

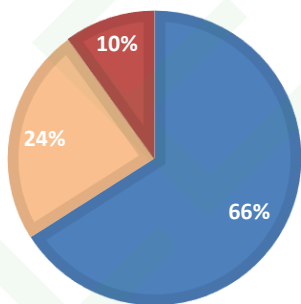
Bio-Ethanol: A more sustainable way to produce Hydrogen

More realistic option for Refineries and Factories



GLOBAL H2 DEMAND

- Ammonia, Polymers, Resins
- Hydrocracking, Hydrotreating
- Iron, Steel, Factories



Bio-Ethanol to H2

Producing Hydrogen In a sustainable way with Steam Reforming of Bio-Ethanol (SRE)

By Eliseo Curcio



Introduction

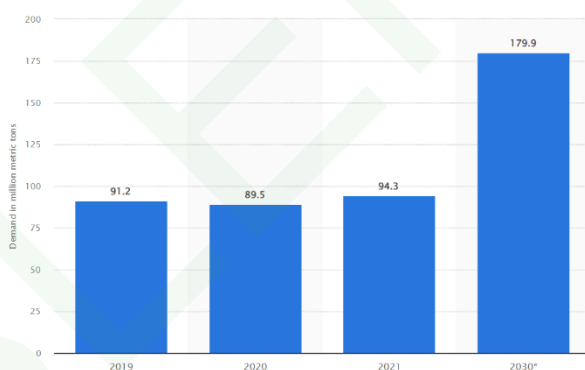
Hydrogen, often heralded as the fuel of the future, offers a beacon of hope for a sustainable energy transition. Its versatility and potential for clean energy production make it an invaluable asset in our collective quest for a carbon-neutral future. Hydrogen's role extends well beyond its potential in power generation and as a fuel, serving critical functions across several industrial sectors. The bulk of hydrogen production and consumption is dominated by refineries, chemical plants, and steel factories, which together account for around 90% of its usage. These sectors leverage hydrogen primarily for processing and manufacturing purposes, underscoring its importance in industrial applications rather than energy alone.

Recent years, however, have seen a growing interest in hydrogen's potential within the power and fuel markets. This shift is driven by the challenge of competing directly with established industrial users of hydrogen, such as refineries, which have long-standing, optimized processes for hydrogen use. As a result, investors and innovators are targeting the power and fuel sectors, hoping to carve out a niche in these emerging markets for hydrogen. The prospects for hydrogen in the power sector appear more promising, supported by continual advances in technology and the escalating demand for clean energy sources. The integration of hydrogen into power generation could offer a flexible, low-carbon alternative that complements intermittent renewable energy sources, such as wind and solar.

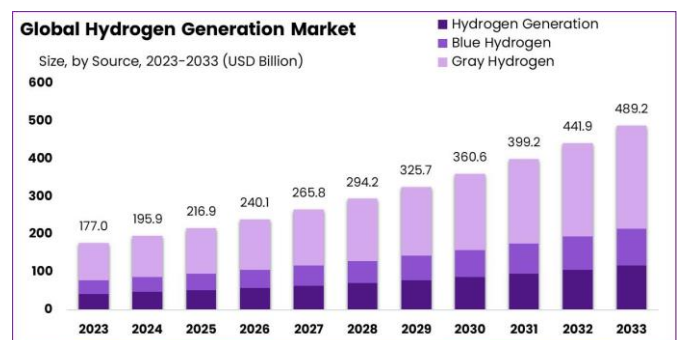
Conversely, the fuel market presents a more challenging landscape for hydrogen. Despite its potential for decarbonizing transport, particularly in heavy-duty and long-haul applications, hydrogen faces significant hurdles. These include infrastructure limitations, the high cost of hydrogen fuel cell technology, and safety concerns related to storage and transportation. Overcoming these barriers will require concerted efforts in research, policy support, and market development to make hydrogen a viable and competitive option in the fuel sector.

Hydrogen energy is in the spotlight as governments worldwide strive to achieve their net-zero emissions goals by the middle of this century. The most optimistic forecasts for global hydrogen demand, proposed by the Hydrogen Council and BloombergNEF (specifically the green scenario), anticipate that by 2050, hydrogen could account for 22 percent of total global energy demand. If a supply-side decarbonization-only scenario were achieved, the Energy Transitions Commission predicts hydrogen would represent about 18 percent of the global energy supply. The global demand for hydrogen (Fig.1) is expected to nearly double from 2021 to 2030, with 2021's worldwide demand at 94.3 million metric tons per annum. Currently, most hydrogen consumption occurs in the chemicals and refining sectors, predominantly produced using fossil fuels.

The Hydrogen generation (Fig.2) market is projected to reach 489.2 US dollars by 2033, with a steady Compound Annual Growth Rate of 10.7%. Most of the Hydrogen market will be dominated by Grey (Natural gas) and Blue Hydrogen (CCS) with a small share reserved for the green one.



1: Hydrogen demand Worldwide from 2019–2021, with a forecast for 2030 (million metric tons). Ref. Statista



2: Global Hydrogen Generation Market (USD Billion). Ref. Market

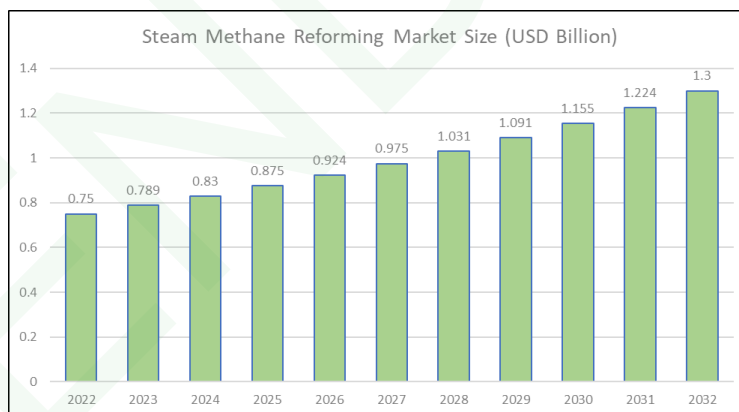
SMR OBSTACLES

The enactment of new policies, such as the Inflation Reduction Act (IRA) for green hydrogen hubs, has led numerous companies to invest in advanced technologies for hydrogen production. The possibility of producing green hydrogen is now a widespread consideration. Is green hydrogen the only solution for Refineries? Can it resolve the energy crisis and address GHG emissions issues? Are refineries and factories on board with obtaining hydrogen through completely renewable means? This publication aims to address these significant questions.

Green Hydrogen is not the sole method for hydrogen production. Currently, most hydrogen is produced from natural gas or coal. The traditional process, known as Steam Methane Reforming (SMR), is the primary method utilized by refineries and factories to obtain the needed hydrogen. Unfortunately, SMR has downsides, notably the CO₂ produced, which is considered one of the most harmful GHGs. SMR plants emit between 7-13 kg of CO₂ for each kg of hydrogen produced. Every refinery operates an SMR unit, which is not inexpensive. The cost of SMR depends on several factors, such as plant capacity, technology adopted, efficiency, and location, but on average, a SMR unit costs between 300-700 million USD.

This highlights the significant investment refineries make to produce hydrogen. Now, institutions, governments, and environmental associations are urging refineries and hydrogen producers to shift their production towards more sustainable alternatives. However, for someone who has invested nearly a billion dollars in hydrogen production, shifting business models is not readily appealing. For a modest-sized green hydrogen production facility (e.g., 10 MW), the capital investment is around 15-40 million USD, excluding land costs. It is challenging for refineries to change their business plan and move away from SMR towards more sustainable methods. For these reasons,

SMR will stay here for a long time, as also highlighted by the market size (Fig.3). In light of this, I believe other alternatives must be explored to make the transition more affordable. One possibility is continuing to use the SMR unit but processing a different raw material, allowing refineries to leverage their existing infrastructure while working towards more sustainable processes in the coming years. What alternatives to natural gas or coal could be processed in the SMR to achieve this?



3: Global SMR Market Size. Ref. Precedence Statistics.



New Feedstock for Steam Reforming

In light of new regulations for clean fuels, such as the Low Carbon Fuel Standards (LCFS), a debate has emerged between supporters of zero-carbon emissions and carbon neutrality. This debate is particularly pronounced between bio-ethanol producers, mostly in the Midwest of the US, and proponents of zero-emission vehicles (ZEVs). Despite the ongoing battle between biofuels and zero-carbon fuels, the mobility industry (primarily automotive and aviation) is expected to be dominated by biofuels, such as bioethanol, biodiesel, renewable diesel, bio-methanol, and Sustainable Aviation Fuel (SAF), in both the present and the long term.

The EPA's Renewable Fuel Standard (RFS) program exemplifies the increasing demand for biofuels, with the Renewable Volume Obligation (RVO) rising annually. While ammonia, hydrogen, and electric vehicles present interesting alternatives, they may be more suitable for a niche market rather than mass adoption. Would you be comfortable driving a car with a tank pressurized to hundreds bar with compressed hydrogen? Or containing ammonia, known as one of the most toxic chemicals? How are these producers mitigating safety concerns?

Large companies, including Shell, have reconsidered their investments in hydrogen for the automotive industry, recognizing that these investments may not pay off in the long term. This outcome was foreseeable when decisions are made without the input of experienced engineers and market experts. Why Bio-ethanol? Bio-ethanol is a versatile fuel, actively used in countries like Brazil, where high-concentration E85 blends are common. In the US, the current limit is up to 10% ethanol content, with higher concentrations gradually appearing nationwide but not fully available for everyone. Although not a zero-emission fuel, bio-ethanol has a lower carbon intensity (CI) index compared to gasoline. Given the significant production of ethanol in the U.S. (over 15 billion gallons in 2021), part of it can also be utilized for alternative purposes. US is the biggest Ethanol producer in the World. Why not adopting what we have in our backyard?

Bio-ethanol has potential for hydrogen production through direct steam reforming of ethanol (SRE), providing an effective way to replace coal and or natural gas.

Exist different approaches that will be discussed in this publication to produce H₂ through SRE, but mainly It doesn't require to buy new equipment, i.e. new steam reforming unit, because the traditional one is suitable to process also bio-ethanol. Let's review a table (Fig.4) to understand differences between SMR and SRE.

	Material	Sustainable	CI [gCO ₂ e/MJ]
SRE	Bio-Ethanol/ Biomasses	Yes, depending origin of feedstock	30-50
SMR	Natural Gas / Coal	No, unless RNG is adopted	70-90

4: Comparison of SRE vs SMR

Green Hydrogen-1

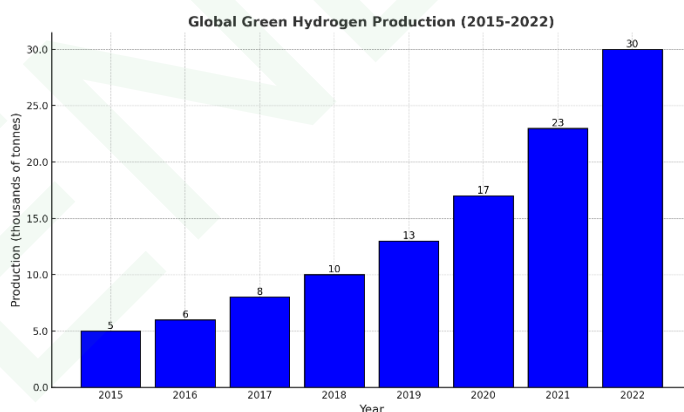
As illustrated in the preceding charts (Fig.5), the production of green hydrogen, both globally and within the United States, has experienced a notable increase over the last two to three years. This surge can largely be attributed to the concerted efforts by governments and climate organizations to align with the Paris Agreement's objective of mitigating global temperature rise by 2050. Furthermore, as highlighted in the introduction, this expansion is supported by a comprehensive suite of policies and incentives implemented by governments.

How is Green Hydrogen Produced?

Green hydrogen is generated through a process known as electrolysis. This method involves the decomposition of water (H₂O) into its basic components—hydrogen (H₂) and oxygen (O₂)—utilizing electric power. When the electricity utilized for this process is derived from renewable sources, such as wind, solar, hydroelectric, or geothermal power, the hydrogen produced is termed 'green hydrogen.' This is in contrast to 'grey' hydrogen, which is generated from fossil fuels through steam methane reforming (SMR) without carbon capture, and 'blue' hydrogen, where the CO₂ emissions from SMR are captured and either stored or utilized.

Key Steps in the Production of Green Hydrogen:

1. **Electrolyzer Technology:** The heart of green hydrogen production lies in the electrolyzer, which comprises an electrolyte and electrodes (an anode and a cathode).
2. **Water Input:** High-purity water is introduced into the electrolyzer. The purity level is vital to mitigate the degradation of the electrolysis system and to maximize hydrogen production efficiency.
3. **Applying Electricity:** The application of renewable electricity to the electrolyzer propels an electrical current through the water, splitting water molecules into hydrogen and oxygen gases at the electrodes.
4. **Gas Collection:** Hydrogen and oxygen gases are separately collected. Hydrogen gas can then be compressed, stored, and transported for use in energy storage, as fuel for fuel cell vehicles, and as an industrial raw material.



5: Global Green Hydrogen Production (2015–2022). Ref Statista

Types of Electrolyzers:

- **Alkaline Electrolyzers (AEL):** Utilize an alkaline solution as the electrolyte. AELs are recognized for their established technology and relatively lower costs, albeit with lower efficiency compared to some newer technologies.
- **Polymer Electrolyte Membrane (PEM) Electrolyzers:** Employ a solid polymer electrolyte and can operate at higher pressures and efficiencies than AELs. They are capable of rapid startup and shutdown, making them ideal for integration with intermittent renewable energy sources.
- **Solid Oxide Electrolyzers (SOEL):** Function at significantly higher temperatures than AEL or PEM electrolyzers, achieving higher efficiencies and potentially lowering the overall energy requirements for hydrogen production.

The primary advantage of green hydrogen lies in its ability to significantly reduce greenhouse gas emissions in comparison to traditional hydrogen production methods, assuming the electricity used is sourced from renewable energy. The scalability and economic feasibility of green hydrogen production are on an upward trajectory, thanks to technological advancements in electrolyzers, decreasing costs of renewable electricity, and increasing policy support aimed at decarbonizing energy and industrial sectors.

Green hydrogen seems to be the perfect way of producing Hydrogen. Let's see the pros and cons of green hydrogen (Fig.6). Certainly, the concept of green hydrogen presents a theoretically ideal solution to the challenges associated with greenhouse gas (GHG) emissions. Despite the long-standing availability of electrolyzers, water, photovoltaics (PV), and wind turbines, it is only recently that the industry has recognized the potential of these resources for green hydrogen production. In the United States alone, investments in green hydrogen projects have surpassed 15 billion dollars. However, the crucial aspect to monitor is whether these investments will lead to successful hydrogen production or if they will result in bankruptcy within the next five years.

Pros of Green Hydrogen	Cons of Green Hydrogen
Environmental Benefit	High Costs
Zero emission	Production costs higher than Blue H2
Sustainable production	Difficult to keep it constant
Reduces dependency on imports	Less-energy efficient than direct electricity use
Can be stored and transported	Significant investment needed for infrastructure
Can be blended with natural gas	Large quantity of water needed
Versatile	Security and health issue
Can be used to produce other green product	Significant land/resources use for renewable energy

6: Pros and Cons of using Green Hydrogen.



Hydrogen Production from Bio-Ethanol

Taking ethanol as the reforming material for hydrogen production, this method is characterized by the following advantages: (1) ethanol is much easier and safer for transportation, storage and direct utilization as a kind of liquid fuel; (2) the materials for ethanol are widely available, and it can be produced not only with biomass like sucrose, starch and oil, but also with agriculture and forestry waste; (3) the hydrogen content of ethanol is very high, and therefore much more hydrogen can be produced with the same weight of ethanol compared with other fuels; (4) the boiling point of ethanol is very low, and therefore gaseous ethanol can be easily achieved for reforming and hydrogen production; (5) ethanol is biodegradable and therefore the bio-toxicity is relatively low; (6) there are not any sulfur components, and therefore sulfur-containing pollutant gases are not a problem during the reforming procedure and (7) ethanol can be miscible with water in any ratio. Nowadays, among all the ethanol reforming technologies, catalysis reforming has been a mature process in industry, and studies on different ethanol reforming processes have also attracted wide attention.

The traditional SRE process is an endothermic reaction. It is the main way of producing Hydrogen. However, this generates also CO₂ as the same as using traditional SMR, but in lower amount. There are also other reactions associated with using bioethanol (Fig.7).

Reforming Process	Chemical Material	Hydrogen Yield (H ₂ /EtOH)	Characteristic
SER	C ₂ H ₅ OH/H ₂ O	2.5-5	Endothermic reaction. Slow reaction and large volume. CO ₂ emissions associate.
Dry Reforming	C ₂ H ₅ OH/CO ₂	1.5-1.9	Endothermic reaction. Low conversion. No CO ₂ emissions.
Partial Oxidation Reforming	C ₂ H ₅ OH/O ₂	0.8	Exothermic reaction. Low selectivity. Coke formation.
Autothermal Reforming	C ₂ H ₅ OH/O ₂ /H ₂ O	2-3.8	Equilibrium reaction and no external heat sources are needed. High H ₂ selectivity, low CO selectivity.
Catalytic Ethanol Reforming	C ₂ H ₅ OH/Steam/Air	High	High conversion and H ₂ selectivity. High cost of catalyst. Catalyst deactivation. Coke formation.
Plasma Ethanol Reforming	C ₂ H ₅ OH/Steam/Air	High	There are different Plasma processes available. It requires a pure feedstock. Possible dissociation of bio-ethanol. High cost. High conversion. Low CO ₂ emissions.
SESRE	C ₂ H ₅ OH/Steam/Air	High	Combination of traditional SER (or with catalyst) and CO ₂ capture. No CO ₂ emission. High selectivity and conversion.

7: Different Bio-Ethanol Reforming Processes to produce Hydrogen.

The most adopted process is the traditional endothermic reaction (SER) with formation of water and CO₂. This process unfortunately as mentioned produced carbon emission. For this reason another process recently was developed to sequestrate the amount of CO₂ produced during the ethanol reformer. **This process is called Sorption-enhanced steam reforming of bio-ethanol (SESRE)**

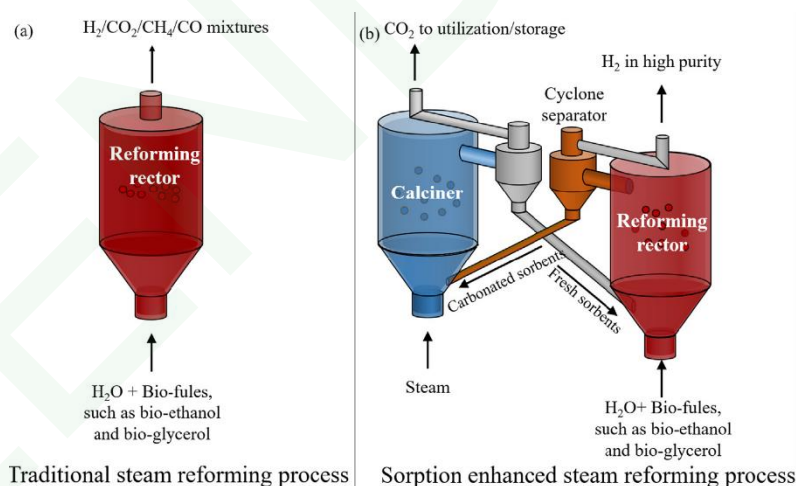


Sorption-Enhanced Steam Reforming of Bio-Ethanol (SESRE)

Let's examine the process of Sorption-Enhanced Steam Reforming of Ethanol (SESRE) as depicted in Figure 8. In the conventional Steam Reforming (SR) process, illustrated in Figure 8a, the mixture of steam and bio-ethanol is reformed into a mixture of H_2 , CO_2 , CH_4 , and CO upon passing through the reforming catalyst loaded within the reactor. Conversely, in the SESRE process (Figure 8b), steam and bio-ethanol are reformed into H_2 and other bio-products such as CO_2 , which is then captured by sorbents. This significantly improves the purity of H_2 while concurrently reducing CO_2 emissions. Subsequently, the carbonated sorbents are transferred to the calcination reactor and regenerated at high temperatures. The calcination process is designed to produce a pure CO_2 stream for storage or local reuse, for instance in the production of methanol or other significant chemicals.

The sorption-enhanced process not only scrubs CO_2 in situ from the product gases but also alters the chemical equilibrium and shifts the reaction pathways according to Le Châtelier's Principle. Should the CO_2 generated in the calcination reactor be geologically sequestered or permanently utilized, it could result in a net negative CO_2 emission. Additionally, the spent sorbents can be effectively recycled in industry owing to their low toxicity. There are two principal reaction pathways that may occur during the SESRE process: the dehydration route and the dehydrogenation route. The dehydration route begins with ethanol dehydration and the formation of ethylene, which subsequently decomposes into carbonaceous species, i.e., CH_4 and C (coking).

The formation of C can also result from the Boudouard reaction and methane decomposition. The absorbed CH_4 then undergoes steam reforming of methane and the Water-Gas Shift (WGS) reaction, producing CO_2 and H_2 . The dehydrogenation route initiates with the dehydrogenation process, yielding H_2 and acetaldehyde, a critical intermediate, which is then converted into CH_4 and syngas. The CH_4 intermediates subsequently undergo steam reforming of methane, followed by a WGS reaction to produce CO_2 and H_2 . The reaction mechanism of SESRE via metal catalysts and CO_2 sorbents, though not fully understood, is presumed to follow these two reaction pathways: dehydration and dehydrogenation. Regardless of the pathway, the SRE process converts H_2O and ethanol into CO_2 and H_2 , with sorbents capturing CO_2 in situ, thereby shifting the reaction route and releasing high-purity H_2 .



8: Traditional SRE Vs SESRE. Ref. Yongqing et al.

Conclusion

Hydrogen is poised to play a pivotal role in the future, not merely as a fuel but more significantly as a chemical and for power generation. Presently, greener options are increasingly accessible for new investors or producers who enjoy greater flexibility in terms of location, land, and proximity to water, sun, or wind resources. However, for refineries and factories, such as steel plants, the situation is markedly more complex. Refineries, in particular, are under pressure to mitigate carbon emissions by adopting new strategies.

I maintain that green hydrogen does not currently serve as a viable alternative for refineries. Given the substantial investments made in Steam Methane Reforming (SMR) technology, abandoning SMR in favor of green production is neither feasible nor economical. Effective emission mitigation should begin with an assessment of the existing infrastructure. Many facilities already operate sizable SMR units. One of the most promising approaches involves utilizing these existing steam reformers but switching to more sustainable feedstocks, such as bio-ethanol, which is more sustainable than coal or natural gas and results in lower carbon emissions.

Another option is to integrate Steam Reforming of Ethanol (SRE) with adaptive in-situ carbon dioxide sequestration. This method involves an absorption process linked directly to the steam reformer reactor, potentially reducing CO₂ emissions to zero. While traditional SMR can also be paired with Carbon Capture and Storage (CCS), the use of natural gas or coal cannot match the sustainability of biofuels. This strategy offers refineries dual benefits: it initiates a shift towards more sustainable and low-carbon feedstocks and allows for a gradual transition to producing cleaner, greener products without committing to the impractical investment in "green" hydrogen.

The development of Dual-Functional Materials (DFMs), which typically comprise a catalytic component and a sorption component, is considered fundamental to the SESRE and SESRG processes. Nonetheless, the deactivation of these DFMs, caused by various factors, presents a significant challenge in their industrial application for high H₂ production.

Therefore, the application of more advanced techniques is essential to precisely understand the reaction mechanism and, consequently, to develop durable and effective DFMs for the SESRE and SESRG processes.

This methodology represents a sustainable avenue for hydrogen production. Refineries can leverage this process to incrementally transition towards cleaner solutions. Although Steam Methane Reforming (SMR) combined with Carbon Capture and Storage (CCS) remains an alternative, it still relies on non-renewable feedstocks and produces a higher concentration of CO₂ emissions in comparison with SESRE.



References

- IRENA website: <https://www.irena.org/>
- Bloomberg : <https://www.bloomberg.com/>
- Department of Energy: <https://www.energy.gov/>
- EIA: <https://www.eia.gov/>
- Statista: <https://www.statista.com/>
- Precedence Statistics: <https://www.precedencestatistics/>
- Market: <https://market.us/>
- Yongqing Xu, Megna Wu et al. Elsevier
- JianHua Yan, ChangMing Du. Elsevier
- EPA : <https://www.epa.gov/>
- LCA Greet Model : <https://www.energy.gov/eere/greet>
- Personal Information and data gathered during my career