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The principles of Hydrogen synthesis and a manufacturing model: A Review

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ABSTRACT

This review discusses the potential of hydrogen as a sustainable fuel source in the context of the global search for the perfect fuel that emits no carbon dioxide. We will illustrate the various hydrogen types and highlight their differences. Three types of hydrogen synthesis are described. Grey and blue hydrogen, which are obtained from natural gas through steam methane reforming, and green hydrogen, which is the focus of our review and is obtained from water electrolysis, We will examine the cells used in the process of electrolysis from the inside out, as well as the different types of them, how they work and their efficiencies, along with the material that electrodes are made of. A real-life model of several steps describes how it's done in the manufacturing field and covers the water treatment step, of which there are two types: seawater desalination and raw water treatment, both of which are necessary steps to be done to the water used before passing it through the cell. The review also describes a 2016 study that measured solar-to-hydrogen efficiency over two days, demonstrating the potential for using solar power to produce hydrogen. The article concludes that hydrogen is a promising solution for clean energy and that existing facilities can be altered to produce "green" hydrogen. Additionally, the use of renewable energy sources like wind and solar power can make the manufacturing process even cleaner.

Introduction

As the demand for environmentally friendly fuels grows, and it is well known that fossil fuels are running out of supply and are not environmentally friendly due to CO_2 emissions from the combustion process, hydrogen appears on the horizon as an ideal solution to the problem. It is environmentally friendly, and the combustion of hydrogen gas produces only water vapor. Mainly, there are three types of hydrogen, "not in terms of isotopes" but in terms of synthesis. "Grey hydrogen," as the first type, is obtained from natural gas through the process of steam methane reforming (SMR) [1], in which natural gas, of which 95% is methane, is mixed with very hot steam at temperatures of around 700 to 1000 °C, while a catalyst is used under a pressure of 3-5 bar, where a chemical reaction creates hydrogen and carbon monoxide.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

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The problem with this method of "Grey hydrogen" is that, as you can see on the right-hand side of the equation, there is carbon monoxide as a product of synthesizing hydrogen, which causes severe harm to the environment. A good approach has been applied which takes us to the second type of hydrogen, which is "Blue hydrogen". Nothing really is different from grey hydrogen; it's the same synthesizing approach but instead of releasing the carbon monoxide in the atmosphere, it's buried deep down in the ground after being captured [1]. The capturing CO_2 emissions process is called CCUS: carbon capture, usage, and storage, which has a flow as the below Fig. 1.0 shows [2].

Green hydrogen, on the other hand, is the focus of this paper; green hydrogen is synthesized from electrolysis of water, resulting in the two gases Hydrogen and Oxygen with no CO_2 emissions, as opposed to blue hydrogen synthesis; we also need to know that hydrogen synthesized from water accounts for only 4% of global hydrogen production; this low percentage is due to the high cost of this operation.

Green hydrogen is synthesized in four ways, but we will be focusing only on two types, which are AWE and PEM. It should be noted that we will use (HER) as a hydrogen evolution reaction and (OER) as an oxygen evolution reaction.

1.1 Types of water electrolysis

- Microbial Electrolysis
- Solid Oxide Electrolysis **(SOE)**
- Alkaline Water Electrolysis **(AWE)**
- Proton Exchange Membrane Electrolysis **(PEM)**

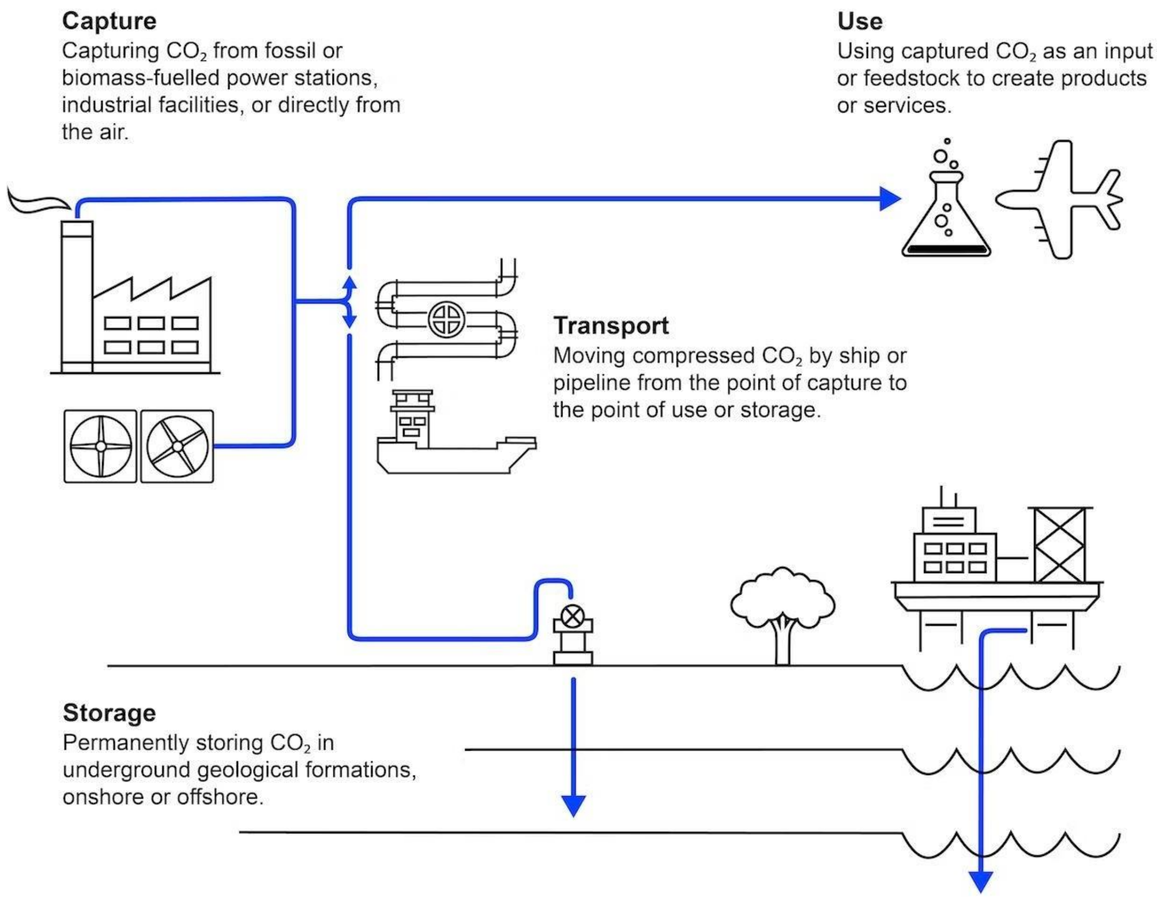

Fig 1.0: About CCUS - iea.org"

1.1.1 Alkaline Water Electrolysis (AWE)

Alkaline electrolysis uses an alkaline solution like NaOH or KOH as the electrolyte, and at the cathode, hydrogen is reduced to one molecule of H_2 gas (Fig 1.1) as follows:

$$\textbf{HER: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

while the two resulting hydroxyl groups go to the anodic electrode through the diaphragm and are oxidized as follows:

$$\textbf{OER: } 2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$$

So every oxygen atom bonds to another oxygen atom and forms an oxygen molecule. The whole process is handled between 40 and 90 ^oC with a KOH/NaOH concentration range of 25 to 30 percent, and we must note that potassium hydroxide is preferred over sodium hydroxide due to its higher conductivity than NaOH and in terms of thermodynamic consideration [3][4]. We should mention that electrodes are made from nickel and that the alkaline solution becomes less effective at high current densities (like the one in industry, 100–400 mA/cm^2) and high temperatures, causing corrosion for other types of electrodes if nickel is not used because we know it resists corrosion [3].

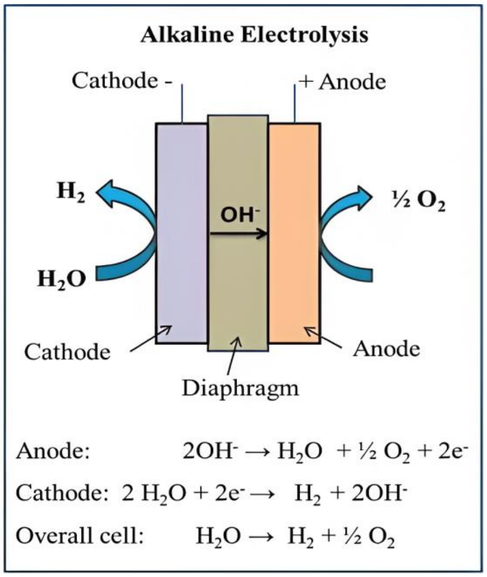

Fig 1.1: Hydrogen production by PEM water electrolysis

1.1.2 Proton Exchange Membrane Electrolysis (PEM)

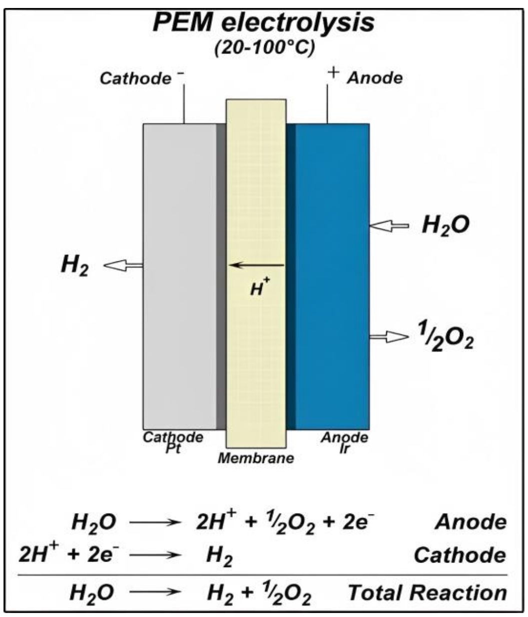

Fig 1.2: Hydrogen production by PEM water electrolysis”

A proton exchange membrane, also known as a polymer electrolyte membrane, is a method in which a polymer membrane separates the two electrodes, the cathode, and the anode, and is designed to pass only protons to the cathodic electrode, where this helps separate the two gases oxygen and hydrogen [5]. The two electrons pass through the circuit and recombine with the two protons to form hydrogen gas (Fig 1.2).

$$\textbf{OER}: \quad H_2O \text{-->} 2H^+ + \frac{1}{2}O_2 + 2e^-$$

$$\textbf{HER}: 2H^+ + 2e^- \text{-->} H_2$$

The whole process is being handled between 20 and 100 ºC, PEM electrolysis was confirmed to be more effective than AWE, while it maintains an energy efficiency range of 85% to 90% and the latter maintains 75% to 85% [5].

Also, PEM is producing highly pure hydrogen with a purity rate of 99.9%. PEM uses electro-catalysts for anode and cathode made of iridium, platinum, and rubidium, the prices of which have been rising in recent years, which is the problem with this approach [5].

2. Green Hydrogen manufacturing

Here we can preview the details about how hydrogen is manufactured in industry, and generally we have two scopes here: water treatment and the manufacturing process.

Water treatment is a very necessary step, so let’s first discuss a little thing that will show us why it’s necessary. There are two types of water: raw or river water, which is almost the main source of water, and on the other hand, saline water, or "sea water," which is full of ions. Raw water is way easier to treat than saline water, and even in terms of cost, it's effective. Moreover, raw water is still convenient in comparison to the cost of treating saline water. However, there may be restrictions on the use of raw water in some countries where it’s made to be used only for drinking purposes as it's considered the main source of water and sometimes for agricultural purposes, so it depends on you which type you will be using. Either way, both water options must be treated so we can prevent the ions we mentioned from corroding the equipment and pipes. As we know, water is not perfectly neutral; it has a slight acidity and is contaminated with ions.

2.1 Raw Water Treatment

It mainly consists of three stages Coagulation, Sedimentation and Storage (Fig 2.1).

After water is fetched from the reservoir, it goes through pipes to be reserved in a tank. After that, it passes through coagulation devices and clarifiers, which remove dirt and other particles suspended in the water. Alum $Al_2(SO_4)_3 \cdot 18H_2O$ and other chemicals like chlorine or polyelectrolyte are injected into the water to form tiny sticky particles called "floc," which attract the dirt particles. The combined weight of the dirt and the chemicals injected becomes heavy enough to sink, which leads us to the second step, which is the sedimentation. The heavy particles "floc" settles to the bottom, and the clear water moves to the filtration step. The water passes through two main filters, the first one made of layers of sand and gravel, and the second one made of carbon or charcoal, that help remove even smaller particles and get rid of bad smell, taste, color, and any residuals of chlorine or organic matter. Finally, the produced water is moved to a storage tower or tanks where it can be stored and used as needed; in our case, it will be used to produce hydrogen.

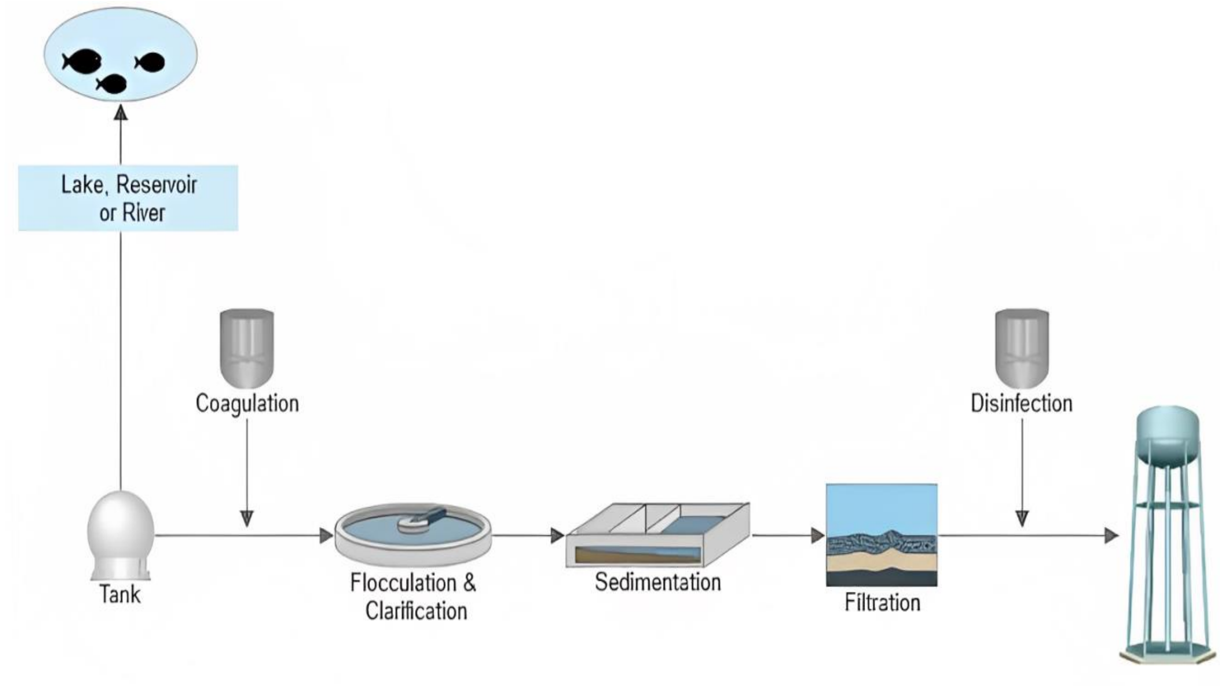

Fig 2.0: Raw Water Cycle

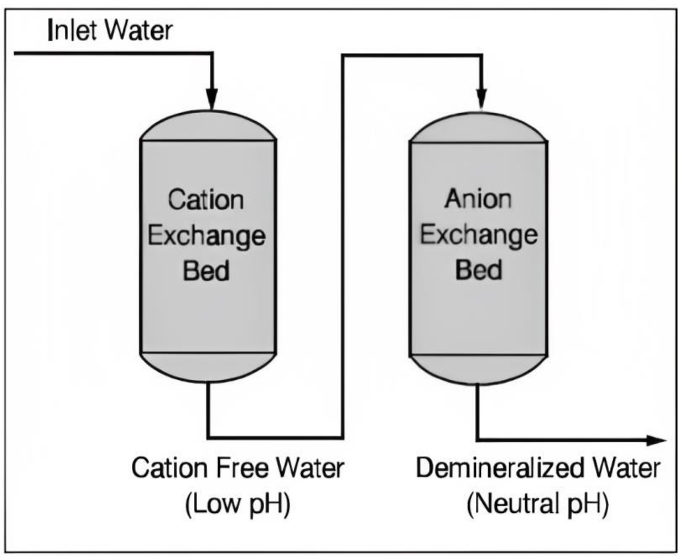

Fig 2.1: Ion Exchange Device

Some manufacturing approaches add an extra step for treating water through an Ion Exchange Device (Fig 2.1) [6]. The extra step ensures the conductivity of water is at its desired value, and it also gets rid of water acidity, which, as we said earlier, causes corrosion to equipment and pipes. Water must have a basic nature to be used in hydrogen production, so we create this basic nature by injecting basic chemicals after the outlet of water from the IED because the outlet is neutral pH water.

2.2 Sea Water desalination

First, let's define desalination [6]. It's defined as the process by which mineral salts dissolved in water are removed. There are several ways to desalinate water, like reverse osmosis, multi-flash, multi-gig systems, and nanofiltration; however, we will discuss the most popular unit only [6].

RO Units: RO, which stands for "reverse osmosis," is the most used process and consumes less energy than the rest, as it is based on the use of semipermeable membranes that allow the water to pass but not the salt (Fig 2.2). These membranes are made of ultra-thin polyamide, and the scientific base that RO uses is simple, as we know from osmotic pressure law:

$$\Pi = iMRT$$

And the water flows from the low-concentrated medium to the higher one; if only a "reverse" pressure greater than osmotic pressure was applied, the water would flow to the lower-concentrated side, providing us with desalinated water; see the next figure for more clarification.

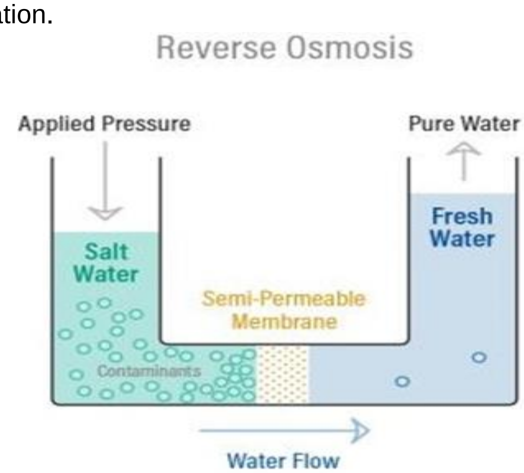

Fig 2.2: Ion Exchange Device

3. Current supplied to Hydrogen cells

Nowadays, there are many types of power sources, with differences in terms of efficiency and cost [7].

Wind energy: Wind is a cheap, erratic resource that can be used to produce power. When wind resources are scarce throughout the day, wind-generated electricity can be stored and subsequently used in fuel cells to provide electricity [7][8]. Using enormous wind turbines that are installed on land (onshore), in saltwater, or in freshwater, wind energy captures the kinetic energy of flowing air (offshore). Although wind energy has been used for thousands of years, onshore and offshore wind energy technology has advanced recently to optimize the amount of electricity produced by using higher turbines and bigger rotor diameters [8]. Even though average wind speeds vary greatly from place to place, most locations in the world have the potential for considerable wind energy deployment [8]. In fact, the technological potential for wind energy is greater than the worldwide power output. Strong winds may be found in many locations across the world, but often distant areas are the greatest for producing wind energy [8]. Offshore wind energy has a lot of promise.

Solar cells: Is one of the renewable energy sources to generate green hydrogen, and it can be obtained either directly or indirectly from sunlight [9]. Although this resource is plentiful, it is dispersed and only accessible for a few hours each day. Solar energy is the most abundant of all energy resources and may even be harnessed in cloudy weather [7][8]. The speed at which alternative energy is intercepted by the world is about 10,000 times greater than the speed at which humankind consumes energy. Solar technologies can deliver heat, cooling, natural lighting, electricity, and fuels for a bunch of applications [9]. Solar technologies convert sunlight into current either through photovoltaic panels or through mirrors that concentrate radiation [10]. Although not all countries are equally endowed with alternative energy, a major contribution to the energy mix from direct alternative energy is feasible for each country. The cost of producing solar panels has plummeted dramatically within the last decade, making them not only affordable but often the most affordable type of electricity [10].

Solar panels have a lifespan of roughly 30 years and are available in different shades depending on the kind of fabric employed in their manufacturing.

There are many types of solar cells, and sure, the higher efficiency of the cell, the higher efficiency of the electrolyser, but in terms of cost, this will cause some limits to our options, but it's up to your budget [11][12]. Table 1 shows the most popular types and their efficiencies.

Table 1: The most popular types and their efficiencies.

Panel Type	Efficiency
Monocrystalline	20%<
Polycrystalline	15-17%
Copper Indium Diselenide	13-15%
Amorphous Silicon	6-8%

There are some parameters that can be controlled in the solar cell to maintain a higher efficiency. The recombination is one of the parameters that causes a lower current output. Some electrons combine with positively charged particles in the cell; this must be solved by alternating their crystal structure. Temperature is also an important factor; the solar cell works best at low temperatures, so cooling must be maintained. Solar panels are usually able to process 15–22% of solar energy into usable energy, which will be enough for the electrolysis process [11][12].

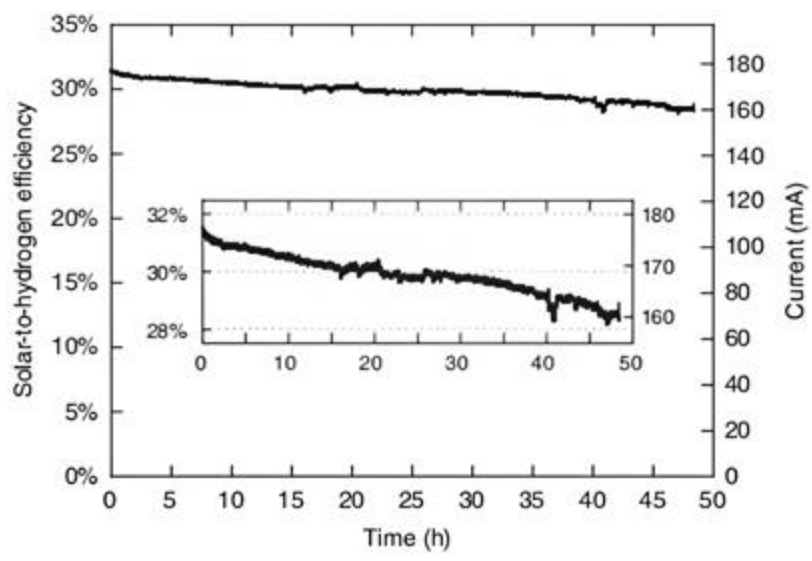

Fig 3.0: STH Efficiency "Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30% "

An approach was held in 2016 the paper "Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30% " over two continuous days, Solar to Hydrogen STH efficiency was measured (Fig 3.0), the solar cell and the electrolyser had a near match in terms of maximum point of power of solar cell, PV-electrolysis performance was nearly optimum, although the graph shows a decreasing in efficiency over the time, but this was due to the catalyst and membrane degradation[13][14][15] .

3.1 Rectifier

Despite the source of your electrical current, a rectifier is a necessary device in the whole process. If the current is not DC, in other words, if the current you have is an alternating current, then the two electrodes of the electrolyser will switch continuously between anode and cathode, the reaction can't be operated with AC at all. A rectifier converts AC to DC, so the anode and cathode don't interchange positions.

Generally, to produce $1m^3/h$ of hydrogen gas, you need 600 amperes, which is usually what a single rectifier power module produces. So, if a gas holder with a capacity of 12m3 needs to be filled with hydrogen, we will need 12 rectifier modules to produce 7200 amperes. We should note that whatever number of rectifiers you use, there's always an extra module called a control module.

3.2 Interference Removal Stage & Storage

After hydrogen is synthesized, it passes through a water pool to remove any contamination by letting it hang in water or dissolve, and the hydrogen as a gas rises from the water towards the pipes to the storage stage, where hydrogen is being stored as condensed or liquefied. Hydrogen in condensed form is stored in tanks under a pressure of 350–700 bar; on the other hand, in liquefied form, it requires a very low temperature, as hydrogen boils at −252.8°C at the regular atmospheric pressure [16].

By this point, you should have a good understanding of how hydrogen is made; see the Figure 3.1 below for a brief overview.

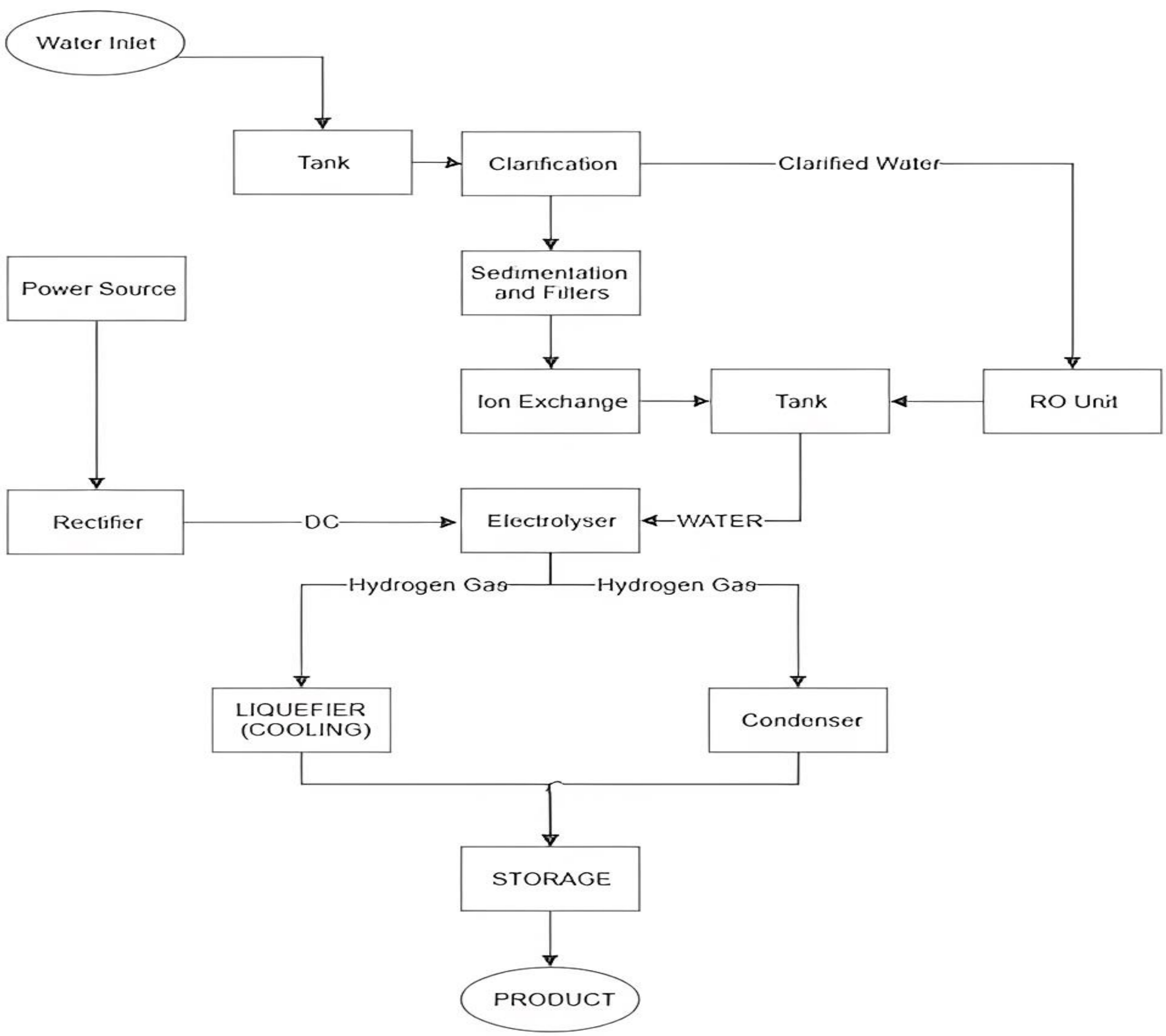

Fig 3.1: The Overview for hydrogen production

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