

# Methods to Produce Hydrogen



## **FOREGROUND**

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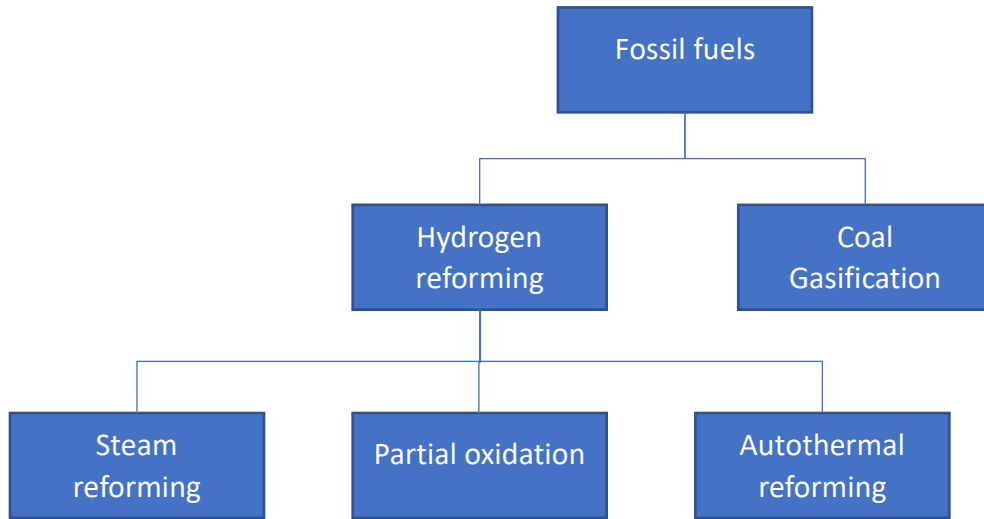
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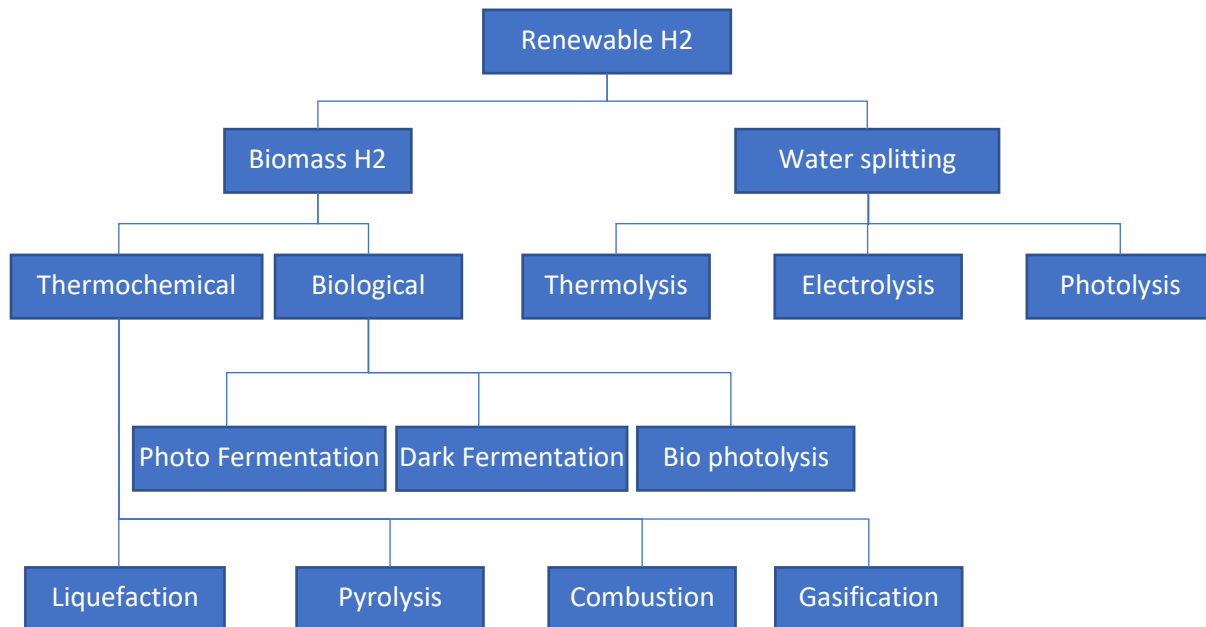
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# 1 Introduction to hydrogen production technologies

There are many different methods and processes that can be used to produce hydrogen. The below figures illustrate the most known methods for producing hydrogen. These methods can be divided into two main groups. The fossil fuel and the renewable one.



**Figure 1.1 – Hydrogen from fossil fuels production methods**



**Figure 1.2 – Renewable methods of producing hydrogen**

The below sections describe the most common methods for producing hydrogen that can potentially be found today and in the future at harbour and port sites. It also presents some of the most advanced and innovative approaches for producing hydrogen, some being at commercialisation stage and others being



at pre-commercial stage. Note that not all of the above methods are described in the below, only the ones that are currently at an advanced staged of deployment, but also only the methods that are currently most likely to be installed in a harbour setup.

## 2 Renewable Hydrogen - Electrolysis of water to produce hydrogen

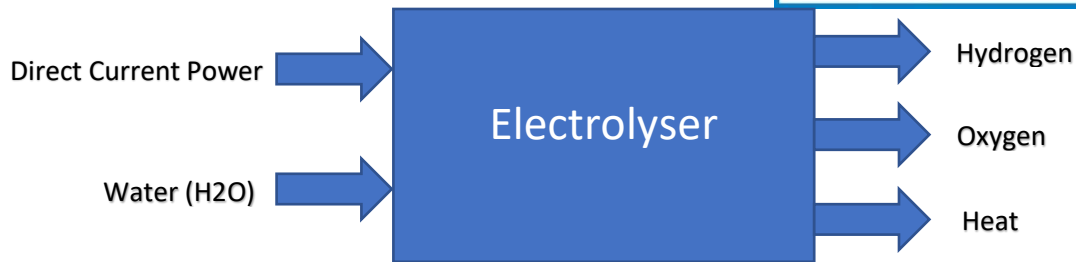
The electrolysis of water is by far the method of choice for producing hydrogen from green energy. It is currently believed to be the main technology that can support the deployment of large-scale renewable energy. If the deployment of large-scale electrolyzers connected to green energy is successful, this will provide the appropriate foundations for transiting from an oil and gas focused energy system onto a complete clean energy economy.

Electrolysis is a technology that can easily be used within a harbour or port setup, but also at offshore locations coupled with renewable power such as wind, wave, tidal, ocean current, offshore solar farm etc. Hydrogen produced at ports and harbour facilities could be both used locally but also exported via H<sub>2</sub> vessels in compressed or liquid form (see module on transporting hydrogen). In addition, hydrogen can be produced via electrolysis at a site that is further away from a harbour, but the hydrogen produced can be injected into pipelines to transport the gas to a port or harbour. At the harbour, the hydrogen fuel can be dispensed into a boat for export of H<sub>2</sub>. As such, and as the scale of hydrogen through electrolysis is believed to become a major player in H<sub>2</sub> fuel with Gigawatts of installation around the world, hydrogen electrolysis is a key technology to understand for port and harbour operators.

The technology for electrolysing water is what some would qualify as being an old technology. The reason behind this is that it was first developed in the 19<sup>th</sup> century. However, and since then, electrolyzers have been further developed to reach the status of mature technology. This is especially true for the alkaline electrolyser type, and less so for the other technology types such as Solid Oxide Electrolysers (SOE).

Electrolysers are used for producing both hydrogen and oxygen from water. The main idea behind the technology is to pass a Direct Current (DC) through water. The current causes the water to split into its components, that is hydrogen and oxygen. In essence, an electrolyzer is a device that uses power and water (H<sub>2</sub>O) as its inputs. As the current flow through the water, it will split the H<sub>2</sub>O to produce hydrogen gas (H<sub>2</sub>), oxygen gas (O<sub>2</sub>). During this process, heat is produced. The heat can be captured and used or released in the atmosphere.

Of importance, hydrogen gas produced from electrolysis of water is said to be free of emissions (or “green”) if the gas is produced from an electrolyser that is supplied by a renewable source of energy. In most cases, the hydrogen gas is stored as a fuel to be used later (when needed). Though O<sub>2</sub> is also produced during the process, the oxygen is in the vast majority of cases released to atmosphere. The below figure illustrates a basic electrolyser schematic.



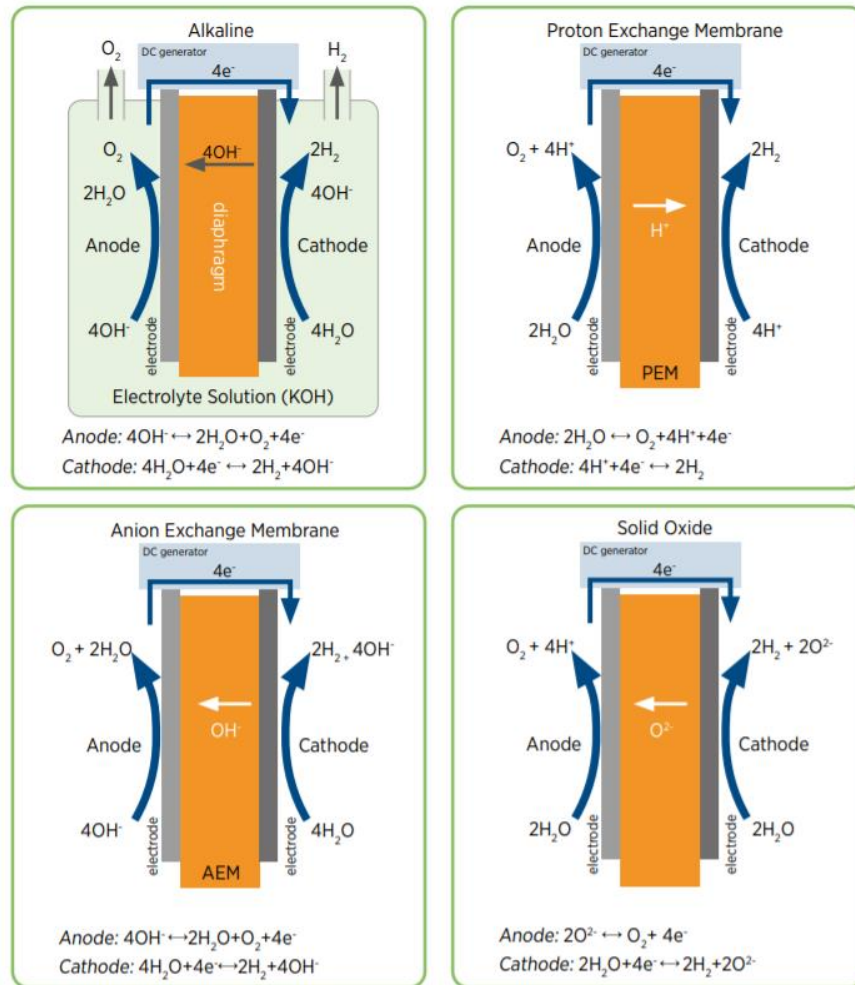
**Figure 2.1 – Basic outline of an electrolyzer (input: H<sub>2</sub>O and DC current, output: H<sub>2</sub>, O<sub>2</sub>, Heat)<sup>1</sup>**

There are four main types of electrolyzers. All of the different types of electrolyzers type have the same functions, being to produce hydrogen (and oxygen if required locally). However, they differentiate in the way they operate. The main difference lies in the type of electrolyte being used. It is usually the type of electrolyte that gives the name of the electrolyser. For example, any electrolyser that uses an alkaline electrolyte is known as an alkaline electrolyser. Below summarises the four main types of electrolyzers currently available on the market:

- Alkaline electrolyzers – commercially available.
- PEM (Proton Exchange Membrane) electrolyzers – commercially available.
- AEM (Anion Exchange Membrane) electrolyzers – commercially available.
- SOE (Solid Oxide) electrolyzers – near commercialisation.

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<sup>1</sup> Courtesy of Pure Energy Centre – [www.pureenergycentre.com](http://www.pureenergycentre.com)



**Figure 2.2 – The difference between the most advanced type of electrolysis units<sup>2</sup>**

## 2.1 Alkaline electrolysis

This is probably the most known electrolyser of all types. It has been commercialised for decades and the CAPEX/OPEX are well known. An alkaline electrolyser has a liquid electrolyte, which is in most cases potassium hydroxide (KOH) or sodium hydroxide (NaOH). When DC current is applied to the electrolyser, water is split into hydrogen and oxygen. Oxygen is produced at the anode. Hydrogen is produced at the cathode. The below figure shows an alkaline electrolyser.

<sup>2</sup> [https://irena.org/-/media/Files/IRENA/Agency/Publication/2020/Dec/IRENA\\_Green\\_hydrogen\\_cost\\_2020.pdf](https://irena.org/-/media/Files/IRENA/Agency/Publication/2020/Dec/IRENA_Green_hydrogen_cost_2020.pdf)





**Figure 2.3 – A hydrogen electrolysis unit as installed<sup>3</sup>**

Alkaline electrolyzers are available in all shape and forms. They come in small, medium, large and very large systems. Some of these are multi-MW in size with the capability of generating over 1000 Nm<sup>3</sup>/h of hydrogen – this is more than (5MW). Alkaline electrolyzers have an efficiency that starts at its low-end from 60% and end at its high-end at 82%<sup>4</sup>. They are many different models and manufactures, the most common models produce hydrogen at atmospheric pressure, at 5 bar, 10 bar and with the most common nowadays being the 30-bar output pressure option (no compression needed up to 30 bar). As a rule of thumb, the higher the pressure output of an electrolyser, the higher the price.

## **2.2 Proton Exchange Membrane (PEM) electrolysis**

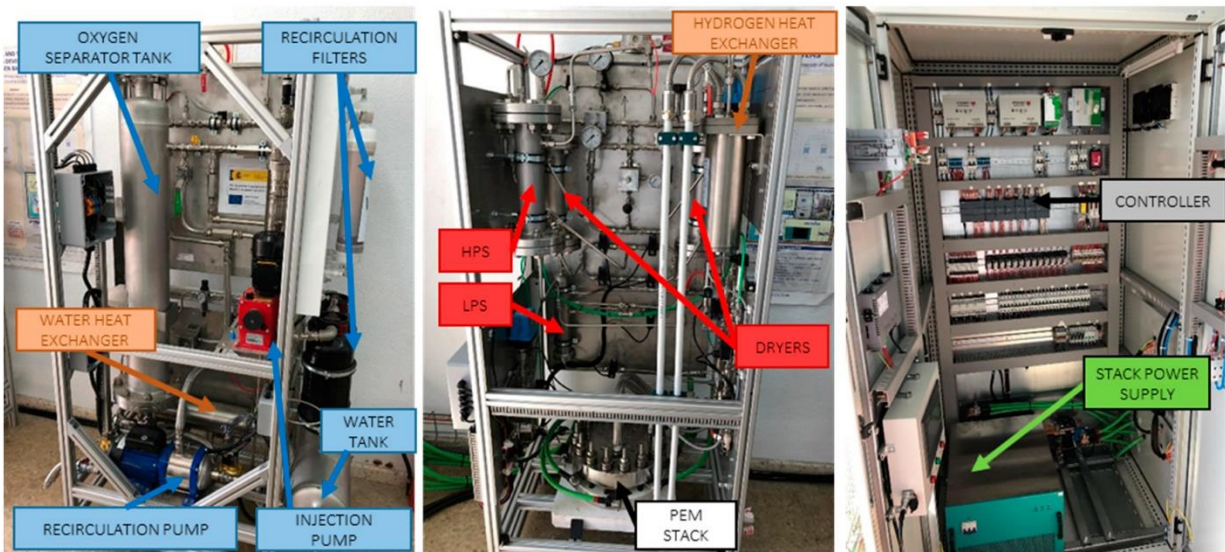
A Proton Exchange Membrane (PEM) electrolyser uses a Solid Catalyst and a Solid Polymer Electrolyte. The only liquid found in a PEM electrolyser is the water that is injected to produce the hydrogen. In other words, there is no toxic chemicals used in a PEM electrolyser. These types of electrolyzers are also known by scientists as Polymer Electrolyte Membrane (PEM) hydrogen production units.

PEM catalysts are fairly expensive and as such, it is commonly agreed that PEM electrolyser technology is more expensive than other hydrogen production technologies. In recent years, PEM electrolyzers are starting to become more price competitive in comparison to alkaline electrolyzers. They are also becoming more commercially available and they are now considered as an established technology. Note that in a PEM H<sub>2</sub> production system, hydrogen is produced at the cathode while oxygen can be captured (or released) at the anode.

<sup>3</sup> Courtesy of Pure Energy Centre – <https://pureenergycentre.com/first-african-wind-hydrogen-system-launched/>

<sup>4</sup> <https://spiral.imperial.ac.uk/bitstream/10044/1/51653/9/1-s2.0-S0360319917339435-main.pdf>

Similar to the alkaline electrolysis units, PEM electrolyzers can be found in small, medium and large scales. As these are compact in size (when compared to alkaline), PEM electrolyzers are the preferred option when space is critical. PEM electrolyzers are still based on a new technology which lacks full long-term field operational data history. Nevertheless, this technology has showed promising results with over 100,000 hours of continuous field operation successfully demonstrated and achieved. The below figure illustrates a typical PEM electrolyser - (left) a water management subsystem, (middle) the hydrogen electrolyser stack and balance of plants (dryer, heat exchanger for cooling, etc.), and (right) the power supply, the overall control system.



**Figure 2.4 – A typical hydrogen PEM electrolysis unit<sup>5</sup>**

In addition to the size being compact when compared to alkaline, PEM electrolyzers do not require the management of toxic chemicals (e.g., KOH for alkaline). Avoiding the management of a toxic liquid electrolyte is a strong commercial offering as PEM systems can produce a hydrogen gas purity of up to 99.999%. The high-level hydrogen gas purity is directly produced from the electrolyser and it is the level of purity that a Fuel Cell (FC) requires to operate. Any impurity into the hydrogen gas supply to a fuel cell could dramatically reduce the FC lifetime. That is why, fuel cell manufacturers insist on knowing the purity of hydrogen gas that will be fed to their fuel cell prior to authorising the use of their fuel cells in any given application.

On the other hand, other applications such as Hydrogen Internal Combustion Engine (H2ICE) or even Hydrogen Gas Turbines (H2ICE) do not require such purity levels.

There is another important criterion that plays in favour of PEM electrolyzers. PEM technology has the ability to load follow the variable generation of renewable energy such as wind and solar systems. The technology has demonstrated the ability to cope with electrical transients from renewable system, though longevity of the catalyst still needs to be proven in the field. Currently, the technology has been

<sup>5</sup> [https://www.mdpi.com/2079-9292/9/5/871/htm#fig\\_body\\_display\\_electronics-09-00871-f010](https://www.mdpi.com/2079-9292/9/5/871/htm#fig_body_display_electronics-09-00871-f010)

demonstrated to operate up to 200 bar output pressure, but the vast majority of systems available in the field produce hydrogen at 30 bar<sup>6</sup>. There are studies to reduce the use of Platinum below 0.1 mg/cm<sup>2</sup> using nanoparticles, efficiency of the system will remain almost the same and PEM life will be extended<sup>7</sup>.

### 2.3 Anion Exchange Membrane (AEM) electrolysis

Anion Exchange Membrane (AEM) electrolyzers are new to the market place. They use a liquid electrolyte in order to produce hydrogen and oxygen gases. They have one major advantage when compared to PEM electrolyzers, that is they are not manufactured using rare and noble metal electrocatalysts. These noble metals are used in PEM electrolyzers, hence their high costs. As such, AEM are based on low-cost metal catalysts leading to this type of technology being much cheaper than PEM hydrogen production systems.

It is only recently that AEM have achieved full commercialisation. Currently, AEM electrolyzers can only be found in small systems, though there is work to design and build larger systems. The below figure illustrates an installation using an AEM electrolyser.



Figure 2.5 – A hydrogen AEM electrolyser<sup>8</sup>

The main downside of AEM electrolyzers is their performance efficiency<sup>9</sup> which can be much lower than PEM. AEM have a high internal resistance of the electrode assembly, leading to the low efficiency factor. However, as the cost of this technology is much lower than the PEM one. As such, there is a strong demand for the electrolyser technology from laboratories.

<sup>6</sup> <https://www.fch.europa.eu/sites/default/files/2%20Water%20Electrolysis%20Status%20and%20Potential%20for%20Development.pdf>

<sup>7</sup> <https://www.nature.com/articles/s41929-022-00796-1>

<sup>8</sup> Courtesy of Pure Energy Centre – [www.pureenergycentre.com](http://www.pureenergycentre.com)

<sup>9</sup> Immanuel Vincent, Dmitri Bessarabov, “Low cost hydrogen production by anion exchange membrane electrolysis: A review”, Renewable and Sustainable Energy Reviews, Volume 81, Part 2, January 2018, Pages 1690-1704

## 2.4 Solid Oxide Electrolysis (SOE) units

Solid Oxide Electrolysers (SOE) are similar to the AEM in that they are new to the market place and at a pre-commercialisation stage. This electrolyser technology is also known as Solid Oxide Electrolyzer Cells (SOEC). They operate at a very high temperature and use a solid electrolyte to produce hydrogen. The most common electrolyte material used in SOEC is yttria-stabilized zirconia (YSZ). There are ongoing studies to improve the process.

SOE have attracted substantial attention from the market place in recent years because they are more efficient than PEM, Alkaline, and AEM. The reason for having a better efficiency is associated to their operating temperature. In essence, an SOE can operate at very higher temperatures. Because they operate at high-temperatures, they have a lower need for electricity to produce hydrogen (and oxygen). The rationale for calling this type of electrolyser Solid Oxide is due to the fact that they use Solid Oxide materials as the electrolyte.

SOE have also been named as High Temperature Electrolysis units (HTE). The downside of these electrolysers is found in that they cannot operate without having a source of heat. In other words, SOE are highly efficient, but this is only the case if there is a “free” supply of heat available. As such, the operation and installation of SOE electrolysers depends highly on finding a site where there is excess heat (high quality heat – meaning high temperature) that is accessible and supplied to the electrolyser.

The main assumption made by SOE manufacturers is that there are many sites that flare high quality heat because there is no heat load demand locally. Therefore, the cost of capturing the “flared” heat and using it will be cheap. As the heat is cheaper than electricity (in this particular case), then installing an SOE will make sense as the OPEX will be low compared to the OPEX for PEM, Alkaline and AEM electrolysers. This is due to the fact that an SOE operates at a high temperature, and thus will use less energy to split water into H<sub>2</sub> and O<sub>2</sub>.

The heat required to operate an SOE varies between 500°C and 1000°C. As a rule of thumb, and under the condition that there is a low-cost source of high temperature heat, SOE will outperform other type of electrolysers. A good example for the installation of an SOE is at a steel plant. It is known that a lot of heat is available at such a plant as waste and usually flared in the atmosphere as there is no nearby customers to buy the excess heat. If the heat is captured and fed to an SOE, the electrolyser could produce hydrogen to reduce the steel plant’s emissions.

Carbon emissions is a big issue for steel plants. The part of the process that constitute the vast majority of the emissions occur during the iron ore reduction process. It is within this process that pig (crude) iron is made. The crude iron is later modified to become crude steel.

Today, steel production plants are aiming to incorporate processes that reduces their overall emissions. Hydrogen gas is of primary importance to steel plants in their CO<sub>2</sub> reduction pathway, especially so that hydrogen could be produced with green energy. The overall idea is to inject hydrogen gas instead of using coke to make steel. When the iron ore reduction process is started, hydrogen gas is fed. The H<sub>2</sub> gas will react with iron oxide in the same way carbon monoxide would react. However, the only by-product of the

process will be water and not carbon dioxide. The below figure illustrates a reversible hydrogen oxide cell. This is a device that can operate as an SOE but it can also work as a FC.



Figure 2.6 – A reversible hydrogen solid oxide cells<sup>10</sup>

## 2.5 Comparison between electrolyzers

The below table summarises the different characteristics of the above electrolyser technologies. Overall, all of the technologies have advantages and disadvantages associated with them. For instance, it is best to operate alkaline systems in a steady state operation, where there are no much electrical power fluctuations. Similarly, alkaline electrolyzers are able to produce hydrogen at 20% of their maximum production capacity.

This means that for a 1MW electrolyser, the minimum operating power of the electrolyser will be 200 kW (20% of 1MW). It is, however, generally accepted that most manufacturers favour to operate their electrolyzers at around 80% of maximum capacity. This is what manufacturers would call the sweet point of alkaline electrolyzers. The sweet point relates to the optimum operation of the electrolyser. If operated at 80% of the maximum capacity of the electrolyser, the electrolyser will be producing hydrogen efficiently

<sup>10</sup> <http://www.fchea.org/in-transition/2019/11/25/hydrogen-in-the-iron-and-steel-industry>



(highest efficiency factor around the sweet point). Operating around the sweet point will also increase the lifetime of the stack, reducing the degradation effect if operated at lower or higher power.

Alkaline electrolyzers are nowadays associated with one major drawback. They have a relatively low current density (if compared to other electrolyser technologies). Due to this low current density, alkaline stacks are larger than other technologies. This means that, wherever space is of essence, say in a submarine, then other technologies may be privileged.

There is another downside to alkaline systems, that is the electrolyte. As the electrolyte is liquid, it reduces the response time of the electrolyzer. This means that Alkaline electrolyser may not produce as much hydrogen when compared to PEM under the same conditions (i.e., when renewable electricity is fed to the stack, alkaline electrolyser will produce a little bit less hydrogen than its counterpart PEM system). Finally, the maintenance cost of alkaline electrolyser may seem a little high when compared to PEM, but to date, PEM OPEX is still higher than alkaline, even though it is a maintenance requirement to change the electrolyte on an annual basis.

On the positive side, Alkaline electrolyzers are much cheaper than the other technologies. They are also trialled and tested in the field for decades. They have been sold and installed globally by thousands.

In terms of PEM electrolyzers, there is one major drawback, which is related to the capital cost of purchasing such system. PEM electrolyzers require the use of rare noble materials and polymer membranes. Because of these two factors, PEM electrolyzers costs are higher than alkaline and AEM types. In addition, PEM technology requires expensive manufacturing processes and techniques. The maintenance costs are also high, but signs are showing that these costs are lowering as the industry mature and understand better the dynamics of the overall electrolyser system.

On the plus side, PEM electrolyzers have a solid electrolyte which leads to faster electrochemical kinetics (e.g., faster response to electrical change). This makes PEM hydrogen systems highly suitable for operating with greatly fluctuating renewable energy sources such as wind generation.

AEM electrolyzers use low-cost materials but have the lowest efficiency of all electrolyzers. They are currently only commercially available in small size, though there is research focused at developing larger units.

SOE electrolyzers are still at pre-commercialisation stage. They can only be installed where high value heat is available. They achieve very high efficiency.

It is important to factor in the consumption of water for all of the different electrolyser technologies. As an example, a 1 MW electrolyzer will produce around 200 Normal Cubic Meters of H<sub>2</sub> per hour (Nm<sup>3</sup>/h) (this equates to about 16.75 kilograms/hour of H<sub>2</sub> at normal temperature and pressure (NTP) – 1atm, 20°C). Note that about 170 Litre/hour (L/h) of deionized water would be required to produce this amount of hydrogen. Also note that a 1MW electrolyser may produce less hydrogen when factoring in valve, detectors, pumps, etc. power consumption.

Electrolyser type	Electrolyte	Operating temperature	Typical size	Efficiency $\eta$ (LHV)	Technology maturity	Main advantages	Challenges
Alkaline	Liquid electrolyte with Alkaline solution (KOH or NaOH)	40-90°C	< 2.7MW (larger systems under development)	59-70%	Mature and commercially available	<ul style="list-style-type: none"> <li>• Low capital cost</li> <li>• Relatively stable</li> <li>• Mature technology</li> <li>• Low temperature</li> <li>• Lifetime: 60 000-90 000 hours</li> </ul>	<ul style="list-style-type: none"> <li>• Corrosive electrolyte has impact on reliability/durability</li> <li>• Gas permeation / Slow dynamics / compactness</li> <li>• Electrolyte management (aqueous)</li> </ul>
Polymer electrolyte membrane (PEM)	Solid polymer membrane (Nafion)	50-80°C	< 1.6M (larger systems under development)	65-82%	Demonstration project and Early market commercialisation	<ul style="list-style-type: none"> <li>• Solid electrolyte reduces corrosion and electrolyte management problems</li> <li>• Low temperature / compact</li> <li>• Quick start-up and load following</li> <li>• Lifetime: 20 000-60 000 hours</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive catalysts (noble)</li> <li>• Sensitive to fuel impurities</li> <li>• High OPEX</li> <li>• High CAPEX</li> </ul>
Anion exchange membrane (AEM)	Solid polymer-based anion exchange membrane in KOH or K <sub>2</sub> CO <sub>3</sub> solution	50-70°C	< 4.8kW (larger systems under development)	62%	Laboratory scale and small demonstration project	<ul style="list-style-type: none"> <li>• Non-noble metal catalyst</li> <li>• Non-corrosive electrolyte</li> <li>• Compact cell design</li> <li>• Low cost</li> <li>• Absence of leaking</li> <li>• High operating pressure</li> <li>• Lifetime: ~30 000 hours</li> </ul>	<ul style="list-style-type: none"> <li>• Low current densities</li> <li>• Durability</li> <li>• Membrane degradation</li> <li>• Low efficiency</li> </ul>
Solid oxide (SOEC)	Solid ceramic membrane	500-1000°C	Not available	81-86% Up to 100% with heat recovery	Laboratory scale and demonstration project	<ul style="list-style-type: none"> <li>• Enhanced kinetics, thermodynamics:</li> <li>• Lower energy demand.</li> <li>• Low capital cost</li> <li>• Lifetime: &lt; 10 000 hours</li> </ul>	<ul style="list-style-type: none"> <li>• Mechanical unstable electrodes (cracking effect)</li> <li>• Safety issue: improper sealing</li> <li>• Long start-up time</li> <li>• Limited number of shutdowns</li> </ul>

**Table 2-1 - Electrolyser technologies**

### 3 Conventional method from fossil fuel

Producing cheap and bulk hydrogen has been the focus of large companies to supply refineries and other major industrial sites.

In the last century, producing hydrogen at large scale focused solely on methods that use hydrocarbons as the primary input to the process. These methods are still, to date, accounting for more than 90% of worldwide hydrogen production.

Most of the sites for hydrogen production are near a port or harbour location and as such this is an important technology to understand for port and harbour operators.

There are two main methods used to produce hydrogen at such a scale. These are Steam Methane Reforming (SMR) and a process known as gasification. Nowadays, governments and companies are investigating coupling SMR and gasification plants with bulk underground storage. The aim is to store the SMR and gasification processes' by-product, that is CO<sub>2</sub>. Storing the by-product CO<sub>2</sub> is known as Carbon Capture Utilization and Storage (CCUS).

The aim of CCUS is to capture the CO<sub>2</sub> produced during the production of hydrogen through SMR and gasification and then inject the CO<sub>2</sub> in underground cavities. The overall idea is that if the CO<sub>2</sub> is buried in underground cavities, then the CO<sub>2</sub> will not be vented in the atmosphere, and as such this will help in achieving carbon-neutral operations. The below sections briefly describe both the SMR and gasification methods.

#### 3.1 Steam Methane Reforming (SMR)

Steam Methane Reforming (SMR) is by far the most used process to produce hydrogen, with over 90% of H<sub>2</sub> being produced through SMR. SMR is a highly mature technology that uses natural gas as the feedstock.

As the feedstock is natural gas, SMR plants are located near gas pipelines, where the gas is available in large quantities. The below figure illustrates a small-scale SMR installation used to produce hydrogen from natural gas or LPG.





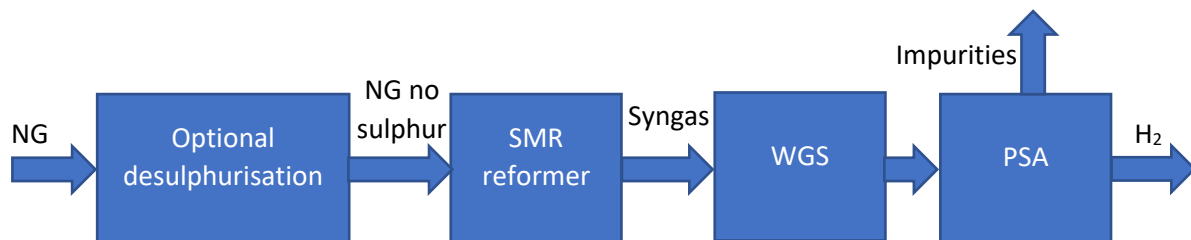
**Figure 3.1 – An SMR hydrogen production system (small scale)<sup>11</sup>**

The most common SMR methods to produce hydrogen are:

- Steam reforming
- Oxygen with partial oxidation
- A combination of both methods shown above. This method is known as autothermal reforming.

### 3.1.1 Steam reforming

The below figure illustrates a simplified SMR hydrogen system.



**Figure 3.2 – A simplified SMR plant**

In a steam SMR process, natural gas (methane) and high temperature steam (around 700°C–1,000°C) are injected over a catalyst (usually nickel-based) – this is the SMR reformer. The output of the process is aimed at dissociating the methane and produce hydrogen, carbon monoxide, and a small amount of carbon dioxide gas. The mixture of these different gases is better known as Syngas.

A Water Gas Shift (WGS) process is then used. The aim of this process is to convert the carbon monoxide produced in the SMR reformer into carbon dioxide and to produce even more hydrogen from water or steam. A Pressure Swing Adsorption (PSA) is then used to clean the hydrogen from impurities. The

<sup>11</sup> <http://www.kakoki.co.jp/english/products/p-001/index.html>

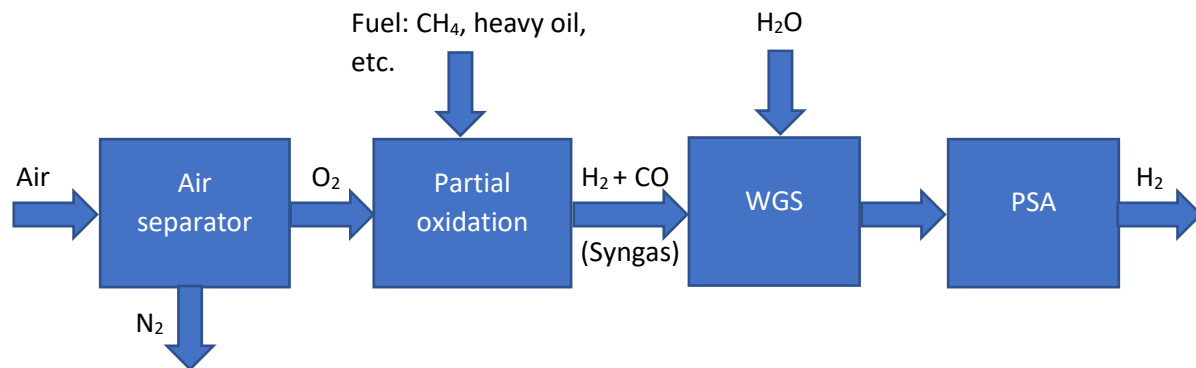
produced hydrogen can then be used (stored, shipped, or locally used). CO<sub>2</sub> is released in the atmosphere at the different stages of the SMR plant.

Steam reforming is an “endothermic” process. This means that a source of heat must be fed to the process in order for the reaction to occur. In the case that the feedstock to the SMR process has a high content of sulphur, then a desulfurization (desulphurization) unit is used. Such unit will avoid poisoning of the nickel catalyst used for reforming. SMRs can have many different feedstocks. These include natural gas, methane, propane, pentane, butane, ethane and naphtha.

### 3.1.2 Partial oxidation

The partial oxidation is a very mature technology. The process differs from the above steam reforming method in the way that it is “exothermic”. This means that heat is produced during the process. Natural gas including methane or heavy hydrocarbon fuel such as heating oil is mixed with a small quantity of oxygen (most of the time this is air or oxygen is extracted from the air).

With the injection of low quantities of oxygen, the output of the partial oxidation process is a mixture of hydrogen, carbon monoxide and some carbon dioxide. Nitrogen is also found at the back of the partial oxidation process if air is used instead of pure oxygen. A WGS process is then used to react water with carbon monoxide, creating carbon dioxide and hydrogen.



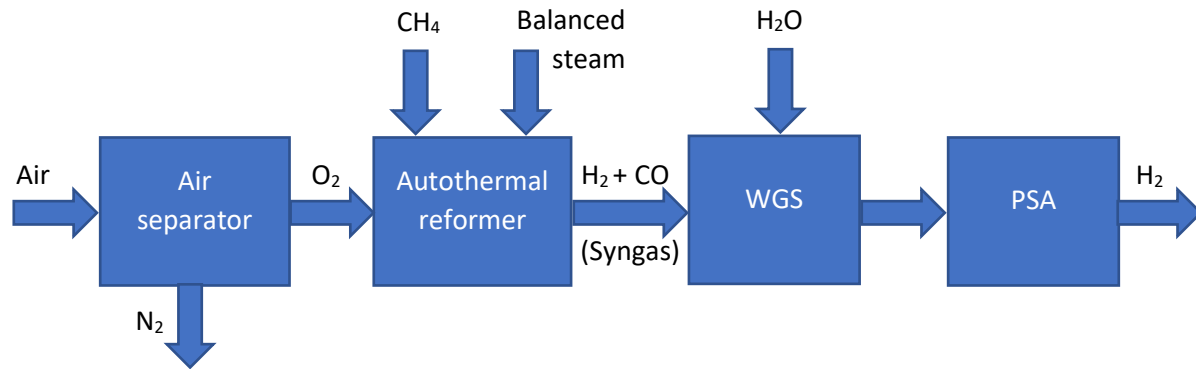
**Figure 3.3 – A simplified partial oxidation system**

The advantage of the partial oxidation process is found in that it is much faster than the above SMR option. The reactor used in the process is also smaller, hence when space is of essence, this technique of producing hydrogen is favoured. However, the downside of the partial oxidation process is that it produces lower quantities of hydrogen per unit of the input fuel. This is why SMR is by far the most used method for producing H<sub>2</sub>. Note that this process is also known as coal gasification because it is mainly used for plants that have coal as a feedstock.

### 3.1.3 Autothermal reforming process

The autothermal reforming process combines both steam reforming and partial oxidation processes to produce hydrogen. A mixture of air/oxygen (partial oxidation process) added to water vapor (steam

reforming) makes up the autothermal system. The process is setup in a way that the ratio of the two oxidants (air and water vapor) is continuously monitored and then adjusted. The overall aim is to avoid introducing or discharging heat into the process. If the monitoring and adjustment process is successful, then the autothermal reaches the state of “isothermal”.



**Figure 3.4 – A simplified autothermal reforming process**

Reaching the isothermal states is important as this occurs only if the temperature of the autothermal system remains constant. This is the reason why continuously adjusting air/oxygen and vapor is required. By adjusting these two variants (air/oxygen, steam), the transfer of heat into the system or out of it occurs at a slow pace. Therefore, the system is able to reach thermal equilibrium and this is maintained through time. The heat/steam is produced and at times recirculated to increase efficiency.

### 3.1.4 Brief comparison of SMR most common technologies

In summary, the first H<sub>2</sub> production method described above (steam reforming) is based on catalytic technology. It is accepted that it is an “energy efficient technology” for producing H<sub>2</sub>. This is true for from light type of hydrocarbons such as NG, refinery off-gases, LPG and Naphtha. Partial oxidation in its vast majority a non-catalytic technology. The advantage of this technology is that it can have heavy hydrocarbon feedstocks. The downside is that it has a lower energy efficiency than the steam reformation. The autothermal solution is no used as much as the other technologies, though it is probably the best option for operation with large scale methanol (MeOH) production plants.

Overall, the major downside of the different SMR and steam reforming technologies is that they produce high volume of GHGs and are nowadays pointed out as being a technology that is harmful to the environment.

## 3.2 Coal Gasification (CG)

Coal Gasification (CG) is a process used to extract hydrogen from coal but also to produce syngas. Usually, coal is burnt to produce power. However, and in order to produce hydrogen, there is a need for coal to be gasified (not burnt). During the gasification process coal makes compounds. These compounds are reacted with water. It is then that hydrogen produced.

The gasification technique can be used to produce two main types of hydrogen. Both have the same quality hydrogen, but they differ in the quantity of hydrogen being produced during the process. The first



type of hydrogen produced using gasification is known as “brown hydrogen”. The second type is “black hydrogen”.

Brown hydrogen is produced from brown coal while black hydrogen is derived from black coal. Obviously, the colour of coal is always black and brown coal does not relate to its colour. The quantity of hydrogen produced from brown coal is higher than the amount of hydrogen produced from black coal. In other words, it is possible to extract more hydrogen from brown coal than black one for the same quantity/tonnage of coal. Black coal has higher quantities of CO<sub>2</sub> and as such, more CO<sub>2</sub> is released in the atmosphere when using black coal to produce hydrogen. It is worth to note that the quantity of hydrogen for both coals is only marginally different. It is the oxygen quantity that differs substantially between the two coal, but also the CO<sub>2</sub> emitted during the process, black coal being the most emitting.

To put this into context, coal gasification produces more CO<sub>2</sub> than SMR technology. An average 18 to 20 kg of CO<sub>2</sub> is released to the atmosphere for each and every kg of hydrogen gas produced<sup>12</sup>. This means that if the gasification process is used to produce 1 ton of hydrogen, then between 18 to 20 ton of CO<sub>2</sub> will be released.

On the other hand, an SMR hydrogen plants produces an average 8 to 12 kg of CO<sub>2</sub> for each kg of hydrogen<sup>13</sup>. Though the GHG emitted through SMR can be halved the emissions generated by the gasification process, both processes are highly polluting and have a highly negative impact to the environment. This is why many countries are investigating the need to implement Carbon Capture Utilization and Storage (CCUS).

### 3.3 Carbon Capture Utilization and Storage

Carbon Capture, Utilization, and Storage (CCUS) is a what people would call a new field. The idea behind CCUS is simple. It is to capture CO<sub>2</sub> before it is released to the atmosphere and then re-direct it to an underground storage. The technology is mainly used nearby an SMR or coal gasification plant. But this is not enough, there is also a need for appropriate geological underground cavities that can take the CO<sub>2</sub>. These cavities must have very specific properties to not allow the CO<sub>2</sub> to escape back to the atmosphere.

In general terms, CCUS projects are being developed to avoid the release of CO<sub>2</sub> in the atmosphere when producing H<sub>2</sub> in large quantities by SMR and coal gasification techniques. There are a number of processes associated with CCUS. The first process is the capture of the CO<sub>2</sub> during the production of hydrogen. The CO<sub>2</sub> is usually captured in the waste stream flue gas – this is where the “CC” comes from, meaning Carbon Capture. The CO<sub>2</sub> that has been captured is then re-Used – this is where the “U” comes from, meaning Utilization. The utilization in this particular field means that the CO<sub>2</sub> has not been released in the atmosphere. It does not matter that the CO<sub>2</sub> is not actively being used, as long as it is not released to the atmosphere. In the case of CCUS, the CO<sub>2</sub> is ultimately injected into a “permanent safe Storage” – this is where the “S” comes from, meaning storage.

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<sup>12</sup> <https://www.valvemagazine.com/web-only/categories/technical-topics/10419-hydrogen-s-role-in-reducing-industrial-carbon-emissions.html>

<sup>13</sup> Hylantic White Paper - 2020



Though large quantities of CO<sub>2</sub> is still being produced, the CO<sub>2</sub> is buried underground and as such the authorities qualifies that hydrogen production using SMR or gasification methods have not damaged the environment. This claim is somehow true, though some scientists believe that incident can occur with CCUS if CO<sub>2</sub> was to find its way out of the storage system.

The rational for developing the CCUS technology is to eliminate the “chicken and egg” problem associated with hydrogen fuel. What it is believed is that there is a need for large scale H<sub>2</sub> production in order to start the shift for CO<sub>2</sub> emitting society to a non-emitting one.

As CCUS can be developed at large scale using a multitude of feedstock (coal, heavy and light oil, naphta, natural gas, methane, ethane, etc.), the large amount of hydrogen made available will provide a much faster path to a transition to a clean hydrogen economy.

Obviously, the renewable hydrogen industry thinks otherwise, and believe that the substantial sums of money invested into CCUS could be used to develop further renewable sites and that the cavities used for storing the CO<sub>2</sub> could be used for hydrogen storage.

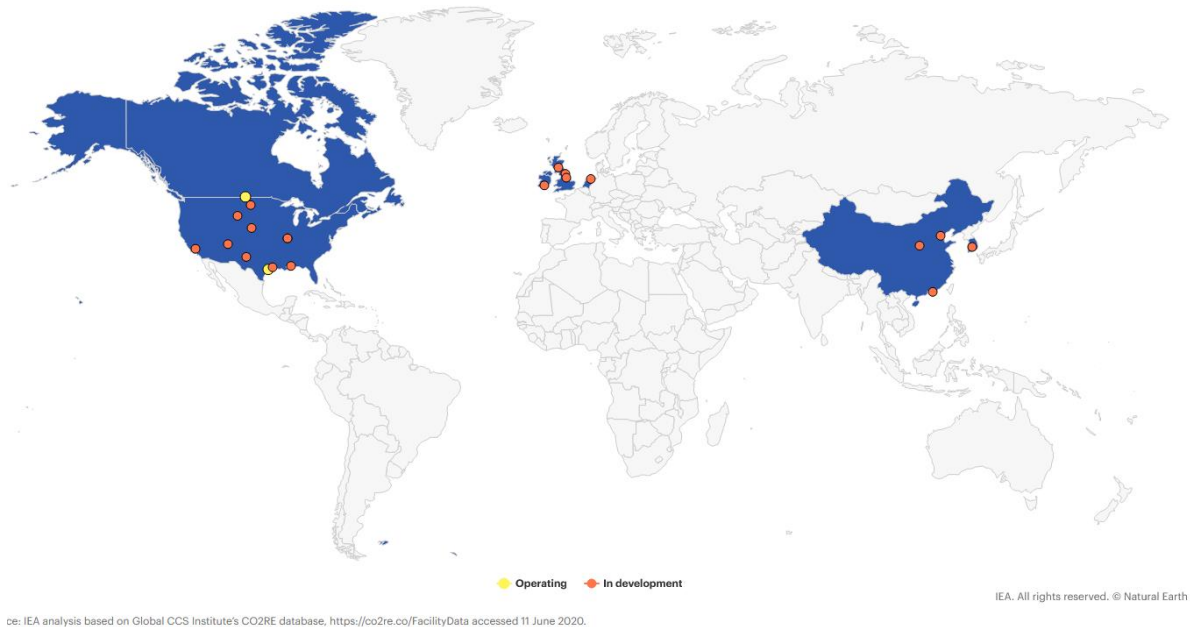
However, there is another reason behind the development of CCUS technologies. This lies in that the oil and gas industry can employ their current knowledge and expertise for the deployment of CCUS, hence creating a lower resistance to the shift towards or net zero carbon economy. Obviously, using CCUS to support the further deployment of SMR and CG systems will help addressing some of the environmental, societal and economic issues with climate change. However, the CCUS solution will not completely address the release of pollutants from fossil fuels in the atmosphere.

There is another reason behind governments’ support for the wide deployment of CCUS. It is related to costs. Currently hydrogen being produced from renewable energy and electrolyzers is still fairly high. It is, however, anticipated that because of the share scale of SMR, Gasification, and CCUS hydrogen production, that the price of hydrogen per kg will drop dramatically. The belief is that the price will drop to the level similar to what is currently being paid for an equivalent litre of diesel / petrol. If this occurs, it is also believed that the hydrogen economy will be a success as people will start shifting to a low carbon economy.

There are two main methods used in CCUS system, the pre-combustion and the post-combustion one. It is only in the pre-combustion method that hydrogen is produced and CO<sub>2</sub> is captured then stored in underground caverns. In a post-combustion method, the hydrocarbon (NG, methane, etc.) is used as the feed to a turbine (or engine, etc.) to produce heat and power. When the hydrocarbon has been burnt, the CO<sub>2</sub> is captured and stored underground (no hydrogen production system in this case).

In other words, a post-combustion carbon capture refers to a process that captures the produced carbon dioxide just after the hydrocarbon (i.e., NG, methane, etc.) has been combusted. This is typically done in flue gas chimneys located at power plants. Capturing CO<sub>2</sub> gas in a post-combustion is still nowadays a difficult task to perform due to the need in removing NO<sub>x</sub> and other pollutants prior to sending CO<sub>2</sub> underground. There are many methods to accomplish this, including the use of solid sorbents, solvents, and membrane solutions. The post-combustion process is also known as post-ignition.

About 19 large scale CCUS projects are operational around the world. There are currently many other schemes being developed<sup>14</sup>. The below figure illustrates the different CCUS operational projects and the ones under development<sup>15</sup>.



**Figure 3.5 - Operational and under development CCUS projects around the world**

The projects that are currently being designed and engineering with pre-combustion carbon capture technology show that it will cost about \$60 per ton to capture and store the CO<sub>2</sub> produced. These costs are based on the use of an Integrated Gasification Combined Cycle (IGCC) power scheme. The cost of storing CO<sub>2</sub> underground is believed to be too high. The Department of Energy (DoE) in the USA has set a target of \$30 per ton of CO<sub>2</sub> captured and stored in order for this technology to be viable<sup>16,17</sup>.

## 4 Recovering by-product hydrogen and waste to hydrogen

There are many processes that produce hydrogen as a by-product. Such processes can be found in petroleum refining (at refinery sites) and a number of chemical industries sites. Caustic soda and chlorine are two electrochemical processes where hydrogen is produced. In most cases, this hydrogen is considered as a “waste” by-product. As the hydrogen is considered a waste, it is, therefore, generally

<sup>14</sup> <https://www.drax.com/technology/5-projects-proving-carbon-capture-is-a-reality/>

<sup>15</sup> <https://www.iea.org/reports/ccus-in-power>

<sup>16</sup> <https://www.energy.gov/fe/science-innovation/carbon-capture-and-storage-research/carbon-capture-rd/pre-combustion-carbon>

<sup>17</sup> <https://www.energy.gov/fe/science-innovation/carbon-capture-and-storage-research/carbon-capture-rd>



flared instead of being utilised. And quite a substantial amount of waste by-product hydrogen is flared at port and harbour's locations where it is produced. The flared quantities are large, while H<sub>2</sub> fuel could be utilised in a better way.

Nowadays, the sites that produce hydrogen as by-product are being investigated in order to use the waste streams hydrogen rich gas to fuel high temperature fuel cells to generate electrical power and heat (i.e., operating as Combined Heat and Power (CHP) systems).

It has been documented that there are nearly 150 manufacturing facilities in the USA where hydrogen or hydrogen rich waste stream are available. The potential gas from these facilities could be captured and utilised.

On the other hand, and though this is not related to recovering by-product hydrogen from a given process, it is possible to utilise other type of waste streams to produce hydrogen or use the hydrogen rich gas being produced at a waste stream plant. The USA has around 40,000 waste treatment sites. These sites could be targeted to install anaerobic digestors, producing biogas and hydrogen rich gas. The produced gas from the waste stream could then be fuelling fuel cells to generate power (and heat) – high temperature fuel cells can operate directly from natural gas and biogas. Worldwide, it is anticipated that there is well above 100,000 MW of power that could be harnessed from waste streams and by-product hydrogen<sup>18</sup>.

In addition to the above, many agriculture waste streams can be targeted to produce hydrogen gas. It is known that sugarcane bagasse, wheat straw, cotton stalk, sugarcane trash, rice straw, and sorghum stover are raw materials that can be used to hydrogen production.

Asia as a continent produces a high quantity of these, and most farmers and countries do not attach a commercial value to these. By converting such low commercial value agricultural waste into hydrogen gas could provide a solution to two main problems. The first one is related to increasing the income of local poor farmers. A waste purchase economy could be developed, increasing the income to small farmers.

The second problem would be to reduce emissions. Currently, most of the produced agricultural wastes in Asia is burnt in small to large fire. These fires release substantial number of particulates, but also harmful gases NO<sub>x</sub>, SO<sub>x</sub>, and others. For instance, and just focusing on India, there is about 350 million tons of agricultural waste produced on an annual basis. Unfortunately, most of this waste is being burnt as, at the moment, there is no other alternative<sup>19</sup>. There is a third problem that producing hydrogen could resolve, that is the import of fuel. By producing hydrogen from agricultural waste, import of fuel could be reduced, creating a new local fuelling economy.

The above illustrates that by-product hydrogen may play a part of the answer to the global warming, though substantial investment may be needed to make this transition happen.

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<sup>18</sup> [https://www.energy.gov/sites/prod/files/2014/03/f12/waste\\_cox.pdf](https://www.energy.gov/sites/prod/files/2014/03/f12/waste_cox.pdf)

<sup>19</sup> <https://www.teriin.org/article/producing-hydrogen-agriculture-waste-microbial-way>

## 5 Waste plastic

Plastic is one of the worse pollutants of all times. It is found in the seas, oceans, rivers, and almost everywhere on land. A lot of plastic transits through harbours and ports and a lot of waste and waste management companies are locate in harbours and ports.

This makes harbours and ports a perfect location to deal with waste plastic and that in a positive, by converting to hydrogen fuel. As ports and harbours use substantial amount of fuel, converting waste plastic to fuel could provide a win-win situation for both waste management companies and harbour authorities.

There are many different types of waste streams, each being managed differently based on the feedstock. Some waste stream management methods include incineration, landfill, biogas plants, etc. Around the world, and though still not perfect, there are a number of processes and systems that have been put in place to collect and at times recycle plastic.

However, it is now possible to convert waste plastic into hydrogen gas. The most known technologies, including the most recent developments in plastic recovery and waste are summarised in the below table.

The technology that is most advanced for hydrogen production from plastic is known as the DMG (Distributed Modular Gasification). The reason behind this is that it is a technology that results in a very small amount of residual waste (at the end of the process). However, it is also a technology that does not release GHG emissions.

The advantage of DMG technology is found in that it can use different types of waste streams as input to the hydrogen conversion process. This includes non-recyclable plastic, but also some waste that is difficult to recycle such as tires. These are two of the most difficult known waste products to recycle. The below figure illustrates the high-level operation of a DMG based waste plastic syngas/hydrogen plant<sup>Error! Bookmark not defined.</sup>



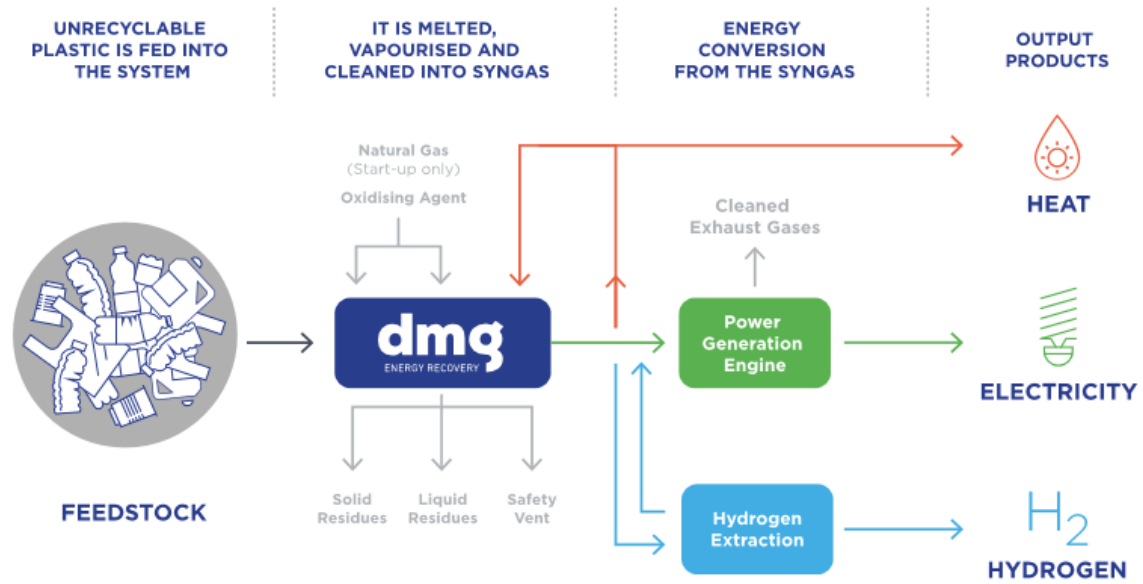


Figure 5.1 - The DMG plastic syngas/hydrogen production system<sup>20</sup>

<sup>20</sup> <https://www.edisongroup.com/publication/fuelling-the-hydrogen-economy/25046/>

## 6 Conclusion

In this module, a comprehensive review of the state-of-the-art technology for hydrogen production is presented. There are conventional methods from fossil fuel which apparently are more economical but these methods have the lack to produce greenhouse gases and for this reason will most likely be avoided.

There have been analysed various water splitting techniques. These techniques offer a practical solution for clean hydrogen production from renewable resources.

The developments of important components, such as electrolyte and electrode materials, have been reviewed. For SOE working at high temperature, there are various studies on what are the best option of electrolytes because of its high ionic conductivity and low cost.

The fundamental mechanisms of electrochemical reactions at the electrodes have not been fully understood yet. The effect of impurity segregation on the electrode long-term stability needs to be further investigated.

The fuel cells can be in tubular or planar form. Although tubular fuel cells have higher mechanical strength than the planar, planar cells are preferred due to better manufacturability and higher electrochemical performance. With the developments in both experimental and mathematical modeling investigations, it is anticipated that water electrolysis will play an important role in hydrogen production and contribute much to the coming hydrogen economy.

Incineration	Pyrolysis	Standard gasification	Plasma arc gasification	DMG process
Combustion in unrestricted amounts of oxygen to give CO <sub>2</sub> and H <sub>2</sub> O	Combustion in absence of oxygen to give syngas	Combustion in limited amounts of oxygen to give syngas	Combustion in limited amounts of oxygen to give syngas	Combustion in limited amounts of oxygen to give syngas
>850°C	300–850°C	>650°C	>5,000°C	>1,000°C
Heat from burning waste raises steam for steam turbine	Syngas impure so burnt to raise steam for steam turbine	Syngas impure so burnt to raise steam for steam turbine	Syngas pure so potentially used to power more efficient gas turbine or fuel cell	Syngas pure so potentially used to power more efficient gas turbine or fuel cell
Non-combustible material forms non-toxic bottom ash	Non-combustible material forms toxic char	Non-combustible material forms non-toxic bottom ash	Non-combustible material forms non-toxic bottom ash	Non-combustible material forms non-toxic residue.
Potential airborne pollutants treated with toxic chemicals. Still risk of emitting furans and dioxins.	Reduced amount of airborne pollutants. Still risk of emitting furans and dioxins.	Reduced amount of airborne pollutants. Still risk of emitting furans and dioxins.	No airborne pollutants	Airborne pollutants reduced in process and then further scrubbed.
Typically, 50–300k tonnes of waste processed/year	Typically, 25–150k tonnes/year	Typically, 60–650k tonnes/year	Typically, 20–700k tonne/year,	Potentially <12k tonnes/year. Process designed so two trains can be installed under local authority permit.

Table 6-1 - Comparison between plastic waste combustion technologies<sup>20</sup>

There are a number of projects around the world that use plastic as the feedstock to produce hydrogen. Though not located at a harbour or port, a project using plastic as a feed to produce hydrogen fuel was launched in Japan. More precisely in the Kawasaki town. This project provides a good example of what can be done with plastic.

The hydrogen produced from a plastic waste is used to provide power for a hotel. Most of the hotel plastic waste, which includes plastic tooth brush and many other different plastic products are collected. These are then transported to a plastic processing plant. At the plant, the plastic is converted into hydrogen. A hydrogen pipeline is used to transport the hydrogen from the H<sub>2</sub> plastic plant to the hotel. The fuel cell installed in the hotel can then produce electricity, some of which have qualify this heat and power as being plastic heat and power<sup>21</sup>.



**Figure 6.1 - Plastic recycling producing H<sub>2</sub> to supply heat and power to a hotel in Kawasaki**

Other hydrogen plastic-based projects are in the pipeline in many different countries. One of them is located in the United Kingdom near Cheshire<sup>22, 23</sup>. Though DMG technologies is currently privileged to produce H<sub>2</sub>, there are a number of technologies that are of interests.

One such technology use sunlight and a process called photocatalyst in order produce H<sub>2</sub> from plastic. This process has a great potential future when compared to pyrolysis. The reason is that it can operate at low temperatures, while pyrolysis requires really high-temperatures between 500 to 800°C to convert plastic to H<sub>2</sub>.

The first stage of the process is the mix cheap cadmium sulphide quantum photocatalyst onto the plastic that requires conversion. When this is done, the plastic can be added to an alkaline solution. Finally, the

<sup>21</sup> <https://www.h2-view.com/story/energy-from-waste-plastics-the-worlds-first-hydrogen-hotel/>

<sup>22</sup> <https://www.edie.net/news/5/Plans-to-build-UK-s-first-plastic-to-hydrogen-recycling-plant-unveiled/>

<sup>23</sup> <https://www.rechargenews.com/transition/turning-plastic-waste-into-hydrogen-first-commercial-plant-moves-step-closer/2-1-733678>

plastic with the cadmium and in the alkaline solution is exposed sunlight. At that time, the production of hydrogen is initiated. Formate, acetate, and pyruvate are by-products to the process, but these are organic and well known<sup>24</sup>.

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<sup>24</sup> <https://www.thechemicalengineer.com/news/producing-hydrogen-from-plastic-waste/>