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HYDROGEN PRODUCTION VIA STEAM REFORMING OF NATURAL GAS WITH INTEGRATED CARBON CAPTURE: A BRIEF OVERVIEW

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Abstract: *This article presents a succinct analysis of hydrogen as a critical component of the future energy landscape. Hydrogen produces three times as much heat as gasoline but has a 50% lower lifecycle carbon footprint than traditional fossil fuels. The benefits and characteristics of hydrogen, as well as the methods for producing it, will be discussed. With 96% of global hydrogen production currently dependent on fossil fuels, it is becoming increasingly clear that both traditional and pilot hydrogen production technologies must be investigated in order to contribute to the goal of reducing greenhouse gas emissions.*

While hydrogen is classified as a zero-emission fuel at the end of use, its environmental impact is determined by its manufacturing process. Thus, the provenance of hydrogen is critical in determining whether it can truly be classified as 'clean' energy.

An overview of hydrogen availability, properties, and potential sources is provided, as well as an analysis of hydrogen production methods. Furthermore, the relationship between hydrogen and renewable energy, as well as its environmental and climate benefits, are thoroughly discussed. Currently, the vast majority of industrial hydrogen production relies on fossil fuels, primarily natural gas and coal, either directly or indirectly through electricity generation. According to projections, this trend will persist for the foreseeable future unless significant changes are made to the energy system. As a result, hydrogen generators continue to be a significant source of CO_2 emissions, contributing to climate change and threatening ecological stability. In light of these challenges, there is an urgent need to reduce or eliminate CO_2 emissions from fossil fuel-based hydrogen production in order to fully realize hydrogen's potential as a sustainable fuel.

The main methods for reducing CO_2 emissions in hydrogen production from fossil fuels fall into three categories: (1) coupling hydrogen plants with carbon capture and storage (CCS) technologies; (2) hydrocarbon dissociation to separate hydrogen and carbon; and (3) combining hydrogen production with carbon-free energy sources such as nuclear or solar. This article reviews and analyzes the current state of these technological approaches, offering insights into how they can significantly reduce emissions. A short- and medium-term outlook is also provided, outlining how new technological advancements could lead to a shift to low- or zero-emission hydrogen production from fossil fuels.

Finally, the future of hydrogen as a clean energy source is heavily dependent on overcoming current technological and economic barriers. Hydrogen adoption will necessitate advancements in production technologies, improvements in storage, transportation, and quality of hydrogen as fuel, and the development of a robust infrastructure. Furthermore, because hydrogen has a fast flame speed and a short ignition delay, combustion systems must be closely monitored to avoid problems such as pre-ignition and backfiring.

Policy incentives, such as renewable hydrogen subsidies and carbon pricing, will be required to accelerate the transition to a hydrogen-based energy economy. When combined with renewable energy sources, hydrogen has the potential to significantly reduce carbon emissions and contribute to global climate goals.

Keywords: *Hydrogen, carbon capture, natural gas, steam reforming*

1. Introduction

The continued growth of the global population and economy, combined with rapid urbanization, has resulted in a significant increase in energy consumption. Traditionally, energy supply has relied on hydrocarbon (fossil fuel) resources, which are limited by geological distribution and the feasibility of extraction [1]. The use of fossil fuels as the primary energy source since the advent of mechanical transformation has contributed to a significant rise in carbon dioxide (CO_2) and other greenhouse gases (GHGs) in the atmosphere, which is the main cause of global warming. As a result, decarbonizing the energy supply requires a shift to cleaner, more cost-effective, and renewable energy sources in order to ensure future energy sustainability and global security.

Hydrogen, as a carbon-free energy carrier, is most likely to play an important role in a world with severe constraints on greenhouse gas emissions. Free hydrogen is rarely found in its pure form within the Earth's crust, as it is typically bound to other elements. However, it can be synthesized from compounds found in natural or industrial sources. Hydrogen is the most abundant element in the universe, accounting for roughly 75% of total matter; in the Earth's crust, it is the tenth most common element.[2] Hydrogen is not found in Earth's atmosphere since the Earth's gravitational pull is not strong enough (unlike Jupiter and Saturn) to retain the light-weight H_2 molecules.
Three isotopes of hydrogen are available: protium, deuterium, and tritium. Consisting of one proton and one electron, protium is the main component of hydrogen, the simplest element. Although it is the lightest element, hydrogen has the highest energy content per unit mass among all fuels. A brief presentation of its properties is given in Table 1 below.

Table 1: Hydrogen properties

Properties	U.M. (S.I.)	Reference
Date of discovery/Author/Formula	1766/Henry Cavendish/H_2	[3]
Isotopes	^1H (99.98%). ^2H. ^3H. (^4H-7H Instable)	[3]
Equivalences: Hydrogen in solid. liquid. and gaseous states at p = 981 mbar and T = 20 °C	1 kg = 14.104 l = 12.126 m^3	[4]
Molecular mass	1.00794	[5]
Vapor pressure at (-252.8 °C)	101.283 kPa	[5]
Gas density at the boiling point and pressure of 1 atm	1.331 kg/m^3	[5]
Specific gravity of the gas at 0°C and 1 atm. (air = 1)	0.0696	[5]
Specific volume of the gas at 21.1°C and 1 atm	11.99 m^3/kg	[5]
Specific gravity of the liquid at the boiling point and 1 atm	0.0710	[5]
Specific volume of the liquid at the boiling point and 1 atm	67.76 kg/m^3	[5]
Boiling point at (101.283 kPa)	-252.8℃	[5]
Freezing/Melting point at (101.283 kPa)	-259.2℃	[5]
Critical temperature	-239.9℃	[5]
Critical pressure	1296.212 kPa. abs	[5]
Critical density	30.12 kg/m^3	[5]
Triple point	-259.3℃ la 7.042 kPa. abs	[5]
Latent heat of fusion at the triple point	58.09 kJ/kg	[5]
Latent heat of vaporization at the boiling point	445.6 kJ/kg	[5]
Solubility in water (vol/vol) at 15.6°C	0.019	[5]
Viscosity of the dilute gas at 26°C (299 K)	9×10^{-6} Pa s	[5]
Molecular diffusivity in air	6.1×10^{-5} m^2/s	[5]
CP	14.34 kJ/kg (℃)	[5]
Cv	10.12 kJ/kg (℃)	[5]
Ratio of specific heats (CP/Cv)	1.42	
Lower heating value. based on weight	120 MJ/kg	[6]
Higher heating value. based on weight	141.8 MJ/kg	[6]
Lower heating value. based on volume at 1 atm	11 MJ/m^3	[6]
Higher heating value. based on volume at 1 atm	13 MJ/m^3	[6]
Stoichiometric air-fuel ratio at 27°C and 1 atm	34.2 kg/kg	[6]

Flammable limits in air	4%-75%	[6]
Explosive limits	18.2 to 58.9% vol.	[6]
Maximum burning rate in air	2.7/3.46 (m s-1)	[6]
Maximum flame temperature	1526.85 ℃	[6]
Autoignition temperature / in air	400℃ /571℃	[6]

Hydrogen can be produced from renewable energy sources such as solar, wind, and nuclear power through processes such as direct thermal conversion or electrolysis. However, in the short term, a more practical approach involves producing hydrogen from conventional fossil fuels, utilizing conversion technologies that incorporate CO2 sequestration to mitigate environmental impacts [7].
Understanding the characteristics and parameters associated with various types of hydrogen is critical for assessing their environmental impact, economic viability, and overall potential in the transition to a low – carbon energy economy.
The following table presents a concise classification of the various types of hydrogen based on their energy source.

Table 2: Hydrogen color classification

<table>
<tr><th colspan="2">Nomenclature</th><th>Technology</th><th>Electricity source</th><th>Green gas emissions</th></tr>
<tr><td rowspan="7">Hydrogen through electric energy</td><td rowspan="5">Green Hydrogen</td><td rowspan="7">Electrolysis</td><td>Wind</td><td rowspan="6">Minimal</td></tr>
<tr><td>Solar</td></tr>
<tr><td>Hydro</td></tr>
<tr><td>Geothermal</td></tr>
<tr><td>Tidal</td></tr>
<tr><td>Purple/Pink Hydrogen</td><td>Nuclear</td></tr>
<tr><td>Yellow Hydrogen</td><td>Mixed-source grid energy</td><td>Medium</td></tr>
<tr><td rowspan="6">Hydrogen production through fossil fuels</td><td rowspan="2">Blue Hydrogen</td><td>Natural gas reforming and CCUS</td><td>Natural Gas</td><td rowspan="2">Low</td></tr>
<tr><td>Gasification and CCUS</td><td>Coal</td></tr>
<tr><td>Turquoise Hydrogen</td><td>Pyrolysis</td><td rowspan="2">Natural Gas</td><td>Solid carbon (by product)</td></tr>
<tr><td>Grey Hydrogen</td><td>Natural gas reforming</td><td rowspan="2">Medium</td></tr>
<tr><td>Brown Hydrogen</td><td rowspan="2">Gasification</td><td>Brawn coal (lignite)</td></tr>
<tr><td>Black Hydrogen</td><td>Black coal</td><td>High</td></tr>
</table>

Hydrogen is extensively used in industries like oil refining, ammonia and methanol production, and iron and steel manufacturing. Between 1975 and 2018, hydrogen production quadrupled, reaching 115 million tons per year globally. Currently, fossil fuels account for more than 95% of hydrogen production, resulting in the emission of approximately 830 million tons of CO_2 per year [8].
48% of hydrogen is produced through steam reforming of natural gas (SR), 30% from petroleum fractions, 18% via combustion activation, and only 4% through electrolysis due to its higher production costs (ranging from €0.61 to €1.30 per liter of gasoline equivalent, compared to €0.33 to €0.57 for SR). Additionally, electrolysis requires electricity, which remains largely dependent on fossil fuel combustion for the foreseeable future [8].
Other renewable-based hydrogen production methods, such as aqueous phase reforming, photo electrolysis, and thermochemical water splitting, are still in the experimental stage. Biomass

fermentation has reached commercial scale, but it remains more expensive than steam reforming, with production costs of up to €0.86 per liter of gasoline equivalent [8].

2. CO_2 capture from hydrogen plant process streams

CO_2 capture is the first stage of the carbon capture and storage (CCS) chain, and it is typically the most energy-intensive and costly process. In many cases, carbon capture, especially from flue gases, along with its purification and compression (usually to pressures between 100 and 135 atm for economical transport) accounts for the majority of the overall costs associated with CCS [9].
Currently, significant research and development efforts are underway worldwide to improve the efficiency and cost-effectiveness of the CO_2 capture process. While many of these initiatives focus on capturing CO_2 from coal-fired power plants, which are the largest stationary source of CO_2 emissions, it is worth noting that existing carbon capture technologies can also be used in hydrogen production facilities.
In recent decades, significant research has focused on finding efficient and cost-effective CO_2 sorbents. A wide range of materials are now commercially available for CO_2 capture via various technological processes, including activated carbons, zeolites, alkali and alkaline earth metal oxides, ionic liquids, polymeric membranes, and metal-organic frameworks (MOFs).

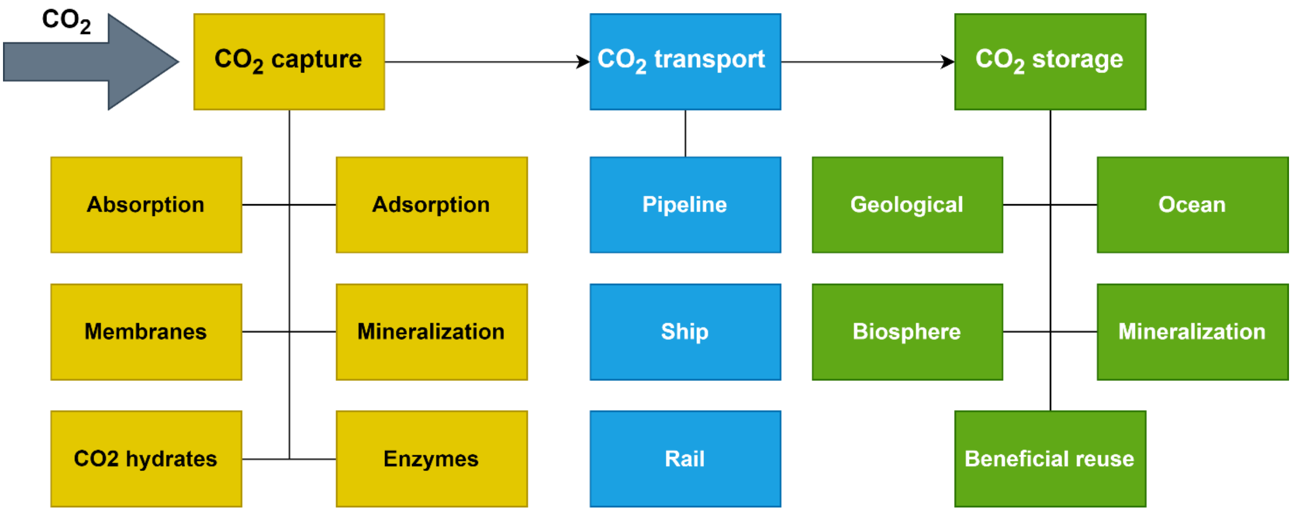

Fig. 1. Overview of Current and Emerging CO_2 Capture and Storage Technologies [9]

3. Integration of Steam Methane Reforming with Carbon Capture and Storage

The steam methane reforming (SMR) process is the most common industrial method for hydrogen production, having been used for decades to produce hydrogen efficiently. As a mature technology, natural gas SMR operates at or near the theoretical efficiency limits and is responsible for producing nearly all of the hydrogen (in the form of a mixture of hydrogen and carbon monoxide) used in the chemical industry, as well as supplemental hydrogen for refineries.
Tessie du Motay and Marechal were the first to document the process of converting hydrocarbons into hydrogen in the presence of steam in 1868, and SMR was first used in industry in 1930 [10]. This process uses methane, naphtha, and fuel oil as feedstocks.
The SMR process is catalytic in nature and involves multiple steps and harsh reaction conditions. It is a reaction between natural gas or other light hydrocarbons and steam that produces a mixture of hydrogen, carbon monoxide, carbon dioxide, and water through a series of three reactions. In the conventional SMR process, as shown in Figure 2, the first reforming step is a catalytic reaction of methane with steam introduced into the reformer furnace, which produces hydrogen and carbon monoxide via an endothermic reaction.

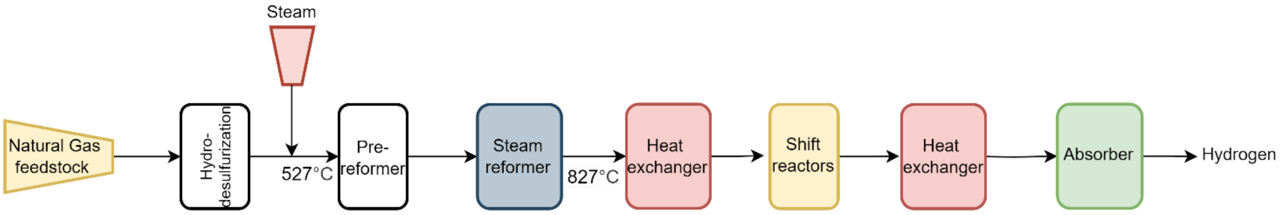

Fig. 2 Overview of Current and Emerging CO2 Capture and Storage Technologies [11]

PSA is a commonly used technique for removing CO_2, water, methane, and CO from off-gas streams. The traditional steam methane reforming (SMR) process requires multiple complex reaction steps to purify hydrogen (H_2), resulting in high capital investment and reduced efficiency. According to Myers et al.,[12] the combined costs of the water-gas shift reaction and PSA account for approximately 30% of the total expenditure on hydrogen production.

4. Conclusions

Hydrogen is emerging as a key energy carrier to facilitate the decarbonization of global energy and industrial sectors; thus, the production of hydrogen from renewable energy sources has garnered significant interest in recent years. Extensive research is underway to advance hydrogen (H_2) generation technologies. Hydrocarbon reforming is currently the most advanced and widely used technology. To reduce reliance on fossil fuels, considerable efforts are being directed toward the development of alternative hydrogen generation methods utilizing renewable resources, such as biomass and water.
To diminish dependence on fossil fuels, considerable efforts are underway to devise alternative hydrogen production techniques utilizing renewable resources like biomass and water. Despite the potential of these technologies, the most efficient way to produce green hydrogen—namely, steam methane reforming combined with carbon capture – is still up to seven times more expensive than producing conventional fossil fuels.
To address these economic challenges, various governments and institutions are increasingly providing subsidies and financial incentives for hydrogen generation. These subsidies aim to reduce production costs, stimulate research and development, and accelerate the adoption of hydrogen technologies. These initiatives are vital for a sustainable energy future and promoting the global shift away from fossil fuels by facilitating the transition to hydrogen as a clean energy carrier.

References

[1] Dawood, Furat, A. Martin, and G. M. Shafiullah. "Hydrogen production for energy: An overview." *International Journal of Hydrogen Energy* 45, no. 7 (2020): 3847-3869. https://doi.org/10.1016/j.ijhydene.2019.12.059.
[2] Baykara, S. Z. "Hydrogen: A brief overview on its sources, production and environmental impact." *International Journal of Hydrogen Energy* 43, no. 23 (2018): 10605–10614. https://doi.org/10.1016/j.ijhydene.2018.02.022
[3] Blumenthal, G. "Kuhn and the Chemical Revolution: A re-assessment." *Foundations of Chemistry* 15, no.1 (2013): 93–101. DOI:10.1007/s10698-011-9129-6.
[4] Huertas, Gaja P., Maria del Mar Llompart Jaume, Raed Kouta, Jean Marc Le Canut, and Xavier Francois. *Standards, codes and regulations of Hydrogen Refueling Stations and Hydrogen Fuel Cell Vehicles*. Final Degree Project (2014), IMSI Department-Fuel cell, UTBM University.
[5] Rivkin, C., R. Burgess, and W. Buttner. "Hydrogen Technologies Safety Guide," 2015. www.nrel.gov/publications; https://www.nrel.gov/docs/fy15osti/60948.pdf.
[6] Tabkhi, F., C. Azzaro-Pantel, L. Pibouleau, and S. Domenech. "A mathematical framework for modelling and evaluating natural gas pipeline networks under hydrogen injection." *International Journal Hydrogen Energy* 33, no. 21 (2008): 6222–6231. https://doi.org/10.1016/j.ijhydene.2008.07.103.
[7] Saeidi, Samrand, András Sápi, Asif Hussain Khoja, Sara Najari, Mariam Ayesha, Zoltán Kónya, Bernard Baffour Asare-Bediako, Adam Tatarczuk, Volker Hessel, Frerich J. Keil, and Alírio E. Rodrigues. "Evolution

paths from gray to turquoise hydrogen via catalytic steam methane reforming: Current challenges and future developments." *Renewable and Sustainable Energy Reviews* 183 (September 2023): 113392. https://doi.org/10.1016/j.rser.2023.113392.

[8] International Energy Agency. "Global Hydrogen Review 2024." 2024. www.iea.org.

[9] Muradov, N. "Low to near-zero CO_2 production of hydrogen from fossil fuels: Status and perspectives." *International Journal of Hydrogen Energy* 42, no. 20 (2017): 14058-14088. https://doi.org/10.1016/j.ijhydene.2017.04.101.

[10] Barelli, L., G. Bidini, F. Gallorini, and S. Servili. "Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: A review." *Energy* 33, no. 4 (2008): 554-570. https://doi.org/10.1016/j.energy.2007.10.018.

[11] Go, K. S., S. R. Son, S. D. Kim, K. S. Kang, and C. S. Park. "Hydrogen production from two-step steam methane reforming in a fluidized bed reactor." *International Journal of Hydrogen Energy* 34, no. 3 (2009): 1301–1309. https://doi.org/10.1016/j.ijhydene.2008.11.062.

[12] Myers, D. B., G. D. Ariff, B. D. James, J. S. Lettow, C. E. Thomas, and R. C. Kuhn. "Cost and Performance Comparison Of Stationary Hydrogen Fueling Appliances." Engineering, Environmental Science, Report (2002), Corpus ID: 30167057. https://www.nrel.gov/docs/fy02osti/32405b2.pdf.