OPTIMIZATION, EXPERIMENTAL PERFORMANCE AND TECHNO-ECONOMIC EVALUATION OF PEM AND ALKALINE ELECTROLYZERS

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I certify that in my opinion the thesis submitted by Syed Arslan Hassan NAQVI titled “OPTIMIZATION, EXPERIMENTAL PERFORMANCE AND TECHNO-ECONOMIC EVALUATION OF PEM AND ALKALINE ELECTROLYZERS” is fully adequate in scope and in quality as a thesis for the degree of PhD.

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ABSTRACT

Ph.D. Thesis

OPTIMIZATION, EXPERIMENTAL PERFORMANCE AND TECHNO-ECONOMIC EVALUATION OF PEM AND ALKALINE ELECTROLYZERS

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This study presents the highly efficient and innovative prototypes of a hydrogen generation system. The study was carried out on two types of water electrolyzers, Alkaline and PEM. The protype of both types of electrolyzers were developed to generate the Hydrogen gas in an efficient and cost-effective way. The prototype of the PEM electrolyzer was comparatively of larger scale, developed for the industrial application. The performance of both the electrolyzers was evaluated and amount of hydrogen production through these electrolyzers was calculated. The techno-economic as well as enviro-economic analyses were performed for these electrolyzers. The annual profit (ΔYY) and simple payback period (SPP) for these prototypes were also determined. A novel and special chemical mixture, made up from the combination of ammonia, ethyl alcohol, urea, and deionized or distilled water is used in this innovative study to increase the output of Hydrogen gas and reduce its cost. In PEM electrolyzer, the Cr-C coated SS304 bipolar plates were used in the electrolysis cells. The super strong magnets were also mounted on the outer surface of the electrolysis cells of both electrolyzers to improve the performance and efficiency. The performance of the electrolyzers was determined through the experiments and the optimization of the different parameters. In the small-scale study of Alkaline electrolyzer, the rate of hydrogen gas production was obtained as 6 g L^{-1} while the annual profit (ΔYY) is found to be as 1,771.14 € y^{-1} and the simple payback period (SPP) is calculated as 2.2 y. For Alkaline electrolyzer, the best results were obtained at 30 A current and 12 V voltage. On the other hand, PEM electrolyzer, the production of hydrogen gas (1 MW) for industrial scale was found to be as 6 m^3 h^{-1}, whereas the annual profit (ΔYY) and the simple payback period (SPP) were calculated as 646,000 € y^{-1} and 2.32 y respectively. The optimum results for PEM electrolyzer were obtained at 30 A current and 10 V voltage. These results indicate that this system can produce hydrogen more efficiently and economically. The rate of carbon emissions through this system is 0%, hence sustainable and environmentally friendly.

Keywords **:** Alkaline electrolyzer, PEM electrolyzer, Techno-economic analysis, SS304, Hydrogen.

Science Code : 91441

ÖZET

Doktora Tezi

PEM VE ALKALİ ELEKTROLİZERLERİN OPTİMİZASYONU, DENEYSEL PERFORMANSI VE TEKNO-EKONOMİK DEĞERLENDİRMESİ

Syed Arslan Hassan NAQVI

Karabük Üniversitesi
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Bu çalışmada, bir hidrojen üretim sisteminin yüksek verimli ve yenilikçi prototiplerini sunmaktadır. Çalışmada iki tip su elektrolizörü, Alkali ve PEM üzerinde gerçekleştirilmiştir. Her iki tip elektrolizörün prototipi, Hidrojen gazını verimli ve uygun maliyetli bir şekilde üretmek için geliştirilmiştir. PEM elektrolizörünün prototipi, endüstriyel uygulama için geliştirilmiş, nispeten daha büyük ölçekliydi. Hem elektrolizörlerin performansları değerlendirilmiş hem de bu elektrolizörler dan üretilen hidrojen miktarı hesaplanmıştır. Bu elektrolizörler için tekno-ekonomik ve çevresel-ekonomik analizler yapılmıştır. Bu prototipler için yıllık kar (ΔYY) ve basit geri ödeme süresi (SPP) de hesaplanmıştır. Hidrojen gazının verimini artırmak ve maliyetini düşürmek için bu yenilikçi çalışmada amonyak, etil alkol, üre ve deiyonize veya damıtılmış su kombinasyonundan oluşan yeni ve özel bir kimyasal karışım kullanılmıştır. PEM elektrolizörde, elektroliz hücrelerinde Cr-C kaplama SS304 bipolar plakalar kullanılmıştır. Performans ve verimliliği artırmak için her iki elektrolizörün elektroliz hücrelerinin dış yüzeyine de süper güçlü mıknatıslar monte edildi. Elektrolizörlerin performansı, deneyler ve farklı parametrelerin optimizasyonu yoluyla belirlendi. Alkali elektrolizörün küçük ölçekli çalışmasında paslanmaz çelik SS304 elektroliz hücere plakalar kullanılmıştır, hidrojen gazı üretim oranı 6 g L^{-1} olarak elde edilirken, yıllık kar (ΔYY) 1.771,14 € y^{-1} ve basit geri ödeme süresi (SPP) olarak bulunmuştur. 2.2 y olarak hesaplanır. Alkali elektrolizör için en iyi sonuçlar 30 A akım ve 12 V gerilimde elde edilmiştir. Öte yandan endüstriyel ölçekte (1 MW) hidrojen gazı üretimi 6 m3 h^{-1} olan PEM elektrolizörünün yıllık karı (ΔYY) ve basit geri ödeme süresi (SPP) olarak hesaplanmıştır. 646.000 € y^{-1} ve 2.32 y sırasıyla. PEM elektrolizör için optimum sonuçlar 30 A akım ve 10 V gerilimde elde edilmiştir. Bu sonuçlar, bu sistemin hidrojeni daha verimli ve ekonomik olarak üretebileceğini göstermektedir. Bu sistem aracılığıyla karbon emisyonu oranı %0'dır, dolayısıyla sürdürülebilir ve çevre dostudur.

Anahtar Kelimeler: Alkali elektrolizör, PEM elektrolizör, Tekno-ekonomik analiz, SS304, Hidrojen.

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SYMBOLS

Δm_K	The amount of unburned coal, [kg/d]
ΔY	Annual of PEM fuel cell profits, [€/y]
$m_{K,Hid}$	The amount of hydrogen-enriched coal consumption, [kg/d]
C_{el}	Daily coal price, [€/kWh]
C_{En}	Daily coal price, [€/ton]
En_{el}	Consumption of electric energy from the mains electricity, [kWh/d]
En_K	The consumption of coal energy amount, [kcal/d]
Hu_K	Lower heating value of coal, [kcal/kg]
$Hu_{K,Hid}$	Lower heating value of hydrogen-enriched coal, [kcal/kg]
m_K	Consumption of coal amount, [kg/d]
Y_{cost}	Investment cost of PEM fuel cell system, [€]
$Y_{En,el}$	Cost of an electric energy consumption, [€/d]
$Y_{En,Hid}$	Energy economic, [€/d]
$m_{LG,Hyd}$	[kg y^{-1}] hydrogen-enriched LG consumption amount
Δm_{LG}	[kg d^{-1}] amount of unburned LG
ΔYY	[€ y^{-1}] annual profit of alkaline electrolyzer profits
C_{el}	[€ kWh^{-1}] LG price
C_{En}	[€ ton^{-1}] LG price Enel [kWh y-1] consumption of electric energy
En_{LG}	[MJ y^{-1}] consumption of LG energy amount
LHV_{LG}	[MJ kg^{-1}] lower heating value of LG
$LHV_{LG,Hyd}$	[MJ kg^{-1}] lower heating value of hydrogen-enriched LG
m_{LG}	[kg y^{-1}] consumption amount of LG
Y_{inv}	[€] investment cost of alkaline electrolyzer prototype system
$YY_{En,el}$	[€ y^{-1}] consumption cost of the electricity
$YY_{En,Hyd}$	[€ d^{-1}] techno-economic of the energy cost amount

ABBREVIATIONS

€	Euro
d	day
el	electric
En	Energy
h	hour
Hid	hydride
K	Coal
k	kilo
m	mass
HHO	Hydroxy or oxyhydrogen
Hyd	Hydride
KOH	Potassium Hydroxide
LG	lignite
LHV	Lower heating value
PEM	Proton Exchange Membrane
MEA	Membrane Electrode Assembly
SPP	Simple Payback Period
HHV	Higher heating value
Hid	Hydride
SWOT	Strengths, Weaknesses, Opportunities and Threats
toe	tons of oil equivalent
ton	tonnes
W	Watt
y	year
YY	cost

PART 1

INTRODUCTION

Energy is the most important element as well as the one of the necessities in today's life of human beings. It is also a basic raw material needed to increase agricultural and industrial productivity. An increase in a country's energy consumption is an indicator of economic and social development. With ever-expanding economies, technological developments, rising living standards, growing populations, and increasing consumption, energy has become one of the most fundamental and strategic components of human life. Traditional energy sources are limited and concentrated in certain geographic regions around the world, and the negative environmental impacts of traditional energy sources are driving countries to look for new and clean energy sources. Especially since the 1960s, the United States, Japan, and European countries have focused scientific research on developing alternative energy sources [1–4].

According to WEC (World Energy Council) projections, 1.3% increase in the use global energy is expected by 2050. Despite the increasing share of renewable energy, the increase in global energy consumption is still largely obtained by fossil fuels. Ensuring of providing sustainable as well as cost-effective hydrogen production processes is a challenge to future hydrogen economy. In line with the world's clean energy choices, all new technology revolves around hydrogen [5,6].

Numerous environment related issues, i.e., acid rain, climate change globally, and depletion of ozone layer in stratosphere, are due to or related to the way the energy was being produced, transformed, and used. There are now many different potential remedies to the existing environmental issues brought on by the harmful pollution releases. Systems using hydrogen energy seem to be one of the best options and can have a big impact on sustainability and in making the environment better. Currently, the primarily use of hydrogen is in the form of chemical substance instead of a fuel, with a market worth around $50 billion USD for the 40 Mt production annually. Much of its present use is in oil refineries, where it is being used to desulfurize the crude oil for making petrol, diesel, and other products. Hydrogen is also used in the manufacturing of ammonia and methanol production as well as in pharmaceutical products manufacturing. There would be drastic increase in the demand of hydrogen in future to meet the needs of industries as well as of traditional fuel for transportation provided that future population growth will result in a greater need for food and other commodities. The rise in greenhouse gas (GHG) emissions in the atmosphere is a result of the rising demand for food and energy [3].

The most basic technology for hydrogen production is electrolysis technology. The basic material for electrolysis is water, and the products obtained by the chemical reaction are high-purity hydrogen and oxygen gases. Not only hydrogen, but also oxygen itself is a product obtained by alkaline electrolysis, a type of electrolysis, and is a very valuable product.

Research into clean, sustainable, and cheap energy sources is increasingly being conducted around the world. In particular, the use of clean energy sources in cities helps reduce the increasing pollution rates in cities. In fact, producing hydrogen from hydrocarbons does not reduce overall air pollution. However, it is important to decide where to produce. Wind energy, solar energy, etc. are clean and renewable sources of energy. The process can also produce hydrogen gas, making it the cleanest system in the world. However, establishing these clean energy sources in the centers where energy is consumed poses major problems. Solar panels cover large areas and urban land is highly valued. Wind turbines, on the other hand, have negative characteristics such as interfering with electromagnetic waves, producing noise, and physically occupying a specific area. Wind turbines are dynamic parts and needed to be installed over large areas for safety reasons. The use of solar panels is increasing in vast deserts, barren and undeveloped lands far from cities. The transmission costs and losses of electricity generated by solar power plants are high. This is the only way hydrogen can be produced on the surface of a solar panel and transported to the desired location using a system similar to natural gas. In this scenario, hydrogen is an important source of energy carrier.

In this view, there is an increase in research and development interest related to hydrogen generation through water electrolysis systems. On the one hand, these technologies make it possible to produce an unlimited source of fuel for the transportation and automotive industries without generating greenhouse gases or other emissions.

After drying and removing oxygen impurities, electrolysis, a very easy technique, is used to produce hydrogen, which has a purity of 99.999 % by volume. The source of electrical energy utilized to continue the electrolytic reaction is one of the crucial parameters affecting hydrogen generation because of the financial and environmental implications. During electrolysis process, the current flows between the two electrodes that are spaced apart and submerged in an electrolyte and ultimately the molecules of water split into hydrogen and oxygen by applying the electrical energy [3].

PART 2

LITERATURE SURVEY

Energy is becoming increasingly significant in the world as the world's demand for energy is rising on regular basis. With population expansion, industrialization, and technical advancements in emerging countries, in particular, this circumstance will raise the need for energy in the coming years. The amount of energy used today reveals a nation's degree of development. Globally, the fossil fuel reserves are being reduced on a daily basis, endangering the habitats of future generations and irreparably harming the planet. Every year, the world's demand for energy rises by about 4 to 5 percent. However, the fossil fuel reserves that can meet this demand are shrinking much more quickly. Even the most optimistic projections suggest that oil reserves will run out in next fifty years and will be unable to meet the latest energy demands. The need for renewable energy sources, i.e., Hydrogen is continuously rising due to this steady depletion and diminishing of oil, coal, and natural gas reserves. Compared to traditional energy sources, renewable energy sources have a lower environmental impact. Because they are renewable and, unlike conventional fuels, do not significantly endanger the environment or human health, renewable energy sources are less expensive than fossil fuels [1–3,7–12].

11,164 million tons of oil equivalent in terms of world energy consumption have been consumed as of the beginning of the twenty-first century. This is due to the fact that a significant amount of the global energy demand is fulfilled by the conventional fossil fuels such as furnace oil, coal, and natural gas. This is the fact that the fossil fuels contribute to climate change and global warming and may diminish soon. As the second largest energy consumer after industry, accounting for 30% of all delivered energy globally, the transportation sector is among those most adversely impacted by this circumstance. A clean and sustainable fuel option is hydrogen (H_2) from renewable energy sources [13].

The increase in a country's energy consumption is an indicator of economic and social development. Constantly growing economies in parallel with developing technology, rising living standards, increasing human population, and increasing consumption have made energy the most basic and strategic element of human life. The fact that traditional energy sources are limited and concentrated in certain geographical regions around the world, and the negative environmental effects of traditional energy sources have led countries to search for new and clean energy. Especially after the 1960s, the USA, Japan and European countries focused on scientific studies to find and develop alternative sources of energy. One of the most important challenges which is faced by the human races is the availability of abundant sustainable renewable energy resources [1,2].

The environmental effects of constant reliance on conventional energy sources, such as pollution, greenhouse gas emissions, and climate change, are extremely problematic. As a result, there is a growing concern about the requirement to switch to a sustainable renewable energy system on global scale. Renewable hydrogen has been identified as a possible energy source for the future in this regard. Hydrogen may be utilized as a fuel in practically all applications where fossil fuels are now employed without emitting any negative pollutants. The most hydrogen is found in water, which requires considerable energy to divide. The energy needed to split water is larger than the energy that can be released from the hydrogen created according to the rules of thermodynamics. Therefore, hydrogen is a useful fuel. Consequently, like electrical energy, hydrogen is also an energy carrier practically [14].

There is increasing interest in hydrogen as a potential transportation fuel and energy carrier. Fossil fuel use dominates the current energy infrastructure, contributing to greenhouse emissions. Because it is good for the environment and loses two electrons when it is oxidized to water, hydrogen has the potential to be an ideal energy carrier. Although elemental hydrogen is the most abundant element in the nature, it is not abundant on Earth. The world's energy issues, energy infrastructure, the environmental benefits of hydrogen as an energy carrier, and the widespread use of hydrogen in the future all require overcoming numerous obstacles. Future utilization of hydrogen at broader scale will require scientific advancements as well as the development for more energy and cost efficient distribution and treatment techniques [6,15,16].

2.1. HYDROGEN AND HYDROGEN ENERGY

The word hydrogen is derived from the Greek word hydro (water) and genes (making/forming). Hydrogen is the first element in the periodic table. It is the lightest, most basic & plentiful element in this universe. It is believed that hydrogen accounts for more than 75% of the universe's mass. It is seldom de-earthed due to its strong chemical reactivity. Hydrogen is also the most abundant element in water, which covers 60% of our world. Animals, people, plants, fossil fuels, and other chemical components all contain hydrogen in various forms. The concept of utilizing hydrogen as a fuel is quite ancient, the process of hydrogen splitting was developed by Henry Cavendish in 1766 and the invention of fuel cells by William Robert Grove in 1839 [2,17,18].

Hydrogen gas is a colorless, odorless, tasteless and non-toxic gas. It diffuses faster than gasoline in the environment and is flammable and explosive. Among other elements, hydrogen is the most lightweight element with the density per unit volume of about 1/14 that of air. High energy density. There is no free-form H_2 in space. Hydrogen exists as a compound in many substances in nature but is found on planets as a component of natural gas, organic matter, or water. Hydrogen has significant advantages over major drawbacks in the energy sector such as be an alternative energy source and reduce greenhouse gas emissions. As a primary energy source, hydrogen has the ability to generate energy directly and tends to facilitate energy production. The energy of hydrogen can be stored for future use, thus reducing the impact of energy generation from non-renewable sources. Hydrogen's flammability makes it possible to use it on a large scale in automobiles in the near future. In fuel applications, hydrogen has an energy density per unit mass that is 2.6 times that of gasoline [3,6,19,20].

Hydrogen is the most widely available chemical element in nature. Hydrogen energy is a clean energy that is used in many fields. Hydrogen energy is the chemical energy released within a molecule as a result of the pure decomposition of hydrogen. This energy can be harnessed by converting it into heat and electricity in a number of ways. In addition, it can be said to be a clean energy source because it releases water and steam when it decomposes. Hydrogen is usually obtained from water and when utilized, the by-product obtained is either water vapor or water itself. So, hydrogen can be continuously produced.

In nature, hydrogen is found as a combination rather than in its free form. Water is the most well-known chemical. When hydrogen is utilized as a fuel in energy systems, all that is released into the environment is water and/or water vapor. In general, hydrogen is 1.33 times more efficient than fossil fuels. It is also the lightest known gas and extremely flammable. Its primary advantage is that when burned, it produces only clean water and no hazardous emissions like carbon dioxide, which other fuels generate. With the exception of water vapor, which pollutes the environment and heightens the greenhouse effect, no gases or dangerous compounds are created during the energy production from hydrogen.

In addition to water, wind, wave, biomass, and solar energy, hydrogen gas can be produced in a variety of ways. According to research, the price of hydrogen is approximately three times higher than that of other fuels at the present time. The availability of hydrogen as a common energy source will depend on technological advancements that can cut production costs. In recent years, hydrogen energy has appeared as one of the most suitable and sustainable alternative energy resources in terms of its properties, possibilities, and fields of application. Hydrogen has been considered as one of the clean energy carriers for many years and has been the subject for scientific research. Especially with the oil crisis of the 1970s, it began to replace traditional hydrocarbons from fossil sources in their use in both stationary and mobile applications. In the near future, hydrogen will actively participate in the research and development of sustainable energy as an energy carrier.

Since 2003, some car brands have produced fuel cells or side-by-side tanks in some models. Hydrogen fuel cells are the biggest obstacle for very large and heavy models. It is included in surveys and inventories related to training solid, gaseous, or cosmic models of hydrogen-powered vehicles. It is developed as a hydrogen-powered internal combustion engine. NASA and some aircraft manufacturers are also working to develop aircraft and spacecraft powered by gas turbines and fuel cells [1,2,6].

2.2. HYDROGEN IMPORTANCE AND RESEARCH SIGNIFICANCE

Discovered in the 15th century and classified as combustible in the 17th century, hydrogen is the fuel with the highest energy per unit mass ever discovered. The energy in 1 kilogram of hydrogen gas is approximately same as the energy in 2.8 kilograms of gasoline or 2.1 kilograms of natural gas. Hydrogen as a fuel is almost 1.33 times more efficient as compared to petroleum fuels. Hydrogen releases water or water vapor when burned instead of toxic greenhouse gases, making it the ultimate alternative to fossil fuels. However, it costs three times more than conventional fuel. It is good to be a common source of energy for technology development and cost reduction methodologies [21,22]. Water, coal, natural gas, and other energy sources can all be possible energy sources for hydrogen generation. The plan is that the world's renewable energy sources will be converted into electricity, which will then be used to produce hydrogen through water electrolysis [23].

Since the environmental concerns are increasing day by day, the environmental sustainability has become increasingly significant. To achieve environmental sustainability, the renewable or green energy resources needs to be preferred rather than conventional fuels derived from fossil fuels. The alternative energy resources., solar, geothermal, wind, and hydro energy, do not harm the environment. Now many countries are building the infrastructure to support the use of these green and alternative energy resources. The hydrogen derived from these sources contributes to environmentally sustainable development. Hydrogen, which can easily be obtained from a variety of sources, releases no greenhouse gases, and can be safely supplied anywhere through pipes.

Hydrogen is a vital carrier of energy; widespread utilization of hydrogen will provide both more cost-effective and more efficient in the energy sector as well as ensure that it is not releasing the toxic emissions and not polluting the environment. Hydrogen is regarded as a very important resource in line with the current and anticipated state of oil, import dependence, carbon dioxide emissions from fossil fuels, and emission restrictions imposed by the Kyoto agreement. The future of hydrogen is influenced by number of factors, including the costs of production and infrastructure, government support for policies and incentives, and also the consumer and society's acceptance to latest technologies.

2.3. HYDROGEN APPLICATIONS

Like conventional fuels, hydrogen can be utilized as a fuel to produce heat as well as power in engines and evaporators. It may also be used in fuel cells to produce electrical energy as a result of a chemical reaction. Normal reaction pathways for combustion will result in much lesser generation of air nitrogen and NO_X components at high temperatures as compared to fossil fuels. Contrarily, the combustion of conventional fuels, which contain carbon, results in the emission of CO_2. Vehicle emissions are very critical in residential areas. The advantages of utilizing hydrogen as a fuel in vehicles and power generation are evident. Emissions produced are in extremely small quantities at high temperature operations are not created at all when used as a fuel. The widespread usage of hydrogen as a fuel will have a substantial impact on carbon emissions reduction. Hydrogen energy has application in many areas of industry, i.e., transportation, space rockets, oil production, etc. It also uses for heating and cooling systems. This energy can also be mixed with gasoline, ethanol, and methanol to reduce pollution and improve transport efficiency. It can also be converted to electricity with hydrogen fuel cells and used as direct fuel in cars. Environmentally friendly hydrogen energy is used for electricity generation, in cars, planes, ships, submarines and trains, in medium and long-range missiles, in space transport, in residential buildings. It has a very wide range of applications in defense industry as well and will soon surpass all fuels. World standards have been established for hydrogen. It is possible to use hydrogen in combustion engines, fuel cells, turbines as well as marines. Hydrogen has an application in cooking too [24–27].

2.4. HYDROGEN STORAGE

In the hydrogen distribution system, liquid or gaseous storage options are available. Most of the time, gaseous hydrogen is stored in caves underground where natural gas is depleted. Even though hydrogen has more properties that can leak than other gases, this method doesn't cause leaks in storage. France, where this method successfully stores city gas (a mixture containing hydrogen) in the cave, can be provided. Additionally, hydrogen gas is stored in a depleted natural gas cave near Amarillo, Texas, while helium gas, which is more susceptible to leakage, is stored there. The energy required to pump the gas into and out of the cave is crucial to this method. The generated hydrogen can be kept in storage and moved using tankers or pipelines. In the future, hydrogen could be transported using natural gas pipes. Both liquefied and high-pressure gas tankers as well as pipelines may transport hydrogen in a gaseous state. Studies have been done on the ability of zeolite environments to store gaseous hydrogen. However, liquid hydrogen storage methods rather to gas ones are prioritized in terms of their energy content [20,27–31].

Metal hydrides can be used to transport hydrogen in a compressed form—as a gas, a liquid, or a solid. The amount of hydrogen to be carried and the route that it will take determine the least expensive mode of transportation. The quantity of hydrogen to be transported and the route taken determine the most cost-effective mode of transportation. The road, sea, rail ways, and pipelines are the modes of transportation for hydrogen. Numerous processes can be used to create hydrogen, which can then be transferred using natural gas pipelines or tankers or stored underground in caves when natural gas is depleted.

Hydrogen is portable and can be stored in pipelines or tankers. Being a low-density gas, the gaseous state takes up a lot of space. These products are stored in gas formulations in pipes or tanks. The safety and durability of tanks or tanks used for pressure storage are very important. Liquids and chemicals can also be stored. Energy is consumed to revive hydrogen. In a simple formula, 3 units of energy are required to consume 1 unit of liquid. Hydrogen is the second most difficult gas to liquefy after helium. It is possible to store hydrogen in a form of liquid or a gas, or even in the form of chemical compound. However, due to its low density, the takes up a lot of space. For this purpose and it is compressed and stored into a tank or pressure vessel. Liquid hydrogen doesn't occupy much space. However, liquefying the hydrogen requires a lot of energy. To store solid hydrogen metal hydrides are used. Hydrogen gas with metal hydrides drawn out like a sponge and stored in the pores. Metal hydrides are quite heavy [20,27,29–31]. The methods for Hydrogen storage are illustrated in Figure 2.1.

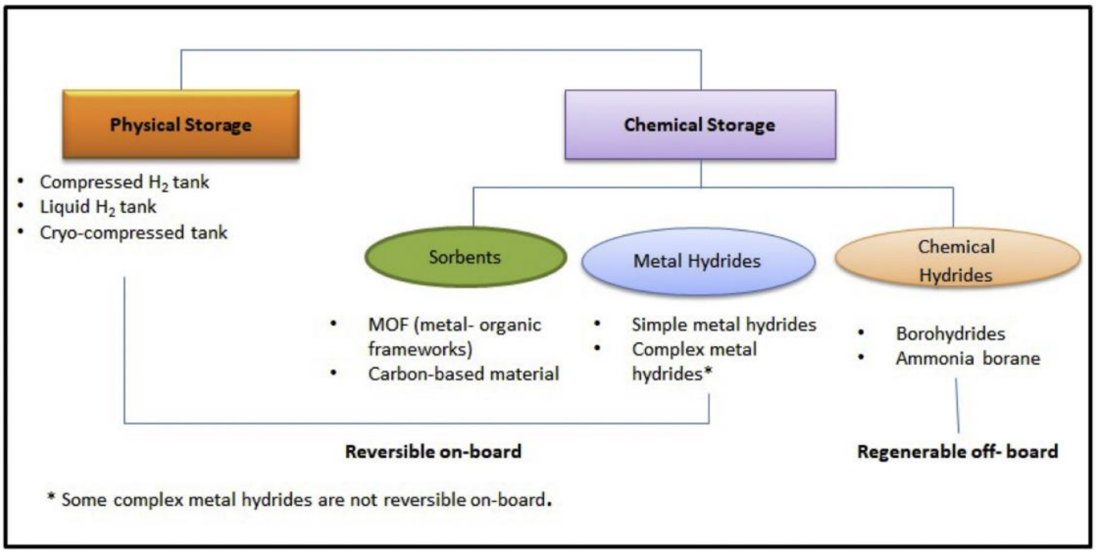

Figure 0.1. Methods for the Storage of Hydrogen [24].

2.5. Hydrogen Economy

Engineers at General Motors came up with the idea for the hydrogen economy in 1970, envisioning hydrogen as a fuel for all modes of transportation. The rapid advancement of fuel cell technology opens the door to additional alternative energy sources like hydrogen, natural gas, methanol, and ethanol. On the other hand, hydrogen is advantageous because it produces water as a by-product [32]. A time when hydrogen produced from non-greenhouse gas emitting sources provided the majority of our energy is referred to as the "hydrogen economy" [33]. Hydrogen economics is more than just a suggestion to alter the fuel mix. It requires the creation and application of a variety of technologies that transport energy from conventional or alternative energy sources to various end uses using hydrogen. Instead of being an energy source, hydrogen is a carrier that stores and transmits energy from other sources [34].

The most important component of the hydrogen economy is the production of hydrogen and CO_2 gas, which is released along with the energy consumed/consumed in this production. Today, with a capacity of about 40 million tons, representing just 2% of global energy demand, and a market share of about $50 billion in annual production, hydrogen is used in many industries as a chemical rather than a fuel. New technologies for the production, storage, distribution, and use of hydrogen are being developed, especially through research activities, public funding, and the projects to promote the use of hydrogen in the developed and industrialized countries. At the same time, a major part of being successful in the hydrogen economy is raising public awareness of the technology and creating a culture of safety. Hydrogen is gradually being introduced into the energy sector, mainly due to the cost of producing the fuel [17,19,34,35].

The anticipated economic, social, and environmental benefits of hydrogen economics are clearly defined, despite some benefits that are up for debate. When consumed with minimal waste and leakage, hydrogen generally qualifies as an environmentally friendly and abundant energy carrier. In terms of harmony between the economy, environment, and energy, the 21st century will be the hydrogen era. It is anticipated that the transition to a hydrogen economy will take several stages over a long period of time [2,34].

The enhanced vapor formation of natural gas in centralized and distributed applications will primarily produce hydrogen in the short term. The opportunity to lessen the amount of carbon dioxide released into the atmosphere is presented by this process. This is due to the fact that depleted natural gas fields and coal deposits contain high-purity carbon dioxide, a by-product of vapor build-up that can be collected, utilized, or stored. Fuel cells that make use of hydrogen will open up opportunities for the electrical service industry in the medium term and enable on-site electricity generation. Fuel cells will produce thermal energy for industrial processes, underfloor heating, and hot water, in addition to electricity. Hydrogen will increasingly come from coal and biomass pyrolysis or gasification at this point [2].

Long-term potential for renewable hydrogen systems will be created by enhanced hydrogen markets and expanding hydrogen infrastructure. Wind turbines or photovoltaic energy technology, for example, will power electrolysis, which will generate hydrogen for fuel cells. Hydrogen will be used by fuel cells to supply electricity or support intermittent energy sources during high demand times. Advanced technologies that use sunlight and water to produce hydrogen and store it at a high energy density also emerged and developed during this time. The establishment of the hydrogen economy will depend on the commercialization of cutting-edge hydrogen production, storage, and utilization technologies. The future hydrogen of economy is also dependent on the development of processes for producing hydrogen that are cost-competitive, sustainable, and clean [2].

2.6. HYDROGEN GENERATION METHODS

Hydrogen is widely available, and the challenge is to extract this gas, from compounds such as water, hydrocarbons, and other organic matter, in an efficient way [21]. Hydrogen can be produced in various ways for use in both the chemical industry and the energy sector. The process of hydrogen generation is sustainable as well as green and eco-friendly. The process of producing hydrogen depends first on the field of application and then on the energy used and the resources required for its production. To produce hydrogen, electrical, thermal, photonic, or biochemical energy is used in the process of separating, converting or breaking down chemicals such as biomass, water, fossil fuels, various hydrocarbons or H_2S. These necessary energy sources can be either conventional energy source (coal, gasoline, natural gas, etc.) or alternative energy sources (hydroelectric, solar, wind, biomass, etc.) [3,25,36]. Hydrogen generation methods along with their sources, and handling processes are represented in Figure 2.2 & 2.3.

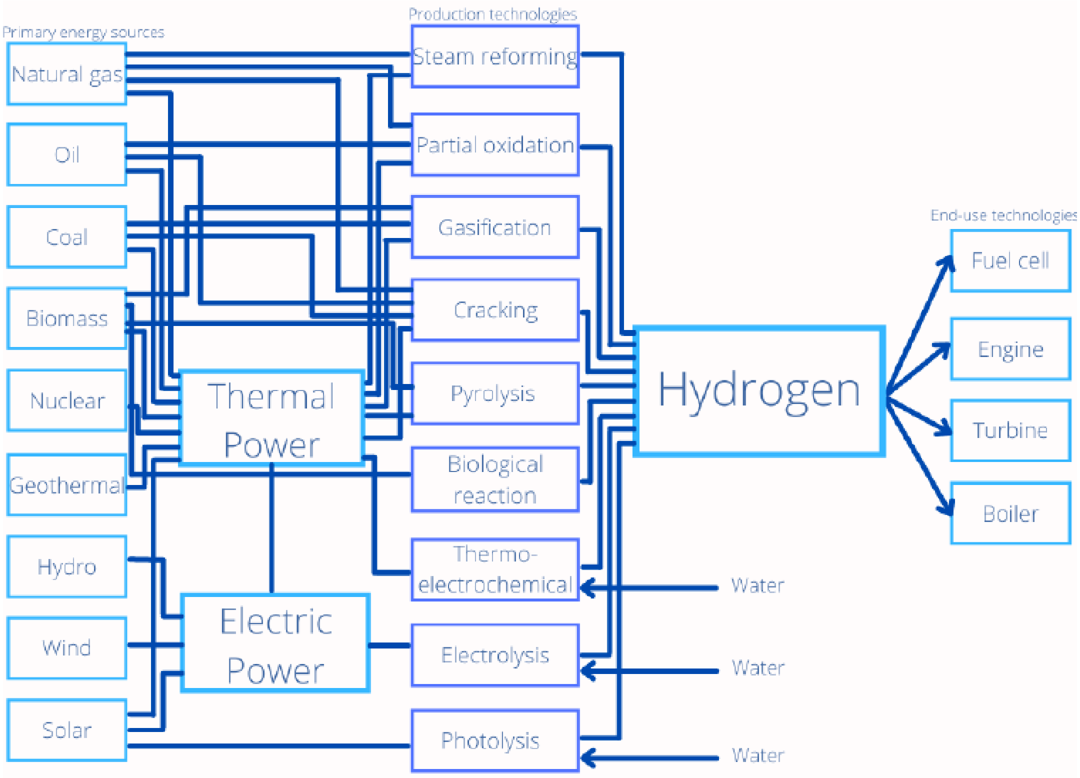

Figure 0.2. Hydrogen generation methods according to energy sources [37].

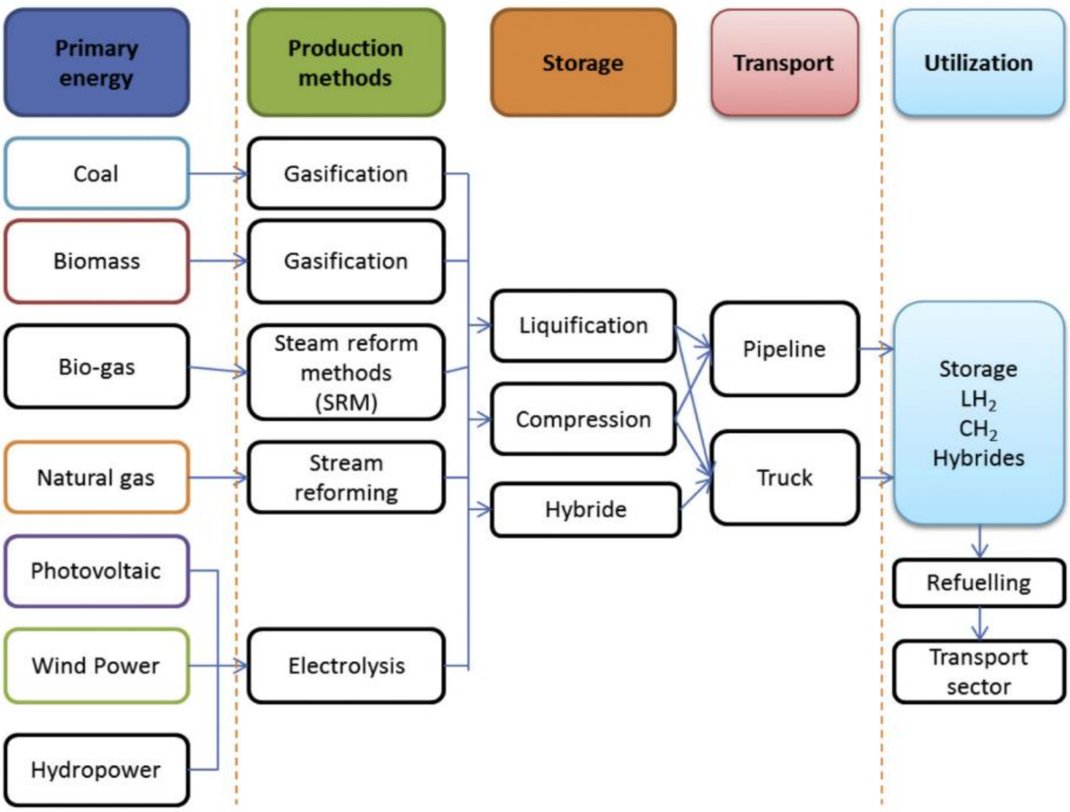

Figure 0.3. Hydrogen energy source, production methods and handling processes till end stage [38].

2.6.1. Electrolysis

The process or method through which electric current breaks down water into oxygen and hydrogen through electrochemical reactions in called as electrolysis. It is regarded as the basic and most straightforward method for producing hydrogen. The high temperature electrolysis takes place at temperatures between 700 and 1000 ℃ to separate apart hydrogen and oxygen from water vapor. In terms of electricity consumption, this method is comparatively more efficient than traditional electrolysis. At present, worldwide round about 4% of hydrogen is generated through electrolysis [39–46].

2.6.2. Pyrolysis

The pyrolysis process converts biomass into solid, liquid, and gas-phase compounds in an oxygen-free atmosphere by heating at a pressure of 100-500 kPa and a temperature of 500-900 ℃. Since there is no water or air, CO and CO2 do not form, so there is no need for PrOx reactors. The material should not be dried if water and air are being used. There are three temperature ranges that are used to define pyrolysis processes: low (below 500 ℃), medium (between 500 and 800 ℃), and high (above 800 ℃). When it comes to converting organic compounds that have a lot of energy, the rapid pyrolysis method is usually the one that is used most often. Process products in the form of solid, liquid, and gas are produced through rapid pyrolysis. Because it yields process products with a high energy content, double pyrolysis of organic wastes and a mixture of coal has become the method of choice in recent years. Slow pyrolysis of biomass yields a lot of coal, whereas quick pyrolysis yields a lot of high-temperature gas and a lot of low-temperature tar. Slow pyrolysis is not favored in hydrogen generation since the major result is coal [39–47].

2.6.3. Steam Reforming

The process of generating hydrogen from natural gas is called as steam reforming. This is the least expensive technique of producing hydrogen. Natural gas and steam in the 700-1000℃ range are treated with a nickel catalyst in this process. The bonds of methane molecules are ruptured as a result of the endothermic process, yielding hydrogen and carbon monoxide. Carbon monoxide and dioxide as well as other greenhouse gases are the primary byproducts of this process. One ton of hydrogen generation produces 9-12 tons of carbon dioxide, depending on the quality of raw materials such as rich gases, natural gas, etc. High-temperature water vapor and methane react endothermically to create hydrogen and carbon monoxide in this process. In the second phase of this reform, the carbon monoxide released in the first stage is reacted with water using an exothermic water-gas exchange reaction below 360℃, resulting in the production of hydrogen once more. Other than hydrogen, carbon dioxide is released here as a by-product [39,41,47,48].

2.6.4. Partial Oxidation

By using partial oxidation, it is made from hydrogen, natural gas, or other hydrocarbons. A hydrogen-rich syngas is produced by partial combustion of a fuel-air or fuel-hydrogen combination. The water-gas exchange process produces hydrogen and carbon monoxide. When the mixture or combination of fuel with air or oxygen is partially burnt in a partial oxidation reactor, this process is known as partial oxidation. There is a contrast between thermal partial oxidation and catalytic partial oxidation [39,41,47].

2.6.5. Thermolysis

The process of breaking down water into its constituent parts at high temperatures is known as thermolysis. At temperatures above about 2500℃, water breaks down itself. However, as the structure of membrane materials cannot withstand high temperatures, various catalysts are used in studies to lower the decomposition temperature [40–42,47].

2.6.6. Thermochemical Water Decomposition

The lack of catalysts in thermochemical water decomposition makes it an advantageous method. Thermochemically transformed chemicals can all be recycled.

The Decoupling of oxygen and hydrogen does not require a membrane, the reaction temperature ranges from 600 to 1200 K, and it requires little electricity [39,41,42,47].

2.6.7. Gasification

In comparison to current hydrogen production methods, coal gasification is among easiest methods for hydrogen production. Along with steam coal is oxidized partially in this method. The process of coal gasification takes place at high temperature, ranging from 800-1300°C and pressure from 30 to 70 bar. The syngas along with hydrogen, carbon monoxide and carbon dioxide are produced as a result of this process. In gasification and thermochemical biofuel reform, by drying or supercritical vapor gasification, moisture must be kept at a specific level when biomass is utilized to generate hydrogen. Fixed bed, mobile bed, and fluid bed types can all be employed in the gasification process. Thermochemical techniques are used to produce hydrogen from liquid biofuels [41,49,50].

The gasification of coal is also the method by which hydrogen is produced using coal. To break the coal's molecular bonds, a controlled mixture of gases and steam is used in the coal gasification process. The result is a mixture of H_2 and CO gas. Since this gas can be used as fuel, so it is the primary product of the hydrogen source, and it is valuable too. Coal that is gasified can be used to generate electricity more effectively than conventionally burnt coal for combustion process [49–51].

Gasification of coal or biomass is the standard CO_2 partition technique. In a low-oxygen environment, coal or biomass is processed with steam at high pressure and temperature as a raw material for hydrogen production. The synthesis gas, which includes methane, hydrogen, carbon monoxide, carbon dioxide, and nitrogen, is the end result of this reaction. The gasification process's thermal efficiency is decreased when biomass is dehydrated. Adding catalysts to fluidized bed or stationary reactors can improve thermal efficiency [40].

2.6.8. Photoelectrolysis

Photon and electrical energy are both converted into chemical energy during photoelectrolysis, which results in the production of hydrogen. Crystal structure, surface properties, corrosion resistance, and reactivity of the photon-absorbing material all affect a photoelectric system's performance. The process of converting the photon's energy into chemical energy is known as photocatalysis. The photon that strikes the photocatalyst creates two electron holes and is then broken down into its constituent parts by the electric charge that results [40–42].

2.6.9. Photo-Fermentation

Photosynthetic bacterial hydrogen production is another name for photo-fermentation processes. Chlorophyll, phycobilins, and carotenoids are the examples of light-trapping pigments that are utilized during this process. In photolytic organisms, light energy is separated from the collected rays and transferred to membrane reaction centers with algae. Daylight changes over water into protons, electrons, and oxygen. catalysts for nitrogen; Hydrogen, ammonia, and adenine diphosphate are the byproducts of its reaction with nitrogen and the protons and electrons of adenine triphosphate. These microscopic organisms can be utilized in a wide range of conditions. Utilizing sun radiations, organic acids, or biomass, photosynthetic bacteria can produce hydrogen under the influence of their nitrogen. Photo-fermentation is a biohydrogen production technique that makes extensive use of organic acid-rich waste and wastewater as substrates. Green algae use catabolism of the endogenous substrate to release electrons for use in photosynthesis during the process of photo-fermentation, in which energy is obtained from sunlight. water made from sunlight; transformed into oxygen, protons, and electrons. Due to its significant hydrogen conversion rate values, hydrogen production through photo-fermentation is considered a promising method for hydrogen production even though it has a relatively lower hydrogen yield by converting organic substrates. In the literature, maximum hydrogen efficiency of 80 percent and light conversion efficiency of 9 percent have been measured. even if photo fermentation results in high hydrogen yield values; The enzyme that makes active hydrogen and the intensity of the light limit the economic viability of hydrogen production. Additionally, favorable process conditions like the carbon-to-nitrogen ratio, the configuration of the reaction tanks, the age of the microbial seeds, and the intensity of the light are effective in increasing the yield of hydrogen [52–57].

2.6.10. Dark Fermentation

In the absence of light, dark fermentation is the process of converting biochemical energy, stored in organic matter, into other forms of energy. Its main advantage is that it can generate hydrogen from organic waste. As a result, the risk of organic waste polluting the environment is reduced. It is particularly adaptable for use in wastewater treatment facilities. Under anaerobic conditions, metabolic means are used by either obligatory anaerobic or facultative anaerobic microorganisms to produce hydrogen through dark fermentation. Because oxygen is not present in these conditions, microorganisms must seek an alternative terminal electron acceptor, such as a proton. When an electron is transferred to a proton, hydrogen is produced. The most common pathways by which biomass is converted into hydrogen are acetate and butyrate. In order to obtain pure hydrogen, separation is required. Acetic, butyric, and other organic acids are produced as well by this process. By directing the metabolic flow toward the production of organic chemicals, the produced acids affect the yield of hydrogen. Furthermore, acids add complexity to the system. Costs go up as a result of this [58–66].

2.7. WATER ELECTROLYSIS TECHNOLOGY

Electrolysis is a very basic method or technology for producing hydrogen gas. Water along with an electrolyte serves as the primary component for electrolysis process and generates high-purity hydrogen and oxygen gases through a chemical reaction. Water electrolysis is basically the process of splitting or separating hydrogen and oxygen from water by supplying electric and thermal energy. The electrochemical reaction of this separation through water electrolysis is given as follows [67]:

$$H_2O \longrightarrow H_2 + \frac{1}{2} O_2 \tag{2.1}$$

Hydrogen may be created through several sources using various technologies, and it has been used in industry for more than a decade. The only cutting-edge technology to generate hydrogen gas through alternative energy resources is the advanced water electrolysis, despite the fact that several techniques have been created and are still being worked on. Water electrolysis is only found to be the realistic way to produce this gas through alternative energy resources such as solar, hydropower, and wind energy [68,69].

The process for water electrolysis is very straightforward and easy to start. Water electrolysis has the potential to link several industries such as power, chemistry, heating, and so on. Due to the greater costs of electrolyzers and their lesser efficiency, only 4% of hydrogen is generated by electrolysis of water. Power-to-Gas technology, which converts power (obtained from renewable sources) into a storable gas by electrolysis of water, has grown in popularity in recent years. This Power-to-Gas technology holds the promise of future renewable and sustainable energy systems since it is both cost-effective and ecologically beneficial. As a result, water electrolysis will become increasingly crucial for hydrogen synthesis in the future. The key obstacles of employing water electrolysis on a bigger scale are lowering energy consumption and costs while increasing durability and performance [70,71].

Water electrolysis has the potential to be an essential means of connecting various industries, including heating, chemistry, electricity, and others. Due to the higher costs of electrolyzers and their lower efficiency, only 4% hydrogen is produced through water electrolysis. Power-to-Gas technology, which involves electrolysis of water to transform renewable electricity into a storable gas, has gained popularity in recent years. This Power-to-Gas technology has the potential to be the future's renewable and sustainable energy systems because it is both cost-effective and good for the environment. As a result, hydrogen synthesis will require water electrolysis in the future. A reduction in energy consumption and cost, as well as an increase in its durability and performance, are the primary obstacles that must be overcome when using water electrolysis at a larger scale [67,70,72–78]. In water electrolysis, the water used for electrolysis process needs to be distilled and deionized [3].

2.8. TYPES OF ELECTROLYSIS TECNOLOGY

The best way to obtain pure hydrogen is to electrolyze water. Water electrolysis is a simple, efficient, low maintenance and easy to control technology. Water electrolysis is suitable to be utilized with both, conventional and alternative energy resources. There are various techniques for producing hydrogen by water. Three common categories of electrolysis are:

- Alkaline Water
- Proton Exchange Membrane
- Solid Oxide

The electrolysis process is mainly consisting of redox reactions that produce oxygen and purified hydrogen gas. Each type of electrolysis comprises an electrolyte and two electrodes, though which current flows and transfer of ions takes place. Solid oxide electrolyzers are still in the development stage, but alkaline electrolysis and proton exchange membrane electrolysis are widely used for commercial purposes. Commercial alkaline and proton exchange membrane electrolyzers typically operate at temperatures below 100℃, while solid oxide electrolyzers operate at temperatures between 800℃ and 1000℃ with water in the vapor phase. The advantage of the higher operating temperature is that the electrical energy required for hydrogen production is greatly reduced. Efficiency and current density are the two most important factors for electrolysis. The efficiency of electrolysis depends on the ideal and actual energies driving the reaction. The catalysts or electrocatalysis play a vital role in enabling and facilitating the electrolysis process. Platinum is the most commonly used heterogeneous catalyst applied to the surface of the electrode [26,78–80].

2.8.1. Alkaline Electrolysis

An alkaline electrolysis system consists of a liquid electrolyte in a closed container and a conductor placed within the electrolyte. It consists of electrodes and DC supply. Liquid electrolyte is a solution, made up of water and solid particles of KOH (potassium hydroxide), NaCl (sodium chloride), or NaOH (sodium hydroxide), used to increase the electrical conductivity of water. The direct current is applied to this liquid electrolyte to make the ions travel from anode to cathode. In order to maximize the ionic conductivity of alkaline electrolyzers, an aqueous solution of an electrolyte is used. These hydroxide ions (OH^{-1}) are present in the solution are the charge carriers. As a result of this, the hydrogen gas is produced at the cathode side and the oxygen gas at the anode side. Alkaline electrolysis is the oldest and simplest electrolysis method, but it has the drawback of requiring maintenance due to the corrosive action of the liquid electrolyte while generating hydrogen and oxygen gases. [77,78,81–83].

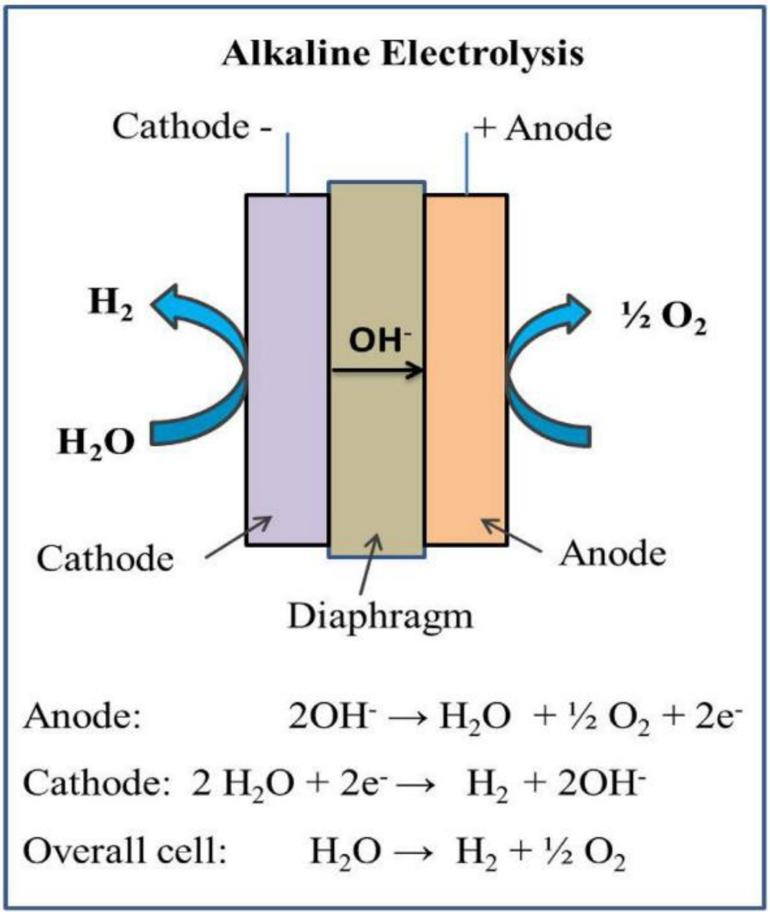

Figure 0.4. Alkaline water electrolysis schematic illustration [84].

2.8.2. Pem Electrolysis

PEM electrolysis is named after the proton permeable membrane used as the solid electrolyte. Unlike alkaline electrolysis, PEM electrolysis uses deionized water instead of liquid electrolyte to avoid poisoning by solid electrolyte, anode and cathode catalysts. The proton-permeable membranes used are completely electrically insulated, allowing only protons to pass through. The PEM electrolyzer consists of a DC power source, electrodes through which current flows, and a membrane. In PEM electrolysis, when the current applies the water splits into ions and hydrogen and oxygen gases are generated. The released oxygen and unused water exit the cell through the anode. A field effect induced by the applied potential causes positively charged hydrogen ions to pass through the membrane and combine with electrons from the cathode catalyst to produce hydrogen gas. PEM electrolyzers use solid electrolytes, which makes them safer and more compact than alkaline electrolyzers. The efficiency of the PEM electrolysis process increases at elevated pressures and current density to generate highly purified hydrogen gas, without the use of compressors. Therefore, no cleaning process is required in PEM electrolysis. PEM electrolyzers can also be used in variable generation renewable energy sources due to the fact that they can operate at high pressures without compressors. Despite these advantages of PEM electrolysis, its drawbacks are its high price, low operability, and the need to use deionized water [26,45,85,86].

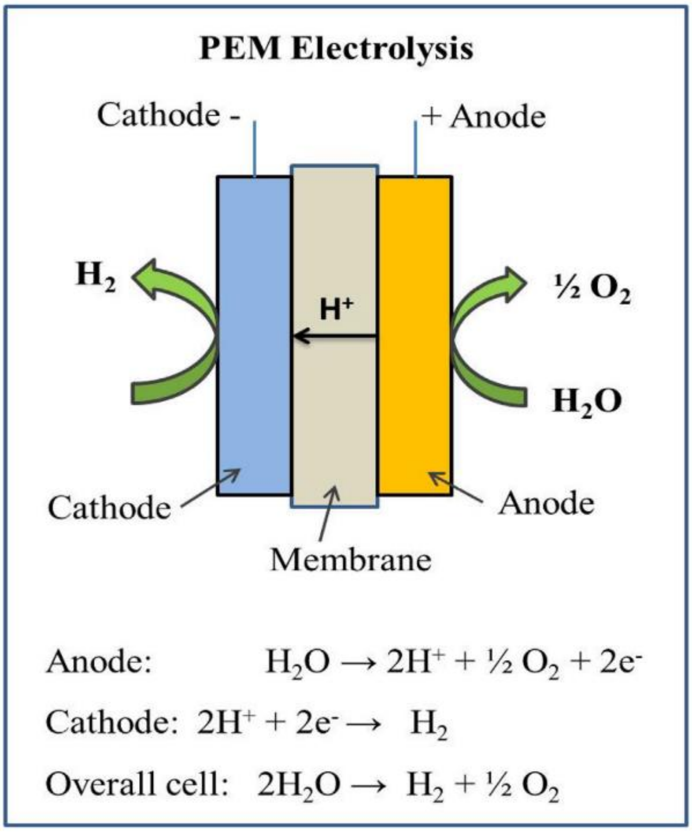

Figure 0.5. PEM water electrolysis schematic illustration [84].

2.8.3. Solid Oxide Electrolysis

Solid oxide electrolysis, uses electrical energy to separate hydrogen and oxygen at high temperature, is not the new technology, but it is the least advanced of the three electrolysis methods. The operating temperature for this process is within the range of 7000 – 1000 ^{0}C the cell voltage is between 1.2 – 1.3 V. Since it consumes less power than alkaline electrolysis or PEM electrolysis, high electrolysis efficiency can be obtained. However, this method is in the research and development stage because the electrodes and the membrane with ionic conductivity are frequently affected by high temperature operation. The current density of this method is usually low due to its working at high temperature. Solid oxide electrolysis is more efficient given the cell voltage and required temperature. The oxide ions at cathode travel through the solid electrolyte towards the anode and recombine to form oxygen molecules. In this method, the material used for the membrane is typically an ion-conducting ceramic [67,87].

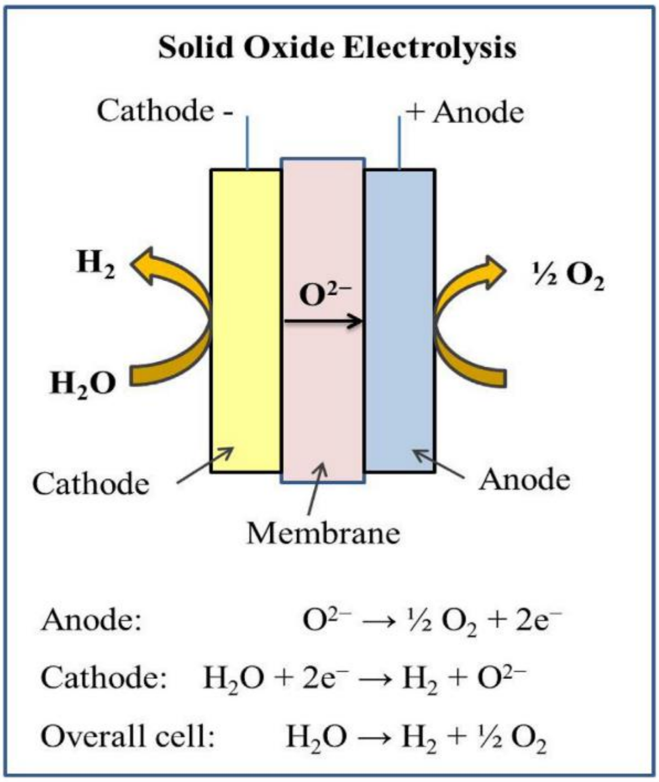

Figure 0.6. Solid Oxide electrolysis schematic illustration [84].

2.9. ELECTROLYZERS

Water electrolysis has been the solution since the early 20th century to meet the demand for hydrogen used in chemistry and industry. This technology uses electricity to split water molecules in a device called an electrolyzer, producing oxygen and hydrogen gases. An electrolyzer is basically an electrochemical device that converts electrical and thermal energy into chemical energy. The decomposition of water is caused by a direct current flowing through the electrodes or electrolysis cells immersed in the electrolyte solution. The electrolyzers can be either small scale or large scale based on the need of the production. [28,88].

2.10. ELECTROLYZERS VERSUS FUEL CELLS

The working principle of the electrolyzers is completely opposite to the working principle of the fuel cells. In an electrolyzer, the electrical energy is used to split water molecules into hydrogen and oxygen. The overall chemical reaction for the electrolyzer is as follows (Eq. 2.2) [28]:

$$2H_2O + \text{Electricity} \longrightarrow 2H_2 + O_2 \qquad (2.2)$$

whereas an electrochemical device, known as fuel cell coverts the chemical energy directly into electrical energy. In fuel cells, basically, hydrogen and oxygen react with each other to produce water and electricity as shown in the chemical equation below (Eq. 2.3) [28,89]:

$$2H_2 + O_2 \longrightarrow 2H_2O + \text{Electricity} \qquad (2.3)$$

2.11. HHO CELL AND OXYHYDROGEN GAS

The HHO (oxyhydrogen) cell is a technology that has become more popular in recent years. An apparatus in which the Water is converted into HHO gas is the HHO cell. As a fundamental principle, the electrolysis process requires an electric current to separate the water. The current utilized is direct current, and the value of direct current changes with system size. The HHO cell is composed of electrodes, plastic gaskets or diaphragms to be placed between them, and the end plates that keep the system together. The size and combination may differ depending on the system being utilized. Oxyhydrogen is an explosive flammable gas in nature. It can be utilized in applications that required explosion or combustion. It is suitable for applications requiring combustion and explosion. HHO gas is a hydrogen-oxygen gas mixture. This gas combination can be used for metal cutting and welding. Theoretically, hydrogen has double the mass of oxygen. This combination is known as by several names such as brown gas, hydroxy gas, or knallgas [69,90]. Yull Brown discovered this gas and got patient in 1977 and mentioned it as a Brown gas [91].

HHO is commonly known as a mixture of hydrogen hydrides produced by a variety of methods, but here we mainly discuss production by the electrolysis of water. Two gases, hydrogen and oxygen water, are produced by immersing an electrically lifted metal plate in any electrolyte, and the combination of both hydrogen and oxygen, produces both gases. Most chemists call it a mixture of oxygen and hydrogen. This encounter can be added to the air intake of petrol/diesel engines to increase engine efficiency. It has always been known that hydrogen can improve engine efficiency, but only hydrogen is worth it, and other base gases such as water vapor can do the same. However, the energy per gram to mix hydrogen, HHO's October calculation is relatively 100 times higher, and the calculation of energy supply using pure compressed hydrogen mixed.to develop alternative energy sources. countries focused on scientific research [92].

2.12. ELECTROLYZERS VERSUS HHO GENERATOR

If the hydrogen generator or electrolyzer contains the same exit for both of the produced gases (H_2 and O_2) by separating H_2O as a result of chemical reaction, and molecular bond is used to keep these two gases combined then it will be labeled as oxyhydrogen or brown gas (HHO) generator. The water electrolysis procedure is used to produce this HHO gas through the electrolyzer. The basic difference between electrolyzer and HHO gas generator is that the electrolyzer has separate exits or storage tanks for both gases (hydrogen and oxygen). Contrastingly, the oxyhydrogen gas

(HHO or OH_2G) generator has common exit or storage tank for both gases produced. [93]. During combustion process, if hydrocarbon fuels are burned with HHO gas, it may enhance the fuel efficiency by 25 to 28 percent [94].

Previous studies similar to current research work having slight differences such as reactions carried out with benzene, diesel, and some other kinds of fuels or alcohols combined with oxyhydrogen (HHO) gas are briefly discussed below:

Compression and spark engines (SI) running with diesel fuels have been researched and experimented by various researchers to explore the effects of oxyhydrogen gas as an additive to fuels and to assess the functioning of engines. Earlier investigative studies related to the subject under discussion manifest that brake thermal proficiency can be increased by mixing diesel and HHO gas. It is also helpful in decreased emissions of HC, CO, and CO_2. However, some earlier studies reported higher rates of NO_x emissions [95–99]. In an investigative study, how a combination of oxyhydrogen and compressed natural gas (CNG) as an additive fuel in a non-modified diesel engine is explored [100]. The results were impressive in terms of engine's performance and its impact on environment. One of the investigative studies on the same matter manifested how hydroxy gas combined with gasoline (petrol and benzene) showed positive outcome such as HHO gas and diesel combined illustrated [101–104]. Theoretical work was initiated to explore practicality of internal combustion engine while producing oxyhydrogen gas [105]. Experimental research for the production of brown gas through water electrolyzer in leak proof plexiglass fashion was performed using three different types of electrodes and electrolytes such as KOH, NaOH, and NaCl [106]. The same reaction was experimented with a mixture of hydrogen and ethyl alcohol and the results were astonishing on the reciprocating of combustion engine when seen in comparison with fuel consisting of benzene [107].

Stainless steel is a material that is easily available, even in large quantity across the globe, and it is not much expensive too. This study utilized stainless steel material to avoid corrosion and because it was cost competitive. The mostly used type of this material is SS304. This goes well with some acidic, alkaline solutions as well as water.

The chemical composition of stainless steel is (wt.%) is: C, 0.08; Mn, 2; Si, 1; Ni, 8-12; Cr, 18-20; N, 0.1; S, 0.03; P, 0.045 [108–110].

These experimental works are beneficial for transport and automobile industries. The technologies researched in the studies like the present and those related to this provide a chance for fuel production that is pollution free and omits the probability of greenhouse gases produced as a by- product. In order to gain benefit from these studies practically, two steps are necessary. First, the paperwork or theories by different national or international scholars, institutes and organizations need to be recognized globally. Second, the reports and support policies by different local or international organizations and industries who implemented hydrogen as prime energy carrier on experimental level can apply these theories and experiments on a larger scale, converting the dream of hydrogen as basic source of energy in 21st century a reality. When seen in this context, research and experiments centered on generation systems of water electrolysis-based hydrogen production are getting recognition in recent times with a special focus on systems utilizing renewable energies. The previous studies and recent researches on the subject matter are considered helpful for the field with the results predictions to be astonishing, beneficial and new improvements in the field of energy production without pollution [111].

These systems enable the production of an unlimited supply of fuel for the transportation and automotive industries without the production of greenhouse gases or other pollutants. On the other hand, integration of these systems in through electrolysis systems as the penetration of these energy sources in the system for generating electricity is increasing, so there is a significant potential for water electrolyzers to help in stabilizing, regulating, and integrating the renewable sources of energy to the grid stations. There are now two primary categories of industrial electrolysis equipment, Alkaline and Proton Exchange Membrane (PEM). The primary distinction between them is the Membrane. A membrane that conducts ions serves as the electrolyte in the second category of electrolyzers, allowing H^+ ions to go from anode towards the cathode and recombine to produce hydrogen, they are called as PEM electrolyzers [111,112].

Due to their beneficial characteristics, alkaline advanced electrolyzers are currently the most widely utilized electrolyzers. As per the higher heating value for hydrogen, i.e., 3.5 $kWhNm^3$, the electrolysis-based systems can have a global energy efficiency as high as 73%. Additionally, there are commercial units available that can produce hydrogen at rates ranging from a few Ncm^3min^{-1} to thousands of Nm^3h^{-1}. In addition, PEM electrolyzers now have a higher capital investment cost than alkaline ones, it's primarily due to the usage of electro-catalysts. The electro-catalysts are generally based on noble metals, i.e., platinum, titanium, etc., these metals are expensive (approximately 200 $ for 1 Nm^3h^{-1} hydrogen production) but the need for high-quality water as well as for certain building materials. There are comparatively few industrial scale demonstration projects and almost no use of water electrolyzers powered by renewable energy sources. Due to the underdeveloped market for energetic hydrogen, these units are expensive. Additionally, the price of electrical energy has a significant impact on the price of the hydrogen produced [111].

According to an NREL report, an electrolysis plant with 100% capacity factor operating for over 40 years and powered by commercial electrical energy, can account up to 70% of the total cost for generating hydrogen. One of the most important manufacturers of water electrolysis equipment, Technologies (a subsidiary of Statoil Hydro in Norway), claims that the price of electrical energy can account up to 90% of an electrolyzer's total operating costs [113,114].

If this energy came from renewable sources, the price of electric energy would even contribute more to the cost of hydrogen. As a result, there is a need to increase the water electrolyzers' overall energy efficiency, particularly by minimizing the use of electrical energy in the electrolysis systems, without making impact on the performance. In this context, alkaline electrolyzers have undergone a number of advancements in recent years. New configurations of electrolysis cells have been created related to the electrolysis stack design. The majority of manufacturers use a configuration known as zero-gap. The energy efficiency can rise by 15–30% in this setup [114,115].

Numerous studies have been conducted with the goal of enhancing performance of electrolysis process even more. The impact of the gas bubbles produced by electrodes placed at various distances apart in order to look into the possibility that there is an ideal separation that maximizes the efficiency of electrolysis. When using high performance electrodes made using the vacuum plasma spraying (VPS) technique, it was possible to achieve the low voltages of approximately 15 % at the cathode and anode [114,116].

However, for weak grid applications, this makes the water electrolyzer system a crucial aspect of the renewable hydrogen energy systems. The technological challenge of the electrolyzer, which is a vital component, is to make it run efficiently on the electricity from renewable energy sources. The most popular water electrolysis technology is the alkaline electrolyzer. Due to stainless steel's exceptional corrosion resistance and excellent conductivity in this concentration range, aqueous solutions of water and typically 20-30 weight percentage of potassium hydroxide (KOH) have historically been employed as the electrolyte in conventional alkaline water electrolyzers. However, alternative electrolytes such as sodium chloride (NaCl), sodium hydroxide (NaOH), and others have also been employed [68,83,112].

The liquid electrolyte makes it possible for ions to move between the electrodes. The current densities in the range of between 100 and 400 mA cm^{-2} are generally used to run the advanced, highly developed commercial alkaline electrolyzers. An alkaline electrolyzer is primarily composed of a cell frame, electrolyte, anode cathode, and separating diaphragm. The two most common types are the bipolar and unipolar design configurations. The electrodes, anodes, and cathodes are suspended alternately in the unipolar design, and the electrical connections of the individual cells are physically and electrically connected in parallel. However, the individual cells in the bipolar design are connected in series [68].

The chemical compositions of three distinct varieties of stainless steels: AISI (316, 304, and 321) were chosen. They are utilized in a variety of applications and have variable corrosion resistance characteristics despite having only slight variations in the amount of alloy additives. The most popular stainless steel is AISI 304, which is utilized because it is less expensive and has better anticorrosion qualities. The alkaline solutions, air atmosphere and natural water as well as certain acids can be used with AISI 304. AISI 306 type of stainless steels demonstrates corrosion resistance qualities against aggressive chemical conditions and is a most widely used acid-resistant material. The third type of stainless steel, AISI 321, exhibits great strength against inter-crystalline corrosion. This type of stainless steel is suitable to use between the temperature range of 400-800 ℃ [110].

Advanced alkaline electrolyzer type can function between 2 and 65^0C and absolute pressures ranging from 5 to 26 bar. In a bipolar stack structure, 22 x 300 cm^2 circular electrolysis cells are linked in series. Each electrolysis cell is made up of an anode and a cathode that are connected and squeezed to produce a zero-gap configuration. An inorganic ion-exchange membrane separates the electrodes. This indicates that in order to have a highly efficient operation, very little space exists between the various components of the cell stack. For the needed high conductivity, 30 percent by weight KOH aqueous solution serves as an electrolyte. The water used in the electrolysis process is deionized using an ion exchange resin bed, resulting in a permanent conductivity of less than 5. The production range is between 33 and 100% of the nominal production rate, which is 1 Nm^3 h^{-1} at an average DC current of 120 A [82]. Hydrogen, that is primarily taken into account in this study, is the synthetic fuel. It has the potential to supply and provide electricity to different industries in future, because it allows the flexible energy storage and distribution. So, all the hydrogen production processes, or steps must be feasible in terms of both cost and environment (thermal or electric). The most useful and effective way to store energy is by electrolysis, which is produced utilizing electricity from renewable sources like the wind, solar or hydropower. Currently, the majority of industrial hydrogen production through the means of water electrolysis is by using KOH electrolyte (30% by wt.), at a temperature of 80 ℃ and the cell voltage ranges between 1.65 V to 1.80 V. Alkaline electrolysis research has mostly looked into electrocatalytic materials to improve current density and lifespan. Electrocatalysts, which are to be deposited on the surface of electrodes, are most frequently made up of nickel-based alloys. Latest research demonstrates that technically less sophisticated or advanced materials for electrodes, need to be used to reduce the cost of the electrolysis systems [117].

Rashid, M. et al., investigated the thermodynamics, energy requirements, and efficiency of electrolysis processes. The electrolysis of alkaline water, proton electrolyte membrane electrolysis, and high temperature electrolysis have all been studied and compared [118]. Grigoriev, S. et al., used PEM electrolysis to produce hydrogen and performed the analysis of the literature data and experimental results concludes that significant development of PEM electrolyzers is expected in the near future, and their cost is approaching the cost of alkaline electrolyzers [119]. Barbir F., in his study, discussed the use of PEM electrolysis, electrolyzer sizing, output pressure, oxygen production, as well as integrated systems related to water consumption, and the efficiency [120]. De Brujin, F.A. et al., used fuel cell experiments and cyclic voltametry to investigate the effect of CO2 on the performance of PEM fuel cells [121]. Grandia, L. M. et al., provided findings from several trials with a 5-kW commercial alkaline water electrolyzer working under typical dynamic circumstances of wind energy systems in the research [122]. Leng, Y. et al., descried the high-performance, long-lasting alkaline membrane water electrolysis in solid-state membrane cells. An alkaline membrane electrolysis cell using iridium oxide as the anode catalyst and platinum black as the cathode catalyst demonstrated a current density of 399 mA/cm at 1.80 V at 50°C. These preliminary water electrolysis findings in the solid-state membrane cell were encouraging for low-cost hydrogen generation [123].

Marini, S. et al., presented our original results demonstrating that an improved alkaline electrolyzer with performance comparable to PEM electrolyzers may be produced without platinum group metals and with catalysts with good stability and durability [124]. Santos, D.M. et al. discussed the electrochemical foundation of alkaline water electrolysis and examined the key process restrictions. As a result, further research is required to solve the durability and safety difficulties that continue to impede the widespread application of alkaline water electrolysis [125]. Pletcher, D. and Li, X. performed a review, that emphasized the potential benefits of zero-gap alkaline water electrolyzers for more inexpensive and efficient water electrolysis technology. While chemical stability improves, the structural alterations necessary to achieve mechanical stability and high conductivity appear to be incompatible [126]. Ganley, J.C.'s work included experimental tests that involved the electrolysis of large concentrations of potassium hydroxide solutions at high temperatures and pressures. At 400℃ and a vapor partial pressure of 8.7 MPa, the highest cell performance was obtained utilizing a cobalt-coated nickel anode. Hall D.E. in his study examined electrodes for alkaline membrane water separation electrolysis and the electrochemical workings properties at 80℃. It was possible to attain an oxygen generation efficiency equivalent to that of coatings formed from nickel powders, nickel particles, and nickel-iron alloy powder [127].

Chen, L. et al., conducted research to use nickel hydroxide to separate the creation of hydrogen and oxygen in alkaline water electrolysis. This might be a viable option to facilitating the transition from renewable energy to hydrogen [128]. Herdem, M.S. et al., in their work performed thermodynamic modelling and simulations were used to analyze the performance of a clean energy system that combined the principles of coal gasification and alkaline water electrolyzer to create hydrogen. As a result, this system's total energy and exergy efficiency were determined to be roughly 55-58%. The hydrogen supplied by the coal fed to this system has a weight ratio of approximately 0.126, and despite the fact that the system produces hydrogen from coal, the greenhouse gases generated by the system are fairly low [129]. Nikolic, V.M. et al study's described an effort to improve the efficiency of alkaline electrolytic hydrogen generation by using ionic and complex forms of in-situ activating chemicals. In comparison to the inactivated system, cobalt and tungsten-based ionic activators applied directly to the electrolyte during the electrolytic process lower the energy consumption per unit mass of hydrogen generated by around 15% [130].

Linkous, C.A., in his study, selected the suitable samples from several polymer groups based on previous studies assessing thermohydrolytic stability, and each sample was converted to ionomers by sulfonation and then converted to membranes for evaluation. Thermal conductivity analysis and performance testing in particular were used to investigate sulfonated polyetherether. The results were comparable to those obtained with commercial perfluorocarbon sulfonates [131]. Ahmadi, P. et al., performed energy and exergy analysis in their study and reported hydrogen production via an ocean thermal energy conversion (OTEC) system combined with a solar proton exchange membrane (PEM) electrolyzer. The integrated OTEC system's energy and exergy efficiency were 3.6 and 22.7%, respectively, while the PEM electrolyzer's exergy efficiency was obtained as 56.5% and the amount of hydrogen produced was 1.2 kilograms per hour [132]. Marshall, A. et al., set out to create electrocatalytic materials that would improve the performance of PEM water electrolysis cells. In general, when Nafion 115 is used, the optimal cell voltage at 80℃ typically noted was 1.567 volts [133].

The paper by Kazim, A. presented a comprehensive exergy analysis of a 10 kW PEM fuel cell at various operating temperatures, pressures, cell voltages, and air stoichiometry [134]. Grigoriev, S.A. et al., research concluded that both anodic and cathodic circuits affect gas purity can lead to the formation of explosive gas mixtures. To avoid these risks, this article investigates two different solutions: the first is chemical modification of solid polymer electrolytes to reduce cross-permeability events, and the second is the use of catalytic hydrogen/oxygen recombiners to keep the hydrogen level at levels consistent with safety requirements. It was possible to keep the hydrogen content in the electrolysis cell below 30% by using gas recombinators [135]. Ni, M. et al., conducted the energy and exergy analyses to investigate the thermodynamically detailed electrochemical properties of hydrogen production by a PEM electrolysis plant. Heat generation due to irreversible losses in the PEM cell was investigated and compared to the PEM cell's thermal energy demand. It has been discovered that a PEM electrolyzer normally operates exothermically, with heat generation exceeding thermal energy demand due to excessive capacitances [136].
Alkaline and proton exchange membrane electrolysis have received the majority of attention in water electrolysis studies (PEM). Since 1920, alkaline water electrolysis has been employed extensively in industrial settings. The advantages of this technology include inexpensive startup costs and no reliance on noble metals; nevertheless, low pressure and low current density have a negative impact on the size of the system and the cost of producing hydrogen [3].

This study proposes the prototypes of two electrolyzers, Alkaline and PEM. To the best of authors’ knowledge and review from the literature, no similar study has been carried out previously, especially where a unique chemical formula is used to make a special chemical mixture to be used in the Alkaline and PEM electrolyzers. The main objective of introducing this unique and novel chemical solution is to increase the efficiency of generated hydrogen or oxyhydrogen gas as well as minimize the production cost. For Alkaline electrolyzer, this unique and novel chemical composition is formed by mixing the distilled or deionized water with ethyl alcohol, ammonia, and urea. Whereas, for PEM electrolyzer, solution of methyl alcohol, ammonia, urea, and deionized or distilled water is used. For both electrolyzers, the electrolysis cell stacks were also magnetized to enhance the efficiency of the hydrogen or oxyhydrogen gas produced through water electrolysis.

PART 3

MATERIALS AND METHOD

3.1. DESIGN AND PROTOTYPE OF PEM ELECTROLYZER

The prototype design of PEM electrolyzer was developed and tested in this study. Since it was developed for industrial scale so 12 electrolysis cell units or stacks were used to generate hydrogen and oxygen gases separately. Each electrolysis unit of the PEM electrolyzer was comprised of 4 electrode plates. From the literature review, it is evident that the bipolar plate membrane with C-Cr coating comes up with good results and long material's life. Two cathodes made of SS304 bipolar plates coated with Cr-C and two anode plates make up each electrolysis cell. The single cell was put to the test for 200 hours. It was determined through contamination analysis for the membrane electrode assembly (MEA) that the C coating is well stable chemically [22,137]. Commercial MEAs with an active electrode area of 50 cm^2 and a platinum charge of 0.5 mg cm^{-2} for the anode and cathode were employed. 316L stainless steel (Cr-C coated) 304SS foil with a thickness of 0.1 mm at a reduced cost was chosen as the material for bipolar plates [137–139]. For this study, the plates were made up of stainless-steel SS304 material. The dimensions of each plate were 12.5 x 12.5 x 2 cm. Each side of the plate was plated with C-Cr, which acted as a membrane for this PEM electrolysis stack.

To prevent produced gases from mingling, a diaphragm or separator should be utilized between the electrode plates. An electrolytic cell is made up of the electrodes, the diaphragm, and the electrolyte. The energy needed for the reaction can be reduced thermodynamically by raising the temperature or pressure, and energy losses in the electrolytic cell can be reduced by lowering the main resistances by raising the conductivity of the electrolyte, which will increase the efficiency of the electrolytic system [3]. The diaphragm was placed between the electrode plates, in order to keep the anode and cathode separate from each other. The gap between the electrolysis cells was maintained to pass the electrolytic solution and allow the flow of electrons between them, and finally separate the created gases, which are hydrogen and oxygen. The size of the diaphragm was 1 mm, which is nearly zero gap configuration, and it was made up of polymer material. Table 3.1. shows the list and cost of all materials used to develop the PEM electrolyzer prototype.

The housing, made up of plexi-glass material, was developed for electrolysis stack. To strengthen this stack, it was further protected by metal plates and tighten using nuts and bolts. As it was developed for industrial scale, so it was made sure that no leakage is there. A separate tank, made by plexiglass, was used to carry the electrolytic solution and for the non-stop of that electrolytic solution to the electrolysis units of the PEM electrolyzer. Finally, the housing, which was again made by plexiglass material cover and all 12 electrolysis units and gas collected area is developed to collect the produced hydrogen and oxygen gases. The prototype for PEM electrolyzer is shown in Figure 3.1.

Figure 0.1. Prototype for PEM electrolyzer.

3.1.1. Hydrogen Generation Via PEM Electrolyzer

Hydrogen and hydroxide ions move toward the cathode and anode, respectively, during the electrolysis of water. The two compartments are separated by a C-Cr membrane. On the anode side of the bipolar plates, the membrane is plated. Due to the low cost and ease of manufacture of Cr-C coated SS304 bipolar plates, they are employed to provide electrical conductivity for the cathode and the anode. Finally, the oxygen gas from the anode and hydrogen gas from the cathode are collected using gas receivers. The KOH (potassium hydroxide) boosts the H_2O input to the cell and creates the chemical compound with the proton exchange membrane in a hydrogen-producing PEM (proton exchange membrane) electrolyzer system. Because in the membrane electrolyzer, the crosslinked mixture produced the best results. A C-Cr coated bipolar plate membrane in in KOH electrolyte shows good performance and gives the best results at 70°C. The technique and precise technical aspects are also detailed in full in this experimental investigation. Hydrolysis of reactive metals, such as Cr-C coated SS304 bipolar plate, has been intensively researched for use in hydrogen generation. The metals were hydrolyzed because the process is exothermic. In the experimental investigation, hydrogen was produced using the hydrolysis procedure. At 80°C, the electrodes were hydrolyzed for one hour in a wastewater solution containing a combination of water and waste with 15% electrolytic KOH [22,137]. Figure 3.2. shows the schematic of PEM electrolysis cell.

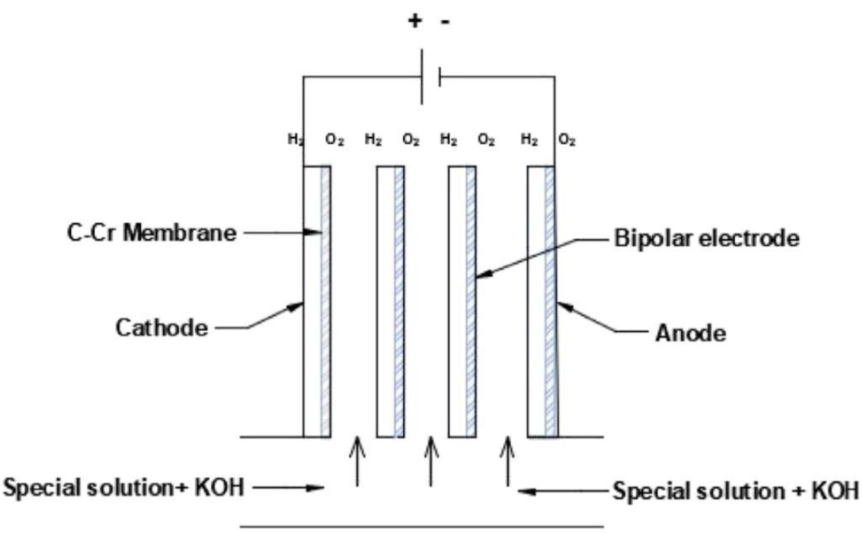

Figure 0.2. Schematic of PEM electrolysis unit.

3.1.2. Cr-C coating and Magnetizing of PEM Electrolysis Stack

Figure 3.3. shows the PEM electrolyzer single electrolysis cell stack exploded view. The bipolar plates of the electrolysis cells were made of SS304 material, and one side of these plates was coated with C-Cr. A total of nine magnets with housings were attached from both sides of the flow channel end plate. The plexiglass was used to cover and connect the plates together to form a single electrolysis cell unit. [22].

To upgrade the performance of electrolysis cell stack and generated hydrogen gas, 9 magnetic magnets were employed on each side of stack. Plates were magnetised from both sides, with the upper pole, - S (negative), and bottom pole, + N (positive) pole (Figure 3.4.). Applying a voltage of 10 V and the direct power supply of 30 A intimates the chemical reaction. Furthermore, the anode and cathode in the system were subjected to 220 V as the energy input and 12 V as the power supply output. The voltage reducer reduces the average voltage of 12 V in the cells to 10 V, resulting in a direct current of 30 A for energy generation. All of 12 cell stacks were magnetized in this electrolyzer prototype [22].

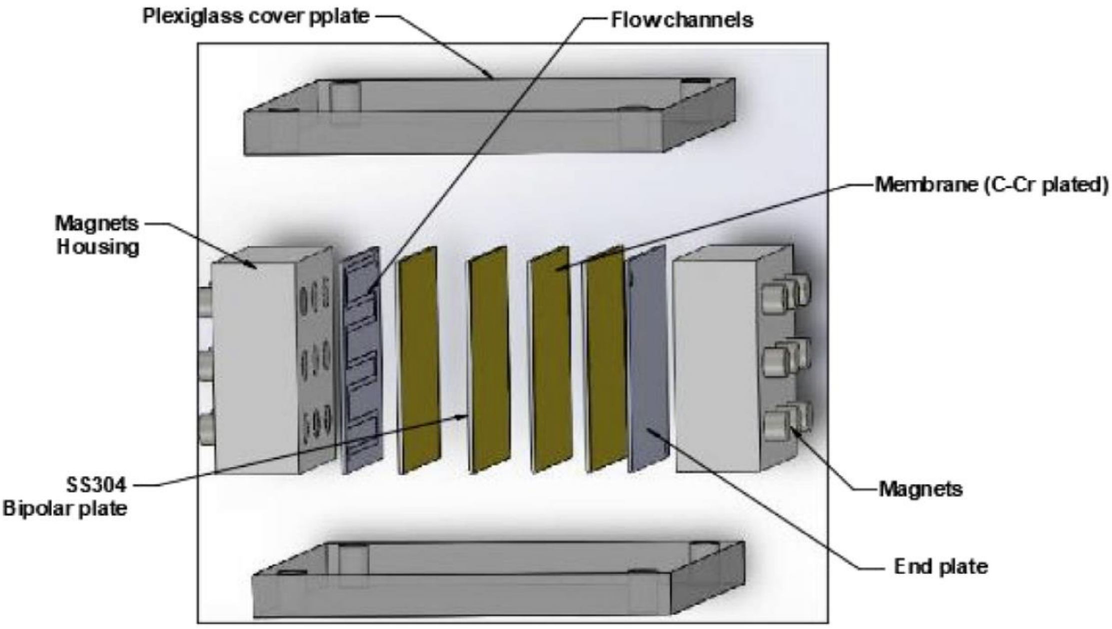

Figure 0.3. Design and magnetizing of PEM electrolysis stack

Figure 0.4. PEM magnetized electrolysis cells unit.

3.1.3. Septic Chemical Solution for PEM Electrolyzer

In an ordinary PEM electrolyzer, electrolysis takes place using an electrolyte or aqueous solution, made up of deionized or demineralized water and any type of an electrolye to produces hydrogen and oxygen gases. In this study, a unique and new chemical composition is introduced which is used instead of water to get the improved performed from the electrolyzer. It was made by mixing ammonia, urea, and methyl alcohol with deionized or distilled water. Figure 3.5. presents the unique and special chemical mixture.

Figure 0.5. Spetic chemical mixture for PEM electrolysis.

3.1.4. List of Materials for the Prototype of PEM Electrolyzer

Table 0.1. List of materials for the prototype of PEM electrolyzer [22].

No	Tools and equipment of machine and materials	Item	Unit price (€)	Price (€)
1	N35 80x80x20 mm magnetic magnet	200	2,000	400,000
2	Cr304 stainless steel 1 mm thickness ∅ 100x200 cm 30 plate	30	2,500	75,000
3	Plexiglas plaque 20 mm 10 plate	10	2,500	25,000
4	Plexiglas plaque 10 mm 12 plate	12	2,500	30,000
5	Wired hose 1 1/4" 100 m length	1	500	500
6	Variable unions and valves	1	1,500	1,500
7	Switch mode regulator adaptor 12 V 30 A	50	2,000	100,000
8	Condenser and fan	50	3,000	150,000
9	Vacuum pump	12	2,500	30,000
10	Cord tyre 200 m length	1	1,000	1,000
11	Solenoid coil 12 V	50	500	25,000
12	pH metre measuring device	12	1,500	18,000
13	Thermometer	12	250	3,000
14	Hydrogen gas nozzles	100	100	10,000
15	PLC panel	4	3,000	12,000
16	Pressure-resistant hose 3x100 m length	1	1,000	1,000
17	Several consumables and specialty adhesives	1	15,000	15,000
18	Special chassis casing	2	9,000	18,000
19	Electrical panel	2	5,000	10,000
20	Various cables 4x100 m length	1	15,000	15,000
21	Labour costs	1	300,000	300,000
22	Software programme	1	100,000	100,000
23	Other cost	1	160,000	160,000
	Total cost of PEM electrolyser prototype (included VAT), Y_{cost} [€]			1,500,000

3.2. DESIGN AND PROTOTYPE DEVELOPMENT OF AN ALKALINE ELECTROLYZER

The present study also focused on the design and development of alkaline electrolyzer prototype from scratch. The basic motive behind this small-scale innovative and investigative study is to evaluate and enhance the efficiency of hydrogen and oxy-hydrogen gas production. Oxyhydrogen gas was produced by utilizing five stacks of electrolysis cells. Each one of these was composed of four electrolysis cells. These cells were further secured by plexi-glass frame seals and tighten firmly with the help of nuts and bolts to avoid any kind of leakage. Each electrolyzer plate was separated by placing 1mm polymer diaphragm between them to keep anode and cathode separate and allowing the regulated flow of water and hydroxyl ions. This resulted in separated hydrogen and oxygen gases production. Moreover, the electrolyzer cell plates were of 12.5 x 12.5 x 2 cm in size and the diaphragm was 1mm thick that equals to zero-gap configuration. All electrolysis cells were joined with electric current supply to let the electrons to flow. A separate tank, which was also made up of plexi-glass material was attached with the experimental setup to make continuous supply of electrolytic solution to electrolysis cell stacks or units. To keep the electrolyte mixed with water continuously and avoid coagulation of the electrolyte at the bottom of water tank, a recirculation pump to was also installed to this system. The plates for electrolysis cells, also called as electrodes, were made up of SS304 AISI304 stainless steels. The prototype of alkaline electrolyzer is shown in Figure 3.10.

The cell stacks compromising of electrode plates were also tested, after cleaning process (Figure 3.6.). For alkaline solution, which is to be used for electrolysis process, the potassium hydroxide (KOH) is added as an electrolyte. The distilled or deionized water was used to wash them completely to remove all residuals of unreacted KOH. To get rid of all remaining particles of unreacted KOH, the deionized water at room temperature was again employed to immerse electrode plates in that for 30-45 minutes. The same procedure was again repeated twice to thoroughly remove all traces of KOH escaping chemical reaction and completely clean the electrolysis plates [140].

Figure 0.6. Testing of alkaline electrolysis cells stack

3.2.1. Hydrogen Generation Via Alkaline Electrolyzer

As compared to other electrolyte solutions, the electrolyte (KOH) contains higher thermal conductivity and lower corrosion problems. KOH in amounts 6 grams per liter of deionized water provides best possible results in producing oxyhydrogen gas [106,141]. So, the 6 grams of KOH in 1 liter of deionized water was mixed to make the alkaline solution. The continuous supply of electrolytic solution of KOH to electrolysis cell stacks or units through the separate tank, attached with electrolysis stacks. The capacity of the attached tank was 6 liters. So, the electrolytic or aqueous solution of KOH for this tank was made using 6 liters of deionized water and 36 grams of electrolyte KOH. The electrolytic solution from the tank was continuously passing through the recirculation pump to make sure the uniformly mixed aqueous solution of

KOH electrolyte enters the electrolysis unit. All the five electrolysis cells stacks had continuous supply of this electrolyte or aqueous solution. Further, in order to mobilize the electrons, a current of 30 A and 12 V voltage was applied to all electrolysis cells stacks from its positive to negative end, so that conductivity may occur. Moreover, the operating pressure of 1 atm and temperature of 70℃ was maintained for aqueous solution (KOH). Fatouh et al. carried out similar research in their study. They are of the view that production rate of hydrogen may increase to 143% in alkaline electrolyzer if the temperature of electrolyte (KOH) is increased to 20℃. Because a raise in temperature results in higher thermal energy of KOH ions, boosting thermal performance of the electrolyte. The prime production rate of hydrogen or mass flow was achieved at 70℃ and 12V [142].

Multiple electrolysis cells are connected in parallel or series in industrial electrolyzers. The two most common configurations for electrolysis are: monopolar and bipolar. To reduce cell overvoltage, it is essential to reduce the distance between the electrodes and the membrane in both bipolar and monopolar configurations. Monopolar electrolyzers require very high currents and a low-voltage electrical supply between 1.9 and 2.5 V, which can be upto thousands of amperes depending on the range of hydrogen production. Due to differences in intracellular ohmic resistance, those in monopolar electrolyzers have an uneven distribution of current across each cell. The monopolar arrangement is totally measured, and one cell is secured and fixed while the others keep on working regularly. Each electron is unipolar in a monopolar electrolyzer because it receives an external current. Parallel connections connect the cells in a monopolar electrolyzer. Regardless of the number of electrode pairs in the electrolyzer, the voltage in the tank is the same as that in any single cell. The construction of monopolar electrolyzers is straightforward and dependable, using relatively inexpensive components. The unipolar (left side in the figure 3.7) and bipolar (right side in the figure 3.7) cell design configuration are illustrated below [143,144].

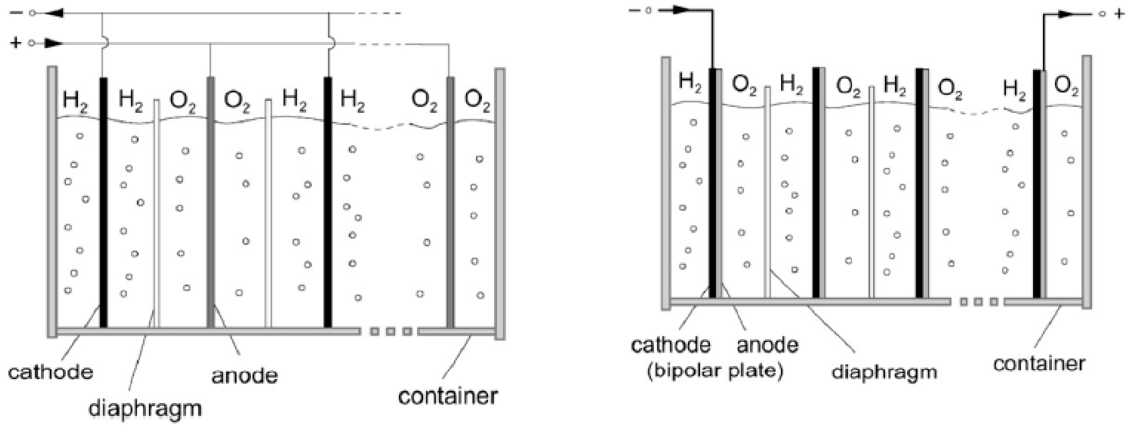

Figure 0.7. Unipolar and bipolar cell design configuration [145].

The alkaline reaction occurs when the base electrolyte (KOH) in an electrolyser is provided with DC supply. Potassium having positive charge (K+) travels towards negatively charged electrode (cathode) while hydroxide with negative charged (OH-) is inclines to move towards positively charged electrode (anode). Reduction occurs at anode and water is divided into hydrogen and hydroxide ions. On the other hand, oxidation of hydroxide ions occurs at cathode producing water and oxygen as illustrated in Figure 3.7. The complete equation of the reaction and cathodic and anodic electrochemical reactions are as shown below [142]:

Anode: $2OH^- \longrightarrow 0.5O_2 + H_2O + 2e^-$ (3.1)

Cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ (3.2)

Electrolyte: $4H_2O \longrightarrow 4H^+ + 4OH^-$ (3.3)

Overall reaction: $2H_2O \longrightarrow H_2 + O_2$ (3.4)

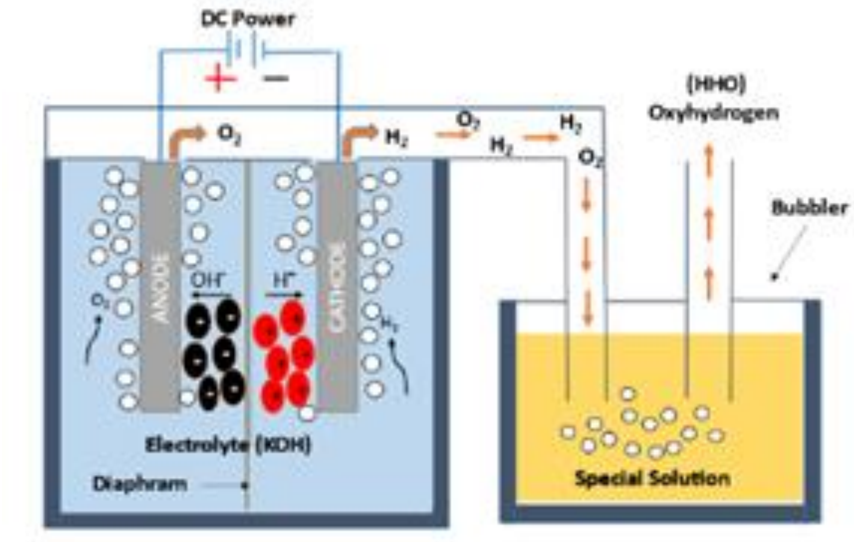

Figure 0.8. Schematic of Alkaline electrolyzer with special chemical solution.

The oxyhydrogen gas generated by all of five electrolysis units of the electrolyzer prototype was firstly passed through the water bubbler first before going to the atmosphere or storage tank. For the purpose of extraction of produced gas, two small vacuum pumps were also installed to the electrolyzer and the vacuum pressure was maintained at 0.025 atm helping in efficiently sucking the produced gas molecules, even those gas molecules which were partially separated. This results in an increased efficiency of the produced gas. Usually, the demineralized or deionized water is used in the bubbler but to increase the efficiency of generated hydrogen or oxyhydrogen gas, the novel and unique in nature chemical composition was made to be used, in place of deionized water, in the bubbler. This novel and unique chemical mixture was made by combining the deionized or demineralized water with urea, ammonia, and ethyl alcohol (Figure 3.9.). The efficiency of this electrolyzer was also measured by changing the bubbler liquid solution with this unique chemical composition. The digital mass flow meter was used to measure the OH_2G or HHO gas generated by this prototype of alkaline electrolyzer. The mole ratio of produced HHO gas is 2:1 that represents that it has two molecules of hydrogen and one of oxygen.

3.2.2. Magnetizing of Alkaline Electrolysis Cell Stack

18 circular magnets (9 on each side) were used to create magnetic field around all the five electrolysis cells units or stacks. The type of magnets utilized for this study were

of Neodymium, N35 grade. This type is observed as one of most powerful type of magnets. The dimensions of N35 magnet, used in this study, was 80 x 80 x 20 mm. The electrolysis cell unit with magnetic field around is shown in Figure 3.8.

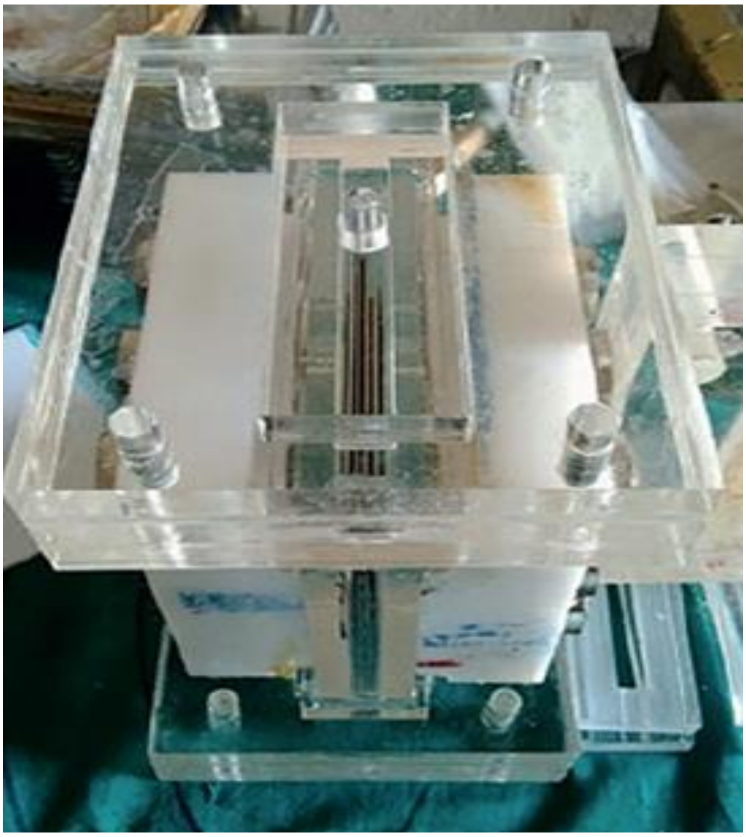

Figure 0.9. Magnetized alkaline electrolysis cells stack.

Figure 0.10. Special chemical solution for alkaline electrolyzer.

3.2.3. The Prototype of Alkaline Electrolyzer

The present study can be summarized by stating that utilizing water electrolysis hydrogen gas is produced and for this purpose a prototype of alkaline electrolyzer is constructed innovatively. The bubbler utilized innovative and specific chemical solution instead of water. Magnetized electrolysis cells stacks were used to enhance the quality of produced gas (HHO). This in turn also improves the quality and functioning of alkaine electrolyzer by producing enriched as well as cost competitive gas. The list of materials along with unit cost is shown in Table 3.2.

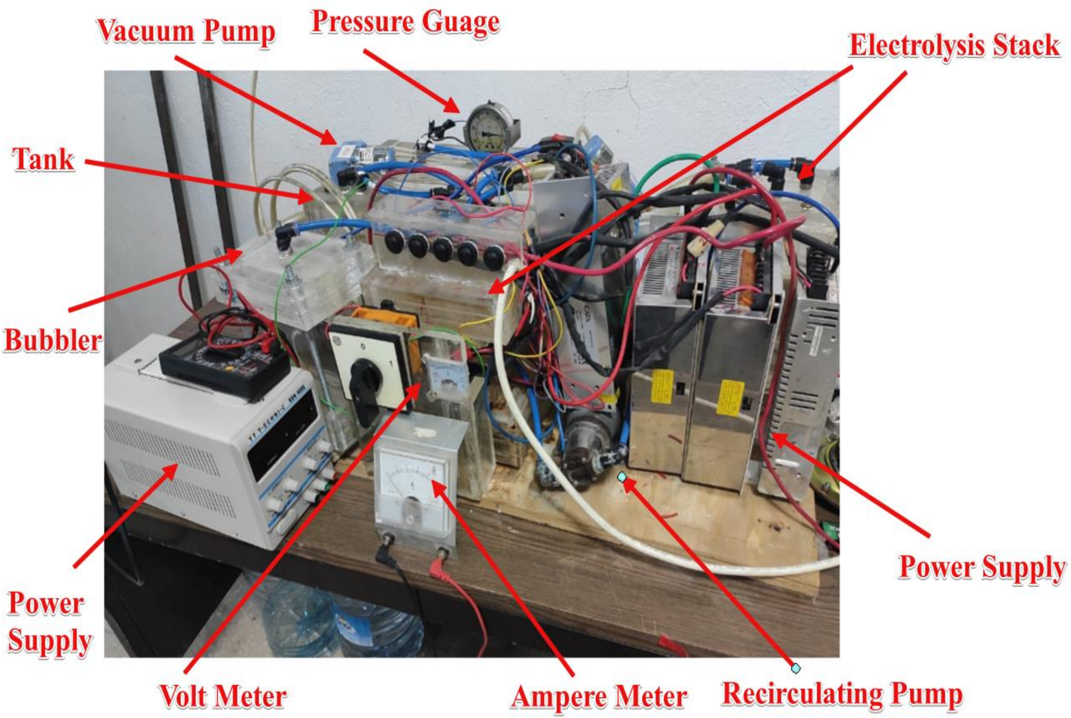

Figure 0.11. Alkaline electrolyzer prototype.

3.2.4. List of Materials for the Prototype of Alkaline Electrolyzer

Table 0.2. List of materials and cost per unit for the small-scale alkaline electrolyzer system [146].

No	Equipment and materials of the materials and tools	Pieces	Price (Unit, €)	Price (Total, €)
1	Plexiglass plate casing for electrolysis cells	5	160	800
2	Plexiglass tank for electrolysis solution	1	100	100
3	SS304 stainless steel plates	20	10	200
4	Neodymium N35 80 x 80 x 20 mm magnets	100	5	500
5	Recirculation pump	1	50	50
6	Vacuum pump for H_2 gas collection	2	50	100
7	Pressure and vacuum gauge	1	30	30
8	Thermometer	1	10	10
9	pH meter	1	30	30
10	Gas nozzle	30	3	90
11	Silicon pressure resistant hose & pipe tubes (3 m)	1	20	20
12	Power supply (12 V)	6	5	30
13	Digital multi-meter	1	20	20
14	Ampere meter	1	20	20
15	Voltmeter	1	20	20
16	Mass flow meter with software	1	200	200
17	Potentiometer	5	8	40
18	Rheostat	5	20	100
19	Different thickness cables (5 meters)	1	30	30
20	Nuts, screws, etc.	50	2	100
21	Plexiglass water bubble casing	1	30	30
22	Flame arrester	1	90	90
23	Chemicals	5	20	100
24	Other item costs	1	100	1200
	YY_{invt}: Total cost of alkaline electrolyser prototype (including VAT)			3,910

PART 4

WATER ELECTROLYSIS AND TECHNO-ECONOMIC ANALYSIS

Since one mole of hydrogen requires two electrons, the minimal voltage that can be supplied under normal circumstances is V_{min} = 2.46/2 = 1.23 V. Catalysts are necessary for electrolysis in order to increase reaction speed and current density. The cost of producing hydrogen through electrolyzers, available commercially, is ranges from 2.5-3.5 dollars at a cost rate of ¢5/kWh for electricity, whereas the cost which is acquired from an ideal electrolysis system (with no losses) is approximately 1.95/kg dollars [3]. The techno-economic analyses were performed for both electrolyzers: PEM and Alkaline. The annual profit (ΔYY) and simple payback period (SPP) for these prototypes were also calculated.

4.1. PEM ELECTROLYZER PROTOTYPE

4.1.1. Techno-Economic Analysis

In the prototype application of PEM electrolyzer, 12 cells stacks were used with a voltage of 10 [V] and a total current of 3.5 [kWh] with 30 [A] current. In this system, approximately 6 [m^3/h] H_2 gas was produced and prepared for use in the desired processes. The lower heat value for H_2 gas mixture was assumed to be 70 [MJ/kg] and the hydrogen gas energy produced was determined to be 1.05 [MW] if the gas density was 1.45 [g/cm^3].

Application of this system to the power plant (1 fluidized bed boiler) can be calculated from mass and energy balance equations. The consumption (used amount) of coal energy amount (En_K) is given in Eq. 4.1 as follows:

$$En_K \text{ [kcal/d]} = m_K \text{ [kg/d]} \times Hu_K \text{ [kcal/kg]} \quad (4.1)$$

where m_K is consumption of coal amount [kg/d], Hu_K is a lower heating value of coal that is ensured approximately 3000 [kcal/kg].

The amount of hydrogen-enriched coal consumption ($m_{K,Hid}$) is found from Eq. 4.2 as below:

$$m_{K,Hid}[kg/d]=\frac{m_K\left[\frac{kg}{d}\right] \text{ x } Hu_K[\frac{kcal}{kg}]}{Hu_{K,Hid}[\frac{kcal}{kg}]} \qquad (4.2)$$

where $Hu_{K,Hid}$ is a lower heating value of hydrogen-enriched coal that can be taken approximately 7000 [kcal/kg].

The amount of unburned coal (Δm_K) can be given through Eq. 4.3 as follows:

$$\Delta m_K = m_K - m_{K,Hid} \qquad (4.3)$$

In this study, a techno-economic analysis can be determined from energy economic ($Y_{En,Hid}$) equation from Eq. 4.4 as below:

$$Y_{En,Hid} \, [€/d] = C_{En} \, [€/ton] \text{ x } \Delta m_{K,Hid} \, [ton/d] \qquad (4.4)$$

where C_{En} is a daily coal price that can be taken approximately 10 [€/ton] from current marketing price.

A cost of an electric energy consumption ($Y_{En,el}$=amount of energy required for hydrogen production) can be given (measured through) Eq. 4.5 as follows:

$$Y_{En,el} \, [€/d] = C_{el} \, [€/kWh] \text{ x } En_{el} \, [kWh/d] \qquad (4.5)$$

where C_{el} is a daily coal price that can be taken approximately 0.0968 [€] for 1 [kWh] price set by the state, En_{el} is a consumption of electric energy from the mains electricity.

The lower heating value of coal value (enriched with hydrogen gas) used as fuel in fluidized bed boilers can be increased from about 7000 to 10000 [kcal/kg]. Firstly, the cost of initial investment of PEM fuel cell was determined and was given in Table 1 that shows total cost of initial investment of PEM fuel cell was found to (to be) 1,500,000 [€] for 1 [MW]. This result is similar to an application prototype study according to literature. When researched literature, PEM cost that was estimated at 1500 [€/kW] by Calise et al. [147] equals to 1,500,000 [€/kW]. Staffell and Green [148] posed that a long-term target of $3000–5000 for 1–2 kW systems. In this study, the prototype PEM fuel cell hydrogen production system was applied to the power plant and the results are shown in Table 4.1.1. that also shows the hydrogen production energy cost of the PEM electrolyzer prototype.

4.1.2. Simple Payback Period Analysis

An annual profit (ΔYY) of the PEM electrolyzer prototype can be determined from Eq. 4.6 as below [22]:

$$\Delta YY\ [€/y] = Y_{En,Hid} - Y_{En,el} \tag{4.6}$$

Furthermore, a simple payback period analysis (SPPA) can be utilised from previous studies [149–151]. Wang et al. [152] defined as the variables to be optimized based on the minimum simple payback period that Dahlhausen et al. [153] analysed as the financial performance in their study. Weissbach et al. [154] identified the simple payback period as energy payback time. The simple payback period is as follows [22]:

$$SPP[y] = \frac{Y_{cost}}{\Delta Y} \tag{4.7}$$

From Eq. 4.7, Y_{cost} is the investment cost of PEM electrolyzer prototype.

The energy and cost analysis for H_2 gas power through PEM electrolyzer is summarized as below; The H_2 gas equivalent to 1 MW electrical energy on hourly basis is investigated and techno-economic analyses were performed. For this electrolysis system, the annual energy production of 864000 MWh was estimated [22].

4.2. ALKALINE ELECTROLYZER PROTOTYPE

4.2.1. Techno-Economic Analysis

For small-scale system of an alkaline electrolyzer, 5 electrolysis cell units were combined in a single electrolyzer and the direct current of 30 A and voltage of 12 V, which is equal to 3.5 kWh electrical energy in total, was applied to the electrolysis stacks. When 3.5 kWh energy was supplied to this electrolyzer prototype at the vacuum pressure of 0.025 atm and the temperature of 70°C. The lower heat value of H_2 gas mixture was taken as 70 [MJ kg^{-1}] that is equal to 101 [MJ m^{-3}]. Alkaline Electrolyzer generated approximately 1.05 [MW] of hydrogen energy and the density of hydrogen was taken as 1.45 [g cm^{-3}] [22,146].

For this electrolysis system, lignite was taken into consideration for the techno-economic analyses. Therefore, balance equations of energy and can be used the consumption of lignite energy (En_{LG}) can be calculated from Eq. (4.8) as follows [22]:

$$En_{LG} = m_{LG} \text{ x } LHV_C \quad (4.8)$$

where m_{LG} is the amount of lignite consumption and LHV_C is the lower heating value of lignite, which is approximately 21.43 [MJ kg^{-1}] [155].

The amount of hydrogen-enriched lignite consumption is obtained from Eq. (4.9) as below [22,146]:

$$m_{LG,Hid} \text{ LG,Hid} = m_{LG} \times LHV_{LG} / LHV_{LG,Hid} \quad (4.9)$$

where the average lower heating value for hydrogen-enriched lignite was roughly taken as $LHV_{LG,Hid}$ 30.5 MJ kg^{-1} [22],[155].

The unburned lignite (Δm_C) amount can be obtained from the Eq. (4.10) [22,146]:

$$\Delta m_{LG,hyd} = m_{LG} – m_{LG,Hid} \quad (4.10)$$

The techno-economic analysis ($YY_{En,hyd}$) can be calculated from Eq. (4.11) [22,146]:

$$YY_{En,hyd} = CE_{nLG} \times \Delta m_{LG,hyd} \tag{4.11}$$

where CE_{nLG} is a price for lignite for daily basis, as per the average rate in the Turkish market, it can be taken as 102.4 € ton^{-1} from current Turkish marketing price. The electric energy consumption cost ($YY_{En,el}$=yield of energy for hydrogen generation, € y^{-1}) can be calculated from Eq. (4.12) as follows [22,146]:

$$YY_{En,el} = CP_{el} \times En_{el} \tag{4.12}$$

where CP_{el} is a daily LG price that can be assumed approximately 0.182 € kWh^{-1} (0.0002112 € $kcal^{-1}$) is the fixed price set in the market, En_{el} is electricity supply consumption. Annual profits (ΔYY) for this alkaline electrolyzer can be calculated from Eq. (4.13) as follows [22,146]:

$$\Delta YY = YY_{En,Hid} - YYE_{n,el} \tag{4.13}$$

4.3. SIMPLE PAYBACK PERIOD ANALYSIS

As per the previous studies of a similar nature SPPA (Simple Payback Period Analysis) can be performed [22,146],[149–151]. Weissbach et al. [154] clearly stated that the SPPA terminology is same as the energy payback time. Wang et al. [53] elaborated the necessary variables which need to be optimized relying on the minimum simple payback period (SPP) Dahlhausen et al. [153] presented the performance of the financial analysis. The SPP can be calculated and obtained from the equation 4.14. [22,146]:

$$SPP[y] = \frac{Y_{invt}}{\Delta Y} \tag{4.14}$$

Y_{invt} is the cost of investment for the development of prototype for an alkaline electrolyser and can be obtained the from Eq. (4.14).

4.4. WATER ELECTROLYSIS

4.4.1. Workıng Prıncıple of Water Electrolysıs

Water electrolysis is an electrochemical process in which electricity is used to break down water molecules into hydrogen and oxygen, which are the main components. These systems are known as PEM, Alkaline, and High Temperature Electrolyzer, respectively. Under standard conditions, the general chemical reaction is shown below:

$$H_2O\,(l) + \text{Electrical energy} \longrightarrow H_2\,(g) + 1/2O_2\,(g) \tag{4.15}$$

Equation 4.15 shows the electrochemical reaction, which explains the electrolysis process as well as its fundamental principles. Oxygen and hydrogen are the substances that appear in the anode and cathode respectively as a result of this electrochemical reaction that takes place when electrical energy is applied to the electrolyte. As shown in equation 4.15, hydrogen and oxygen convert electrical energy into chemical energy, using only water in the process. The sub-reactions take place at anode and cathode are shown in Eq. 4.16 and Eq. 4.17 respectively:

$$2OH^- \longrightarrow 1/2O_2 + H_2O + 2e^- \tag{4.16}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \tag{4.17}$$

In an alkaline solution, the three stages of the hydrogen production reaction have an impact on the rate of production. The first step in separating the H_2O molecule into the absorbed hydrogen atom and the hydroxyl ion is the Volmer reaction, also known as the discharge reaction in an alkaline environment. A hydrogen molecule must go through one of the usual two stages before it can form. The Tafel reaction, is referred as the combination step, selects the step in which two hydrogen atoms which are absorbed to form a molecule of hydrogen, as a result of the interaction of the H_2O molecule and the H atom, i.e., the Heyrovsky step.

Hydrogen Evaluation Reaction:

$H_2O + e^- \longrightarrow H_{(ad)} + OH^-$(Volmer reaction) (4.18)

$H_{(ad)} + H_{(ad)} \longrightarrow H_{2(ad)} + OH^-$(Tafel reaction) (4.19)

$H_2O + H_{(ad)} + e^- \longrightarrow H_{2(ad)} + OH^-$(Heyrovsky reaction) (4.20)

Oxygen Evaluation Reaction:

$OH^- \longleftrightarrow OH + e^-$ (4.21)

$OH + OH^- \longleftrightarrow O^- + H_2O$ (4.22)

$O^- \longleftrightarrow O + e^-$ (4.23)

$2O \longleftrightarrow 2O_2$ (4.24)

4.4.2. Thermodynamics of Water Electrolysis

The processes that occur in an electrolysis cell can be described using thermodynamic principles. The basic law of thermodynamics is utilized to decide the amount of energy needed for the electrolysis process to take place. The conservation of energy is also another name for this law. In accordance with this law, a system's internal energy changes proportionally to the difference between how much heat is added to it and how much work it does in its environment. The energy required for a water electrolysis reaction is determined by the change in enthalpy when an electrolytic cell operates at constant temperature and pressure. The enthalpy change is denoted by the symbol ΔH. The electrical energy must be part of the energy required for this reaction to occur and corresponds to the change in Gibbs free energy, denoted by ΔG. The process temperature, with symbol T, and the variation in entropy, denoted by ΔS, make up the remaining heat energy. Assuming that electrolysis is an isothermal reversible process, theoretically, the total Gibbs energy needed to produce hydrogen is:

$$\Delta G = \Delta H - Q \quad (4.25)$$

$$\Delta G = \Delta H - T.\Delta S \quad (4.26)$$

$$\Delta G = z.\ F.\ V_{rev} \quad (4.27)$$

The reversible voltage (V_{rev})of the cells is the minimal voltage needed for electrolysis is called Vref. Both chemical reactions, endothermic (H> 0) and a non-spontaneous (G> 0), are the part of electrolysis process. Where ΔG = 237.2 KJ/mol and ΔH = 286 KJ/mol at standard conditions (Temperature = 298 K and Pressure = 1 atm).

$$V_{rev} = \frac{\Delta G}{z.F} \quad (4.28)$$

Where z is the number of electrons transferred per mole of hydrogen, and z = 2. Whereas F is the Faraday's constant and represents the charge on one mole of electrons, and its value is 96487 $Cmol^{-1}$. The value for V_{rev} would be 1.229 V.

4.4.3. Cell Voltage and Losses

Enthalpy voltage (V_{enth}), also called as thermos-neutral cell voltage is the minimal cell voltage needed for the water electrolysis reaction and is given as in Eq. 4.29:

$$V_{enth} = \frac{\Delta H}{z.F} \quad (4.29)$$

The extra voltage potential required during the chemical reaction is the activation voltage, denoted by V_{act} and is represented in the equation 4.30 below:

$$V_{act} = A + B \log (I) \quad (4.30)$$

V_{act} is the coefficient for temperature at standard condition and electrode, where A and B are the anode and cathode constants respectively. There is another type of voltage loss, known as Ohmic voltage, denoted by V_{ohm}. This type of voltage is the combined effect of voltage losses occurs due to the electrodes, electrolyte, and electrical cables resistance and is represented as below in equation 4.31:

$$V_{ohm} = \frac{r}{A} \quad (4.31)$$

V_{cell} is the abbreviation of cell voltage or overvoltage potential and is the sum of ohmic, activation, and enthalpy voltages and can be calculated from the equation 4.32 below:

$$V_{cell} = V_{ohm} + V_{act} + V_{enth} \quad (4.32)$$

However, during the electrolysis of water, the overvoltage potential needs to be overcome in order to reaction takes place. The theoretical decomposition of voltage (E_d) can be calculated from the Nernst equation (4.33):

$$E_d = E_{anode} - E_{cathode} \quad (4.33)$$

The value of E_d is 1.229 V and can be calculated through the voltage potentials of electrodes corelates the equilibrium state of the cathode and anode.

4.4.4. Electrical Circuit Analogy and Resistance Losses

Heat is generated in the system by both concentration and resistance over voltages. Some of the heat generated can be utilized to heat the electrolyte in a well-insulated electrolysis system. As a result, the loss of production caused by high potentials can be reduced. The equation of sum of resistances is represented in equation 4.34.

$$\sum R = R_{ions} + R_{membrane} + R_b + R_c \quad (4.34)$$

Where R_{ions} is the electrolyte resistance, $R_{membrane}$ is the membrane resistance, R_b is the bubbles resistance, and R_c is the circuit resistance. The total cell resistance may be displayed in the electrical circuit to make it easier to identify each source of excess potential in an electrolysis cell, as illustrated in Figure 4.1. R_{anode} and $R_{cathode}$ are resistors because they require an extremely high potential to overcome the activation energies of oxygen and hydrogen production, respectively. The resistance of oxygen and hydrogen bubbles on the electrolyte and electrode surfaces is represented by $R_{bubble,O2}$ and $R_{bubble,H2}$. $R_1$is the diaphragm membrane's resistance.

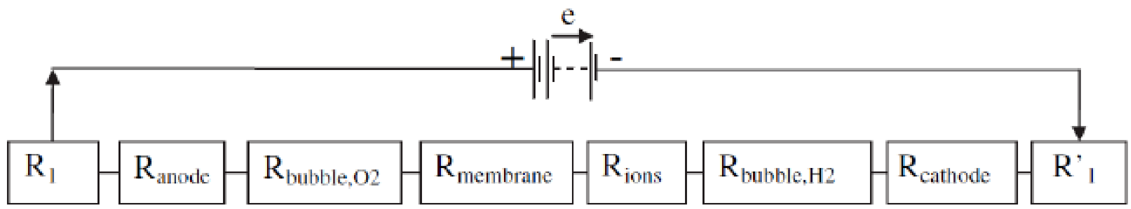

Figure 0. In water electrolysis the electrical circuit analogy of the resistances [156].

4.4.5. Efficiency Analysis and Evaluation

Voltage Efficiency

Voltage efficiency in an electrolysis system can be calculated by taking the difference of voltages at anode and cathode dividing by the cell voltage as shown in the equation 4.35 below:

$$\eta_{volt} = \frac{(V_{anode} \cdot \ V_{cathode})100}{V_c} \tag{4.35}$$

Faraday Efficiency

Faraday efficiency of an electrolysis system can be calculated from the Gibbs free change in energy for water decomposition reaction as shown in equation 4.36.

$$\eta_F = \frac{\Delta G}{\Delta G + Losses} \tag{4.36}$$

It can also be represented in terms of voltage as shown below in equation 4.37:

$$\eta_t = \frac{V_{\Delta G}}{V_c} \tag{4.37}$$

Where $V_{\Delta G}$ is the equilibrium voltage.

Thermal Efficiency

The thermal efficiency of an electrolyzer can be calculated from the following equation (4.38):

$$\eta_{thermal} = \frac{\Delta H}{\Delta G + Losses} \quad (4.38)$$

The thermal efficiency of an electrolysis can also be represented in terms of the voltage, equation 4.39:

$$\eta_{thermal} = \frac{V_{\Delta H}}{V_c} \quad (4.39)$$

Where $V_{\Delta H}$ is thermos-neutral voltage.

Hydrogen Generation Rate Efficiency

Hydrogen generation rate efficiency of an electrolyzer represents the rate of hydrogen generation per unit of electricity supplied to the electrolysis system and it can be calculated from the equation 4.40 given below:

$$\eta_{H2gen\ rate} = \frac{f_{H_{2,gen\ rate}}}{\Delta E} \quad (4.40)$$

Where $f_{H_{2,gen\ rate}}$ is the hydrogen generation rate.

HHV Effiiency

Higher Heating Value (HHV) efficiency of an electrolysis system expresses the HHV of one mole of hydrogen divided by the electrical energy supply to the system and is represented in the equation 4.41 below:

$$\eta_{HHV} = \frac{HHV_{H_2}}{\Delta E} \quad (4.41)$$

Net Efficiency

Net efficiency of an electrolyzer can be calculated from the sum of all over potential losses divided by the system input energy and its formula is given by equation 4.42:

$$\eta_{net} = 1 - \frac{E_{loss}}{E_{input}} \quad (4.42)$$

Electrolysis System Efficiency

The overall efficiency of the electrolysis system can be obtained from the multiplication of net hydrogen generation and higher heating value of hydrogen divided by the total energy input to the system. The equation or formula for the overall efficiency calculation of electrolysis system is given as follows in equation 4.43:

$$\eta_{sys} = \frac{n_{H2,gen} \cdot HHV_{H2}}{W_{Sys}} \quad (4.43)$$

The efficiency of the electrolyzer can also be calculated from the Eq. 4.44.

$$\eta = \frac{E.Q}{Voltage\ X\ Current} \quad (4.44)$$

Where E is calorific value for hydrogen ($Jmol^{-1}$) and Q is the flow rate of hydrogen gas Ls^{-1}.

PART 5

RESULTS AND DISCUSSION

5.1. HYDROGEN GENERATION AND TECHNO-ECONOMIC ANALYSIS RESULTS

5.1.1. PEM Electrolyzer Result Analysis

According to this study's findings, for the H_2 gas production of 6 m^3h^{-1} through PEM electrolyzer prototype there is a need of approximately 3.5 kWh of electric power supply. The summary of the PEM electrolyzer's parameters is shown in Table 5.1.

Table 0.1.Summary of parameters and values for PEM electrolyzer.

Parameter	**Value**
DC Supply	30A
Voltage	10 V
Temperature	70 °C
Pressure	1 bar
Electrolyte	KOH - 100 g/L
Gas	H_2
Production rate	6 m^3/h

Table 5.1, shows the results after performing techno-economic analysis on PEM electrolyzer prototype, the annual profits of PEM electrolyzer is calculated as 6.46×10^5 euros per year and simple payback period (SPP) is found to be as 2.32 years.

After reading the literature, these results appear to be very appealing and accurate. Calise et al. found SPP as 10.3 years [147]. Moradi and Mehrpooya determined that the simple payback period was 4.43 years and that the modelled system produced

9,903,303 kWh of electrical energy in a single year [157]. When compared to previous studies, these findings were found to be very favourable and even superior in some of the parameters.

Table 0.2. PEM electrolyzer techno-economic analysis results [22].

Parameters		Units						
$Hu_{K,Hid}$	7000	[kcal/kg]	-		-		-	
Hu_K	3000	[kcal/kg]	-		-		-	
m_P	6	[m^3/h]	-		-		-	
m_K	1.5×10^6	[kg/d]	-		-		-	
En_K	4.5×10^9	[kcal/d]	18828.0	[GJ/d]	448.1	[toe/d]	5215.4	[MWh/d]
$m_{K,Hid}$*	6.43×10^5	[kg/d]	642.9	[ton/d]	26785.7	[kg/h]	26.8	[ton/h]
En_{el}	70000	[kWh/d]	-		-		-	
$\Delta m_{K,Hid}$	8.57×10^5	[kg/d]	857.1	[ton/d]	35714.3	[kg/h]	35.7	[ton/h]
C_{en}**	10.0	[€/ton]	-		-		-	
C_{el}	0.0968	[€/kWh]	-		-		-	
$Y_{En,Hid}$	8571.4	[€/d]	2.57×10^5	[€/mo]	3.09×10^6	[€/y]	-	
$Y_{En,el}$	6776.0	[€/d]	2.03×10^5	[€/mo]	2.44×10^6	[€/y]	-	
Y_{cost}	1.50×10^6	[€]	-		-		-	
ΔY	6.46×10^5	[€/y]	-		-		-	
SPP	2.32	[y]	27.8	[mo]	-		-	

* 380000 [lt/h] = 380 [m^3/h] = 551000 [kg/h] = 551 [ton/h] = 153 [kg/s] H_2 gas density 1450 [kg/m^3]. H_2 gas is required.

** According to the thermal industry coal price market study, the average current C_{en} (unit price) including VAT was taken as approximately 10 [€/t] based on the power plant fuel.

5.1.2. Alkaline Electrolyzer Result Analysis

The results indicates that the prototype of an Alkaline electrolyzer developed for this study requires approximately 2.8 kWh of electrical energy to produce 6 gL^{-1} of hydrogen gas. The summary of the alkaline electrolyzer's parameters is shown in Table 5.3.

Table 0.3. Summary of parameters and values for Alkaline electrolyzer.

Parameter	Value
DC Supply	30A
Voltage	12 V
Temperature	70 °C
Pressure	1 atm
Vacuum Pressure	0.025 atm
Electrolyte	KOH - 6 g/L
Gas	HHO
Production rate	12 kg/min

The results calculated from techno-economic analysis are illustrated in Table 5.2. After experimental analysis and calculations for the profit per year and payback period of the presented prototype, the annual profit values are come out as 1771.14 euros per year and simple payback period as 2.2 years. These results are very fascinating as compared to the relevant studies in literature.

Table 0.4. Alkaline electrolyzer techno-economic analysis results [146].

Term 1	Value result 1	Term 2	Value result 2	Term 3	Value result 3
LHV_{LG}	21.43 MJ kg^{-1}	En_{LG}	2,143,000 MJ y^{-1}	$YY_{En,Hyd}$	3,045.14 € d^{-1}
$LHV_{LG,Hyd}$	30.5 MJ kg^{-1}	En_{el}	7,000 kWh y^{-1}	$YY_{En,el}$	1,274.0 € y^{-1}
m_{hyd}	6 g L^{-1}	$\Delta m_{LG,Hyd}$	29,737.7 kg y^{-1}	YY_{invt}	3,910 €
m_{LG}	100,000 kg y^{-1}	$C_{en,LG}$	0.1024 € kg^{-1}	ΔYY	1,771.14 € y^{-1}
$m_{LG,Hyd}$	70,262.3 kg y^{-1}	$C_{P,el}$	0.182 € kWh^{-1}	SPPA	2.2 y

The findings of the present study reveal that the results are not only positive as compared to several earlier research in the field but even better than those. ΔYY of the electrolyzer was estimated as 646K euros per year and 2.32 y of SPP [22]. Simple Payback Period for the systems were calculated as 10.3 and 4.43 years [147]. Earlier studies centered on current subject provided theories and experimented in producing models of systems for hydrogen gas production utilizing PEM and alkaline electrolysers. The researchers anticipated that there will be developments in the models and designs with the passage of time and consequently emergence of prime production systems.

PART 6

SWOT ANALYSIS

6.1. INTRODUCTION TO SWOT ANALYSIS

SWOT is an acronym for Strengths, Weaknesses, Opportunities, and Threats. SWOT analysis, first used for business purposes in the 1970s. A SWOT analysis is a technique used to identify the strengths and weaknesses of an organization or system, technology, process, or situation under consideration, and to identify opportunities and threats arising from the consequences of the external environment or situation. Over the years, it has been valued as an analysis and planning tool for various application areas. Basically, the principle of this analysis is examining & analyzing these four parameters of existing structures. Both quantitative and qualitative analyzes can be performed with this method. By studying the generated SWOT matrix, a strategic view of the current program can be created. The main and most important purpose of a qualitative SWOT analysis is to support the strengths and weaknesses of the subject and their situation. Identify opportunities and risks. This method is often used in European regional policy strategies for judgment [158,159].

Similarly, SWOT method MECO (Mediterranean, coastal, CO system) used in coastal management projects such as projects (Sano and Fiero). This analyzes were the first to be discussed and taken up in various workshops. The method was developed in collaboration with DIPTERIS and the Marine Science Department of the University of Las Palmas de Gran Canarias. It was carried out for planning purposes in two coastal areas of the Canary Islands. In short, the SWOT analysis is the best analysis of the resources and functions of various systems and structures in our environment. It was developed as the primary tool for obtaining information that can be used. In other words, the SWOT analysis was used to capture basic information that should be considered during planning [160–162].

It is one of the methods that enables situational analysis in a scientific manner. It simultaneously evaluates the internal and external properties of the system and reveals all the possible factors becoming either strengths & opportunities or weaknesses & threats. For a particular system, SWOT analysis can be used to analyze the following:

- Internal Strengths & Weaknesses
- External Opportunities & Threats [160]

6.1.1. Advantages of Swot Analysis

- The identified strengths through this analysis are used to take the advantage of highlighted opportunities.
- This analysis reveals the weaknesses in the system and pave the path for strategies to convert them into strengths.
- This analysis also points out the threats for the particular system and makes the transformation of the highlighted threats into opportunities, which can add up as a strength in the particular system.
- It also identifies the existing and future threats observed during this analysis and suggest the measures to remove them.
- The weaknesses of the particular system come out through this analysis and necessary steps to eliminate them are suggested.
- By analyzing the strengths, opportunities, weaknesses, and threats, the required actions can be taken and performance of the system can be improved [158–160].

6.2. SWOT ANALYSIS FOR ALKALINE ELECTROLYZER PROTOTYPE

The prototype of an Alkaline electrolyzer, comprising of five electrolysis cell stacks, was developed and tested experimentally as well as economically. The electrical energy (DC) of 30 amperes and the voltage of approximately 12 V was supplied to the system, the mass flow rate of the oxyhydrogen gas obtained was 12 kg min^{-1}. SWOT analysis study was performed for this system and all the parameters of this study was brought under consideration, i.e., Strengths, Weaknesses, Opportunities, Threats.

The small-scale alkaline electrolysis system is a unique, innovative, and different type of prototype for the production of hydrogen gas, when compared to other studies in the literature, which is the strength of this system. From literature review, it is evident that the results obtained after technical and techno-economic analyses; the system is found to be cost-effective, energy efficient, and also environmentally friendly. The obtained results add the strength to the presented system. The novel and special type of chemical mixture used in this system improved the efficiency of the system is also an addition to the strength.

Although the small-scale alkaline electrolysis system exhibits many strengths, it has some weaknesses too. The materials, other than stainless steels, for electrolysis cells could be used and the performance could be compared, especially the materials having higher conductivity values than SS304 could be tried on. The strength of SS304 material could be enhanced by applying the coating (electroplating) of Tin, Nickel, or Chrome on them. The different types of membranes could also be placed between the electrolysis cells to increase the efficiency of this system. But due to limited time constraints and availability of budget for this research work, everything was not possible. The weaknesses can be converted into strengths by trying the alternate options in future and thus improving the performance of this small-scale system and make it more efficient.

Besides, strengths and weaknesses, the system presents some opportunities too. The use of hydrogen as a fuel as well as in other applications is rapidly increasing day by day. With the increasing demand for hydrogen in the market, hydrogen needs to be produced in a more efficient and cost-effective way. The small-scale system for hydrogen production introduced in this study, have several novel additions, i.e., using of special chemical mixture instead of water, magnetizing of electrolysis cells stack, attaching extra vacuum pumps in the system, which increase the efficiency of hydrogen generation process and make it cost effective too. All these strengths create the opportunities for the relevant researchers and scientists to go deeper into this system through research and experimental studies to further increase the performance and efficiency of hydrogen generation. There is an opportunity for integrating the present set up with renewable energy sources, i.e., solar PV or CSP and making it more environmentally friendly, energy efficient, and economical. The prototype of the system may attract the attention of any industrialist, and the industrial scale system may get developed to generate hydrogen at larger scale.

Along with several opportunities, the system has some threats too. If no further interest is shown in improving the performance of system and also to commercialize it, the system may lose its importance. In addition to that, if in future no further research and development study is carried out on this system, the contribution to science and literature related to this novel and innovative system will be stopped.

6.3. SWOT ANALYSIS FOR PEM ELECTROLYZER PROTOTYPE

The industrial scale prototype of PEM electrolyzer was made up of 12 electrolysis cell stacks. The PEM electrolysis system was operated and tested for commercial use by supplying the direct electric current of 30 amperes and the applying the voltage of 10 V. SWOT analysis was also performed for this study, and several strengths and weaknesses as well as opportunities and threats were revealed/disclosed.

The very first strength that was noticed for this PEM electrolysis system is that it is unique and novel in its nature, developed for industrial scale applications and comparatively found to be more efficient and cost-effective, after tested experimentally as well as economically. The Cr-C coating, which acted as membrane and was applied to SS304 electrolysis cell, improved the performance of hydrogen gas production. The unique and novel septic chemical mixture, which has not been used previously, was used in this system instead of water during electrolysis process, which also enhanced the efficiency of the generated gas. Hence, these and other similar additions and changes, added strength to the system.

Though, the system exhibits several strengths, it has some weaknesses too. One of the weaknesses of the system, which is observed, that it is tested by merely using one material (SS304) for electrolysis cells or plates. Although the material was electroplated by Cr-C plating but another type of stainless steel, i.e., SS316 or different type of materials were not used. The comparison of unplated and electroplated SS304 materials as well as comparison of different electrolytes was not made due to time constraints and budget or funds limitations.

The PEM electrolyzer prototype presented in this study reveals some opportunities and threats too. There is an opportunity for the relevant researchers and scientists to integrate this system with renewable energy source, i.e., solar energy and make it more economical, energy efficient, and environmentally friendly. There is also opportunity that this project may gain the attention of the industrialists and get commercialized. Similarly, this study can motivate the relevant researchers and scientists to conduct further research studies related to this work. This would assist in improving the quality and efficiency of the hydrogen gas generation process.

Along several opportunities for this system, there are some threats too. No progress or lack of interest by the researchers and scientists in the relevant study may hinder the development in the relevant study and eventually may close the door of contribution to the literature related to this study. The system presented in this study may also lose its importance if not commercialized and no interest is shown by the industrialists.

PART 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. CONCLUSIONS

The main aim of this study was to design and develop the innovative set-ups for the alkaline and PEM electrolysis systems in an economical way and then optimize these prototypes to get maximum of hydrogen gas by reducing the losses as well as through novel additions in these systems. One of the aims of this study was also to perform the techno-economic analysis for both prototypes. The results obtained through optimization and experiments as well as via techno-economic and enviro-economic analyses are come up with very attractive conclusions. Both electrolyzers (Alkaline and PEM) presented in this study are found be economical, energy efficient, and environmentally friendly.

For Alkaline Electrolyzer: A small-scale alkaline electrolysis system was developed, and its performance was also evaluated. The conclusions drawn from the results obtained through experiments and techno-economic analysis are as follows:

- The small-scale system can generate almost 6 g L^{-1} of hydrogen gas.
- Almost 12 kg min^{-1} of oxyhydrogen (HHO) gas can be produced through this alkaline electrolysis system.
- The electric energy required to generate 6 g L^{-1} of hydrogen or 12 kg min^{-1} of HHO gas is found be as 2.8 kWh.
- The optimum results during the electrolysis are obtained when the current of 30 A and the voltage of 12 V is applied to the system.
- The efficiency of the generated hydrogen or oxyhydrogen gas is improved by up to 20% through using the novel and special chemical mixture (ethyl alcohol,

urea, ammonia, and deionized water) in the bubbler instead of using distilled water only, along with vacuum pumps.

- By creating the magnetic field on both sides of the electrolysis cells stack, the performance of the generated hydrogen or HHO gas is enhanced by 30%.
- The profit per year or annual profit (ΔYY) for this system is to be found as 1771.14 € y^{-1}.
- The simple payback period (SPP) for this system is to be calculated as 2.2 years.

For PEM Electrolyzer: An industrial scale prototype of PEM electrolysis system was designed and developed in this study. Optimization was done and system was tested through experiments as well as through techno-economic analysis. The conclusions made from the obtained results are presented as follows:

- The prototype of PEM electrolysis system can generate 6 m^3 h^{-1} of hydrogen gas.
- The electrical energy required to generate the hydrogen gas of 6 m^3 h^{-1} is found to be as 3.5 kWh.
- The optimum results were obtained, when direct current of 30 A and the voltage of 10 V was applied through this electrolysis system.
- The electroplating of SS304 metal electrodes with Cr-C, helps in resisting and reducing the corrosion and oxidation, and ultimately improve the efficiency of hydrogen generation process.
- The use of septic and novel chemical composition, made up of ammonia, urea, methyl alcohol and distilled or deionized water, increased the hydrogen production rate by 20%.
- By creating the magnetic field on both sides of the electrolyzer stack, accelerates the movement of electrons from North (N) pole towards the South (S) pole, and hence enhance the efficiency of hydrogen gas by almost 30%.
- The annual profit (ΔYY) for the system is to be calculated as 646000 € y^{-1}.
- The simple payback period for this system is found to be as 2.32 years.

- The electrolysis system is found to be 4.5 times more efficient as compared to other hydrogen generation systems, published in the literature.

7.2. RECOMMENDATIONS FOR FUTURE WORKS

It can be realized from the literature survey that hydrogen and its applications will reach to an important point in near future. Whereas, water electrolysis is found to be the best option to generate hydrogen or oxyhydrogen gas at large scale. There is need of more research works in this area by using new and better materials for electrolysis cells in case of Alkaline electrolysis. However, for PEM electrolysis different membranes or coatings as membranes can be tested. The performance of coated and uncoated steels can be compared, which couldn't be done in this study, due to the availability of limited time span and funds. The materials with higher electrical conductivity as compared to stainless steels (especially SS304) can be tried for electrolysis cells or bipolar plates. Thus, the cost can be reduced, and the performance can be increased. Electrolytes, other than Potassium hydroxide (KOH), can be tested in Alkaline as well as PEM electrolyzer and performance can be compared. For example, Sodium Chloride (NaCl) based electrolytes can be tested and comparison can be made with KOH.

Since the world is moving towards the renewable and sustainable energy to make this planet green and make this earth livable. So, the further studies can be conducted by integrating this electrolysis system with renewable energy sources, i.e., solar energy, instead of using power supply. In solar assisted water electrolysis, fuel cells can be added along with electrolysis cells.

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RESUME

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