise in temperature in this type of reaction up to 100°C acts as a catalyst, but the increase in the yield of the reaction is not as significant with the rise in temperature.

The chemical reaction is exothermic in nature in this third step [Cu(s)+2HCl(g) →CuCl2(s)+H2(g)+Q]. The most likely product of this type of reaction is hydrogen.

We notice from Figure 4.8 that the amount of heat produced is rejected from the system to the outside environment. According to the English convention of the sign of work and heat, the sign of the amount of heat in this case is negative. As the temperature of the reaction increases, the quantity of the heat of reaction decreases very little. We can assume with a very good approximation that the value of heat remains unchanged in the closed interval of [0°C – 100°C]. It is preferable to work in this case at ambient temperatures [20-30°C] in order to save the amount of heat supplied and consequently increase the performance of the reaction as well as of the complete cycle.

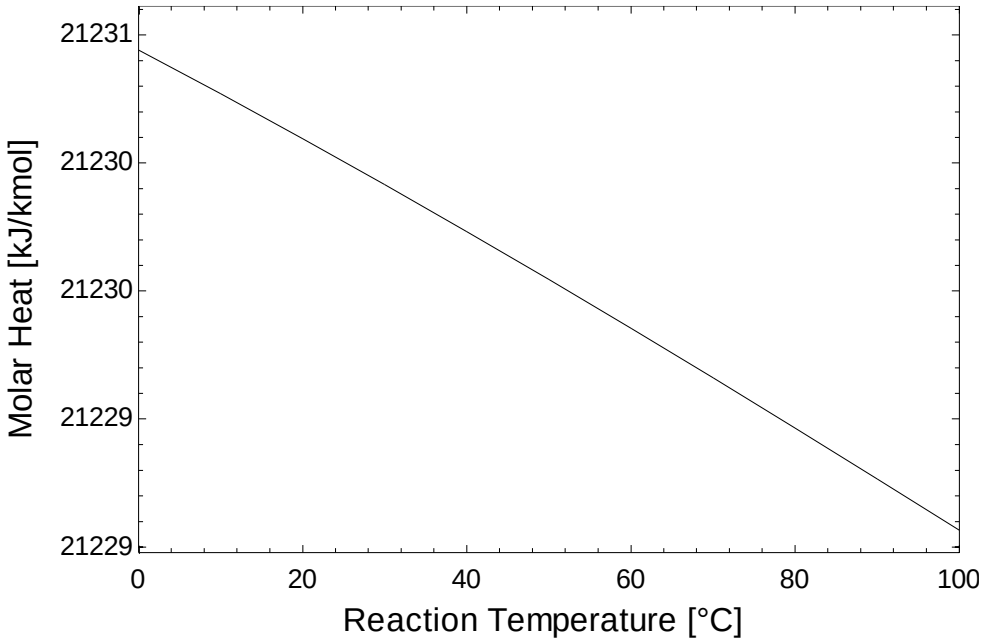

Figure 4.8 Variation of the molar heat transfer with the reaction temperature.

Figure 4.9 shows that the destroyed exergy increases non-linearly with increasing of the reaction temperature and decreases with increasing different surroundings temperatures. This is due to the low exergy of products which are represented in copper-chlorine and Hydrogen compared to exergy of the reactants (Copper and Hydrochloric acid). One can observe that for the case of

ambient temperature 50 °C, the exergy is minimum while at -10 °C the exergy is maximal for this step.

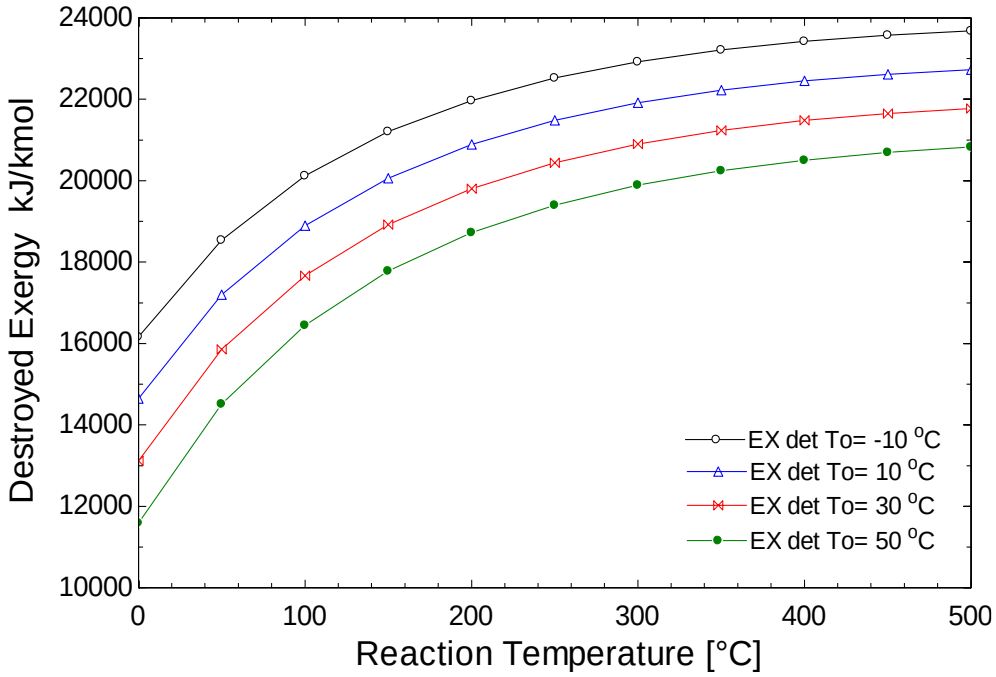

Figure 4.9 Destroyed exergy vs the reaction temperature for several surrounding temperatures.

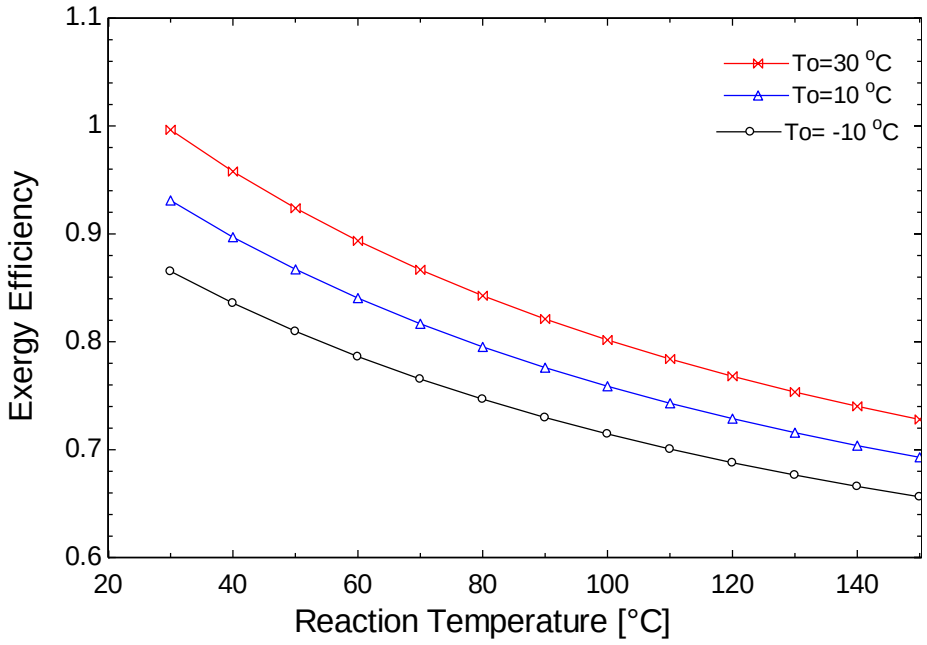

Figure 4.10 Variation of the exergy efficiency with the reaction temperature for different surrounding temperatures.

Exergy efficiency of the third step, Figure 4.10, changes from 0.72 to 0.98, with the external temperatures of -10,10 and 30 °C respectively. It decreases with increasing the reaction temperature up to 140 °C. This is explained by the exergy of products (hydrogen gas and copper chloride) is higher than the exergy of the reactants such as cooper and hydrochloric acid. At high temperature the irreversibility increases and this is the main cause of degradation of the exergy efficiency. This confirms that this chemical reaction is viable at ambient temperatures.

4.4 OVERALL EXERGETIC YIELD

This table represents a summary of the previous figures concerning the quantity of molar heat necessary for each chemical reaction. in addition, the reaction temperature necessary and the surrounding temperature for the proper functioning of all chemical reactions. finally, the exergy efficiency of each reaction, that was 0.624, 0.502 and 0.976 respectively. The exegetic yield of the chemical reactions is calculated without considering the heat losses. The three steps in Table 5.1 are performed at T0=30°C and P0=1 bar. The product of all chemical reactions of exergetic yields is used to calculate the overall exergetic yield. The cycle's overall exergetic efficiency is determined by:

$$\eta_{ex\ overall} = \eta_{R1} * \eta_{R2} * \eta_{R3} \quad (25)$$

Table 4.1 Exergy yield of the chemical reactions

Steps	Reactions	Q kJ/kmol	$T_{rea}{}^{O}C$	$T_0{}^{O}C$	η_{ex}%
1	$CuCl_2$ (s) + Q → Cu(s) + Cl_2 (g)	205844	500	30	0.624
2	H_2O(l) + Cl_2 (g) + Q→2HCl(g)+1/2O_2(g)	101207	450	30	0.502
3	2HCl(g) + Cu (s)→ $CuCl_2$(s)+ h_2(g)+ Q	-21230	35	30	0.976

The exergetic yield of each step is calculated as in Table 4.1, and the overall exergy efficiency of the cycle for hydrogen production is found to be 30.5%.

CHAPTER 5

5 PROPOSED HYDROGEN PRODUCTION UNIT COUPLED WITH THERMAL POWER PLANT

In this study, we carried out an analysis according to the first and second principles of thermodynamics of the copper-chlorine thermochemical cycle by the separation of the water molecule using thermal energy. To provide the cycle proposed in this memorandum with a necessary and sufficient heat source allowing it to operate in good conditions, the Sonelgaz SPE turbine power plant at Hassi R'Mel in the town of Laghouat, 500 km south of the capital Algerian, was chosen because of its thermal capacity. this turbine plant has three (03) GE turbines with a total power of 590.726 MW with an area of 15 hectares. The fuel that powers these turbines is mainly natural gas because of its availability in this region.

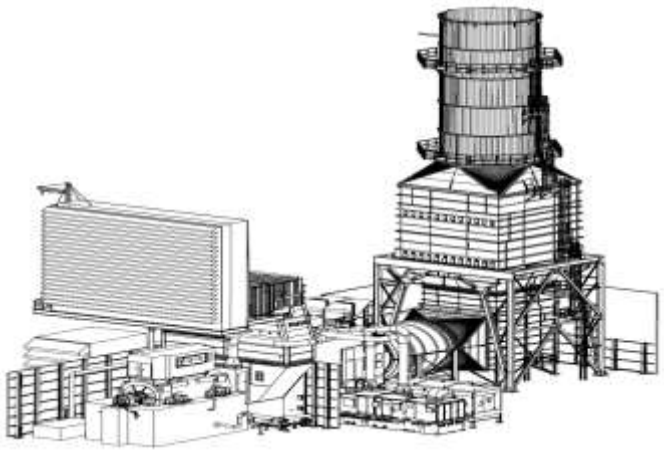

Figure 5.1 HASSI R'MEL turbine power plant [107]

5.1 DESCRIPTION OF THE PROPOSED GAS TURBINE

The MS–9001FA single shaft gas turbine is designed to operate in an installation configured as a single cycle or combined cycle steam and gas unit. The gas turbine has six main sections or groups:

1. Air intake

2. Compressor

3. Combustion system

4. Impeller

5. Exhaust

6. Support systems

This section briefly describes the operation of the gas turbine and the relationship between the main components. Each turbine is connected to an alternator to produce electricity.

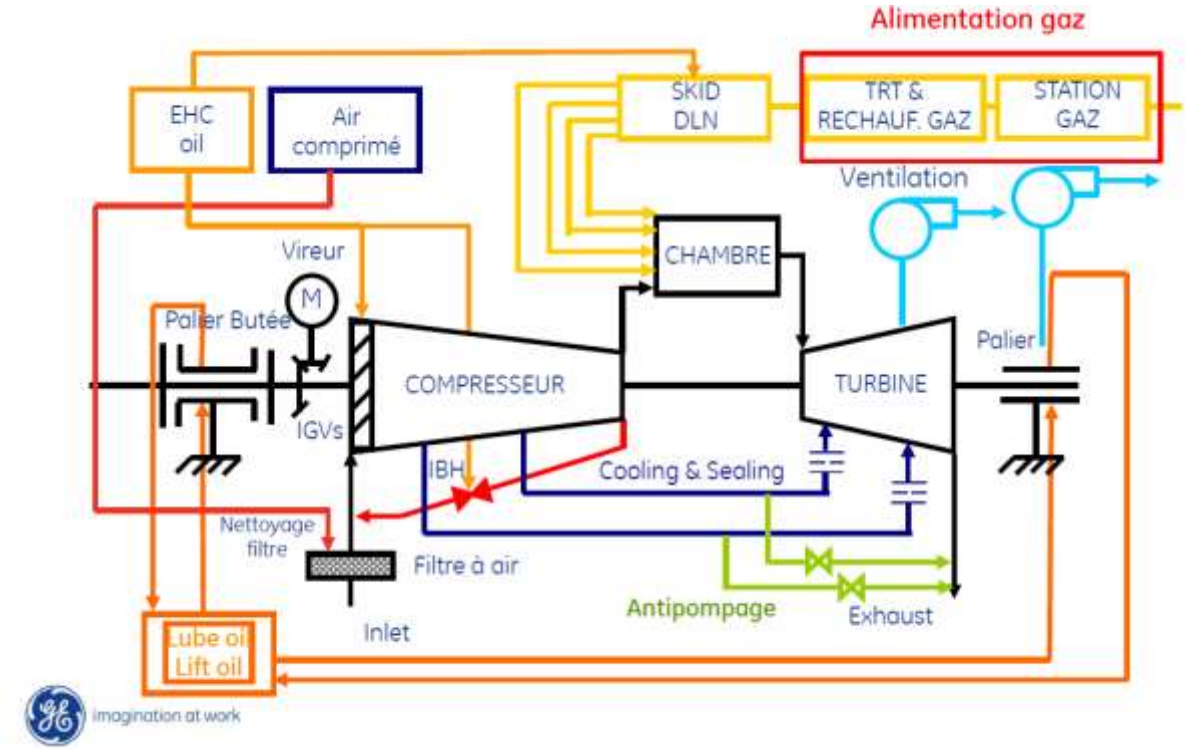

Figure 5.2 Gas turbine overview [107]

5.2 DESCRIPTION OF THE GAS VEIN

The gas stream is the path followed by gas flow from the air inlet through the compressor, combustor and turbine to the turbine exhaust.

When the turbine start system is actuated, ambient air is drawn from the air intake duct, filtered and compressed in the axial flow compressor. The air compressed by the compressor passes through the annular space that surrounds the combustion chambers, then through the spaces between the external bodies and the flame tubes, and enters the combustion zone through the calibrated holes of each flame tube. Fuel from an outside source arrives through lines that terminate in injectors in the end caps of the separate combustion chambers. Injectors introduce fuel into the combustion zone of each chamber where it is mixed with combustion air and ignited by one or more spark plugs. As the fuel explodes in one combustion chamber, the flame is propagated, through interconnecting tubes, to all the other combustion chambers. The hot gases from the combustion chambers pass through separate transition pieces attached to the rear of the chambers'

flame tubes and from there into the three-stage turbine section. Each stage consists of an annular distributor and a row of turbine blades. In each annular distributor, the kinetic energy of the jet is increased with an associated pressure drop which is absorbed by the work of the turbine rotor blades and causes rotation of the shaft used to drive the alternator and produce electricity. After passing through the third stage blades, the gases are directed into the exhaust diffuser. The gases then pass into the exhaust duct where the temperature reaches 500 °C and are introduced to the atmosphere through the exhaust stack [107].

5.3 THE PROPOSED CONFIGURATION

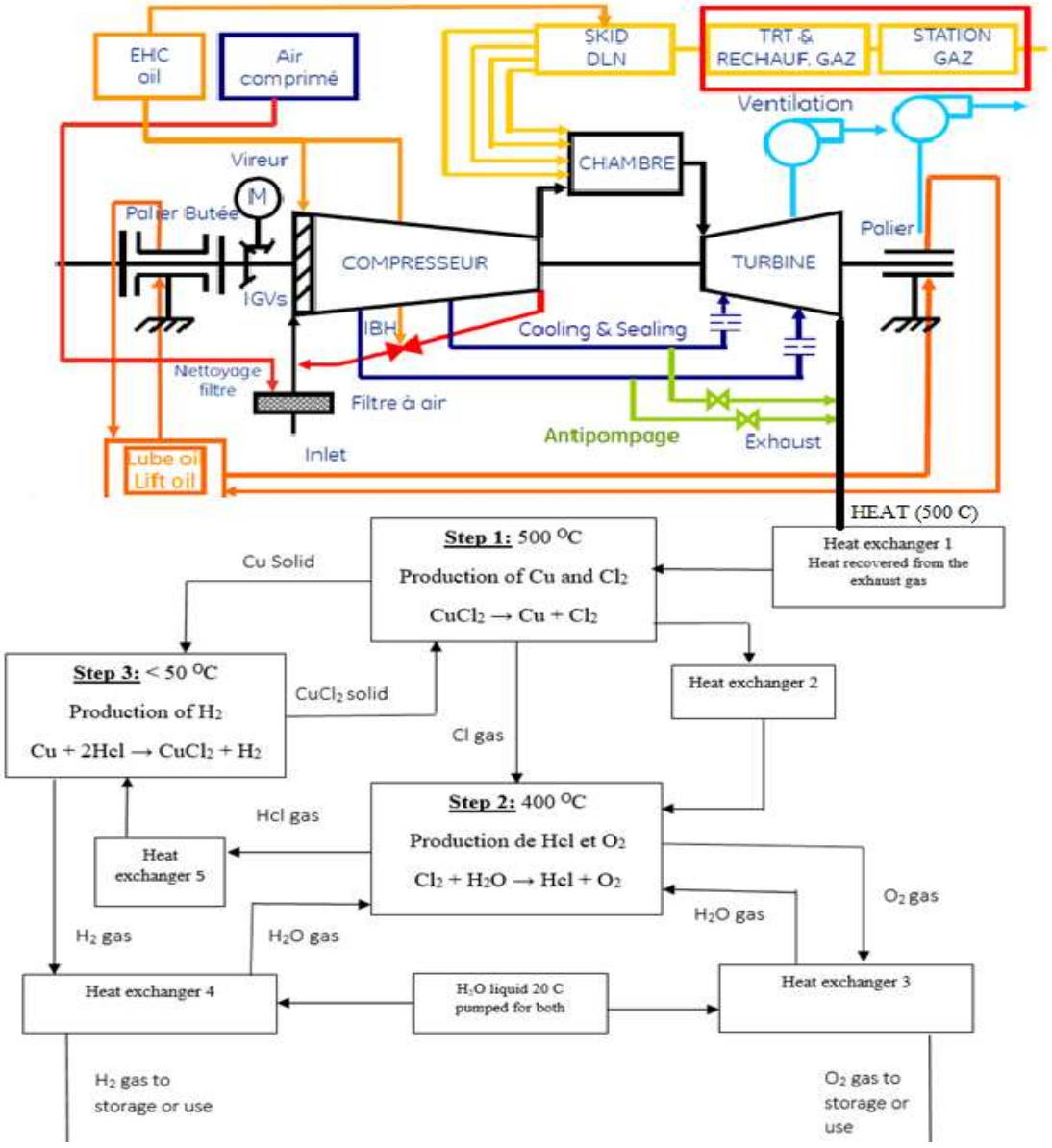

Figure 5.3 New hydrogen production plant: connection between the hydrogen production unit based on the proposed Cu-Cl cycle and the Hassi R'mel thermal power plant.

The new proposal in this research is to connect the hydrogen production unit operating on the basis of the copper-chlorine couple to a thermal power plant designed in a different way. the gases emitted by the turbine exhaust have a temperature of up to 500 °C, which corresponds to the operation of the hydrogen production unit. This new station produces electricity, hydrogen and oxygen, it is a trigeneration plant. The thermochemical cycle analyzed consists of a series of three stages of chemical reactions in which water is decomposed into hydrogen and oxygen through the elements copper and chlorine which will then be recycled.

5.4 PRODUCTION CAPACITY MEASUREMENT:

5.4.1 HYDROGEN PRODUCTION MEASUREMENT

This section represents a summary of the studies discussed in the previous sections. It is a question of making a metrology for the configuration seen on the screen in order to have a clear and clear idea on the quantity of hydrogen produced by this system. for this reason, the author of this thesis proposed to connect the hydrogen production unit based on chlorine and copper to the thermal power plant of electricity production in order to provide the unit with the heat necessary for its operation.

To determine the hydrogen production capacity, the following formula is used [103]:

$$\eta_{\text{ex overall}} = \frac{X_{H2} + X_{O2} + \eta_{\text{isn}}.W_u}{Q_t\left(1-\frac{T_0}{T_{rea}}\right)} \quad (5.1)$$

X_{H2} is the exergy of hydrogen

X_{02} is the exergy of oxygen

η_{isn} is the isentropic efficiency of the gas turbine

W_u is the net work in terms of power of the thermal station [104]

Q_t is the total thermal energy in terms of power recovered from the exhaust gases [104]

T_0 ambient temperature

T_{rea} reaction temperature

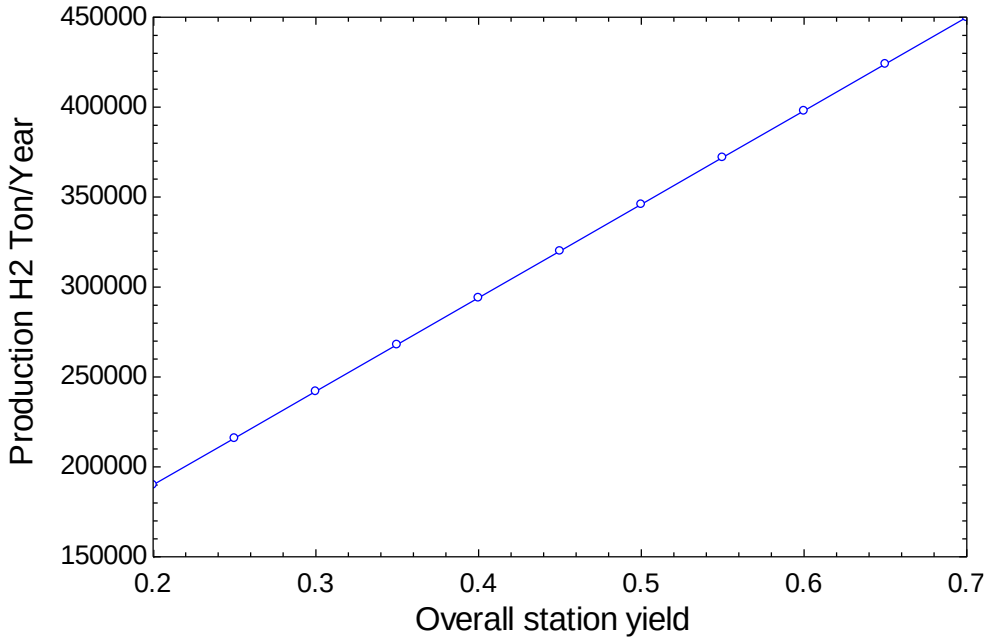

Figure 5.4 Hydrogen production in ton per year as a function of overall station yield.

The graphs in Figure 5.4 representing the variation in hydrogen production in ton per year. This variation in hydrogen production is a function of the variation in the overall exergy efficiency of the thermal power plant. The increase in annual hydrogen production as a function of the overall efficiency of the station is linear. for the overall efficiency of the plant of 34% the system produces 262,800 tons per year of hydrogen.

5.4.2 COST OF THE KILOGRAM OF HYDROGEN

There is an accessible and known cost for the hydrogen supplied by the manufacturers (Air Liquide, Air Products, Linde or others) who market it. It is most often produced by reforming natural gas, therefore highly dependent on the market price of gas, the range of which varies from country to country. By taking an average value of 10€/GJ, we arrive at an approximate cost of 15€/GJ leaving the reforming unit, i.e. still 1.5€/kg.

If we are interested in "clean" mobility, i.e. a fuel cell vehicle powered by hydrogen produced by a renewable source, via electrolysis, the cost at source reaches and/or exceeds double (>€30/GJ) if starting from nuclear electricity and triple or more if the electricity is supplied by a renewable source, ie nearly €5/kg. If we add transport and distribution costs, this price can double again. For example, German public service stations supply hydrogen at €10/kg. This price can be compared to that of gasoline, hit in Germany by the Internal Tax on Petroleum Products at €1.78/litre. For the same distance travelled, for example 600 km, it will take 5 kg of hydrogen, or €50, and 60 liters of gasoline, or €90 [105].

5.4.3 OXYGEN PRODUCTION MEASUREMENT

We can also produce oxygen from the production cycle proposed in the second reaction, the inputs of which are chlorine and water, and the outputs are chlorinated acid in addition to oxygen gas. reaction requires a temperature of up to 400 degrees Celsius, which is provided by the turbine exhaust. In this system, which includes the thermal power plant with the proposed Cu-Cl based unit, it produces hydrogen, electricity and finally oxygen at the same time.

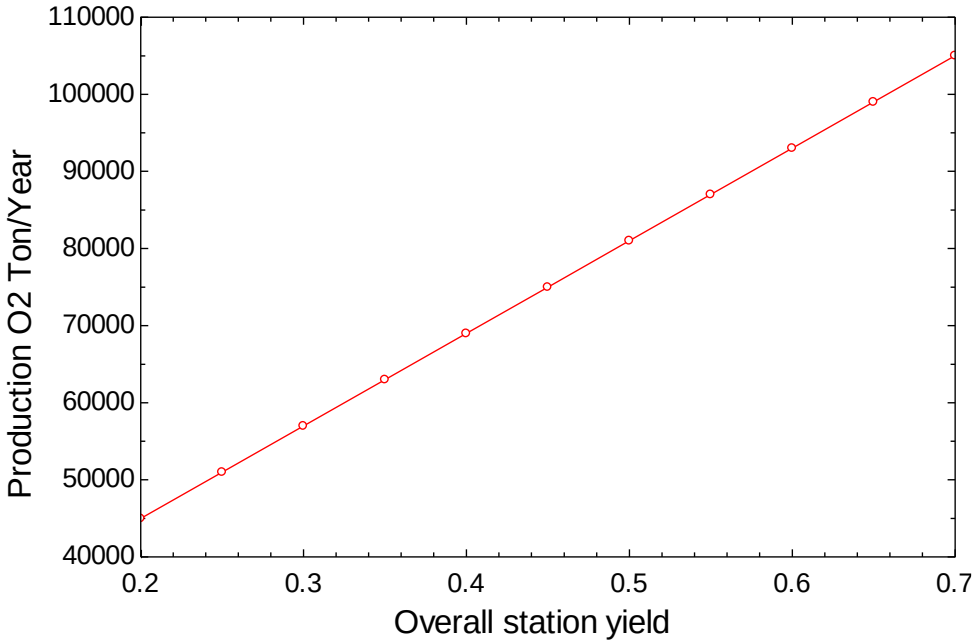

Figure 5.5 Oxygen production in ton per year as a function of overall station yield.

Using formula (5.1) to estimate the oxygen production in ton per year based on the overall performance of the station. The rate of oxygen production increases with the increase in the overall efficiency of the plant. It is obvious that this system with an overall efficiency of the plant of 34%, the production of O2 exceeds 65000 tons per year.

5.4.4 FIELDS USING OXYGEN

There are several areas that use oxygen gas in large quantities [106];

Medical use: Especially oxygen generators in hospitals for patients with respiratory and lung problems

Water treatment: Pure oxygen is used in the production of ozone, which is very useful in a variety of everyday situations, from eliminating odors to providing clean, quality drinking water. By injecting oxygen into your water system, you can increase the efficiency of removing pollutants and impurities.

Metal production: Oxygen dramatically increases gold processing efficiency and ore flow, reducing the cost of cyanide and waste. The steel industry is the biggest user of oxygen. Industrial oxygen generators are also used in the production of other metals such as copper and lead. A continuous supply of plenty of oxygen is essential for the safety of miners.

Military and field hospitals: One-sixth of combat casualties typically require oxygen. This means that a field hospital with several beds needs a lot of oxygen cylinders per day. This leads to high transport costs and logistical problems. The alternative to oxygen cylinders is an on-site oxygen generator that ensures reliable and safe delivery of continuous, medical-grade oxygen without the problems and risks associated with traditional high-pressure cylinders.

Glass production: A better quality of the finished product can be achieved by adding oxygen during the glass melting process. Furnace efficiency is thus improved, flame temperature is increased, nitrogen pollutants and energy costs are reduced.

fish farming: Fish need precise levels of oxygen in the water for optimal growth. Oxygen must therefore be dosed correctly in order to ensure this growth, as well as less disease and stress to maintain high quality. Pure and stable oxygen is essential in modern fish farming.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

In this work, a new thermochemical cycle has been proposed for production of hydrogen at relatively low temperature. This cycle is based on chemical elements consisting of copper-chlorine Cu-Cl for dissociating water molecule into hydrogen and oxygen. The process comprises three physical steps in the form of a closed internal boucle that continuously recycles all copper-chlorine molecules in which the products of the first reaction are the reactants of the following step and so on. The principal reaction is that related to hydrogen production, and the two remaining ones are used to recycle the chemical components for continuity of the process. Study of Gibbs function of the three chemical equations is shown to be negative which means that the equations are spontaneous and thus feasible. Whereas the first law of thermodynamics allowed us to determine the molar heat of the equations, which are respectively 205844 kJ/kmol, 101207 kJ/kmol and -21230 kJ/kmol (exothermic reaction). In addition to determining the appropriate temperature for each equation where the heat calculated for the needs of reactions of the pure thermochemical cycle is a critical detail for the design of thermal sources. The highest temperature for this cycle is 500°C, which is relatively low when compared to other available cycles.

Exergy analysis is a particularly powerful tool for designing and improving thermochemical cycles for hydrogen production. Although the design work can be done using conventional energy analyses, but from a precision point of view, the exergy analysis reveals very important and very concise information about the efficiency of the processes. the power of this measurement tool comes from the fact that the concept of exergy uses and combines a very large panoply (heat, work, enthalpy, entropy, internal energy, Gibbs function, pressure and temperature of the system and of the external environment, volume chemical exergy, etc.) of physico-chemical quantities that directly influence the functioning of thermodynamic systems.

The exergy efficiency of the three steps is found to be 62.4%, 50.2% and 97.6%, respectively, while the overall exergetic yield of the thermochemical cycle is 30.5% which it is promising as compared to that of other different cycles.

because the gas turbine is the main source producing thermal energy, the hydrogen production unit, which operates with a thermochemical cycle based on copper-chlorine couples, has been connected to a thermal power plant producing electricity with three gas turbines at Hassi R'mel. the gases emitted by the turbine exhaust have a temperature that can reach 500 °C, which corresponds to the operation of the hydrogen production unit. the amount of hydrogen and oxygen produced was calculated for this unit. for an overall efficiency of the plant of 34% the system produces 262,800 ton/year of hydrogen and the production of O_2 exceeds 65,000 ton/year. This new station produces electricity, hydrogen and oxygen, it is a trigeneration plant.

The proposed hybrid hydrogen production cycle has the following chemical elements; $CuCl_2$ (powder), HCl (gas), Cu (powder), H_2O (liquid/vapour) H_2 (gas) and finally O_2 (gas), these

elements are not toxic for the health of the operators, they are not also corrosive for equipment, they are not so dangerous, no risk of explosion, they are abundant in shops and their purchase prices are affordable.

RECOMMENDATIONS

From the studies performed along this thesis, many suggestions can be offered in order to focus on the more detailed evaluation, as well as a more realistic system design for the new Cu-Cl based thermochemical cycle of water decomposition and each of its component stages. Future research in this new cycle should help assess the thermal, mechanical, chemical losses of each of the organs of the global hydrogen production system in order to improve efficiency and reduce the costs of the final product.

- An exhaustive thermodynamic, thermal and thermo-fluid simulation study of the global system as well as the pairing between the hydrogen production unit and the thermal power plant, will have to be carried out.

- In order to fully understand the heat recovery system for the cycle, a detailed analysis by the pinch method of the existing heat exchangers in the overall cycle should be carried out in order to determine the best thermal compatibility. The purpose of this study is to determine the material, size and number of heat exchangers and other heat management equipment.

- Building the electrolyser is the most important and difficult step in this cycle. Thermodynamic and electrochemical models will have to be developed to design this device in order to have a more efficient electrolysis process.

- Optimization and economy studies should take place in future research on this subject.

- Other renewable energy sources, such as wind power, geothermal energy, solar photovoltaic energy, biomass, should be considered, to provide heat and electricity necessary for the Cu-Cl cycle and his auxiliaries.

- The electrochemical version could be proposed in future research to improve the efficiency of this cycle.

- As a final recommendation, we propose the integration of this hydrogen production unit with the hybrid cycle proposed in the means of transport. This miniature scale hydrogen production unit will exploit the thermal energy lost with the exhaust gases in the air to supply this unit in addition to the electricity for the operation of the electrolyser. The hydrogen produced will be consumed as fuel in the internal combustion engine of the same vehicle. This will considerably reduce polluting emissions from means of transport. The same system can be installed in conjunction with the gas turbines installed in the pumping and compression stations for the transport of hydrocarbons or any other installations which throw thermal energy into the atmosphere.

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