RSC Sustainability

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Vitta, *RSC Sustain.*, 2024, DOI: 10.1039/D4SU00420E.

ROYAL SOCIETY OF CHEMISTRY

Hydrogen production – a review and its sustainability

View Article Online
DOI: 10.1039/D4SU00420E

Sustainability Statement

Hydrogen is a highly versatile energy vector and its combustion to release energy produces water without any associated emissions. Hence there has been a strong push to transition to Hydrogen as the sole energy which has the potential to limit/arrest the global warming phenomenon. This has essentially resulted in the term 'Hydrogen Economy' which is being discussed around the world. In this context and current scenario, it becomes highly relevant and timely to assess the environmental and ecological sustainability of transitioning to this energy source. This review therefore has been undertaken to assess the sustainability of largescale hydrogen production which will be essential for energy transition.

Hydrogen manufacturing – a review and its Sustainability

View Article Online
DOI: 10.1039/D4SU00420E

Satish Vitta*
Lodha Crown; Palava Phase 2
Khoni 421204; India.

Abstract:

Hydrogen is a highly versatile energy vector and most importantly its oxidation which releases energy is a green process with no associated emissions. Hence it is considered as a green alternative which can supply and simultaneously reduce global warming. This gas however does not occur naturally in sufficient quantities and needs to be synthesized using different resources. The two most feasible methods of producing H_2 are steam methane reforming process and water splitting by electrolysis. Therefore, these two processes are reviewed first and subsequently a complete sustainability analysis has been performed using currently available data. It is found that input raw materials such as methane and water will be required in 'giga tonnage' quantity every year. Although availability of water does not pose supply risk, methane production falls far short of the requirement and becomes a supply risk. The conversion of these into H_2 requires energy and results in the production of 'Gt' of CO_2. For e.g., the production of 1 Gt of H_2 using the steam methane reforming process requires ~ 3.6 EJ of energy and releases ~ 10 Gt of CO_2. The water splitting electrolysis on the other hand requires ~ 198 EJ of energy and releases anywhere from 102 Gt to 220 Gt of CO_2 depending on the electricity generation mix. Additionally, they also create ecological impact in the form of acidification, marine toxicity, particulate emissions and so on which affects all life forms on earth. This analysis clearly shows that complete transitioning to H_2 based energy supply is not sustainable and only a fraction of the energy needs can be supplemented.

Key words: Hydrogen Economy; Sustainability; Methane Reforming; Water Splitting; Electrolysis

*Retired Professor from the Indian Institute of Technology Bombay, Mumbai 400076, India.
Email: satish.vitta@iitb.ac.in

View Article Online
DOI: 10.1039/D4SU00420E

1. Introduction:

1.1. Brief History:

Hydrogen is the most abundant element on earth as well as in the universe as far as current knowledge goes. On earth it is present mainly in combined form with other elements, mostly oxygen and carbon. In the universe it is present as a fuel that sustains and powers stars like the Sun. The presence of hydrogen on earth was discovered way back in the 15th century but it was only in the 18th century it was called 'Hydrogen' by the French chemist Antoine Lavoisier meaning 'water former'.[1] All the elements in the periodic table originate from hydrogen, the building block. It is the starting element in the periodic table with just 1 electron and a proton and commonly perceived to exist only as a gas. Yet this gas has created considerable interest lately across the world and there are worldwide discussions regarding an economy that is powered solely by this element, an 'Hydrogen Economy'.[2-13] So, the question arises – is this all only a 'gas' or is there a solid substance behind these discussions. Before addressing this question, it is important to understand some basic aspects of this element hydrogen, H_2.

Hydrogen is the smallest and lightest element known, highly unstable in monoatomic form and hence exits in the diatomic form, H_2, a molecule. In the presence of elements such as oxygen and carbon, the monoatomic form is unstable and combines to form compounds such as water and hydrocarbons and hence has been predicted to be not commonly occurring even in molecular form. This notion however has been recently challenged after the discovery of several naturally occurring sources/deposits as well as constantly forming sources.[14,15] The exact amount of naturally occurring H_2 is not clearly known as it is being actively explored and current estimates for the flux of gas that emanates from the geological formations varies from 0.1 – 10 Mt per year.[14,16-18] On the other hand, H_2 can and is produced from a variety of sources – gas, liquid and solid and it is used extensively in applications varying from fertilizers for agriculture to fuel for space shuttle. The growth in consumption of H_2 since 1975 for various applications is shown in Figure 1. It can be seen that use of H_2 for methanol production, an alternate fuel, has been steadily increasing including for other applications. The amount of H_2 produced from natural resources such as natural gas or biomass or coal for these applications has reached about 120 Mt in the year 2022 and is growing.

View Article Online
DOI: 10.1039/D4SU00420E

1.2. Colors of H_2:

Before we proceed to discuss the various aspects of H_2 it is important to understand the different variants of H_2 and their environmental connection. Since H_2 can be produced from a variety of sources, both non-renewable and renewable and the source of energy for this production can again be non-renewable or renewable, distinction has been made by attributing different colors.[19-22] It should be noted that the color coding of H_2 is not unique and there is no universal agreement for the color codes. This has been done primarily to distinguish the different ways of production. The different colors and attributes are shown schematically in Figure 2. Firstly, the naturally occurring H_2 gas – its color coded '**Gold**' as it is pristine, does not require any special processing which results in environmental emissions. Another source of H_2 which does not result in any emissions is the process of 'serpentinization' wherein water coming into contact with ferrous salts of Fe, FeO leads to H_2 release according to the reaction;

$$2FeO(s) + H_2O(l) \rightarrow Fe_2O_3(s) + H_2(g) - \Delta H \qquad (1)$$

This reaction requires suitable temperature and pressure and has been known to occur in sub-surface terrains with Fe-containing rocks, typically magnesium silicates. This H_2 is color coded as being '**White**' and has been found in many locations across the earth. Since this is a naturally occurring reaction, the H_2 content is generally low and is normally mixed with natural gas, CH_4. If this process can be externally stimulated by pro-actively pursuing such rock formations, water hydrolysis can be performed naturally and this form of H_2 is referred to as '**Orange**'. This method of production is being pursued and developed actively across the world and has the potential to become a major renewable source. Currently H_2 is produced on an industrial scale using naturally occurring methane gas as source and this process is generally termed the reforming process. Since this process results in the emission of 1 mole of CO_2 for 2 moles of H_2 produced, it is referred to as '**Grey**' H_2. If on the other hand this CO_2 is completely captured and sequestered or utilized (CCUS), the resulting H_2 is referred to as '**Blue**'. A nearly emission free process of producing H_2 will be using renewable energy resources such as Sun, wind and hydroelectricity to reform methane and subsequently sequester the CO_2 emitted. Currently significant efforts are being made to scale up this process for large scale production. If H_2 is produced from coal using gasification as the process, it is colored either ‘**Brown**’ or ‘**Black**’ depending on whether the coal is lignitic or non-lignitic in nature, respectively. H_2 can also be produced by the pyrolysis of natural gas without emitting CO_2 but producing solid C and this is color coded ‘**Turquoise**’. The source of H_2 in the above schemes are naturally occurring fossil fuels. Another nearly infinite source however is water, H_2O which can be split into its constituents. If the source of energy for this splitting is nuclear the resulting H_2 is referred to as ‘**Purple/Pink**’. Another most often discussed hydrogen production route is by splitting of water using completely renewable electricity generation schemes such as solar, wind or hydroelectric. This form is color coded **‘Green’** as it has emissions essentially due to installation and operation of the different electricity generation schemes. These color schemes indeed show the multiplicity of producing H_2 and the variety of processes feasible to produce the gas. All the different forms have varying degree of greenhouse gas emissions at different stages of production, Table 2, clearly showing that a completely emissions free hydrogen is not possible. If one were to transition to H_2 and a H_2 economy, these production processes need to be significantly scaled up. The flip side however is that the environmental foot print of these technologies should be significantly reduced or even eliminated completely. This makes it imperative to understand these processes and evaluate their environmental impact and long-term sustainability. The different large scale production processes currently known which have the potential to be scaled-up are discussed below.

1.3. Hydrogen – gas, liquid or solid:

H_2 as we know exists in gaseous form under normal temperature and pressure conditions. Since this is the lightest element known with a density of 0.08 $KgNm^{-3}$ under normal conditions, it becomes extremely ‘voluminous’ to handle large quantities required for large scale utilization in a hydrogen economy scenario. Hence it becomes important to understand the conditions under which it can exist in a higher density form compared to the gaseous state such as a liquid or a solid.[23,24] The pressure and temperature dependence of existence of the different forms - gas, liquid or solid is shown in Figure 3, the phase stability diagram.

If the gas is cooled at an atmospheric pressure of 10^5 Pa (1 atm.), it condenses into a liquid at ~ 20 K (-253 °C) and if cooled further to < 14 K (- 259 °C) it undergoes transition to a solid state. These transition temperatures depend on pressure but require the gas to be

View Article Online
DOI: 10.1039/D4SU00420E

cooled to at least 33 K (-240 °C) to transform at very high pressures. The density of H_2 changes by about 3 orders of magnitude to ~ 71 $kgNm^{-3}$ on transforming to liquid state, Table 1[25] and thus enhances its transportability as well as its energy density. The energy content of H_2, a technologically important parameter, is defined as the 'heating value' HV when it is converted into H_2O on exposure to oxygen. The corresponding exothermic chemical reaction is written as;

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + \Delta H \qquad (2).$$

The magnitude of heat released as a result of this exothermic reaction is termed the 'highest heating value' HHV and is found to be 142 $MJkg^{-1}$ (12.8 $MJNm^{-3}$) of H_2. In most common practices however, H_2O is in gaseous form, steam and results in loss of heat or energy if this is not recovered. The corresponding energy released on transformation to steam is termed as 'lower heating value' LHV and is found to be ~ 120 $MJkg^{-1}$ (10.8 $MJNm^{-3}$). Converting the gas into liquid increases the energy density by orders of magnitude but requires extraction of large quantity of latent heat to cool the gas. Also, storing and transporting in liquid state requires development of highly thermally insulating containers and pipelines. Hence H_2 is manufactured, stored and transported in compressed gaseous state. Since the mass density in the gaseous state increases with increasing pressure, the energy content increases on increasing the pressure as shown in Table 1 and hence H_2 is transported in pressurized form if not in the liquid state. This will increase the energy density although it is still far below that of gasoline, for example. The volumetric energy density of gasoline is ~ 3 orders of magnitude higher compared to that of H_2 gas but it is non-renewable.

1.4. Objectives of H_2 Economy:

The current scenario of global warming due to emission of various greenhouse gases has necessitated a shift from energy sources such as coal, oil and natural gas to non-polluting alternatives such as Sun and wind. In this context, H_2 is proposed as a clean source of energy with minimal emissions. As an energy carrier it is extremely versatile and can substitute the fossil fuel-based energy carriers currently in use. If a transition to H_2 should occur, then all the different energy requirements along with the current needs in various applications has to be fully met which means the demand will increase manifold from the current level of 120 Mt per year. Hence it becomes imperative to understand and analyze all the different aspects of

View Article Online
DOI: 10.1039/D4SU00420E

H_2 – production to transport to utility. Most importantly, the true gain to the environment as well as its sustainability in the long run needs to be assessed. The sources of H_2 can be broadly classified into non-renewable and renewable sources. The different non-renewable sources are hydrocarbon gases, coal, tar sands, heavy oils and so on. The renewable sources are different types of biomass and water. The most common non-renewable source that is currently used extensively is methane, CH_4 as it has the highest H:C ratio of 4 and the most renewable source is water, H_2O which can be split using electricity. Hence in the present work conversion of CH_4 and H_2O into H_2 are discussed in detail as they hold the highest potential for scaling up to extremely large quantity production. The objective of this work therefore is to review the different aspects of the supply chain and associate wherever possible environmental and ecological factors to these processes. It should be mentioned here that since most of these processes are not performed at large scale, the environmental parameters and materials issues will either be extrapolations or estimates. These however will need to be refined/modified as we gain experience in the future and development takes place.

2. Hydrogen Production:

2.1. Natural Hydrogen:

Naturally occurring H_2 deposits are currently not fully explored and mapped due to a variety of reasons such as economic and geopolitical, including non-availability of accurate detection methods.[15] The concentration of H_2 gas in the naturally occurring deposits varies from region to region as the source is different in different locations. The concentration of H_2 in these deposits can vary from 10 % to > 90 %.[14,15,20,26,27] The most common gases associated with H_2 in these deposits are N_2, CH_4 and a combination of these gases. An interesting aspect of some of these deposits is that there is a constant production of fresh H_2 due to reactions such as serpentinization which means it's a never-ending source. Although these sources exist and new deposits are being discovered, a challenge however is to separate H_2 from the other gases and making it suitable for transportation and consumption. Current estimates show the naturally occurring H_2 gas potential is ~ 0.1 – 10 $MtYear^{-1}$. The industrial requirement, other than being an energy carrier alone is ~ 120 $MtYear^{-1}$, far in excess of current naturally occurring deposits. The current gas requirement is far in excess of naturally occurring resources. Recently however the US Department of Energy awarded a USD 20 million grant program to explore the possibility of extracting naturally occurring H_2,[20] bolstering the search for naturally occurring H_2. Another source is freshly forming H_2 as a byproduct of serpentinization reaction that occurs in ocean ridges. H_2 yields of up to 300 mmol for every kg of rock are predicted due to this reaction and this has been detected along the mid-ocean ridges.[28]

Historically it has been produced from a range of sources such as natural gas to coal to meet the industrial needs. Synthesizing it however has the biggest advantage as it results in nearly pure state with very low quantity of impurities and thus fit for direct use in many applications ranging from production of fertilizers to electricity generation. If one were to transition to H_2 and a H_2 economy, these industrial production processes need to be significantly scaled up. The flip side however is that the environmental foot print of these technologies should be significantly reduced or even eliminated completely. This makes it imperative to understand these processes and evaluate their environmental impact and long-term sustainability. The different large scale production processes currently known which have the potential to be scaled-up are discussed below.

2.2. Reforming:

Reforming is a process which converts naturally occurring hydrocarbons into H_2 and CO_2 (CO). The naturally occurring hydrocarbons can be gaseous – natural gas, liquid – wet biomass or solid – coal.[25,29,30] Most commonly used starting material however is natural gas, CH_4. The main advantage of this source is that it generates 2 moles of H_2 for every mole of CH_4 and releases only 1 mole of CO_2 and is therefore one of the main resources used currently for large scale production.

2.2.1. Natural Gas Reforming:

Natural gas occurs on its own in gas fields or along with oil in oil fields and coal in coal fields. The natural gas content in the gas fields varies depending on the geological location and CH_4 content can vary from 70 % to 95 % with the rest made of higher hydrocarbons such as ethane, propane, butane, pentane and hexane.[31] Non-hydrocarbon gases such as S, N_2, H_2O, H_2S, CO_2 will also be present with CH_4. Most of the higher hydrocarbons undergo liquefaction when they are brought to atmospheric conditions from high pressure gas wells and thus ease the gas separation process. The non-hydrocarbons however should be stripped

View Article Online
DOI: 10.1039/D4SU00420E

completely before reforming process as they tend to poison the reforming catalysts. The cleaning process has to be performed before CH_4 enters the reformer reactors which means a ‘cleaning process plant’ has to be set-up either at the gas well or at the reforming plant. Also, the extracted natural gas has to be compressed and transported through gas pipelines or if it is to be processed at far away distances from the gas well it has to be liquified at 109 K (-164 °C) and transported via cryogenic containers.

The steam-methane reforming (SMR) process, which is the most reliable process known, produces H_2 in several steps or reaction vessels.[25,29,30] The first step in this process is conversion of CH_4 into CO and H_2 based on the reaction;

$$CH_4(g) + H_2O(l) \rightarrow CO(g) + 3H_2(g) - \Delta H \qquad (3)$$

where ΔH is the reaction enthalpy and negative sign indicates endothermic nature of the reaction. This reaction takes place in the temperature range 700 °C – 1000 °C under a pressure of 0.3 MPa to 2.5 MPa. It’s an endothermic reaction overall requiring ~ 252 $kJmole^{-2}$ of CH_4 and a catalyst with an extremely large specific surface area, 60 – 100 nm size, Ni particles. The steam to C ratio in this reaction is extremely critical and should be ~ 2 – 5 to avoid carbon build-up on the catalyst particles which poisons them. If H_2O is supplied in the form of steam, the amount of heat energy required reduces to ~ 206 $kJmole^{-1}$ of CH_4. The reaction product, mixture of CO and H_2 is generally referred to as ‘Synthetic gas’ or ‘Syn gas’. Since CO is a toxic gas which needs to be oxidized before releasing to the atmosphere, this gas mixture is further subjected to water exposure, Water Gas Shift (WGS) exothermic reaction given by;

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) + \Delta H \qquad (4).$$

The temperature of the incoming synthetic gas and steam should be maintained at ~ 400 °C as the above reaction is exothermic in nature releasing 41 $kJmole^{-1}$ of CO. This reaction takes place under a pressure range of 0.1 MPa to 8 MPa. The reaction however does not really go to completion and the product gases will have ~ 2 vol.% of unreacted CO. If ultrapure H_2 is required, the product gas is further subjected to 2 additional stages of WGS reaction at 200 °C and 100 °C to bring down the CO content to < 0.002 vol.%.

The main steam-methane reforming reaction, Eq.(3) is highly endothermic and also the conversion of water to steam requires heat input. In order to overcome some of these heat requisites, two alternatives are explored;

- Supplying the required heat by burning a fraction of incoming CH_4, typically ~ 25 %. This is called allothermal reforming.
- Autothermal reforming – in this process air/oxygen is added to the incoming reactants results which results in an exothermic methane oxidation reaction that supplies the heat needed to push the reaction forward. Both steam reforming and partial oxidation reactions take place simultaneously at ~ 950 °C – 1100 °C and 10 MPa pressure in the presence of a catalyst. The net autothermal reaction is given by;

$$5CH_4(g) + 3H_2O + O_2(g) \rightarrow 5CO(g) + 13H_2(g) \qquad (5).$$

This reaction involves a series of reactions and controlling the mixture of reactants and maintaining proper steam to C ratio will be extremely crucial in this process. A reduced ratio of 0.6 and correct fraction of oxygen/air supplies the heat required and hence no external heat source will be needed to generate H_2. Since no heat is required and all the reactions can take place in a single reactor, it will be a compact process with possibly low capital cost.[32] The products of this process however are still a mixture of gases and H_2 needs to be separated. Also, if air is used it will add N_2 to the product gases while addition of pure O_2 requires its cryogenic isolation from air.

An alternative to steam reforming is 'dry' reforming wherein CO_2 is used instead of H_2O;

$$CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g) + \Delta H \qquad (6).$$

This is again an endothermic reaction requiring about 247 $kJmole^{-1}$ of CH_4 and also a suitable catalyst. The main advantage of this method is that it does not require high purity water and recycles existing CO_2 without leading to any additional emissions. However, this reaction is not fully explored and needs research and development. If one considers the overall steam reforming reaction given by;

$$CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g) + \Delta H \qquad (7)$$

it is seen that for every mole of CH_4 4 moles of H_2 are released with the additional 2 moles coming from H_2O. Hence this process is a combination of methane reforming and water hydrolysis which is why it is a preferred method for industrial production. The result of either steam-methane reforming or dry methane reforming is a mixture of the two gases H_2 and CO_2 which means they need to be separated in an additional process step to get pure H_2.

2.2.2. Plasma Reforming:

View Article Online
DOI: 10.1039/D4SU00420E

Hydrogen is produced in this method by the decomposition of CH_4 into solid C and H_2 gas. The decomposition can be performed either without any solid catalyst at very high temperatures, 3000 °C – 10000 °C or in the presence of a catalyst at lower temperatures.[33] The overall energy consumption for this process is lower than that in steam reforming and ideally it does not have any emissions as C is deposited in the form of soot which can be used for other applications. The life of the catalyst however decreases rapidly due to deactivation by C and hence needs frequent reactivation which will result in CO_2 emissions. Since the process is simple, the reactors can be compact in design. The energy required is solely in the form of electricity which can be a deterrent in many locations. Partial substitution of energy requirement can be made by the addition of steam and oxygen but control of these processes is not well established. The energy utilization and efficiency of the plasma process limits its use and developments in these can render this process competitive for large scale application in the future. It should be noted that use of oxygen or steam in the reformer will lead to generation and emission of CO_2 which has to be stripped from H_2.

2.2.3. Sorbent-enhanced Reforming:

This is a variant of the steam reforming process with the main reforming reaction and gases separation combined into a single process.[34] The CO_2 generated is absorbed by a solid sorbent present along with the catalyst. The constant removal of CO_2 from the reaction chamber shifts the reaction forward and also reduces the reforming temperature from ~ 900 °C to ~ 500 °C. The product output of this process is ~90 % pure H_2 with the rest composed of unreacted CH_4 and small amount of CO_2. The sorbent soaked with CO_2 can be revived by flushing it with steam and the subsequent condensation of steam into water releases the CO_2 for sequestration. Therefore, the reactors are extremely compact and lends itself for sequestration making it very promising for further development and commercialization.

Apart from CH_4 gas, materials such as coal and biomass (both dry and wet) have been proposed and also demonstrated as sources of H_2. Gasification of coal for example does result in producing synthetic gas but the amount of H_2 in this gas mixture is relatively low and does not exceed about 50 % with majority of the cases yielding about 10 % - 15 %. This product gas however contains several harmful and toxic gases, metals and particulates. Similar is the case with biomass, both dry and wet. So, from the perspective of largescale production for H_2

View Article Online
DOI: 10.1039/D4SU00420E

economy, these technologies do not really hold promise either from environmental or economic considerations and hence these will not be discussed in detail here.

The source of H_2 in the different processes discussed above are mainly fossil based hydrocarbons including coal. The other main source of H_2, as mentioned in the introduction section, is H_2O water. In the steam reforming process water also undergoes hydrolysis but in the presence of and together with hydrocarbons. However, H_2O itself can be a source of H_2 when it is separated into components on supply of required amount of energy and in the presence of suitable catalysts. If one were to supply the required energy to split H_2O in the form of heat, i.e., thermal decomposition, then heating to ~ 3000 °C leads to about 50 % of volume decomposition into H, H_2, O, OH^- and O_2. The decomposed gases should be separated to avoid recombination and separation at these elevated temperatures is extremely difficult. Hence pure thermal decomposition is never practiced and alternate forms of energy is used to split H_2O. The most versatile form of energy is electricity, i.e., electrolysis of water and this process is used industrially and is being developed for large scale adaptation. Hence the discussion on splitting H_2O is limited to the various forms of electrolysis.

2.3. Water Splitting by Electrolysis:

Electrolysis is a process wherein H_2O is split into its components H_2 and O_2 using electricity as the source of energy for splitting, as shown in Figure 4. The distinct advantage of this method of producing H_2 is that it can be environmentally neutral, sustainable and completely circular in nature if the primary energy source is renewable in nature such as solar and wind. The splitting of water produces O_2 which is environmentally friendly and this can be used for many applications including medical use. In a truly closed system however it can be used for oxidation of H_2 which releases useful energy and will also result in the formation of H_2O which can either be used again for splitting or released into the atmosphere.

Electrolysis can be performed under different conditions and in the presence of different electrodes and electrolytes, each of which will have differing physio-chemical and electrochemical aspects.[35] There are mainly 4 different configurations of electrolysers;

- Alkaline, AEC
- Proton Exchange/Polymer Electrolyte Membrane, PEM,
- Anion Exchange Membrane, AEM, and

View Article Online
DOI: 10.1039/D4SU00420E

- Sold Oxide Electrolyte, SOC.

The typical cell structure of these 4 different electrolysers is shown in Figure 5.[7] Irrespective of the type of configuration H_2 evolution takes place at the negative cathode while O_2 evolution takes place at the positive anode. The half-cell reactions in the 4 electrolysers and the corresponding standard potentials are given below;

Alkaline:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad E^0 = 0.828\,V\ at\ negative\ Cathode$$

$$2OH^- \rightarrow \frac{1}{2}O_2(g) + H_2O(l) + 2e^- \quad E^0 = 0.401\,V\ at\ positive\ Anode$$

Proton Exchange/Polymer Electrolyte Membrane, PEM:

$$4H^+ + 4e^- \rightarrow 2H_2(g) \quad E^0 = 0\,V\ at\ negative\ Cathode$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^- \quad E^0 = 1.23\,V\ at\ positive\ Anode$$

Anion Exchange Membrane, AEM:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad E^0 = 0.828\,V\ at\ negative\ Cathode$$

$$2OH^- \rightarrow \frac{1}{2}O_2(g) + H_2O(l) + 2e^- \quad E^0 = 0.401\,V\ at\ positive\ Anode$$

Solid Oxide Electrolyte:

$$2H_2O(g) + 4e^- \rightarrow 2H_2(g) + 2O^{2-} \quad E^0 = 1.23\,V\ at\ negative\ Cathode$$

$$2O^{2-} \rightarrow O_2(g) + 4e^- \quad E^0 = 0.33\,V\ at\ positive\ Anode$$

It can be seen that OH^- ions are the migrating species in alkaline and anion exchange electrolysers while both H^+ and O^{2-} ions are the migrating species in the case of PEM and Solid Oxide electrolysers respectively. This means the nature and type of membrane that allows permeation of these differently charged ions in each case have to be different. The ideal thermodynamically reversible full cell voltage varies from 1.23 V to 1.56 V depending on the type of electrolyser. The actual operating voltages V_{op} however will be higher than these values as they operate under adiabatic conditions and the different losses such as electrolyte resistance, electrode overpotentials and electrolyte resistance have to be compensated. The resulting V_{op} therefore can be written as;

$$V_{op} = E^0 + IR_e + IR_{Cathode/Anode} + \eta_{Cathode/Anode} \qquad (8)$$

where I is the cell current, R_e and $R_{Cathode/Anode}$ are resistance of electrolyte and electrodes respectively and η the overpotential at the two electrodes. Currently AEM and SOC electrolysers are very much in research and development stage while the AEC and PEM have proven technological capability with large scale production feasibility. Hence the typical characteristics of these two electrolysers are given in Table 3 together with their operating conditions.[7] The PEM electrolyser operates at a higher pressure compared to other electrolysers which makes a difference for effective storage and transportation. It should however be noted that these are typical parameters and variations are adapted for large scale manufacturing. The AEM and Solid Oxide electrolysers are currently under development and can become operational at large scale in the coming decade. Similar to batteries the electrolyser cells can be combined either in a monopolar or bipolar configuration. These are known as stacks or modules and they can be connected either in series or in parallel depending on the configuration. Typically, the bipolar stack design is used for PEM and operates at a higher voltage and lower current density compared to the monopolar tank configuration of alkaline electrolysers. These stacks are a component of the whole system and the system level components vary depending on the type of electrolyser.

Apart from steam reforming and electrolysis, H_2 can be produced by splitting H_2O using solar energy alone, Photolysis. In this case the required energy in the form of heat for splitting is provided by concentrated sun light produced using a number of heliostats. A variant of this process is photo-thermal electrolysis wherein the infra-red radiation of the solar spectrum is converted into heat while the rest of the radiation is converted into electricity using a photovoltaic cell. The heat generated converts water into steam and the electricity is used to perform electrolysis of the steam. There are certain other processes which are a combination of chemical and thermal energies that are being developed to split water into H_2 and O_2. These thermochemical processes have highly acidic environments and operated at highly elevated temperatures because of which they are currently not amenable to large scale adaptation, specially in the context of hydrogen economy. Hence all these processes including photolysis and photo-thermal splitting will not be discussed and analyzed further.

View Article Online
DOI: 10.1039/D4SU00420E

3. Hydrogen Separation:

Irrespective of the reforming process used, H_2 is produced together with CO_2 and other impurity gases. Hence separation from these other gases is mandatory to produce pure H_2. Separation is achieved mainly by two different methods;

- pressurized adsorption of CO_2 and other impurity gases onto a sorbent, Pressure Swing Adsorption PSA; and
- selective diffusion of H_2 across a membrane known as membrane separation.

In the case of PSA the hot gases from the water-gas shift reactor are pressurized to ~ 4 MPa and passed over a sorbent which adsorbs CO_2 and other gases by physisorption. The sorbent used is either a molecular sieve such as zeolite or activated carbon. The efficiency of separation reduces with time and the sorbent gets saturated with CO_2 and other impurity gases. The separation takes place in a vertical packed bed column reactor and is a bath process. In large scale production plants multiple column reactors connected in parallel are used to enhance productivity and a semicontinuous production capacity, as shown in Figure 6.[36] Reducing the gas pressure in saturated sorbent columns in several discrete steps releases CO_2 and other impurity gases and leads to revival of the sorbent material. Because of this, the separation efficiency is around 90 % while the H_2 produced will be 99.999 % pure. Industrial units ranging in production capacity of 500 – 100000 Nm^3h^{-1} having up to 12 column separators are currently being used.

Cryogenic separation of H_2 by cooling the mixture of gases to < 216 K (- 57 °C) at a pressure of 0.5 MPa enables the liquefaction of CO_2 and thus separates gaseous H_2. This method however is energy intensive but has the advantage of converting CO_2 into liquid, a dense form compared to gas and is more amenable to transportation in cryogenic containers and subsequent sequestration.

Separation of H_2 can also be performed by pressurizing the gases to flow across a membrane. These membranes can either be non-porous or porous and separation takes place mainly due to high diffusivity of H_2 in the membrane due to its smallest size. Typical non-porous membranes are metallic in nature and most commonly used metal membrane is made of Pd and its alloys. Non-porous membranes made of perovskite compounds such as $SrCeO_3$ or $BaCeO_3$ are also used for H_2 separation at high temperatures. The porous membranes on the other hand are molecular sieves made of zeolites or silicates with pore sizes < 1 nm. There are several polymeric as well as mixed membranes also that have been used for gas separation. These can be both porous and non-porous glass or rubbery polymers.[37] The biggest advantage of polymeric is their flexibility compared to inorganic membranes which tend to be brittle in nature. The pure polymeric membranes however have low thermal stability compared to inorganic membranes which can operate well even at 400 °C. In order to exploit the flexibility of polymeric membranes and thermal stability and selectivity of inorganic membranes, mixed membranes made of both polymeric and inorganic materials have been developed and these have been found to exhibit good performance. Typical polymeric membranes are made of polyimide, polysulfone, polybenzimidazoles, polycarbonate, polyethersulfone and so on. Inorganic nanoparticles such as Pd, silica, carbon nanotubes have been incorporated in these polymers to realize mixed membranes with separation properties better than polymer based membranes. The gas flux J_i of the component i across the membrane is a diffusive phenomenon and is governed by the equation;

$$J_i = \frac{D_i C_i}{RT}\left(\frac{\partial \mu_i}{\partial x}\right) \tag{9}$$

where D_i, C_i and μ_I are the diffusion constant, concentration and chemical potential of component i in the gas mixture and R and T are gas constant and temperature respectively. Apart from the concentration gradient across the membrane, the diffusing flux depends strongly on D_i which in turn depends directly on the temperature and inversely on the pressure. The chemical potential gradient which drives the diffusion process becomes extremely large if the overall diffusion distance becomes small, i.e., the membrane thickness becomes very small. Hence the membranes are typically < 10 μm thick and in many cases are mounted on substrates for mechanical stability. In the case of non-porous membranes H_2 has been predicted to diffuse mainly in ionic form, i.e., breakdown of the molecule into a monoatomic state followed by ionization and subsequently the reversal of the processes. In the case of porous membranes however it has been predicted to diffuse predominantly in molecular form. It can be seen that membrane separation is a complex process involving several stages and also the membranes have an associated risk of getting poisoned/contaminated by harmful impurity gases in the gas mixture. Hence for large scale industrial operation the most preferred process is the pressure swing adsorption and industrially this process has been optimized to a large extent.

View Article Online
DOI: 10.1039/D4SU00420E

4. Sustainability Evaluation:

The concept of sustainable development encompasses the three most important aspects – planet, people and prosperity. These in turn have several components which deal with the environment, materials, economics, legislation and so on. The scope of this review is limited to discussion in detail the technical aspects of H_2 production and its environmental consequences defined in terms of embodied energy for the manufacture of H_2 and associated emissions, ecological impact and materials required including input materials such as natural gas and water for the SMR process and electrolytic splitting respectively. The other components such as economics and legislation are equally important and a detailed discussion of these is beyond the scope of current review. However, the important and essential economic and legislative components are mentioned without going into exhaustive details. A concise sustainability, circularity analysis of H_2 production using any of the production methods has to clearly define the 'System Boundaries'. These boundaries are extremely important and can make a considerable difference. In the present work system boundaries are clearly defined and available data analyzed within this boundary limit. The sustainability criteria can limit to environmental and ecological impact assessment or encompass economic and social aspects of H_2 production. The materials and various infrastructure facilities required are estimated using available data/information. The environmental and ecological parameters for the different processes are discussed together with economic factors where feasible.

The projected global energy demand till the year 2050 based on past energy consumption has been estimated by the Energy Information Agency, EIA in the International Energy Outlook 2023 report[38] and this has been shown in Figure 7. It is seen that the energy demand increases from ~ 650 EJ to 1000 EJ at an average rate of 2 % per year. This energy demand can be translated into amount of H_2 gas requirement using the best case scenario of HHV and this has also been shown in Figure 7. It is seen that the amount of H_2 gas required to meet this energy demand increases correspondingly from 4.5 Gt to 7.5 Gt or 50 teraNm^3 to 85 teraNm^3 every year. This requirement is based on the assumption that the total energy requirement will be met solely by H_2 which is not true as renewables are anticipated to directly contribute a significant fraction of the energy demand. Even if one assumes a 50 % energy demand being met by alternatives such as renewables and nuclear, the H_2 gas needed will still be in the range 2.25 Gt to 3.75 Gt per year, which is enormous compared to 120 Mt produced in the year 2020, 3 orders of magnitude less compared to requirement. This means a significant expansion in production capacity has to be achieved at the earliest possible. As mentioned earlier, SMR and electrolysis of water using the alkaline electrolyte cell, AEC are two processes which have the potential for expansion and large scale production and hence the sustainability of these two processes is discussed below. Also, natural gas is a non-renewable fossil source while water is a renewable source which is almost infinite on earth.

4.1. System Boundaries:

4.1.1. Steam Reforming of Methane:

The major resource inputs for SMR are: naturally occurring, non-renewable fossil fuel methane, water and energy. The naturally occurring methane gas has been found in select locations across the earth which means the gas has to be extracted and transported to the site of H_2 production plant. The situation with respect to water may not be all that critical as compared to methane gas but obtaining the requisite quality becomes essential. Energy on the other hand again may be a commodity, access to which is not easy or straight forward. Hence defining a system boundary which either considers all these as a given or explicitly accounts for these becomes important. A typical process flow sheet for SMR can be considered as two independent systems as shown in Figure 8. System 1 comprises of prospecting and producing natural gas which is required for the SMR process while System 2 defines the boundary with input as natural gas and output as high purity H_2. The two are shown separately because natural gas prospecting is an independent operation and does not depend on H_2 production, finding its own use. The System 2 however depends on System 1 as it cannot be operationalized without the feed from System 1, i.e. natural gas. Hence in the literature several studies have considered only System 2 for life cycle studies. In the present work however the sustainability of the SMR process which includes both systems 1 and 2 has been presented.

The three major inputs needed for the SMR process are; 1) Natural gas, 2) Electrical energy and 3) Water. Typical values of these inputs obtained based on actual plant operating conditions in certain cases and plant simulations in others are given in Table 4.[38,39] The different catalysts such as activated charcoal, ZnO, Al_2O_3, Co_2O_3 and CuO that are required are given in Table 5. These can be revived and need replacement once in 2 or 3 years. Apart from these several other inputs such as catalysts, steel , cement and land will also be required. These however will be small as they are mainly infrastructure in nature and last for the lifetime of the plant, typically 20 years or more. Hence these are not discussed as main requirements. The 3 major requirements have been determined based on the H_2 gas requirement and are shown in Figures 9 (a) and (b). It is seen that electricity requirement ranges from 15 to 25 EJ per year while that of natural gas varies from ~ 13 Gt to 23 Gt per year till the year 2050. The SMR process requires fresh water for various operations and the corresponding need ranges from 80 Gt to 140 Gt per year or 80 to 140 T litres.

The environmental impact is generally assessed by the amount of emission of greenhouse gases and is represented in terms of equivalent CO_2 quantity. In the case of SMR process, emissions are due to two distinct sources – natural gas mining & breakdown in the reactor and electricity use for the different processes. The emissions due to electricity utilization varies from country to country as the renewables fraction is different in different countries. The most extensive and reliable data available is from H_2 production facilities in USA and Canada and these are given in Table 6.[39-46] It is seen that on an average 10 kgs of CO_2 is emitted for every kg of H_2 gas produced. This means the amount of CO_2 emission alone will be of the order of 10's of Gt. The actual yearly emissions based on amount of H_2 produced has been determined and is shown in Figure 10. These emissions include those which arise due to natural gas prospecting, processing and decomposition as well as electricity utilization in the different aspects of SMR process. The emissions range from 45 Gt to 75 Gt per year.

4.1.2. Water Splitting by Electrolysis:

As the name suggests the two major inputs for this method of production of H_2 are 'clean' water and electricity. The water used for electrolysis has to be devoid of all impurities – both inorganic and organic as these will not only reduce the cell performance but will also lead to cell life degradation. Hence the water has to be treated before being fed to the electrolysis cell. The other major input is electricity required to split water molecules. This energy can be obtained from a wide variety of resources – non-renewable and renewable and needs to be considered separately. Hence the largescale electrolysis process can be considered as two separate systems from the perspective of sustainability evaluation – System 1 comprising the water treatment and electricity handling sub-systems and System 2 comprising of the actual water splitting process together with H_2 compression and cooling

View Article Online
DOI: 10.1039/D4SU00420E

unit which makes it ready for transportation and further use. These two systems are shown schematically in Figure 11. It should be noted that electricity in the form of direct current will be used for electrolysis which means the alternating form generated by the different electricity generating processes has to be first rectified.

In the case of splitting water by electrolysis in an alkaline electrolytic cell, the main requirement will be for electricity, water and electrolyte, KOH.[40] These are given in Table 7 and the amounts required as per energy demand are shown in Figures 12 (a) and (b). The electricity requirement increases from ~ 900 EJ to 1500 EJ per year while that of the electrolyte increases from 4.5 Mt to 7.5 Mt. The water demand on the other hand varies from ~ 60 Gt to 100 Gt or 60 to 100 T litres per year. The typical cell configurations have Ni-electrodes, stainless steel separators and Polyphenylene sulfide packing and these will be required in millions of tons to install and commission large scale H_2 production.

The water splitting electrolysis process on the other hand does not directly generate emissions but requires electrical energy, the generation of which leads to emissions. Again, based on a country's electricity generation mix, the magnitude of emissions varies.[40,47-51] Since there are no large-scale water splitting units operating commercially, the equivalent emissions have been determined based on the electricity requirement given in Figure 12(a). The yearly emissions due to H_2 production based on two limits of 390 $gkWh^{-1}$ and 820 $gkWh^{-1}$ have been determined[52] and shown in Figure 13. These are about an order of magnitude higher compared to the emissions due to SMR process shown in Figure 10. These can vary from ~ 90 Gt to 160 Gt in the best-case scenario to 200 Gt to 340 Gt in the worst-case scenario. The emissions due to water splitting by electrolysis are essentially due to electricity consumption.

Apart from the environmental consequence of emitting various global warming gases and particulates into the atmosphere, large scale production of H_2 gas also leads to significant ecological emissions and impact. These ecological emissions lead to various effects such as fresh water toxicity which affects both humans and other living organisms. The different ecological impact parameters both due to the SMR process as well as water splitting by electrolysis are given in Tables 8 and 9. If one considers the fact that these parameters are due to the production of just 1 kg of H_2 gas, the intensity of producing giga tons of H_2 gas become extremely severe and require serious consideration.

View Article Online
DOI: 10.1039/D4SU00420E

5. Discussion:

Large scale production of H_2 using either conventional fossil fuels such as methane and coal or splitting of water have been shown to be technologically feasible. Specifically, steam methane reforming has been in use since a long time while water electrolysis is at a very nascent stage. Scaling-up these technologies to meet the current and growing energy demand however requires a relook at these and most importantly analyse carefully the sustainability implications of this energy transition. Sustainability analysis of any process or product is multidimensional in nature and has several components such as technical feasibility, energy, environment and ecological implications, financial requirement, societal and governmental obligations. Specifically, a fast shrinking remaining CO_2 budget for either 1.5 °C or 2.0 °C global warming scenario makes it absolutely imperative to analyse the environmental and ecological sustainability of this transition.

The SMR process has been conventionally used for producing H_2 which is used mainly in NH_3 production and oil refining. The technology therefore has matured considerably and is ready for even larger upscaling. This is evidenced by one of the recent large scale facility becoming operational in April 2021, shown in Figure 14 producing 56000 Nm^3 per hour of 99.99 % pure H_2.[53] The main inputs for the SMR process as mentioned earlier are natural gas, electricity and water. If one considers availability of natural gas, the quantity produced in the world since year 2010 and projected production till the year 2050 are shown in Figure 15. The global production capacity increases steadily from ~ 2.0 Gt in the year 2010 to 3.4 Gt by the year 2050. This is an order of magnitude lower compared to the H_2 based energy demand, clearly showing that natural gas availability will run the risk of severe short fall and hence prospecting and production capacity needs significant increase. The available global reserves as of year 2022 are estimated to be ~ 110 Gt and the amount of methane present in the form of methane hydrates has been estimated to be ~ 5 orders of magnitude higher than terrestrial reserves. The exploration and production of natural gas however has to be done extremely carefully avoiding any leakage into the atmosphere as its global warming potential is ~ 28 times higher than that of CO_2. Natural gas is one of the non-renewable fossil sources used in the reforming process. An alternative would be different types of biomass – solid and liquid which can also be used as input in the reforming process. They are also renewable in nature and hence have been extensively investigated for producing H_2. The biomass can be of different types varying from simple organic waste such as grass, coconut shell, and corncob

View Article Online
DOI: 10.1039/D4SU00420E

to sewage sludge. Two methods of treating these have been investigated at best in laboratory/pilot scale set-ups or purely based on thermodynamic and kinetic modelling of the reactors.[54-56] The output of these processes is a mixture of gases such as H_2, CH_4, higher hydrocarbons and CO which have excellent combustion value. Production of pure H_2 requires further processing including techniques such as pressure swing adsorption. The real environmental benefits of these however needs to be assessed as and when large scale production becomes feasible in the future. An attractive feature of these is that they add value to every day waste and thus lead to ‘valorisation’ of common waste. It should however be mentioned that common organic and agricultural waste already finds use as animal feed and composting to produce organic fertilizers. The amount of electrical energy and water needed to implement natural gas SMR based H_2 production is shown in Figure 9 and these clearly indicate that 10 EJ - 30 EJ of energy will be needed to produce the gas while the water requirement increases to ~ 140 Gt by the year 2050. This water cannot be saline as it affects reactor performance and this huge quantity of fresh water requirement year-on-year imposes considerable load on natural fresh water systems, in direct conflict with human and food production needs. The other most important impact is the magnitude of CO_2 emissions which is 10’s of Gt due to H_2 gas production alone. An alternative to mitigate CO_2 emissions into the atmosphere is to capture and subsequent sequestration and utilization, CCSU and thus change the H_2 from being grey to blue. The current status of CCSU technology however is in its infancy with mainly trials/pilot schemes being in operation. The feasibility of large scale implementation of these schemes is still in debate and needs significant research and analysis. Another alternative to reduce effective emissions is to transition to electrical energy being provided solely by renewable resources such as solar, wind and hydro. Scaling of these is again highly debated and thus making H_2 production a completely green activity needs further developments. Apart from the emissions associated with steam reforming, ecological impact also becomes significant as given in Table 8.[57] The contamination of water resources, as measured by fresh water toxicity amounts to ~ 149 tons for the year 2023 alone and increases with increasing energy demand. The carcinogenic toxicity to humans and terrestrial acidification become millions of tons, clearly showing the disastrous consequences of large scale H_2 production.

An alternative to using natural gas as the source of H_2 is water, H_2O a renewable source. The inherent advantage of this method is that the oxidation or usage product is H_2O

View Article Online
DOI: 10.1039/D4SU00420E

with no associated emissions and being truly circular in nature. The main concern in this method is that it requires electrical energy to split water and this will be in the range of 1000's of EJ per year as shown in Figure 12 and is too large. If this electrical energy can be provided by renewable resources alone, then water electrolysis to produce H_2 will be an ideal sustainable choice, the case of green H_2. One of the truly green H_2 production facility that became operational recently, in the year 2022, in Spain is shown in Figure 16. This plant is based on polymer electrolyte membrane, PEM cell and is capable of producing ~ 360 kg of H_2 every hour which is used mainly to produce 'green ammonia'. This plant is powered by a 100 MWp photovoltaic solar facility located near the adjacent fields as seen in Figure 16. To compensate the varying solar power generation, a 5 MW Li-ion battery system capable of 20 MWh storage is also part of this H_2 production facility.[58] It is seen that green H_2 production requires setting up large and exclusive renewable electricity generation plants such as solar photovoltaics, wind mill farms or captive hydroelectric power stations along with power storage systems such as Li-ion battery systems. Setting up these dedicated electrical power generation plants will require both material and economic resources. In the short term, they will lead to generation of emissions and pollutants as well as create materials supply risks. For e.g. setting up just a 1 MWp Si photovoltaic (PV) power plant will require anywhere from 2.0 t to 7.0 t of 9N purity solar grade Si apart from other materials and will result in emitting about 680 t to 1720 t of CO_2(e) into the atmosphere.[59] This however is not completely feasible and conventional methods of electrical energy generation will be needed. The electricity generation mix varies from country to country and as a result the net emissions also vary. The net emissions considering two extreme limits for CO_2 emission to generate electricity across the world show that they are in the range of 100's of Gt per year, Figure 13, a significant fraction of available carbon limits for global warming. Another major input for water splitting is water which is required in Gt quantities every year. This will lead to stresses in human water consumption requirement as well as food production. The fact that extremely pure water is needed for electrolysis means that water purification will result in generation of 'brine or salt' concentrate and release of this will lead to ecological damage as given by the various parameters in Table 9.[60] Terrestrial toxicity will be ~ 53 million tons while acidification is 0.25 million tons for the year 2023 alone and increases with increasing H_2 production. The ecological impacts are extremely significant and show the non-viability of this technology. An alternative to fresh water electrolysis would be direct sea water electrolysis using renewable electrical energy which will be highly effective and completely sustainable. A recent study has demonstrated the feasibility of such a process using renewable wind energy.[61] An important point to be noted here however is that the water generated due to usage of H_2 can in-principle be reused for electrolysis again, thus completing the cycle. This however requires effective sequestration and transport of water to the electrolysis unit which becomes a logistical near impossibility. The water produced as a result of use cannot be used either for human consumption or agriculture as it is highly ‘demineralised’ and hence has to be released into the atmosphere, if it is not to be sequestered for reuse in electrolysis. The electrolysis process also requires electrode material, Ni of the order of million tons. Although it becomes enormous magnitude wise, it is not a recurring consumable and has a finite life. Its supply however can become critical as it is used in a wide variety of applications ranging from catalysis to stainless steel manufacturing. The other materials that will be needed to implement large scale H_2 utilization will be available in sufficient quantity and may not pose significant supply chain risk.

The case of producing green H_2 is being pursued actively across the world as it is being forecast to play a significant role in decarbonizing energy generation as well as supplement grey H_2 usage in several hard-to-abate applications.[62] The two main factors that limit the large scale adoption of green H_2 are; availability of renewable electricity and capital costs involved in installation of green H_2 plants. Regarding establishing dedicated renewable electricity generation facility, as mentioned earlier with the example of solar PV, it will have associated materials supply risks and short term emissions which need careful planning and execution. Three of the major producers, the European Union, United States of America and Canada have recently specified strict regulatory conditions for green H_2 projects, commonly referred to as the ‘3 pillars’.[63] These requires; 1) the electrolysers electricity consumption to match renewable electricity production timing, 2) electrolysers to source electricity from within the same region and 3) that the renewable electricity is sourced from newly establishes sources. The solar PV and wind mill electricity generation are inherently intermittent in nature and thus require intermediate electricity storage system such as batteries. In such cases will it be considered as violation of first regulation of the 3 pillars is debatable. The two other regulations/pillars imply that both renewable electricity generation systems and electrolysers should be in the same geographical region and they be newly installed. Additionally, the regulations also specify that CO_2(e) emissions should be limited to 3.4 kg and 4 kg per kg of green H_2 produced. An important sustainability factor which becomes crucial is the financial resources required to implement large scale production facilities. The SMR process has been in use for several decades and so the financial resources needed can be estimated with accuracy. It has been found that implementing an SMR plant together with CCSU capability will result in ~ USD 2.5 per kg of blue H_2 produced. The cost for establishing a large industrial scale water electrolysis unit however is not known with the level of accuracy that is built into SMR process costs. It has been estimated to cost ~ USD 5.2 per kg of green H_2 by water splitting using the alkaline electrolytical cell. These clearly show that green H_2 production at a large scale to meet the demands of an H_2 economy has many challenges to face and to become economically and environmentally viable. Irrespective of the technology being used to transition to H_2 based energy production, it would cost trillions of USD to implement and this requires a concrete policy decision by individual countries. One important point to be noted in this context of energy transition is that energy, environmental, ecological and financial costs associated with decommissioning the existing fossil fuel based energy generation and utilization structures have to factored in the sustainability analysis of H_2 based energy supply and thus a 'H_2 economy'.

6. Conclusions:

Hydrogen based energy supply has been projected as an alternative to decarbonise the energy sector and thus reduce or arrest the global warming phenomenon. This has led to the phrase 'hydrogen economy' in several discussions across the world's energy fora. Hence an exhaustive review of known hydrogen production technologies has been performed to assess the potential of hydrogen based energy supply from the perspective of sustainability as defined by embodied energy, environmental, ecological and financial parameters. The various conclusions of this analysis are given below;

1) The SMR process is a mature technology and has the potential to be scaled-up. The current status of this process is that it produces grey H_2 and efforts are underway to make it blue by sequestering the emissions. Another effort that is currently being investigated is to make it completely green by using renewable electrical energy. Even if these efforts succeed, the question of supply chain risk of natural gas is extremely high as the quantities required are about 3 orders of magnitude higher compared to current production. Additionally, the risk of direct methane emission into the atmosphere becomes finite and thus increases the global

View Article Online
DOI: 10.1039/D4SU00420E

warming phenomenon considerably, albeit on a shorter time scale. This technology however cannot avoid the baseline emission of CO_2 due to CH_4 oxidation, i.e. 1 mole of CO_2 for every mole of CH_4 reformed. Hence on a larger scale this technique cannot satisfy all the sustainability criteria and can at best be a partial/temporary method to produce large quantities of H_2.

2) Splitting water to produce H_2 by electrolysis is highly promising from emissions perspective of just the process. This process however requires extremely large quantities of electrical energy, the generation of which results in highly unwanted quantities of global warming gases to be emitted. Several technological as well as legislative measures are currently underway to make green H_2 more sustainable. Unless the electrical energy supply is completely decarbonized this process becomes totally unsustainable from environmental and ecological criteria. It also puts severe stress on fresh water availability which can be overcome by switching to direct sea water electrolysis. Such alternatives which combine sea water electrolysis with renewable electricity are the best way forward in switching to H_2 gas based energy generation.

3) The large scale production of H_2 using either of the technologies results in significant and disastrous ecological impact. Even if both the technologies change to using renewable energy and resort to CCSU measures, the ecological impact will not be mitigated. This becomes extremely critical and has to be completely addressed before transitioning to an H_2 based energy generation and an 'H_2 economy'.

4) In the recent times several naturally occurring H_2 sources have been discovered. Apart from this, methods to produce H_2 exploiting the geological formations such as the serpentinization reaction will be extremely useful in producing green hydrogen with extremely low emissions. Geological explorations to discover new sources will contribute significantly to 'greening' the H_2 based energy sector.

In summary, electrolysis of sea water using renewable electricity or even low carbon emitting nuclear electricity will be the best way forward in the long run for transitioning to extremely low carbon emission method of energy generation. Naturally occurring H_2 as well as that being produced by reactions like serpentinization will contribute to greening of the energy sector. These alternatives are sustainable and need active global support. Based on the overall energy, environmental and ecological considerations it is clear that transitioning to a completely H_2 based energy supply as envisioned by 'H_2 economy' is not feasible based

View Article Online
DOI: 10.1039/D4SU00420E

on currently known technologies. As an energy vector, H_2 can only be a part of the total energy scenario comprising of different renewables including nuclear electricity generation.

Acknowledgements: The author wishes to acknowledge the Indian Institute of Technology Bombay for the provision of facilities.

Declaration: The author has not received any funding for this work and there are no conflicts of interest.

Data Declaration: All the data used in this work is from open literature and is given in at the relevant sections.

References:

1) Holland GB, Provensano JJ. The Hydrogen Age - empowering a clean energy future. Utah: Gibbs Smith; 2007.

2) Davis SJ, Lewis NS, Shaner M, Aggarwal S, Arent D, Azevedo IL, et al. Net-zero emissions energy systems. Science [Internet]. 2018;360(6396). Available from: http://dx.doi.org/10.1126/science.aas9793

3) Global Hydrogen Review 2023 [Internet]. IEA. [cited 2024 Sep 6]. Available from: https://www.iea.org/reports/global-hydrogen-review-2023

4) Madadi Avargani V, Zendehboudi S, Cata Saady NM, Dusseault MB. A comprehensive review on hydrogen production and utilization in North America: Prospects and challenges. Energy Convers Manag [Internet]. 2022;269(115927):115927. Available from: http://dx.doi.org/10.1016/j.enconman.2022.115927

5) Ishaq H, Dincer I, Crawford C. A review on hydrogen production and utilization: Challenges and opportunities. Int J Hydrogen Energy [Internet]. 2022;47(62):26238–64. Available from: http://dx.doi.org/10.1016/j.ijhydene.2021.11.149

6) The Future of Hydrogen [Internet]. IEA. [cited 2024 Sep 6]. Available from: https://www.iea.org/reports/the-future-of-hydrogen

7) IRENA (2020), *Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.50C Climate Goal*, International Renewable Energy Agency, Abu Dhabi.

8) Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. Renew Sustain Energy Rev [Internet]. 2017;67:597–611. Available from: http://dx.doi.org/10.1016/j.rser.2016.09.044

9) Derwent R, Simmonds P, O'Doherty S, Manning A, Collins W, Stevenson D. Global environmental impacts of the hydrogen economy. Int J Nucl Hydrog Prod Appl

View Article Online
DOI: 10.1039/D4SU00420E

[Internet]. 2006;1(1):57. Available from: http://dx.doi.org/10.1504/ijnhpa.2006.009869

10) Hassan Q, Abdulateef AM, Hafedh SA, Al-samari A, Abdulateef J, Sameen AZ, et al. Renewable energy-to-green hydrogen: A review of main resources routes, processes and evaluation. Int J Hydrogen Energy [Internet]. 2023;48(46):17383–408. Available from: http://dx.doi.org/10.1016/j.ijhydene.2023.01.175

11) Oliveira AM, Beswick RR, Yan Y. A green hydrogen economy for a renewable energy society. Curr Opin Chem Eng [Internet]. 2021;33(100701):100701. Available from: http://dx.doi.org/10.1016/j.coche.2021.100701

12) Falcone PM, Hiete M, Sapio A. Hydrogen economy and sustainable development goals: Review and policy insights. Curr Opin Green Sustain Chem [Internet]. 2021;31(100506):100506. Available from: http://dx.doi.org/10.1016/j.cogsc.2021.100506

13) Bockris JOM. The hydrogen economy: Its history. Int J Hydrogen Energy [Internet]. 2013;38(6):2579–88. Available from: http://dx.doi.org/10.1016/j.ijhydene.2012.12.026

14) Zgonnik V. The occurrence and geoscience of natural hydrogen: A comprehensive review. Earth Sci Rev [Internet]. 2020;203(103140):103140. Available from: http://dx.doi.org/10.1016/j.earscirev.2020.103140

15) Boreham CJ, Edwards DS, Czado K, Rollet N, Wang L, van der Wielen S, et al. Hydrogen in Australian natural gas: occurrences, sources and resources. APPEA J [Internet]. 2021;61(1):163. Available from: http://dx.doi.org/10.1071/aj20044

16) Lollar BS, Onstott TC, Lacrampe-Couloume G, Ballentine CJ. The contribution of the Precambrian continental lithosphere to global H2 production. Nature [Internet]. 2014;516(7531):379–82. Available from: http://dx.doi.org/10.1038/nature14017

17) Warr O, Giunta T, Ballentine CJ, Sherwood Lollar B. Mechanisms and rates of 4He, 40Ar, and H2 production and accumulation in fracture fluids in Precambrian Shield environments. Chem Geol [Internet]. 2019;530(119322):119322. Available from: http://dx.doi.org/10.1016/j.chemgeo.2019.119322

18) Frieder Klein, Jesse D. Tarnas, and Wolfgang Bach. Abiotic Sources of Molecular Hydrogen on Earth. Elements. 2020;19–24

19) Incer-Valverde J, Korayem A, Tsatsaronis G, Morosuk T. “Colors” of hydrogen: Definitions and carbon intensity. Energy Convers Manag [Internet]. 2023;291(117294):117294. Available from: http://dx.doi.org/10.1016/j.enconman.2023.117294

20) Hand E. Hidden hydrogen. Science [Internet]. 2023;379(6633):630–6. Available from: http://dx.doi.org/10.1126/science.adh1477

21) Ajanovic A, Sayer M, Haas R. The economics and the environmental benignity of different colors of hydrogen. Int J Hydrogen Energy [Internet]. 2022;47(57):24136–54. Available from: http://dx.doi.org/10.1016/j.ijhydene.2022.02.094

22) Osselin F, Soulaine C, Fauguerolles C, Gaucher EC, Scaillet B, Pichavant M. Orange hydrogen is the new green. Nat Geosci [Internet]. 2022;15(10):765–9. Available from: http://dx.doi.org/10.1038/s41561-022-01043-9

23) Leung WB, March NH, Motz H. Primitive phase diagram for hydrogen. Phys Lett A [Internet]. 1976;56(6):425–6. Available from: http://dx.doi.org/10.1016/0375-9601(76)90713-1

24) https://www.hysafe.org/download/1196/BRHS_Chap1_V1p2.pdf

25) Rand DAJ, Dell RM. Hydrogen Energy: Challenges and Prospects. Cambridge, England: Royal Society of Chemistry; 2007.

26) Brandt AR. Greenhouse gas intensity of natural hydrogen produced from subsurface geologic accumulations. Joule [Internet]. 2023;7(8):1818–31. Available from: http://dx.doi.org/10.1016/j.joule.2023.07.001

27) Prinzhofer A, Tahara Cissé CS, Diallo AB. Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali). Int J Hydrogen Energy [Internet]. 2018;43(42):19315–26. Available from: http://dx.doi.org/10.1016/j.ijhydene.2018.08.193

28) Albers E, Bach W, Pérez-Gussinyé M, McCammon C, Frederichs T. Serpentinization-driven H2 production from continental break-up to mid-Ocean Ridge spreading: Unexpected high rates at the West Iberia margin. Front Earth Sci [Internet]. 2021;9. Available from: http://dx.doi.org/10.3389/feart.2021.673063

29) Boretti A, Banik BK. Advances in hydrogen production from natural gas reforming. Adv Energy Sustain Res [Internet]. 2021;2(11). Available from: http://dx.doi.org/10.1002/aesr.202100097

30) Muritala IK, Guban D, Roeb M, Sattler C. High temperature production of hydrogen: Assessment of non-renewable resources technologies and emerging trends. Int J Hydrogen Energy [Internet]. 2020;45(49):26022–35. Available from: http://dx.doi.org/10.1016/j.ijhydene.2019.08.154

31) Rau F, Herrmann A, Krause H, Fino D, Trimis D. Efficiency of a pilot-plant for the autothermal reforming of biogas. Int J Hydrogen Energy [Internet]. 2019;44(35):19135–40. Available from: http://dx.doi.org/10.1016/j.ijhydene.2018.04.014

View Article Online
DOI: 10.1039/D4SU00420E

32) Kidnay AJ, Kidnay AJ, Parrish WR. Fundamentals of natural gas processing. CRC Press; 2006.

33) Feng J, Sun X, Li Z, Hao X, Fan M, Ning P, et al. Plasma-assisted reforming of methane. Adv Sci (Weinh) [Internet]. 2022;9(34). Available from: http://dx.doi.org/10.1002/advs.202203221

34) Masoudi Soltani S, Lahiri A, Bahzad H, Clough P, Gorbounov M, Yan Y. Sorption-enhanced steam methane reforming for combined CO2 capture and hydrogen production: A state-of-the-art review. Carbon Capture Science & Technology [Internet]. 2021;1(100003):100003. Available from: http://dx.doi.org/10.1016/j.ccst.2021.100003

35) Chatenet M, Pollet BG, Dekel DR, Dionigi F, Deseure J, Millet P, et al. Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments. Chem Soc Rev [Internet]. 2022;51(11):4583–762. Available from: http://dx.doi.org/10.1039/d0cs01079k

36) Dhoke C, Zaabout A, Cloete S, Amini S. Review on reactor configurations for adsorption-based CO_2 capture. Ind Eng Chem Res [Internet]. 2021;60(10):3779–98. Available from: http://dx.doi.org/10.1021/acs.iecr.0c04547

37) Pal N, Agarwal M. Advances in materials process and separation mechanism of the membrane towards hydrogen separation. Int J Hydrogen Energy [Internet]. 2021;46(53):27062–87. Available from: http://dx.doi.org/10.1016/j.ijhydene.2021.05.175
38) US Energy Information Administration. International Energy Outlook 2023. 2023. https://www.eia.gov/outlooks/ieo/pdf/IEO2023_narrative.pdf

39) Spath PL, Mann MK. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming. 2001. https://www.nrel.gov/docs/fy01osti/27637.pdf

40) Gonzales-Calienes G, Kannangara M, Yang J, Shadbahr J, Deces-Petit C, Bensebaa F, et al. Life cycle assessment of hydrogen production pathways in Canada. National Research Council of Canada; 2022.

41) Al-Qahtani A, Parkinson B, Hellgardt K, Shah N, Guillen-Gosalbez G. Uncovering the true cost of hydrogen production routes using life cycle monetisation. Appl Energy [Internet]. 2021;281(115958):115958. Available from: http://dx.doi.org/10.1016/j.apenergy.2020.115958

42) Antonini C, Treyer K, Streb A, van der Spek M, Bauer C, Mazzotti M. Hydrogen production from natural gas and biomethane with carbon capture and storage – A techno-environmental analysis. Sustain Energy Fuels [Internet]. 2020;4(6):2967–86. Available from: http://dx.doi.org/10.1039/d0se00222d

View Article Online
DOI: 10.1039/D4SU00420E

43) Mehmeti A, Angelis-Dimakis A, Arampatzis G, McPhail S, Ulgiati S. Life cycle assessment and water footprint of hydrogen production methods: From conventional to emerging technologies. Environments [Internet]. 2018;5(2):24. Available from: http://dx.doi.org/10.3390/environments5020024

44) Salkuyeh YK, Saville BA, MacLean HL. Techno-economic analysis and life cycle assessment of hydrogen production from different biomass gasification processes. Int J Hydrogen Energy [Internet]. 2018;43(20):9514–28. Available from: http://dx.doi.org/10.1016/j.ijhydene.2018.04.024

45) Siddiqui O, Dincer I. A well to pump life cycle environmental impact assessment of some hydrogen production routes. Int J Hydrogen Energy [Internet]. 2019;44(12):5773–86. Available from: http://dx.doi.org/10.1016/j.ijhydene.2019.01.118

46) Valente A, Iribarren D, Dufour J. Prospective carbon footprint comparison of hydrogen options. Sci Total Environ [Internet]. 2020;728(138212):138212. Available from: http://dx.doi.org/10.1016/j.scitotenv.2020.138212

47) Ghandehariun S, Kumar A. Life cycle assessment of wind-based hydrogen production in Western Canada. Int J Hydrogen Energy [Internet]. 2016;41(22):9696–704. Available from: http://dx.doi.org/10.1016/j.ijhydene.2016.04.077

48) Koj J, Wulf C, Schreiber A, Zapp P. Site-dependent environmental impacts of industrial hydrogen production by alkaline water electrolysis. Energies [Internet]. 2017;10(7):860. Available from: http://dx.doi.org/10.3390/en10070860

49) Kuckshinrichs W, Koj JC. Levelized cost of energy from private and social perspectives: The case of improved alkaline water electrolysis. J Clean Prod [Internet]. 2018;203:619–32. Available from: http://dx.doi.org/10.1016/j.jclepro.2018.08.232

50) Valente A, Iribarren D, Dufour J, Spazzafumo G. Life-cycle performance of hydrogen as an energy management solution in hydropower plants: A case study in Central Italy. Int J Hydrogen Energy [Internet]. 2015;40(46):16660–72. Available from: http://dx.doi.org/10.1016/j.ijhydene.2015.09.104

51) Wulf C, Kaltschmitt M. Hydrogen supply chains for mobility—environmental and economic assessment. Sustainability [Internet]. 2018;10(6):1699. Available from: http://dx.doi.org/10.3390/su10061699

52) CO2 Emissions in 2023 [Internet]. IEA. [cited 2024 Sep 6]. Available from: https://www.iea.org/reports/co2-emissions-in-2023

53) Hydrogen: Forging the future with SMR-X^{TM} technology/Air Liquide [cited 2024 Sep 6]. Available from: http://www.airiquide.com

View Article Online
DOI: 10.1039/D4SU00420E

54) Hajizadeh A, Mohamadi-Baghmolaei M, Cata Saady NM, Zendehboudi S. Hydrogen production from biomass through integration of anaerobic digestion and biogas dry reforming. Appl Energy [Internet]. 2022;309(118442):118442. Available from: http://dx.doi.org/10.1016/j.apenergy.2021.118442

55) Demey H, Ratel G, Lacaze B, Delattre O, Haarlemmer G, Roubaud A. Hydrogen production by catalytic supercritical water gasification of black liquor-based wastewater. Energies [Internet]. 2023;16(8):3343. Available from: http://dx.doi.org/10.3390/en16083343

56) Mohamadi-Baghmolaei M, Zahedizadeh P, Hajizadeh A, Zendehboudi S. Hydrogen production through catalytic supercritical water gasification: Energy and char formation assessment. Energy Convers Manag [Internet]. 2022;268(115922):115922. Available from: http://dx.doi.org/10.1016/j.enconman.2022.115922

57) Cho HH, Strezov V, Evans TJ. Environmental impact assessment of hydrogen production via steam methane reforming based on emissions data. Energy Rep [Internet]. 2022;8:13585–95. Available from: http://dx.doi.org/10.1016/j.egyr.2022.10.053

58) Puertollano green hydrogen plant – Iberdrola, [cited 2024 Sep 6] Available from: https://www.iberdrola.com.

59) Vitta S. Materials and environmental sustainability of scaling Silicon Photovoltaics to 50 TWp. 2024; (submitted).

60) Zhao G, Kraglund MR, Frandsen HL, Wulff AC, Jensen SH, Chen M, et al. Life cycle assessment of H2O electrolysis technologies. Int J Hydrogen Energy [Internet]. 2020;45(43):23765–81. Available from: http://dx.doi.org/10.1016/j.ijhydene.2020.05.282

61) Liu T, Zhao Z, Tang W, Chen Y, Lan C, Zhu L, et al. In-situ direct seawater electrolysis using floating platform in ocean with uncontrollable wave motion. Nat Commun [Internet]. 2024;15(1). Available from: http://dx.doi.org/10.1038/s41467-024-49639-6

62) IRENA (2020), *Green Hydrogen: A guide to policy making*, International Renewable Energy Agency, Abu Dhabi

63) The “three pillars” are gaining momentum in the green hydrogen industry, [cited 2024 Sep 6] Available from: https://www.gh2.org

View Article Online
DOI: 10.1039/D4SU00420E

Property	Value
Density (Gas)	**$8.988x10^{-5}$ gcm^{-3}**
Density (Liquid)	**$70.8x10^{-3}$gcm^{-3}**
Higher Heating Value (HHV)	**142 MJkg^{-1}/ 12.77 MJm^{-3}/ 39.45 kWhkg^{-1}/3.946 kWhm^{-3}**
Lower Heating Value (LHV)	**120 MJkg^{-1}/10.79 MJm^{-3}/33.33 kWhkg^{-1}/2.99 kWhm^{-3}**
Energy density of gasoline	**46 MJkg^{-1}/12.2 kWhkg^{-1}/$9.7x10^{3}$ kWhm^{-3}**
Heat of Vaporisation	**444 kJkg^{-1}**
Ignition Temperature	**585 °C**
Lower Flammability Limit, in air	**4 vol.%**
Upper Flammability Limit, in air	**75 vol.%**
Pressure, MPa	**Energy Content, 10^{3}MJm^{-3}**
20	**2.53**
55	**6.96**
70	**8.86**
80	**10.12**

Table 1: Physical properties of H_2 are given here along with their potential heating values or energy delivery capacity on oxidation. The higher heating value can be realized if the energy in steam is gainfully extracted. The ignition temperature is high but the lower flammability limit is only 4 vol.% which makes it crucial to control leaks. Compressing the gas to different pressure levels leads to increased energy content and hence aids transportation logistics.

View Article Online
DOI: 10.1039/D4SU00420E

Colour	**GHG reduction potential**	**Comments**
Gold	**High**	**Naturally occurring; Extraction related emissions only.**
White	**High**	**Identification of geological formation; extraction related emissions only.**
Orange	**High**	**Identification of suitable silicates; pumping water and extraction related emissions.**
Grey	**Low**	**Source (methane) and energy are from fossil resources; both have associated emissions.**
Blue	**Medium**	**Strongly dependent on emissions sequestration.**
Brown/Black	**Low**	**Source (coal) and energy from fossil resources; both have associated emissions.**
Turquoise	**Medium**	**Pyrolysis of source; Solid carbon hence no emissions; Energy for pyrolysis has emissions.**
Purple/Pink	**Medium**	**Renewable source (water); Nuclear energy (Low carbon footprint).**
Green	**High**	**Renewable source (water); Renewable energy resources.**

Table 2: A comparative statement of different colours of hydrogen with respect to their potential for greenhouse gases, GHG, emissions reduction. The comparison is limited to just three categories, high, medium and low in order to keep it simple and avoid excessive gradation. It can be seen that all forms of hydrogen have associated emissions at different stages of their production including green hydrogen.

View Article Online
DOI: 10.1039/D4SU00420E

Condition	AEC	PEM
Temperature, °C	70 - 90	50 – 80
Pressure, MPa	0.1 – 3	< 7
Electrolyte	KOH (~ 6 $molL^{-1}$)	PFSA Membrane
Separator	ZrO_2 with PPS mesh	Solid PFSA
Positive Anode	Ni-coated Stainless Steel (Perforated)	IrO_2
Porous O_2 Transport Layer	Ni-mesh	Pt-coated Ti (Porous)
Bipolar plate - Anode	Ni-coated Stainless Steel	Pt-coated Ti
Negative Cathode	Ni-coated Stainless Steel (Perforated)	C@Pt nanoparticles
Porous H_2 Transport Layer	Ni-mesh	Porous Ti or C-cloth
Bipolar plate – Cathode	Ni-coated Stainless Steel	Au-coated Ti
Frames and sealing compounds	PSU, PTFE, EPDM	PTFE, PSU, ETFE

Table 3: Typical components of aqueous electrolyte and polymer electrolyte cells and their operating conditions are given. It can be clearly seen that a variety of materials ranging from metals to ceramics and polymers constitute the typical cell, both AEM and PEM. Even nanoparticles are being used for realizing large specific surface areas in the electrodes.

View Article Online
DOI: 10.1039/D4SU00420E

	Ref. 39	Ref. 38	Refs. 40-45, 56, 59, 60
SMR Process			
Natural Gas, kg	**2.55**	**3.25**	**2.76**
Electricity, kWh	**1.31**	**0.4**	**1.8**
Water, kg	**-**	**19.8**	**17.1**

Table 4: The different input requirements for the SMR process to produce 1 kg of H_2 are given here. The nature of electricity mix varies across countries as many European countries have major contribution from renewable resources. The data is from different capacity plants and since the SMR process has been in use for several decades now, these are actual working plant requirements.

View Article Online
DOI: 10.1039/D4SU00420E

Material, kg	
ZnO	**$3.36\text{x}10^{-4}$; replenished every 2 Years (desulfurization)**
ZnO	**$2.35\text{x}10^{-5}$; replenished every 3 Years (catalyst in WGS reactor)**
Aluminum Oxide	**$7.84\text{x}10^{-6}$; replenished every 3 Years (catalyst in WGS reactor)**
Copper Oxide	**$2.09\text{x}10^{-5}$; replenished every 3 Years (catalyst in WGS reactor)**
Co_2O_3	**$2.05\text{x}10^{-5}$; replenished every 3 Years (catalyst in SMR reactor)**
Activated Carbon	**$6.92\text{x}10^{-4}$; replenished every 2 Years (PSA bed)**

Table 5: The different catalyst materials used in the natural gas reforming reactor, water shift reactor and pressure swing adsorption unit are given. These need to be changed once every 2 or 3 years and hence do not come under large scale materials requirement. These are for the production of 1 kg of H_2 gas.

View Article Online
DOI: 10.1039/D4SU00420E

Environmental parameters, kg	Ref. 51	Ref. 39	Ref. 38
CO_2	9.35 (4.69-17.31)	10.5 (7.74-12.6)	10.621
CH_4	2.36×10^{-4}	-	6×10^{-2}
NH_3	2.36×10^{-4}	-	-
CO	0.27	-	6×10^{-3}
NO_2	-	3.48×10^{-5}	-
NO_x	1.68×10^{-3}	4.77×10^{-3}	12×10^{-3}
SO_2	10^{-4}	2.58×10^{-4}	10^{-3}
$PM_{2.5}$	4.44×10^{-4}	-	-
PM_{10}	5.35×10^{-4}	-	-
VOC	9.01×10^{-4}	-	-
Pb	5.07×10^{-8}	-	-
Methanol	2.14×10^{-5}	-	-
Water	-	17.1 (7.5-21.9)	19.8

Table 6: The various environmental parameters of SMR process from different sources in literature. The most commonly reported parameter is CO_2(e) which consists of warming potential of all gaseous emissions. Apart from the gaseous emissions both 2.5 μm and 10.0 μm particulates are emitted into the atmosphere but not all reports mention these parameters. Not all environmental pollution related parameters are reported reliably in several publications. The units are kg per kg of H_2 gas produced.

View Article Online
DOI: 10.1039/D4SU00420E

	Ref. 39	**Ref. 46-50**
AEC Electrolysis Electricity, kWh	**56.1**	**54.3**
Water, kg	**13.05**	**13.3**
KOH, g	**0.81**	**1.2**

Table 7: The water splitting electrolysis plant's main requirement will be electricity apart from water. The water will be from regular brackish sources which has to be purified to be used in the electrolysis unit. Currently there are no electrolysis 'plants' which utilize directly sea water without purification. The electricity mix can vary across countries in the world to include electricity generated from renewable resources. The requirements given are typically to produce 1 kg of H_2 gas.

View Article Online
DOI: 10.1039/D4SU00420E

Ecological parameter, kg	
Freshwater ecotoxicity	**3.12×10^{-8}**
Human carcinogenic toxicity	**1.46×10^{-2}**
Human non-carcinogentic toxicity	**1.52×10^{-3}**
Marine ecotoxicity	**6.13×10^{-6}**
Ozone formation, human health	**1.68×10^{-3}**
Ozone formation, terrestrial ecosystems	**1.68×10^{-3}**
Terrestrial acidification	**1.17×10^{-3}**
Terrestrial ecotoxicity	**3.28×10^{-3}**

Table 8: The different ecological impact parameters due to H_2 production by reforming of natural gas are given. All these parameters are for the production of 1 kg of H_2 gas and the toxicity parameters are with respect to 1,4 Dicholorobenzene except Ozone formation which is NO_x equivalent and acidification which is SO_2 equivalent. These ecological parameters are due to the production of 1 kg of H_2.

View Article Online
DOI: 10.1039/D4SU00420E

Ecological parameter, kg	
Ozone depletion	**$8x10^{-6}$**
Acidification	**1.4**
Terrestrial toxicity	**$3.3x10^{2}$**
Fresh water toxicity	**3.3**
Marine toxicity	**4.7**
Human carcinogenic toxicity	**1.3**
Human non-carcinogenic toxicity	**110**

Table 9: The ecological impact of water spitting into H_2 by electrolysis in an alkaline electrolyte cell is given by these parameters. The different toxicity parameters are given in terms of equivalent 1,4 Dicholorobenzene while acidification is given in equivalent SO_2 level and the Ozone depletion is in terms of equivalent Chlorofluorocarbon 11. The data correspond to a stack unit with 1 m^2 area capable of producing ~ 29.485 tons of H_2.

View Article Online
DOI: 10.1039/D4SU00420E

Methodology:

The different requirements such as energy, materials, electrolytes, water and so on as well as the environmental parameter, mainly CO_2 emission and ecological parameters for each year have been determined based on the H_2 demand corresponding to that particular year. However the global strategy will be for transition to H_2 economy over a period of two to three decades. This means on a year-to-year basis there will be additional/incremental energy, materials, water and so on requirement over the previous year and correspondingly the emissions will be incremental compared to the previous year.

Example Calculation: Consider Year 2023 as the base year !

Energy requirement: 677.11 EJ

Equivalent H_2: 4.7684 Gt @ 142 $MJkg^{-1}$ HHV for H_2

SMR Process Requirements:

Energy for H_2 production: 4.7684 PWh @ 1 $kwhkg^{-1}$ of H_2

Natural gas: 14.305 Gt @ 3 $kgkg^{-1}$ of H_2

Water: 85.8312 Gt @ 18 $kgkg^{-1}$ of H_2

CO_2 emission: 47.684 Gt @ 10 $kgkg^{-1}$ of H_2

Energy requirement for the Year 2024: 692.33 EJ $\cong$ 4.87551 Gt

Additional H_2 over the Year 2023: 0.10713 Gt

Additional Energy: 385.668 GJ

Additional Natural gas: 0.32139 Gt

Additional Water: 1.92834 Gt

Additional CO_2 emission: 1.0713 Gt

AEC Water splitting Process Requirements:

Energy required to produce H_2: 944.136 EJ @ 55 $kWhkg^{-1}$ of H_2

Water: 61.989 Gt @ 13 $kgkg^{-1}$ of H_2

KOH: 4.7684 Mt @ 1 gkg^{-1} of H_2

CO_2 emission:

Additional Energy for 2024 over the year 2023: 21.211 PJ

Additional Water: 1.39269 Gt

Additional KOH: 0.10713 Mt

View Article Online
DOI: 10.1039/D4SU00420E

Figure Captions:

Figure 1: World Consumption of H_2 for different applications ranging from ammonia manufacturing to direct reduction of iron ore (DRI). Refining is for petrochemicals while methanol is an alternate fuel made using H_2.[6] The world consumption has increased steadily from ~ 30 Mt in 1975 to 120 Mt in 2018 with refining and ammonia production being the major users.

Figure 2: H_2 can be produced from a wide variety of natural resources – non-renewable such as natural gas and coal as well as renewable such as water. Depending on the method of production and the CO_2(e) emission potential, it has been attributed different colors which are shown here along with the method of production. Naturally occurring H_2 can also be of different origin and depending on this it has also been color coded. The exact definition of each of these variants is given in the text.

Figure 3: The pressure-temperature or phase stability diagram for H_2 shows the temperature-pressure fields where it exists as gas, liquid or solid. It can be seen that extremely low temperatures and high pressure will be required to transform from one phase to another, including the solid phase. There are several variants within the solid and liquid phases and these are not shown here for simplicity. At room temperature and atmospheric pressure it exists in the gaseous state.

Figure 4: Splitting of Water, H_2O using renewable electricity is a net-zero emission process and is also circular in nature becoming completely sustainable. This is because the product of H_2 combustion will produce H_2O which can be re used if collected at the source and recovered completely. This process can be least harmful both environmentally and ecologically.

Figure 5: The different electrolysis processes with the electrode reactions and the dominant moving ions across the membranes are shown. (a) Alkaline electrolyte solution electrolyser, AEC (b) Polymer electrolyte membrane electrolyser, PEM (c) Anion exchange membrane electrolyser, AEM and (d) Solid oxide electrolyte electrolyser, SOC. Among the 4 different type

of electrolytic cells, AEC has a liquid electrolyte while the others have solid electrolytes/membranes. The SOC process essentially operates at elevated temperatures.

Figure 6: A typical 4 column configuration of pressure swing adsorption facilitates continuous operation of the process leading to enhanced operation efficiency as well as regeneration of the catalyst. This is because multiple columns operate simultaneously and each of the columns has different functionality leading to a continuous mode of operation as far as H_2 separation is concerned. The different colors for the columns clearly indicate the different functions at any stage of the separation process. This configuration will be highly beneficial for large scale gas production.

Figure 7: The energy demand till the year 2050 has been forecast by the US Energy Information Agency's Energy outlook report of 2023 and is shown here together with the equivalent amount of H_2 gas required to generate the yearly energy demand, assuming that complete energy requirement is met by H_2. To convert the energy demand into equivalent H_2 amount the higher heating value has been used which gives the lower limit of gas requirement. The actual has requirement will be higher than the value shown here.

Figure 8: System boundary of the SMR process for life cycle assessment can be split into two distinct stages. Stage 1 concerns natural gas mining, extraction and transport to final usage site while Stage 2 is exclusively concerned with steam methane reforming of natural gas to produce H_2 which can be compressed for transport. The H_2 produced will be of 99.9 % purity and will be in gaseous form. Some life cycle assessments consider only Stage 2 while some consider both stages.

Figure 9: The magnitude of annual electrical energy required to produce H_2 gas using the SMR process is shown in (a). Electrical energy is required mainly in the reforming reactor together with natural gas and water which are shown in (b). Both natural gas and water will be required in Gt quantities every year. The materials needed to construct a H_2 plant with a production capacity of 1.5 MNm^3 per day are mentioned in the inset of (b). Apart from these, different catalyst materials will also be needed as given in Table 4. However, these are not as large in magnitude as cement, steel and Al.

Figure 10: The annual CO_2 emissions due to H_2 production using the SMR process increase with increasing energy demand from about 45 Gt to 75 Gt by the year 2050. This constitutes a significant fraction of annual global emissions. The data includes emissions due to electricity generation and are mainly from production plants in USA, Canada and Europe where there is substantial renewable electricity mix in the overall electricity generation.

Figure 11: System boundary for water splitting by electrolysis can also be separated into two distinct stages for life cycle assessment. In Stage 1 the utility water or sea water is completely purified so that it meets the input quality requirement of water electrolysis. In Stage 2 water is split into H_2 of 99.9 % purity by electrolysis and compressed so that it can be transported for further use. Several studies consider only stage 2 for life cycle assessment as stage 1 is considered as insignificant from energy and emissions consideration.

Figure 12: The electrolysis process requires significant amount of electrical energy annually for splitting water as shown in (a). This increases to ~ 1500 EJ by the year 2050 and becomes highly critical. The corresponding annual requirement of water and the electrolyte KOH are shown in (b). The water requirement is of the order of several Gt each year. The magnitude of other electrolytic cell materials such as electrodes, separators and sealants required to produce 1 kg of H_2 gas are given in inset of (b). It can be seen that these materials supply can become critical with increasing H_2 production.

Figure 13: The amount of yearly CO_2 emissions due to large scale production of H_2 using water splitting by electrolysis are shown here and it is seen that they are a significant fraction of available CO_2 emissions limit for 2.0 °C global warming scenario. Since production by electrolysis has not reached large scale industrial capacity, actual emissions data is not available. Hence the electricity demand is converted into equivalent emissions based on two limits of 390 $gkWh^{-1}$ and 820 $gkWh^{-1}$ across the world.

Figure 14: One of the recent SMR based H_2 production facility (Air Liquide's SMR-X Process) in Antwerp, Belgium produces 99.99 % pure H_2 at 56000 Nm^3 per hour rate. The plant went into operation in April 2021. This shows the complexity of the plant and also the stainless steel structurals required in the form of pipes which carry hot gases.

View Article Online
DOI: 10.1039/D4SU00420E

Figure 15: The quantity of annual global natural gas production and its estimated production till Year 2050 are shown together with the quantity required based on energy demand. It is clearly seen that projected production lags behind requirement indicating severe supply chain risk associated with H_2 production to meet the complete energy demand, H_2 economy.

Figure 16: Green H_2 production facility, Iberdrola established in the year 2022 in Spain. This water electrolysis facility produces 360 kg of H_2 per hour and is powered by solar photovoltaic plant with an installed capacity of 100 MWp. The plant also has Li-ion battery system for streamlined and steady electrical power supply to the plant. This clearly illustrates that green H_2 production requires not only renewable electricity generation system but also a electrical energy storage system.

Hydrogen production – a review and its sustainability

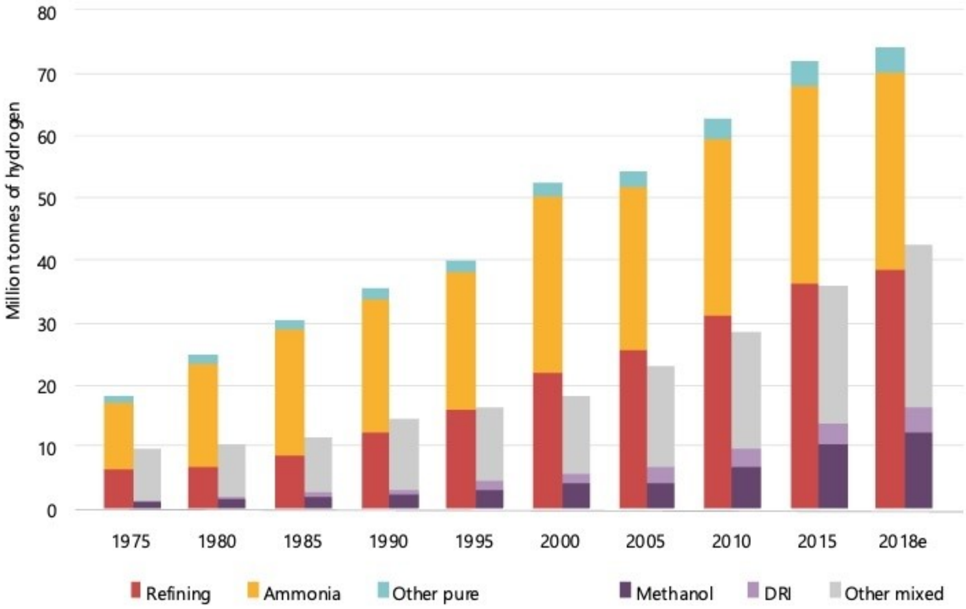
View Article Online
DOI: 10.1039/D4SU00420E

Data Availability Statement

All the data used in this manuscript has been included in the manuscript itself and does not have a separate data set.

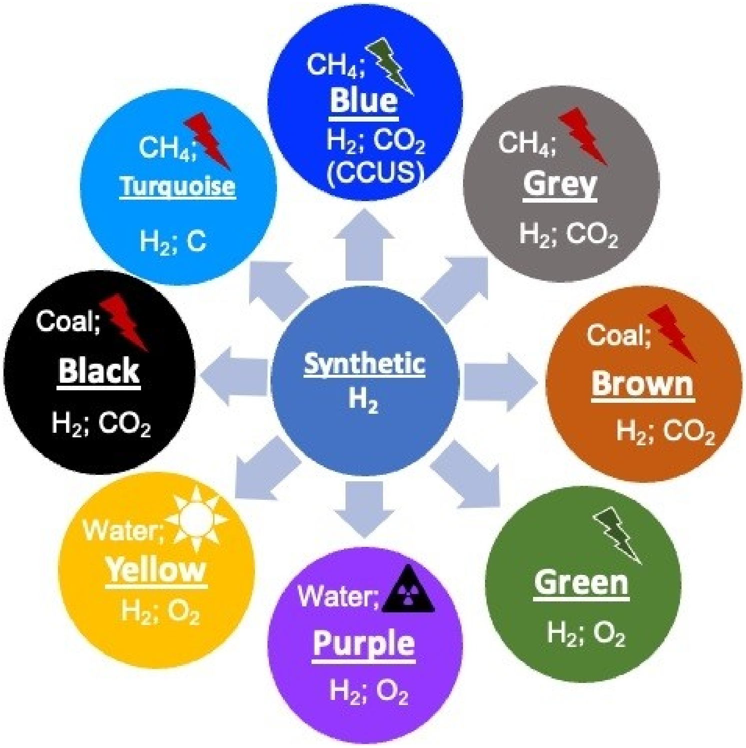
Satish Vitta.

View Article Online
DOI: 10.1039/D4SU00420E



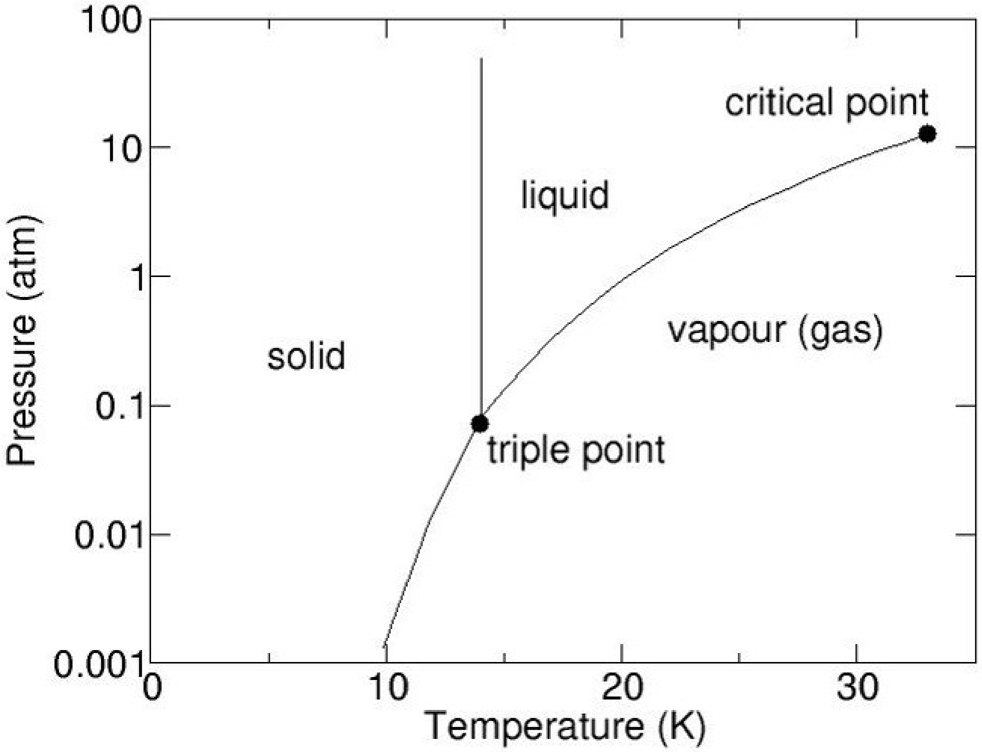
256x165mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



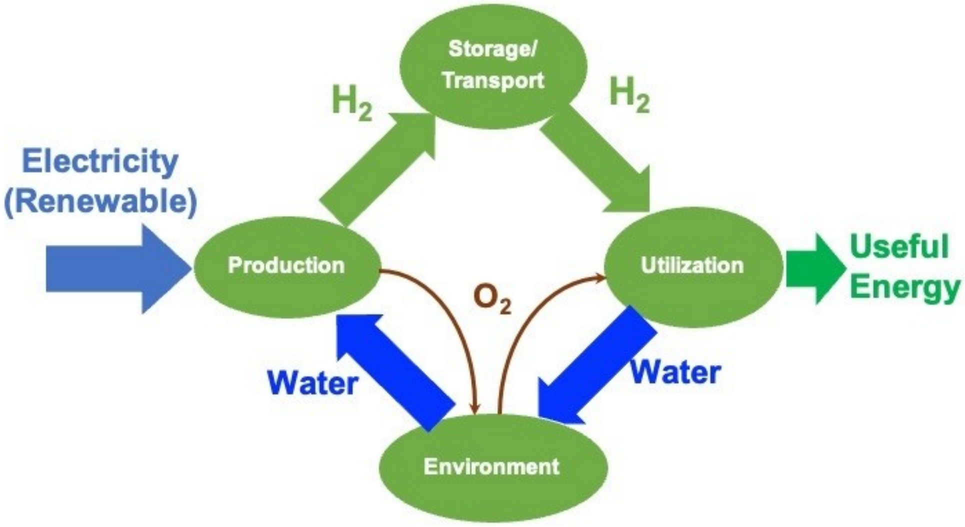
225x167mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



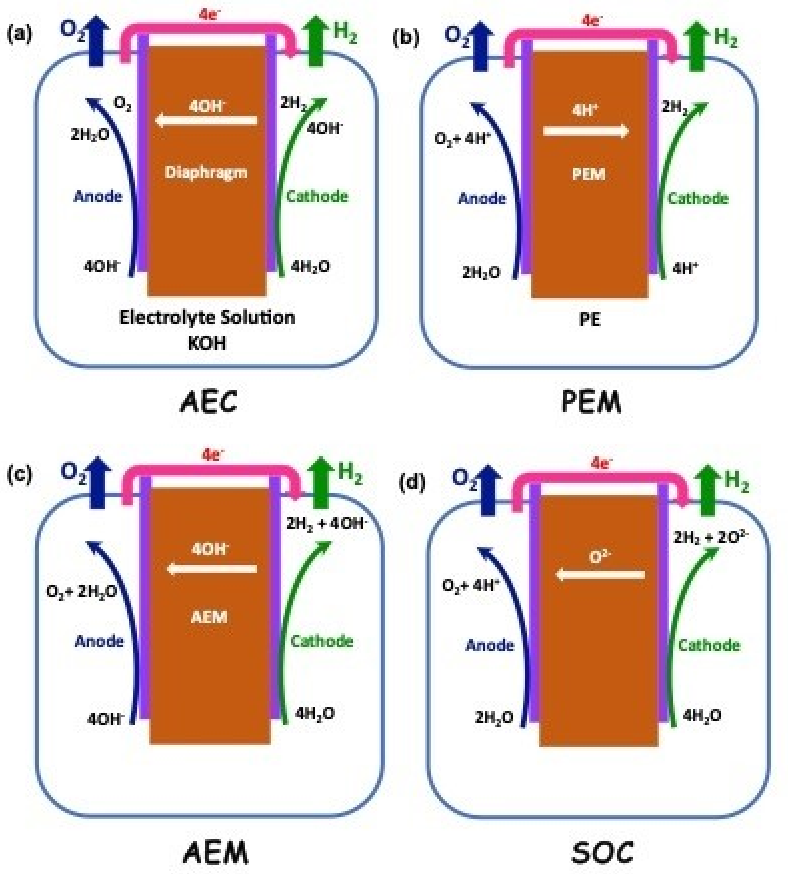
233x176mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



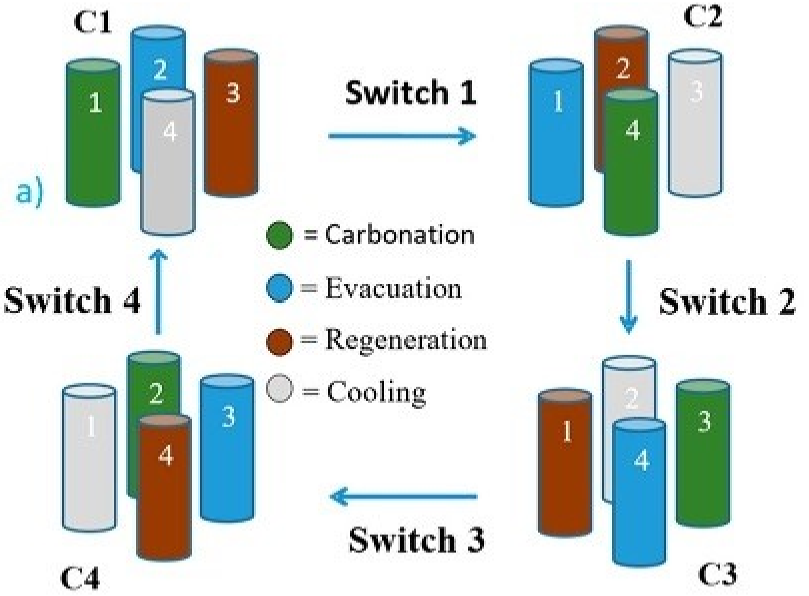
255x150mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



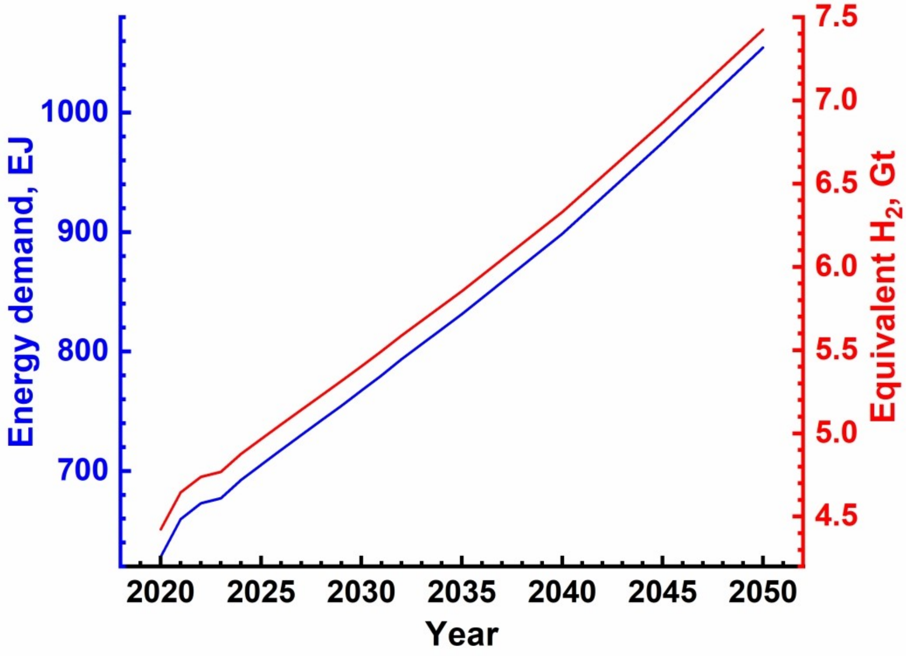
159x162mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



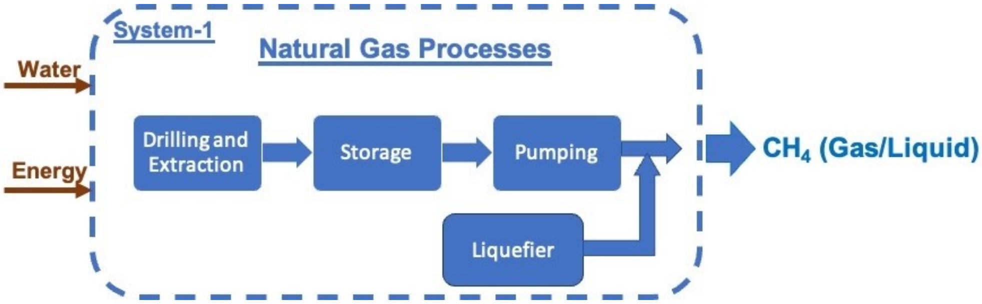
143x105mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



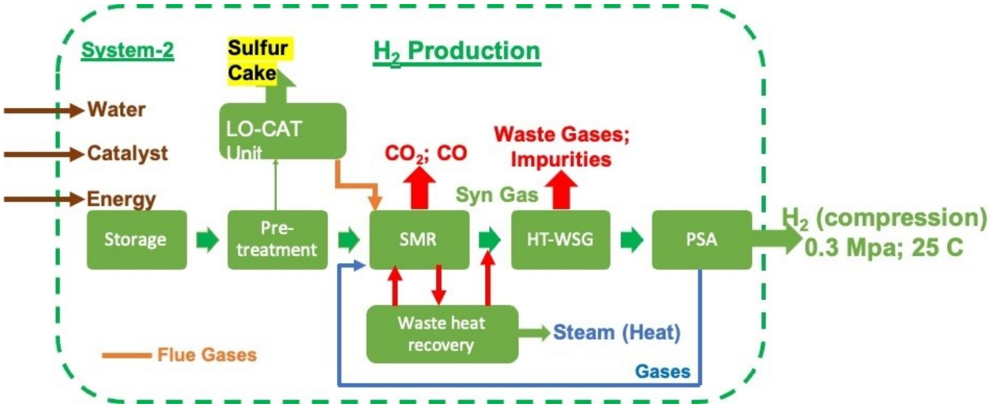
272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



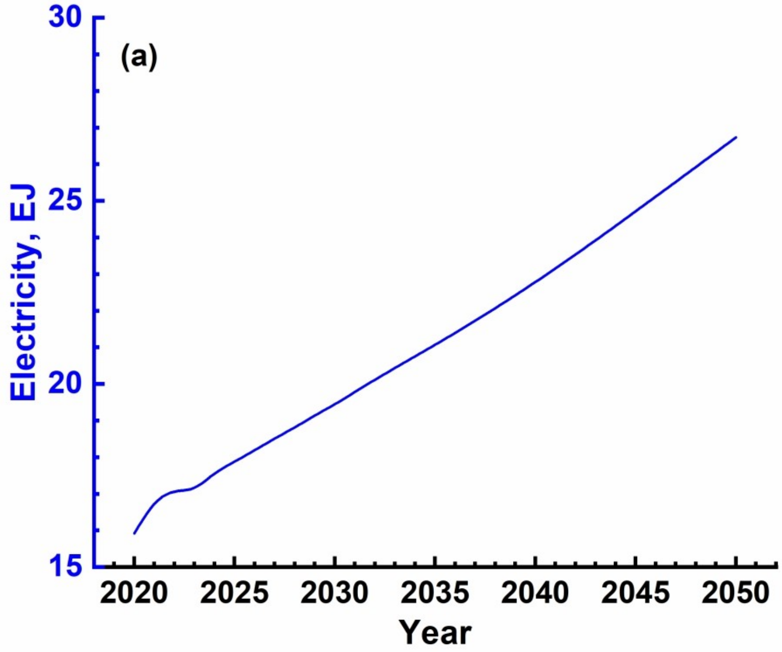
311x92mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



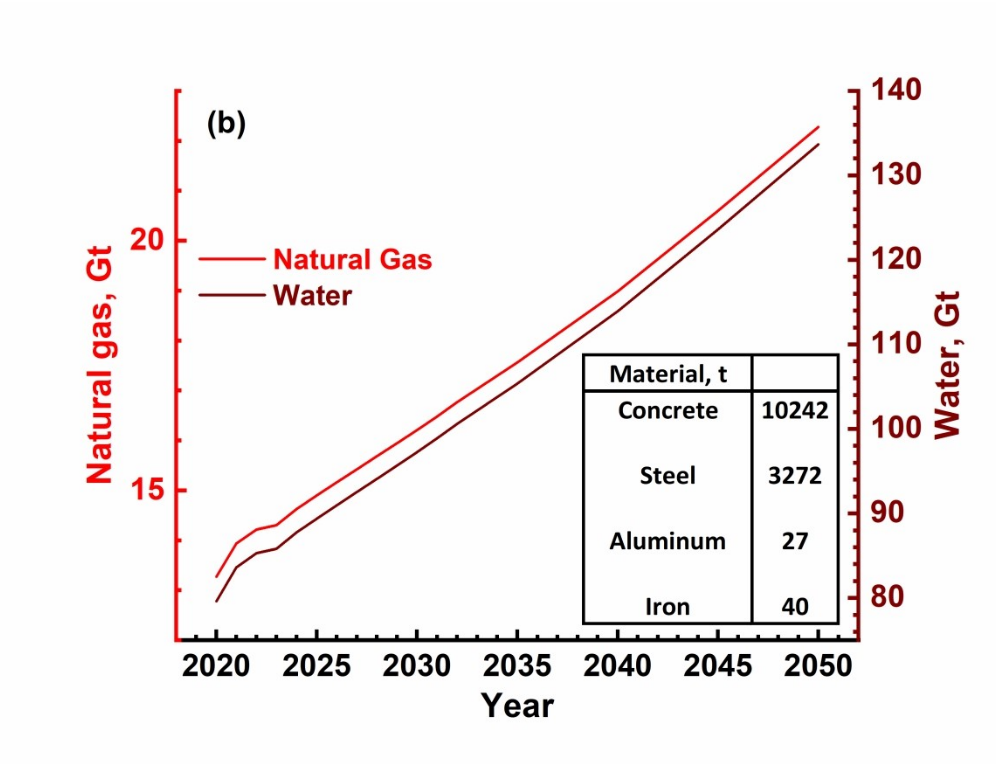
338x135mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



272x208mm (300 x 300 DPI)

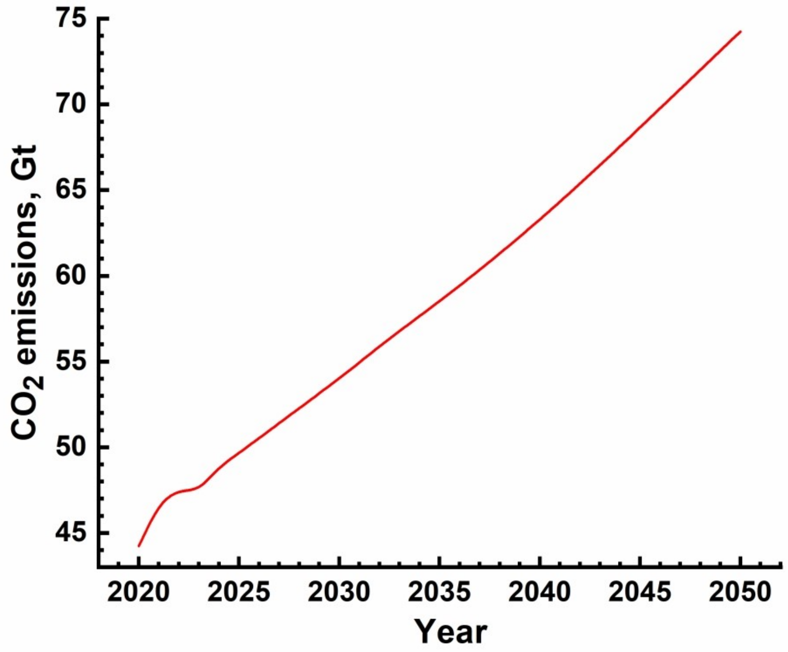
View Article Online
DOI: 10.1039/D4SU00420E



Material, t	
Concrete	10242
Steel	3272
Aluminum	27
Iron	40

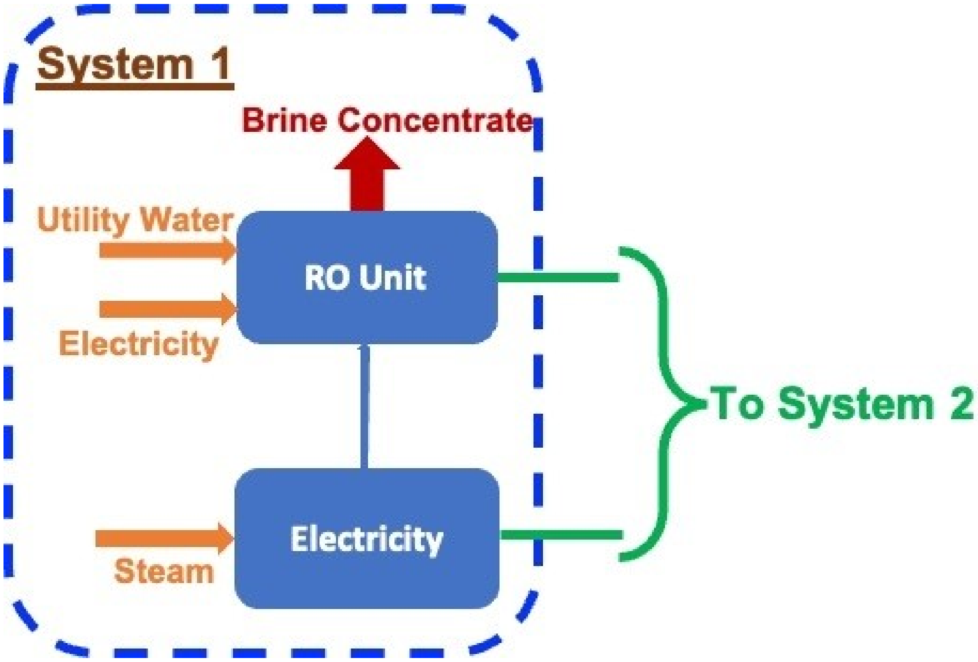
272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



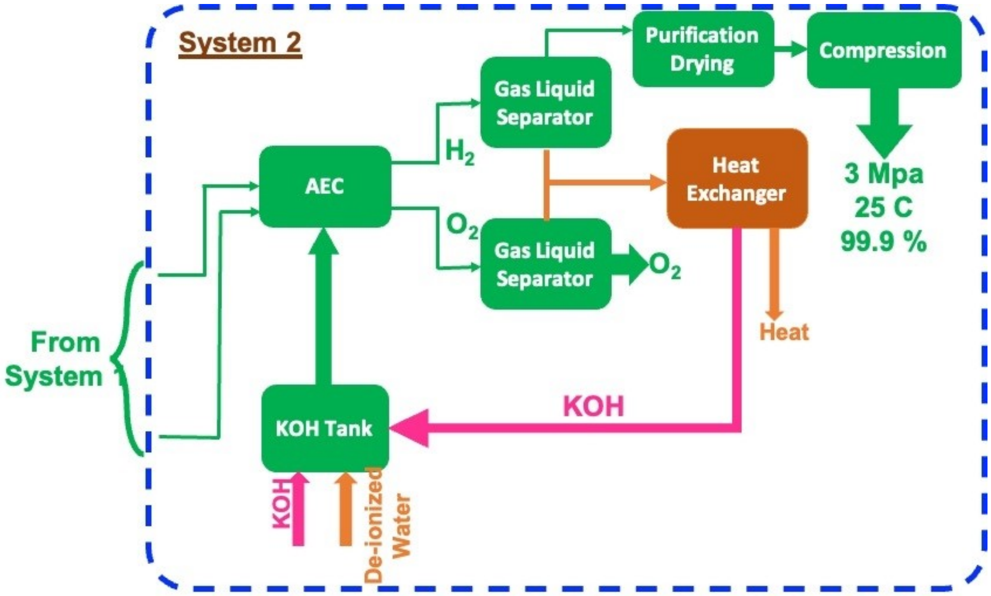
272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



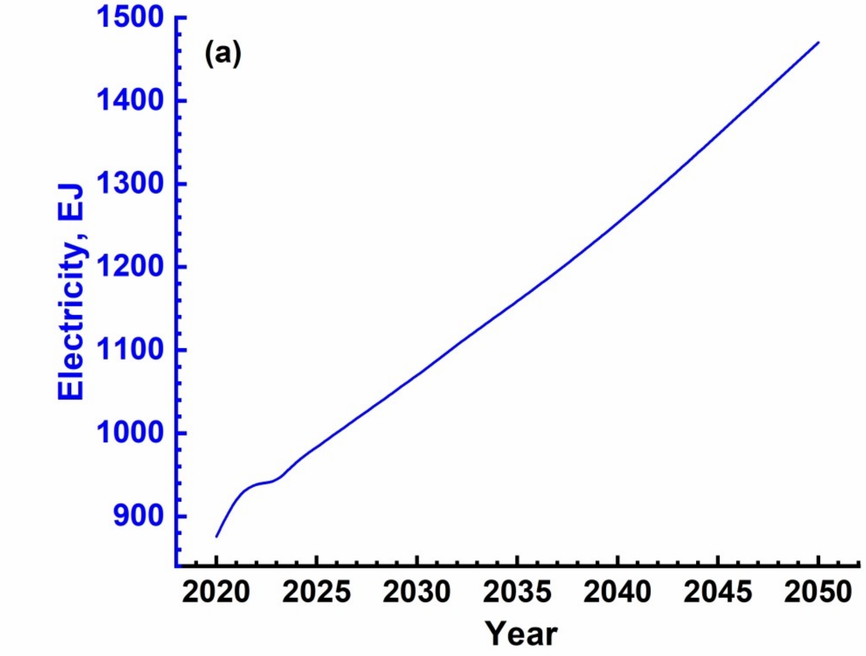
187x122mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



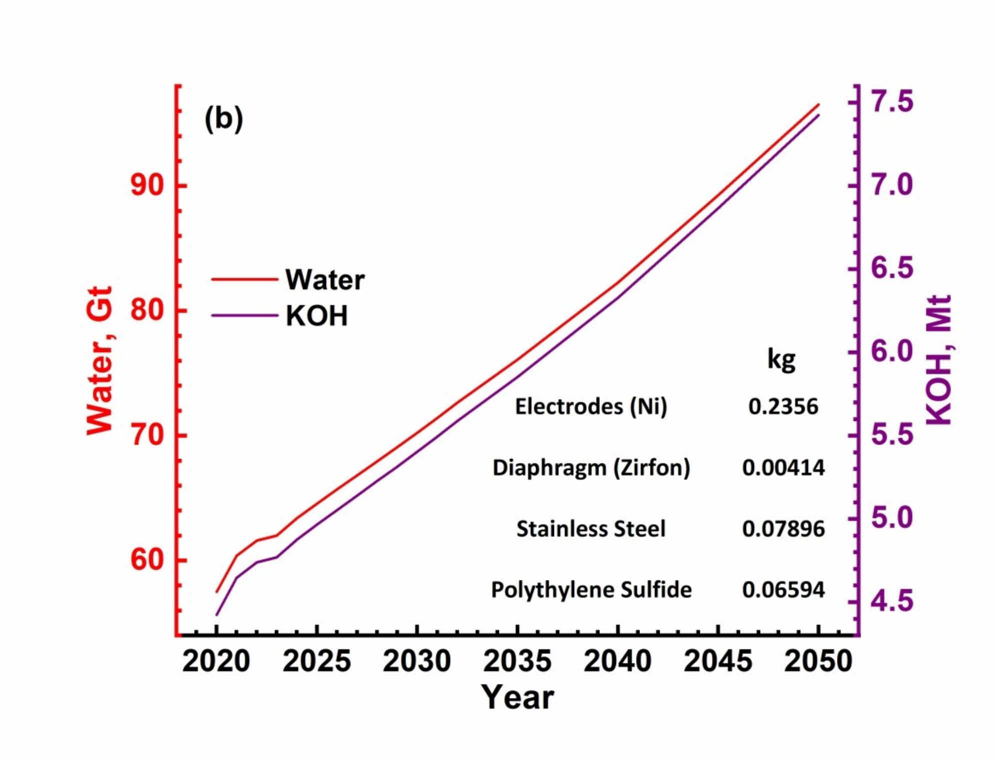
301x179mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



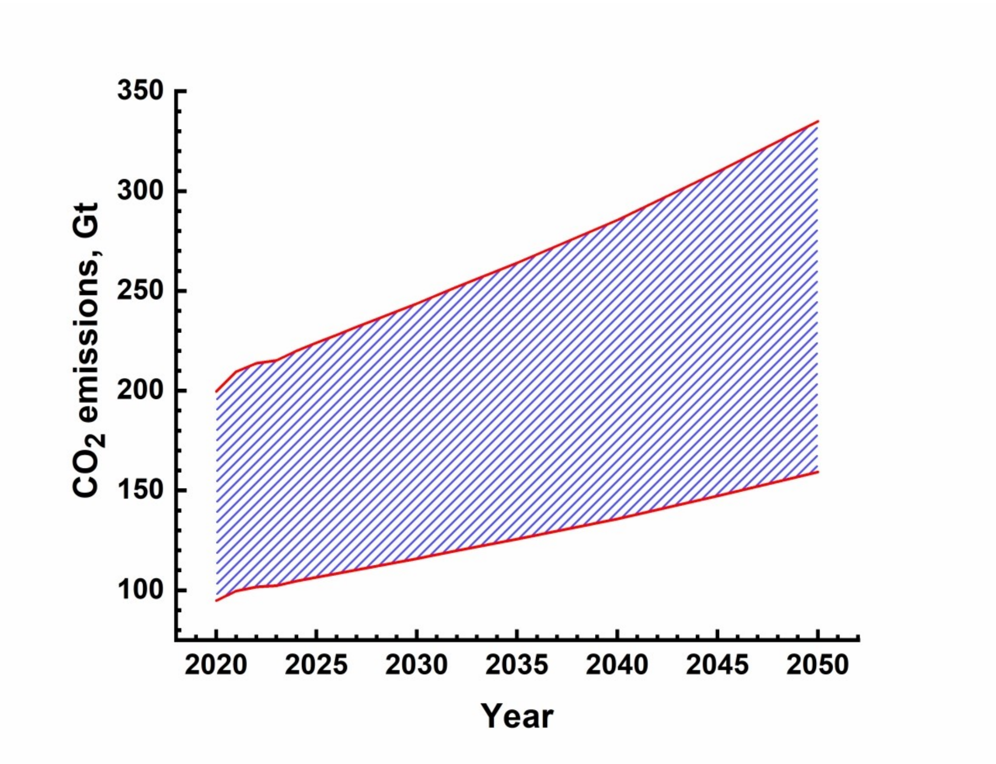
272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E

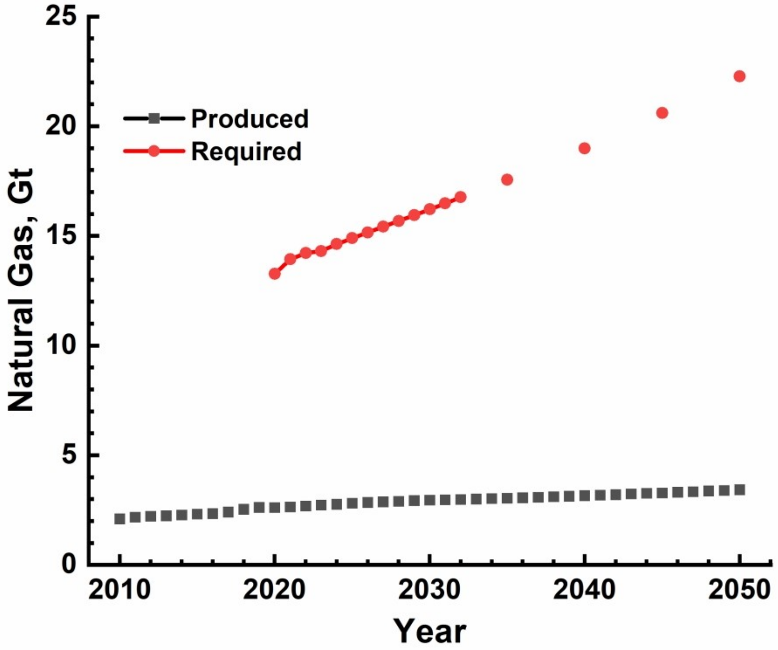


272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E

250x168mm (72 x 72 DPI)

View Article Online
DOI: 10.1039/D4SU00420E



272x208mm (300 x 300 DPI)

View Article Online
DOI: 10.1039/D4SU00420E

318x90mm (72 x 72 DPI)