Hydrogen production by ethanol reform: critical analysis and technological roadmap

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ABSTRACT

Hydrogen (H_2) as a fuel has advantages such as near to zero GHG emissions when produced with renewable energy, high energy power, and many production routes. When it comes to Brazil, there is a huge production potential of green H_2 due to its already established expertise and infrastructure of ethanol production and distribution. Ethanol reform is one of the most promising ways of producing H_2 and can be performed in different processes. Within this context, the main motivation of this paper is to conduct a brief literature review on each of these ethanol-reforming technologies. The article also has the purpose to understand reforming technologies, analyzing the H_2 market in Brazilian scenarios, and foresee a roadmap for the technology. As possible takeaways, according to the literature review, the most used and studied processes are ethanol steam reforming, partial oxidation of ethanol, and ethanol autothermal reforming. Briefly, the objective of this study is contributing to energy management, presenting a promissory hydrogen production technology and analyzing its implementation perspectives.

Keywords: ethanol steam reforming, partial oxidation, autothermal reforming, hydrogen production, technology roadmap.

1. INTRODUCTION

i. Hydrogen

Due to climate changes and global warming forecast, the focus on sustainable development with the reduction of greenhouse gases emission is the top priority worldwide. This necessity was firstly issued in the energy matrix crisis in the 1970s which showed the need for a drastic change in the global energy matrix; at that time hydrogen was first brought up as a viable solution in virtue of its storage capacity and generation of big sums of energy without emitting CO_2 during combustion, being crucial to the decarbonization process in major industrial areas[1,2].

Hydrogen is the most abundant element on Earth and can be found in water, air (mostly in methane), etc. Global hydrogen production nowadays is mainly done using fossil fuels. The four methods for commercial production of H_2 are: steam methane reformation, oxidation, gasification, and electrolysis. Among these, the first three may use fossil fuels [3].The technologies for hydrogen production are classified in different colors depending on the production processes, the kind of energy used, and the related emissions: black-brown (from coal), gray (hydrocarbons without carbon capture and storage (CCS) like natural gas), blue (hydrocarbons with CCS), turquoise (pyrolysis), red (high-temperature catalytic process), green (clean RE electricity) and moss hydrogen that is made from biomass or biofuel [1,4]

The most used source for obtaining hydrogen is steam methane reformers using natural gas. Though, the use of natural gas brings warm to the environment because its production may cause a significant CO_2 emission, around 10T of CO_2 per 1T H_2 produced from natural gas, 12T CO_2 /1T H_2 from oil products, and 19T CO_2 /1T H_2 from coal. In 2019, 70Mt of hydrogen were produced. Among these, 76% were produced by natural gas and 23% by coal. With that, the annual emission of CO_2 was equivalent to UK and Indonesia emissions together [3,5].

A challenge to be overcome is the cost gap in hydrogen production regarding different possible paths. Nowadays, the production from fossil fuels is the lowest cost option in most parts of the world, within a range from 0.5 to 1.7 USD/kg, controlled by regional gas prices. The path utilizing CCUS (Carbon Capture, Utilization and Storage)

technologies, aiming to reduce CO2 emissions in H_2 production, increases the costs in 1-2 USD/kg, and using renewable electricity it is around 3 to 8 USD/kg of produced H2 [6].

ii. **Ethanol**

Brazil is one of the major countries in production and consumption of ethanol as a fuel. This became a reality because of high oil prices in the international market due to the 1st oil crisis in the 1970s. This crisis made the Brazilian government launch the "Proalcool" program in 1975 aiming to reduce the country dependency on oil imports. The program prescribed the use of 10% anhydrous ethanol as an additive to gasoline, with a voluntary component using 100% hydrated ethanol (95% ethanol + 5% water) in modified Otto cycle engines. With the 2nd oil crisis in 1979, Brazil launched the second phase of Proalcool with the goal to use hydrous ethanol to completely substitute gasoline in automobiles, resulting in the development of Flex Fuel technology [7] which allows consumer to choose between gasoline or ethanol during the fueling and mix the fuels in any percentage without damaging the car system [8]. Even though, Flex Fuel technology was developed in the 1990s, it was only established in the Brazilian market by 2003 with the launching of the 1st model and is present in Brazilian's market until nowadays [9].

2. MOTIVATION AND NOVELTY

The main motivation of this study is to conduct a brief literature review on ethanol reforming technologies along with information about its advantages and disadvantages, aiming to understand parameters such as ethanol conversion and hydrogen selectivity. This study provides an assessment of ethanol reforming literature thus validating the use of hydrogen energy on a large scale [10]. The hydrogen market has been promising with high demand for this fuel, so diversify the production technologies is supposedly required.

The global hydrogen demand in 2020 had an increase of 50% since the turn of the millennium [11] and in 2021 achieved a demand of more than 94 Mt (million tons), 5% more than previous years [6] with a USD 117 billion (bn) global market [12]. The road transports were the most focused subject with a growth of 60%, which reflects a fast change of FCEVs (Fuel Cell Engines Vehicles), especially in China, which is the world's largest consumer, mainly in heavy-duty trucks, achieving around 28Mt of H_2 demand in 2021. The demand rank is followed by the United States, Middle East, and Europe as the second to fourth places in global demand [6].

As fuel and industrial feedstock, green H_2 (GH_2) will contribute to decarbonizing the world's energy matrix, creating an opportunity of USD 200 bn investment in Brazil over the next 20 years and 180 GW in energy generation [4]. Brazil is very well positioned to become a powerhouse in support of the global transition and a major player in the hydrogen market due to its geographical position, which facilitates the logistics of hydrogen transportation especially for the US and Europe, its capability of territorial expansion for on and off grid installations, its natural solar incidence near equator and constancy of winds. Brazil can become one of the major global GH_2 producers because of the low cost derived from its natural resources and its clean and integrated power grid, which reduces the need for capital investment [4].

Brazil has a forecast of 9 Mt domestic demand and a total H2 production potential of 12,9 Mt per year in 2040. Therefore, this domestic demand for GH2 represents about 70% of the total supply. Thus, it creates a potential additional market for GH2 of up to USD 5 and 20 billion in 2030 and 2040, respectively [4].

Even with all this potential that Brazil has for the hydrogen market, its government has not defined a clear strategy for this H_2 chain yet. Therefore, some Brazilian states have been taking the lead and are already determining a state strategy for hydrogen roadmap. States like Bahia, Pernambuco, Ceará (northeast region), and Rio Grande do Sul (south) already defined their strategies and are starting to sign MoUs (Memorandum of Understanding) regarding GH_2 production [13,14]. Paraná (south) has also now started discussions and is setting itself as an important national player [15] as well as São Paulo, which recently closed a partnership with GWM (Great Wall Motor), resulting in an investment of USD 10 bn to support the state's energy transition [16]. Many other investment agreements have already been announced in the country.

So far, USD 35 bn has already been announced. These investments regard hydrogen, ammonia, consolidated wind onshore and growing offshore. The Port of Pecém at Ceará, is the main H_2 production hub in the country, with over 20 MoUs and 3 pre-contracts already signed. This hub has an ambitious goal of producing 900 thousand tons of GH_2 per year from an electrolysis capacity of 5 GW [12]. In Brazil, there are 23 offshore complexes with open licensing processes at the Brazilian Institute of Environment and Renewable Natural Resources (Ibama), totalizing 46.6 GW of installed power, then demonstrating the capacity the country has to become an important player in this market [12].

In Latin America, Chile has already designed a clear path to follow and will get to compete in the GH_2 market, with a goal to reach 25 GW electrolysis capacity until 2030, being the only country outside of the European Union with a goal for electrolysers [6]. Along with Chile, Brazil can be the most competitive GH_2 producer by the end of the decade. In addition to the motivations previously mentioned regarding the promising hydrogen market, the main one is focused on the

environmental impact when using this fuel, since hydrogen production from ethanol reforming is an alternative for renewable energy. Although, there are some issues about the reform process that are discussed by the documented studies, such as the emissions generated in the reform process, the energy efficiency due to the need of heat transfer, and the general costs associated with the introduction of a new operation unit. These points are the main criticisms mentioned and the researchers' focus of study when establishing this approach as sustainable and economically viable [10].

Ethanol is mainly produced in Brazil by the fermentation of sucrose, glucose and fructose extracted from sugarcane and also from the sugarcane biomass cellulose fermentation, resulting in the bio ethanol or 2° generation ethanol [17]. Colombaroli et al. (2011) [18] carried out an energetic analysis of hydrogen production through steam reforming derived from ethanol from bagasse fermentation. Carbon dioxide emissions during hydrogen production were lower than their absorption during sugarcane cultivation, leading to negative carbon emissions. It is important to emphasize that the life cycle analysis study may be different in relation to the input parameters considered in the system, but it is noted that even if this ethanol reform system does not have a negative carbon footprint, this possibility exists. In this study, the authors presented results with the steam reforming of ethanol having a thermodynamic efficiency of 56% and an ecological efficiency of 80% in hydrogen production. Eco-efficiency can reach 90% when carbon cycle is considered. General ecological efficiency compares the integrated emissions of pollutants and the thermodynamic efficiency of reform processes [18].

Thus, studying this ethanol reforming process is necessary, especially for an analysis of the Brazilian market. Regarding the criticisms about the sustainable bias, even if the process generates carbon emissions, the carbon footprint of the process will be smaller, with the possibility of being near to zero. When it comes to the energetic feasibility of this system, more robust prototyping studies are needed, but many simulation results and small prototypes are documented, showing the efficiency of this hydrogen production system. About the economic viability of this production system, even with the addition of an unitary production operation and energy demand costs of the process, this technology could facilitate, reduce and optimize critical stages of the H_2 chain, such as storage and transport, the most critical and costly processes in this chain [19].

3. BIBLIOGRAPHIC REVIEW

The first method of analysis performed in this study for the literature review was the search for ethanol reform. According to the Scopus database, the keywords "ethanol reforming" are present in 3040 documents. The publications

number with the theme increased in the 2000s, due to nowadays resurgence of critical environmental guidelines (Figure 1). Directly seeing Brazil, in this period the 1st Flex Fuel model was launched in the region, facilitating and increasing the use of ethanol, which consequently generates an increase on this biofuel research. The document types are mostly articles, conference papers, reviews, book chapters, conference reviews, notes, erratum, books, abstracts, reports, and editorials. Among the documented studies, most of them, 583 to be precise were carried out in China. Brazil is in fifth place with 216 documents.

Over the last two decades, several literature reviews were published on ethanol reforming. These review papers briefly describe the technologies analyzing properties such as thermodynamic analysis, catalyst type, kinetics and reactor design, conversion efficiency, catalyst deactivation, and syngas selectivity. The author's Sun, et al (2012) [20] thermodynamic analysis of ethanol reforming for hydrogen production presents a detailed analysis of the simulated equilibrium compositions and thermal efficiencies of ethanol steam reforming (SR), partial oxidation (POX), and auto-thermal reforming (ATR) over a wide range of temperature, steam-to-ethanol (S/E) molar ratio, and oxygen-to-ethanol (O/E) molar ratio. The simulation results show that the moles of hydrogen yield per mole of ethanol are in the order of SR > ATR > POX. The results were compared with other simulation works and fitted models, which showed a high level of consistency with very small deviations. Thanomjit et al (2015) [21] the performance of a Solid Oxide Fuel Cell (SOFC) system integrated with ethanol reforming processes including Steam Reforming (SR), Partial Oxidation (POX), and Autothermal Reforming (ATR), was examined to identify a suitable reforming process for the SOFC system. The simulation results showed that increasing the reformer and SOFC temperatures can enhance the electrical performance of the SOFC system. The SOFC-SR was found to have the highest electrical performance due to its high hydrogen yield. The study also examines the thermal efficiency of the SOFC system and reveals that the SOFC-POX system shows higher thermal efficiency with increasing oxygen/ethanol and decreasing reformer and SOFC temperatures.

Based on catalyst type and reaction mechanism, Mattos et al.(2012) [22] investigated different ethanol conversion and catalyst deactivation strategies and analyzed the reaction mechanisms involved. The study named carbon deposition as a key mechanism for catalyst deactivation. The best supports were found to be those that were alkaline and inhibited the synthesis of ethylene, which is a precursor to coke formation. Hou et al. (2015) [23] conducted a review of ethanol reforming and various hydrogen production methods based on

the catalyst type and reaction mechanism. According to their findings, Rh-based catalysts had the potential to break C-C bonds effectively. On the other hand, MgO, CeO_2, and La_2O_3 were identified as the best supports because of their basic properties and/or redox capability. Kumar (2021) [24] examined ethanol decomposition and nonoxidative ethanol dehydrogenation as means of converting ethanol into hydrogen. Their study revealed that ethanol breakdown mainly produced aldehydes, acetates, and others in the presence of hydrogen. Anil et al. (2022) [25] evaluated the effects of several noble and non-noble metals on Ni-based catalysts for ethanol conversion and H_2 generation. The study found that the choice of the active metal and the modification of the catalyst morphology (particle size and surface area) were crucial for ethanol conversion and H_2 production.

Focusing on the automotive onboard reforming and design of the reactor, the authors Sall, *et al*. (2013) [26] developed and tested three low-temperature ethanol reformer architectures for automotive-scale applications using exhaust from a V8 engine. The best results were obtained by embedding the catalyst in fibrous metal media with a density gradient, achieving effective catalyst retention and heat-transfer properties. Longitudinal shell-and-tube and finned tube reformers showed a high thermal mass, catalyst settling and unacceptable pressure build. However, a transverse shell-and-tube design, in which banks of parallel, vertical catalyst tubes extended through a transverse stack of exhaust-side heat-exchange plates, showed sustained high conversion with low and stable fuel-side pressure throughout a 500-hour test period. This design has relatively low thermal mass and can be readily packaged on a vehicle. In conclusion, onboard reforming of ethanol- or methanol-rich fuels appears to be a feasible pathway for improving fuel economy and reducing emissions in light-duty vehicles. The development of effective low-temperature ethanol reformers will be an essential step toward achieving more sustainable and environmentally friendly transportation.

Among technologies of ethanol reforming producing hydrogen, the main ones reported in literature are steam ethanol reforming, partial oxidation, and autothermal reforming. So, the study has the aim to analyze the prompting of several publications of literature on ethanol reforming.

3.1 ETHANOL STEAM REFORMING (ESR)

Steam reforming is an endothermic method in which gaseous fuel reacts with water vapor in presence of a catalyst and high-temperature conditions. This process forms a syngas composed mainly of hydrogen, carbon monoxide, carbon dioxide, and methane. Equation 1 demonstrates the overall reaction of ethanol steam reforming, and secondary reactions occur for other components formation.
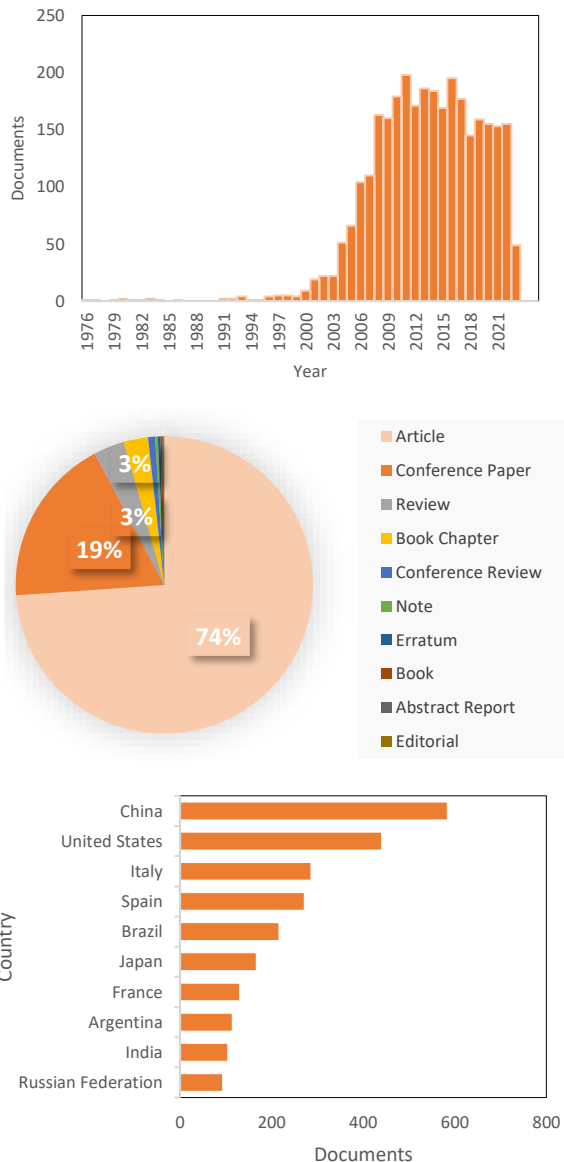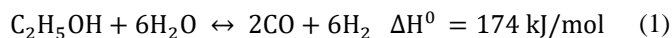

Figure 1. Analysis search result of the Scopus database: a) Documents by year; b) Documents type; c) Documents by country.

$$C_2H_5OH + 6H_2O \leftrightarrow 2CO + 6H_2 \quad \Delta H^0 = 174\ \text{kJ/mol} \quad (1)$$

The most studied ethanol reforming technology is steam reforming, using the keywords "ethanol steam reforming", 2123 documents were found. The search was carried out using article titles, keywords, and abstracts. This study shows many subjects like reaction kinetics, thermodynamics, and catalyst type. The main parameters that directly influence the efficiency of ethanol reforming production process are : i) kinetic conditions which are related

to catalyst type and content, catalyst particle size, and surface area; ii) diffusion condition that is directly related to boundary conditions, such as reaction temperature and pressure, reactor type and size, steam/ethanol ratio, and inlet flow [10,27]. Thus, this present study aims to carry out a critical review of the literature analyzing these important parameters for the system efficiency.

3.1.1   Effect of reaction temperature

When ethanol is converted into hydrogen, it requires higher temperatures compared to methanol due to the presence of C-C bonds which need more energy to break. This poses a challenge for emerging ethanol-to-hydrogen conversion technologies, as reducing thermal energy consumption is critical. To address this issue, catalysts and supports play a crucial role in minimizing energy consumption and research has focused on catalytic ethanol reforming for the past two decades. Table 1 provides information on the catalytic activity of different metals in ethanol reforming at various temperatures.

Analyzing the selected studies, a strong influence of reaction temperature is noted in ethanol steam reforming process. This behavior is expected due to it being an endothermic reaction ($\Delta H^0 = 174\,\text{kJ/mol}$). Liguras et al. (2003) [28] the article discuss the results of experiments on the influence of temperature on the catalytic activity and product distribution of ethanol steam reforming over $1\%\text{Rh}/\text{Al}_2\text{O}_3$ catalyst. The experiments show that ethanol conversion is significant at temperatures above 600°C and increases continuously along with the temperature, achieving complete conversion at 800°C. The selectivity towards H_2, CO, and CO_2 is high, at 800 °C, selectivity towards hydrogen is higher than 95%, while reaction dehydration of ethanol is less, so the selectivity towards ethylene and acetaldehyde is relatively small and decrease at higher temperatures. Methane production is maximized at around 750 °C and can be eliminated by increasing reaction temperature or contact time. The authors also discuss the temperature drops (ΔT) during the reforming process, due to the endothermic properties of the reaction as expected, the temperature drop increases along with ethanol conversion. Although the system is not perfectly adiabatic, and the two curves diverge at higher temperatures (probably due to heat input from the hot furnace), the observed endotherms are in reasonably good agreement with ethanol conversions and can be used as a first approximation of the extent of reaction. This behavior shows the dependence of energy supply throughout the operation of the reforming system.

Diagne et al. (2004) [29] analyze the influence of temperature on the reforming process. It is noted from the results in Table 1, using the Rh (2%)/CeO_2 catalyst a proportional relationship between temperature and ethanol conversion as well as selectivity of H_2 and CO_2, and an inversely proportional relationship to CO selectivity. Using the Rh (2%)/ZrO_2 catalyst, a similar behavior is seen, however, with a smaller influence of temperature on ethanol conversion. The authors associated the decrease of CO_2/CO molar ratio at hot temperatures (above 400°C) to thermodynamic limitations. Water-gas shift reaction (WGSR) (Equation 2) is exothermic and is thus not favored at extremely hot temperatures, while steam reforming is endothermic.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0 = -41.2\,\text{kJ/mol} \quad (2)$$

Wang et al. (2007) [30], Ebiad et al. (2012) [31], and Zhurka et al. (2021) [32] found similar results, an increase in ethanol conversion and H_2, CO_2 selectivity with increasing temperature. Liu et al. (2014) [33] and Llorca *et al.* (2014) [34], on the other hand, presented distinct behaviors in terms of H_2 selectivity. This behavior can be related to the kinetic properties of the catalysts used.

3.1.2   Effect of catalyst type

The choice of a catalyst in ethanol reforming process is important, both noble and non-noble metals are used in this process as well as different catalytic supports. In Table 1, we can see some studies documented in the literature with different catalysts and supports. The catalytic activity of noble and non-noble metals in ethanol steam reforming (ESR) processes is related to the d-character of their metal bonds. The partially filled d-orbitals [(n-1) d $^{1\text{-}10}$ns$^{1\text{-}2}$], which can uptake or give electrons to different reagents, play a crucial role in controlling the different reforming reactions of ethanol. Metals with a filled d-orbital have less capability to break C-C bonds, resulting in lower catalytic performance. Based on previous studies, the sequence of catalytic performance for various metals in ESR processes is Ru ([Kr]4d^{7}5s^1) > Ni([Ar] 3d^{8}4s^2)> Rh([Kr] 4d^{8}5s^1) > Co([Ar] 3d^{7}4s^2) > Pd ([Kr]4d^{10})[35,36]. In Figure 2, the radar diagram shows the comparative hydrogen, carbon monoxide, and carbon dioxide selectivity.

This analysis brought the discussions above, in which can be observed the best performance of the noble metals catalyst. These materials show high hydrogen selectivity (~100%). Noble metals, Rh (Rhodium), Ru (Ruthenium), and Re (Rhenium) are considered promising catalysts for ESR processes. Observed the Table 1, Rhodium on an Al_2O_3 support is active for ESR at elevated temperature (800 °C) with high hydrogen selectivity (95.7%). Ethanol is completely converted at elevated temperature, and the product distribution of CO_2 and CO increases with higher temperatures. Zhurka et al. (2021) [32] also found greater selectivity with the Rh-based catalyst and CeO_2 support.

Non-noble metals also used catalysts such as Nickel (Ni) and Cobalt (Co) for ethanol steam reforming reaction due

Table 1. Literature analysis papers on steam reforming of ethanol

Ref.	Temperature(°C)	Reactor	Catalyst	Steam/EtOH (mol %)	EtOH conversion (wt %)	S_{H2}(%)	S_{CO}(%)	S_{CO2}(%)
[28]	800	Quartz microreactor	Ru(1%)/Al2O3	3:1	42	55	20	10
			Ru(5%)/Al2O3		100	96	65	28
			Rh(1%)/Al2O3		100	95	72	25
			Rh(2%)/Al2O3		100	96	68	32
			Pt(1%)/Al2O3		60	65	25	15
			Pd(1%)/Al2O3		55	50	20	5
[29]	300-450	Fixed-bed reactor	Rh(2%)/CeO2	8:1	58.5-100	59.7-69.1	18.2-3.5	6.5-18.7
			Rh(2 %)ZrO2		100	59.6-71.7	13.1-2.1	11.4-20.3
[32]	300−600	Fixed-bed quartz reactor	Rh/ZrO2-La2O3	3:1	25-65	12-68	58-10	20-92
			Rh/CeO2-ZrO2-La2O3		38-78	30-75	20-0	65-100
			Ni/ZrO2La2O3		20-50	10-55	65-15	10-85
			Ni/CeO2-ZrO2-La2O3		28-65	20-68	28-10	60-92
[37]	420	Fixed-bed quartz reactor	Co(7.9 %)CeO2-Nano	21:1	100	92.6	4.9	84.1
			Co(8.6 %)CeO2-M		100	75.8	30.8	25.4
			Co(8.2 %)ZrO2-N		100	85	22.1	51.6
			Co(8.9 %)ZrO2-M		100	77.3	18.6	35.4
			Co(9.1%)Ce(22.3%)ZrO2-N		100	91.9	6.4	80.8
			Co (5.5 %)Ce(13%)ZrO2-M		100	91.5	12.8	71.7
[30]	350-450	Fixed-bed quartz reactor	Co3(10 %)O4/CeO2-C	3:1	39.1- 82.1	68.1-69.6	5.6-5.0	11.1-14.5
			10%Co3O4/CeO2-I		12.6-18.8	64.0-65.1	0-4.1	4.1-6.4
[33]	400-600	Fixed-bed reactor	Ni(12 %)La-Ce-C	3:1	100	70.3-60.7	12.4-23.6	10.2-16.7
			Ni(12 %)La-Ce-C		83.3-100	66.1-61.3	16.5-22.4	5.2-15.1
[34]	350-450	U-shaped quartz reactor	Na(0.06%)Co(11.1%)ZnO	13:1	100	72.3-72.8	12.4-23.6	10.2-16.7
			Na(0.23%)Co(10.8%)ZnO		100	73.9-73.6	16.5-22.4	5.2-15.1
			Na(0.78%)Co(10.8%)ZnO		100	73.8-73.9	0-8.0	4.0-16.3
[31]	200-600	Vertical tubular quartz reactor.	Ni(2 %)CeO2/ZrO2	8:1	82-100	0-75.3	0-5.2	4.0-23.7
			Ni(10 %)CeO2/ZrO2		98-100	37.5-70.3	15.9-5.28	1.3-23.7

to their ability to break C–C bonds followed by dehydrogenation and dehydration reactions, as well as its assistance in WGSR (Equation 2). Non-noble metals such as nickel and cobalt are popular choices for ethanol reforming due to their affordability. However, they tend to develop carbon deposition on the catalyst surface which leads to the inhibition of catalytic activity. Additionally, these catalysts are not very stable at high temperatures[10,35].
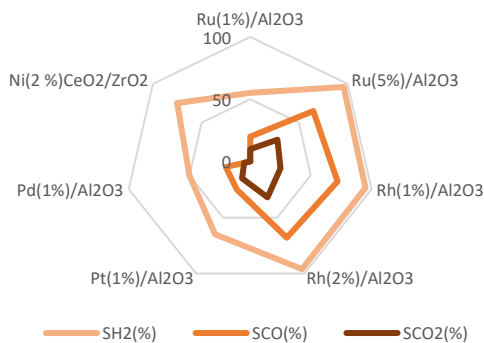

Figure 2 . The radar diagram has been made from the data collected from Liguras *et al*., [14] and Zhurka *et al*., [16], showing the comparative selectivity of hydrogen, carbon monoxide, and carbon dioxide and the ESR production of hydrogen.

3.1.3   Ethanol to steam ratio impact on ESR

The rate of carbon gasification by water can be enhanced by increasing the steam/ethanol molar ratio, which minimizes catalyst deactivation. Nevertheless, adding excess water can raise operating costs because it requires a less energy-efficient reactor to produce steam. It's important to note that the reaction efficiency is not solely influenced by the molar ratios of water and ethanol, but also by the oxygen storage capacity of the supports. This storage capacity boosts the reaction activity at the interface of the catalyst supports by catalytic dispersion.
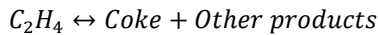
3.1.4   Catalyst deactivation

The ethanol reforming reaction is heterogeneous, meaning it occurs on the surface of the catalyst, and the formation of carbon (coke) can be detrimental to this process by deactivating the catalyst surface. The formation of coke on the catalyst surface during ethanol reforming can arise from three distinct processes. Coke formation at low reaction temperatures is followed by the Boudouard reaction (Equation 3) and reverse gasification of carbon (Equation 4). In contrast,

carbon deposition primarily originates from methane decomposition at high temperatures (Equation 5) [38,39]. Given that a range of factors affect carbon deposition or coke formation, including temperatures, catalyst shape, and support chemistry, this study aims to evaluate the different efficiencies of coke production and catalyst deactivation under various techniques.

$$CO + H_2 \leftrightarrow C + H_2O \quad \Delta H° \ = \ 75 \text{ kJ/mol} \qquad (3)$$

$$\qquad\qquad (4)$$

$$C_2H_4 \leftrightarrow Coke + Other\ products$$

$$\qquad\qquad (5)$$

$$CH_4 \leftrightarrow C + H_2 \quad \Delta H° \ = \ 75 \text{ kJ/mol}$$

The literature indicates that higher steam-to-ethanol ratios are unsuitable for carbon deposition, because increasing the steam/ethanol molar ratio reduces the catalyst deactivation by accelerating carbon gasification, and carbon formation is maximized between 500 °C and 600 °C due to methane decomposition occurring at that temperature [40,41]. However, the carbon decomposition rate decreases as the temperature continues to rise [23]. Comparing the non-noble and noble metals analysis the Table 2, it has seen the mass increase to non-noble metals. Despite non-noble metal, catalysts are more active and less prone to carbon deposition than other noble metal catalysts. Compared to C–H bond breaking (CH→ C + H*), which has a large activation barrier, carbonyl formation (CH* + O→ CHO) occurs predominantly on non-noble metal surfaces, facilitating carbon deposition.

Zhurka et al. (2021) [32] analyze the formation of coke in the catalyst used in the experiments of ethanol steam reforming reactions, the authors compared the amount of carbon deposited on the catalyst bed in terms of catalyst weight mass and carbon fed with Temperature-Programmed Oxidation (TPO) experiments, indicating the superior catalytic performance and stability of Ni/CeO$_2$-ZrO$_2$-La$_2$O$_3$. The results suggested that the choice of support and catalyst composition play a crucial role in figuring out the type and amount of carbon deposition during steam reforming reactions. The formation of distinct types of carbon species can have a significant impact on the catalytic performance and stability of the catalyst, highlighting the importance of understanding the nature and behavior of carbon deposits to design more efficient and durable catalysts for hydrogen production. The TPO profiles of Rh-based catalysts showed only one minor peak, indicating a lower amount of carbon formation compared to the Ni catalysts. This is consistent with their higher catalytic activity and stability. On Rh/CeO$_2$-ZrO$_2$-La$_2$O$_3$, only a very minor peak was detected, indicating minimal carbon deposition (0.01% of carbon fed), which further highlights the synergistic effect of the noble metal and the ceria support.

During ethanol steam reforming (ESR), methane undergoes decomposition over Ni catalysts, releasing highly reactive carbon species. These carbon species can be formed through various processes, including interaction with water, accumulation on the catalyst surface, or dissolution in the lattice crystallite followed by nucleation and the formation of carbon filaments or amorphous carbon deposits. Ni-based catalysts can be deactivated by carbon deposition at low reaction temperatures, which can be prevented by increasing the H$_2$O/C$_2$H$_5$OH ratio or adding O$_2$ gas into the reactor. The acid/base characteristics of supports also play a crucial role in the catalytic performance, product distribution, and catalyst stability during ESR. Ethanol dehydration is triggered by both acidic Al$_2$O$_3$ and basic MgAl$_2$O$_4$ supports[10].

Table 2. Mass based percentages of coke deposited on catalyst samples in terms of total carbon fed and catalyst mass

	Ni/CeO$_2$-ZrO$_2$-La$_2$O$_3$	Ni/ZrO$_2$La$_2$O$_3$	Rh/CeO$_2$-ZrO$_2$-La$_2$O$_3$	Rh/ZrO$_2$-La$_2$O$_3$
m$_{coke}$/m$_c{}^{fed}$	0.25	0.63	0.01	0.09
m$_{coke}$/m$_{cat}$	7.95	24.57	0.39	3.51

Source: Zhurka, et al. (2021) [32]

3.2 ETHANOL PARTIAL OXIDATION (POX)

Partial oxidation is an exothermic process in which ethanol reacts with oxygen in sub-stoichiometric ratios in the presence of catalysts (Equation 6).

$$C_2H_5OH + \frac{1}{2}O_2 \ \leftrightarrow 2CO \ + 3H_2 \quad \Delta H^0 \ = 14.1\ kJ/mol \qquad (6)$$
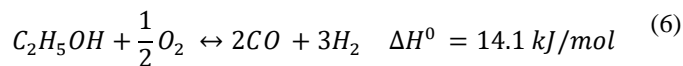
The search was performed in the Scopus database, using the keywords "partial oxidation ethanol" were found 875 documents, search within article titles, keywords, and abstracts. The subjects of these studies are like steam reforming method. Within this context, Table 3 shows some partial oxidation of ethanol studies documented in the literature.

3.2.1 Effect of reaction temperature

The aim of introducing oxygen in the POX process is to accelerate the catalytic reaction and achieve complete conversion of ethanol while increasing hydrogen selectivity at lower temperatures than ESR. Liguras et al. [42] investigated the partial oxidation of ethanol using a Ni/La$_2$O$_3$ catalyst, with reaction temperatures ranging from 500°C to 650°C. The catalyst showed robust activity, with increasing temperature resulting in almost 100% ethanol conversion above 550 °C, accompanied by improved hydrogen selectivity of 97%. The study found that at 550°C, methane selectivity was around 15%

but reduced to negligible levels at 650°C due to thermal decomposition. This contributed to improved hydrogen selectivity. However, at a temperature of 650 °C, trace amounts of CH_3CHO, C_2H_6, and C_2H_4 were detected.

Rodrigues et al. (2009) [43] tested the effect of temperature on ethanol partial oxidation using a Co_3O_4/Al_2O_3/cordierite catalyst. Table 3 showed that the ethanol conversion improved with temperature, while complete conversion was achieved at 770 °C. Within this context, it can be seen that hydrogen selectivity also increased with temperature. The study concluded that at lower temperatures, when the ethanol conversion was about 30%, the dehydrogenation reaction products such as acetaldehyde, ethylene, and diethyl ether had high product selectivity. Like the results observed by Liguras et al. [42], the catalyst demonstrated a relatively strong preference for CO_2 over CO at 500°C, suggesting that it promotes a WGSR (Equation 2). Based on the findings presented in Table 3 after reaching a temperature of 500°C, the significant increase in CO_2 selectivity is interrupted. Thus, the authors concluded that ethanol is adsorbed as ethoxy species (CH_3CH_2OR, where R stands for an alkyl group) which subsequently undergoes a reaction to form acetaldehyde. The acetaldehyde then either oxidizes to form an acetate derivative or decomposes to produce CO and CH_4 when exposed to hot temperatures. Notably, the absence of any significant increase in CO_2 formation at higher temperatures suggests that no acetate derivative formation occurred as an intermediate step.

In a study conducted by Ehrich et al. [44], Co and Ni catalysts were used to partial oxidation ethanol while gradually increasing the reaction temperature from 600 °C to 750 °C. The study revealed that all catalysts successfully converted ethanol to completion at temperatures above 600 °C. Moreover, H_2 and CO selectivity were improved as intermediate oxidation occurred. This intermediate oxidation could be attributed to the partial oxidation of intermediates, such as acetaldehyde or methane, as well as the reverse water-gas shift (WGS) reaction, dry reforming, and steam reforming, which increased with rising temperatures. Previous research has also suggested that the addition of extra oxygen can enhance the reactivity of partial oxidation compared to ethanol steam reforming [34]. Therefore, it can be concluded that the optimized temperature for ethanol reforming over a non-noble metal-based catalyst is 600 °C.

3.2.2 Effect of catalyst type

Literature review indicates that non-noble and noble metals are used as a catalyst in POX (Table 3). The reaction conditions are similar in both ESR and POX, as the temperature ranges, and type of catalyst. Consequently, it shows nearly equivalent product distribution. Among the commonly used noble and non-noble metal catalysts for ethanol partial oxidation, Ru, Rh, Pd, Pt, Co and Ni are often employed (Table 3).

Table 3. Literature analysis papers on partial oxidation of ethanol

Ref.	Temperature(°C)	Reactor	Catalyst	O2/EtOH (mol %)	EtOH conversion (wt %)	S_{H2}(%)	S_{CO}(%)	S_{CO2}(%)
[45]	630	Peripheral reactor	Pd(1%)Al_2O_3	1:1	100	60	50	-
			Pt(1%)Al_2O_3		100	58	43	-
			Ru(1%)Al_2O_3		100	67	53	-
			Rh(1%)Al_2O_3		100	72	60	-
[42]	500	Fixed-bed reactor	Ni(13%)La_2O_3	0.6:1	100	94	30	60
	550				100	94	32	60
	600				100	94	35	58
	650				100	97	40	58
[46]	650		1% Pt/Al2O3 R20	1:1	38	18	-	-
	650		1% Pt/Al2O3 R20-coated	1:1	28	35	-	-
[43]	420	U-shaped quartz reactor	CuO/c-Al 2O 3/cordierite	0.3:1	34.7	1.6	7.9	10.4
				0.5:1	51.3	2.2	13.0	15.2
				0.8:1	78.3	2.7	18.8	17.4
	570			1:1	42.8	7.0	39.6	1.0
	620				73.4	7.3	40.9	1.0
	670				78.4	7.9	41.9	1.7
	720				90.9	10.0	43.2	2.6
	770				96.3	11.5	42.4	1.3
[44]	600-750	Quartz-glass fixed-bed reactor	CoAlZnSG	0.75	-	78-80	75-78	23-19
			NiAlZnSG			90-85	79-80	21-17
			CoAlZnCM			80-88	62-80	16-12
			NiAlZnCM			82-95	76-88	12-9

The available literature suggests that noble metal-based catalysts are typically used for ethanol partial oxidation at temperatures between 500 °C and 600 °C. Non-noble metals, on the other hand, presented studies with higher temperature ranges, up to 750 °C. Hydrogen selectivity is lower in POX compared to ESR and ATR at similar temperatures. Therefore, it can be seen that hydrogen selectivity to non-noble metals is higher (90 %) compared to noble metals, also to ESR reactions. In Figure 3, the radar diagram shows the comparative selectivity of hydrogen, carbon monoxide, and carbon dioxide and the POX production of hydrogen. This analysis brought a higher selectivity for non-noble metals compared to noble metals. Another observation that noticed is concerning the selectivity of the other secondary components CO_2 and CO. Despite the high selectivity for H_2, non-noble metals also show high selectivity for these components that are considered contaminants in certain applications. Nickel-based catalysts are highly used in the literature for the reduction of carbon dioxide, this non-noble material has an affinity and forms strong bonds of its active sites with carbon [47]. Thus, despite the low cost of this catalyst, when hydrogen purity is required in the process, purification unit operations must be included.

3.2.3   Ethanol to oxygen ratio impact on POX

The sub-stoichiometry of the partial oxidation reaction implies that 0.5 moles of oxygen per mole of ethanol is required to produce CO and H_2.
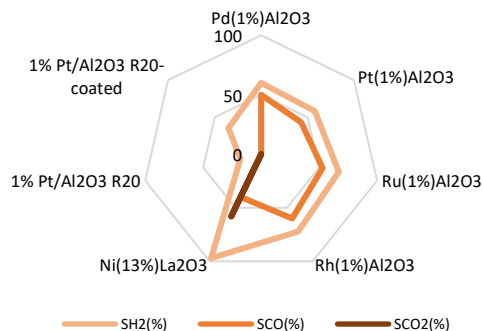

Figure 3. The radar diagram has been made from the data collected from Liguras et. al, [42] and Chiu et. al.,[45] showing the comparative selectivity of hydrogen, carbon monoxide, and carbon dioxide and the POX production of hydrogen.

Rodrigues et al. (2009) [43] investigate the impact of the O_2/EtOH ratio on the reaction, the relative concentrations of O_2 in the feed were varied while keeping the ethanol and total flows constant at 420°C. Since O_2 is the limiting reactant, increasing the O_2/EtOH ratio from 0.3 to 0.8 resulted in a better ethanol conversion (Table 3). When running in an oxygen-deficient environment, this catalyst promotes ethanol dehydration, producing ethylene and diethyl ether.

3.2.4   Catalyst deactivation

In the production of hydrogen via the ESR reaction using different catalysts, coke deposition is a significant problem that can be addressed by operating at high oxygen/carbon ratios and high temperatures. High O/E ratios effectively minimized coke formation [43], and the order of decreasing coke production was POX > ATR > ESR. Rodrigues et al.(2009) [43] used Co_3O_4/Al_2O_3/cordierite and observed relatively low levels of carbon deposition during partial oxidation. According to their findings, the alumina support contained acidic sites that favored the formation of ethylene and ethyl ether, which may have contributed to the undesirable coke deposition.

3.3 ETHANOL AUTOTHERMAL REFORMING(ATR)

Autothermal reforming is a thermally neutral or slightly exothermic process that combines steam reforming and partial oxidation. In this process, the heat generated by partial oxidation can be used for steam reforming, making the system thermodynamically neutral.

$$C_2H_5OH + 1.78\,H_2O + 0.61\,O_2 \leftrightarrow 2CO_2 + 4.78\,H_2 \quad \Delta H^0 = 0\,\frac{kJ}{mol} \quad (7)$$
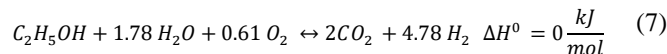
The search was performed in the Scopus database, using the keywords "ethanol autothermal reforming" were found 177 documents, search within article titles, keywords, and abstracts. The subjects of these studies were same to steam reforming and partial oxidation methodology. Therefore, this present study aims to conduct a critical review of the literature analyzing these important parameters. Within this context, Table 4 shows some autothermal reforming of ethanol studies documented in the literature.

3.3.1   Effect of reaction temperature

Hung et al. (2012) [48] also conducted a study to better understand the impact of temperature on the ATR/OSR of ethanol (H_2O: EtOH: O_2 = 3:1:0.3) on various metals (Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au)/Al_2O_3 catalysts at temperatures ranging from 400 °C to 600 °C. The results showed a proportional relationship between temperature and ethanol conversion, that ethanol conversion decreased as the temperature decreased from 600°C to 400 °C, ranging from 93% to 97% for different catalysts, the same behavior is observed with hydrogen selectivity, a decline in as the temperature decreased from 600 °C to 400 °C. The dehydrogenation of ethanol was explained using the dissociation of O–H and C–H bonds, where atomic O (produced from O_2 and H_2O) removes two H atoms from the C–H and O–H of ethanol.

3.3.2   Effect of catalyst type

Regarding the effect of the catalyst, Table 4 and Figure 4 show higher H_2 selectivities for noble materials. At 600 °C, the sequence of hydrogen selectivity was Rh > Ir > Ru > Pt > Au (in the range of 14–94%) and the sequence of ethanol conversion was almost identical and ranged from 93% to 97%.
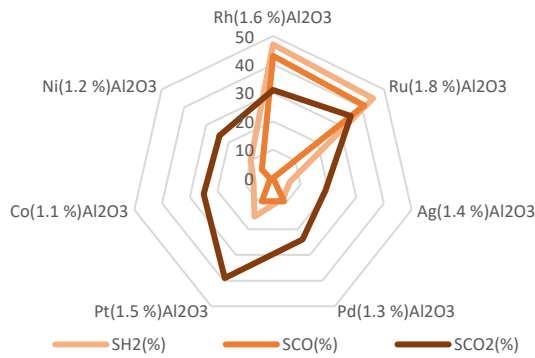

Figure 4. The radar diagram has been made from the data collected from Hung et al. (2012) [48] showing the comparative selectivity of hydrogen, carbon monoxide, and carbon dioxide and the ATR production of hydrogen.

3.3.3   Ethanol to steam ratio impact on ATR

Hung et al. (2012) [48] assessed the effects of O_2 in the ATR technique. They claim that oxygen could rapidly generate atomic O and react with ethanol, breaking the C–C bond and increasing the selectivity of hydrogen and carbon dioxide as oxygen was added. According to the study, the rate of carbon production was reduced in the presence of oxygen.

3.3.4   Catalyst deactivation

As previously mentioned, high O/E ratios effectively minimized coke formation [34], and the order of decreasing coke production was POX > ATR > ESR.

4.   CRITICAL ANALYSIS

Analyzing these three hydrogen production processes using ethanol, it noticed a technological potential. In Table 5, you can find the comparison of ethanol reforming technologies and optimal operating parameters. These data summarize the description and discussion conducted in this study according to the literature review. With this study, it noted that research and development on this topic are necessary, because of the substantial number of studies and the potential of the low-carbon methodology for hydrogen production. Ethanol steam reforming its a well-established technology and method that way the biggest number of studies.

Table 4 . Literature analysis papers on the autothermal reforming of ethanol

Ref.	Temperature(°C)	Reactor	Catalyst	Steam/EtOH/O_2 (mol %)	EtOH conversion (wt %)	S_{H2}(%)	S_{CO}(%)	S_{CO2}(%)
[48]	600	Fixed bed linear Quartz reactor	Rh(1.6 %)Al_2O_3	1.6:1:0.68	84	47	43	31
			Ru(1.8 %)Al_2O_3		83	45	41	35
			Ag(1.4 %)Al_2O_3		75	6	0	19
			Pd(1.3 %)Al_2O_3		78	8	9	24
			Pt(1.5 %)Al_2O_3		78	15	9	39
			Ir(1.8 %)Al_2O_3		95	91	27	63
			Au(1.6 %)Al_2O_3		97	18	3	26
			Co(1.1 %)Al_2O_3		78	7	1	25
			Ni(1.2 %)Al_2O_3		79	10	5	24
			Cu(1.9 %)Al_2O_3		76	9	0	16
[49]	300-450	Fixed bed linear	Rh(1.6 %)Al2O3	13:1:0.5	97	94	41	41
			Ru(1.8 %)Al2O3		96	83	33	45
			Ag(1.4 %)Al2O3		97	14	0	24
			Pd(1.3 %)Al2O3		93	22	12	28
			Pt(1.5 %)Al2O3		95	29	11	28
			Pd(2.8%)ZnO		100	45.8-60.9	1.2-0.1	9.9-22
			Pd(2.8%)SiO2		31.1-48.7	28.8-34.7	28.6-30.6	2.9-0.3
[50]	700	Fixed bed reactor	Ni(11 %)Al2O3	1.6:1:0.68	100	45		
			Ni(20 %)Al2O3		100	95		
			Ni19.4Cr0.6/Al_2O_3		100-97	98-53		
[51]	300-400	Fixed bed quartz reactor	Ni(10 %)/YSZ	4:2:1 (v/v)	100	44.1-50	23.2-24.2	20-14.9
	400		Ni(15 %)/YSZ		100	46.1	27.6	13.8
	400		Ni(20 %)/YSZ		100	40.5	35.6	4.5
[52]	635	Fixed bed reactor	Rh(1%)CeO_2	2:1 :1	100	45	15	8
	760		Rh(1%)CeO_2	4:1:1.8	100	62	16	9

Regarding coke formation, POX and ATR showed relativity low coke formation due to the oxidation of carbon in the presence of oxygen. This process also has the biggest thermal efficiency and lower thermal demand, due to the exothermic POX reaction that provide the necessary heat. But greater selectivity is found at higher temperatures, so these reactions take place at higher temperatures. And compounding the technologies, ESR features higher hydrogen selectivity. Many studies are portrayed in the literature about this technology, so it can observe that the operation conditions, the catalyst materials, the catalyst parameters, the reactors, and the reaction mechanisms already present an established knowledge, even if in a less effective way for POX and ATR.

Thus, there is a need for studies to increase the TRL of these technologies, especially for vehicular applications. As an example, studies of system scale-up, system optimizing (i.e. thermal management: reuse POX reactions), and ethanol reformers prototypes embedded in vehicles, to understand the behavior of these systems under dynamic conditions. According to Sall *et al.* (2013) [26] who developed three low-temperature ethanol reformer architectures (representing a design evolution), were developed and tested at the automotive scale with exhaust from a V8 engine. This technology studied by Sall *et al.* (2013) [26] is for an internal combustion engine. However, the prototypes developed are suitable for an on-board application, so there is a study possibility to apply this system with a fuel cell. In the same context, performing an analogy with the technology roadmap of this study, for this prediction happen it is necessary to invest in all sectors, especially in the short-term regarding research and development.

Table 5 . Comparison of ethanol reforming technologies and optimal operating parameters

Comparatives descriptions		
ESR	POX	ATR
Technology Readiness Level Well–established technology and method to steam reforming	Not well–established technology and methods like steam reforming	Not well–established technology and methods like steam reforming
Coke formation High coke formation	Relativity low coke formation due to carbon oxidation	Relativity low coke formation due to carbon oxidation
Thermal Efficiency Lower thermal efficiency	Higher thermal efficiency	Medium thermal efficiency
Selectivity Higher selectivity de H_2	Lower selectivity compared to the SR. Oxygen in POX techniques triggered oxidation processes, which led to the production of oxygen-containing gases (CO_2 and CO) rather than hydrogen	Lower selectivity compared to the SR. The addition of oxygen in ATR techniques triggered oxidation processes, which led to the production of oxygen-containing gases (CO_2 and CO) rather than hydrogen
Thermal demand Higher demand energy, strong endothermic reaction, and high reaction temperature	The exothermic POX in the reaction system may provide the necessary heat but a high reaction temperature.	The exothermic POX in the reaction system may provide the necessary heat for the endothermic ESR, which maintains thermal neutrality, but a high reaction temperature.
Optimal operating parameters		
ESR	POX	ATR
Catalyst type 1) Noble metals: Ru and Rh 2) Non-noble metals: Ni and Co	1) Noble metals: Pt and Pd 2) Non-noble metals: Ni and Co	1) Noble metals: Ru and Rh 2) Non-noble metals: Ni and Co
Optimum supports Al_2O_3, CeO_2, and ZrO_2	Al_2O_3	Al_2O_3, ZnO, and ZrO_2
Optimum reaction temperature 300°C – 600°C	300°C – 600°C	300°C – 600°C
Range Pressure 1 – 10 bar	1 – 10 bar	1 – 10 bar
Reactors Fixed-bed reactor and quartz-bed reactor	Fixed-bed reactor and quartz-bed reactor	Fixed-bed reactor and quartz-bed reactor

5. TECHNOLOGICAL ROADMAP

Green hydrogen is a promising opportunity for creating sustainable wealth in Brazil and in the world. GH_2 is produced through the electrolysis of water using renewable energy and can be used as a clean energy source in many sectors such as transportation, industry, and power generation. As mentioned anteriorly, despite the many H_2 production ways, the study aims to analyze the perspectives of green and moss hydrogen in the Brazilian scenario. Regarding the roadmap for GH_2 in Brazil, the country has significant potential for the production and exportation of GH_2 due to the availability of renewable resources such as sun and wind, as well as an abundance of water. However, further actions are necessary to set ambitious targets for GH_2 production and to implement public policies that incentivize the development of the hydrogen value chain, including investments in infrastructure, research and development. According to McKinsey (2021), [4] GH_2 will require USD 200 billion in investments and 180GW of additional power capacity from renewable sources. This value of energy required is more than the entire generating capacity in 2020. To produce GH_2 Brazil would need to accelerate the expansion of its power infrastructure by 7% per

year, or 3 percentage points more than the 4% annual expansion rate of recent years.

By 2030 an additional 19-39 GW would be required, or 11-22% of the current capacity. By 2040 this need would be further increased to 129-178 GW. On the other hand, the total potential for renewable energy should not be an issue in 2040, as by then the main potential sources, wind, and solar, should be able to supply 100% of the demand for GH_2. The total wind power capacity by 2040 is estimated at 185-206 GW, with the total potential in Brazil being as high as 247 GW using 100 m turbines; solar energy capacity should be 134-155 GW by 2040 and could reach as high as 307 GW with the best locations. Brazil has a positive historic investment in renewable energy, which the capital cost perceived by renewable energy investors is higher in Brazil than in competing countries (8-9% vs. 7%). In either case, numerous themes must be addressed to allow GH_2 to be developed in Brazil across the value chain. The primary obstacles in power generation and transmission relate to regulations aimed at accelerating the expansion of renewable energy generation. When it comes to on-grid configurations, taxes, and industry charges for power purchase agreements (PPAs) and self-generation over the medium and long term may considerably impact the competitiveness of Brazilian GH_2. Therefore, a monitoring system is needed to track energy generation in near real-time for renewable energy trade agreements. For off-grid configurations, the primary regulatory challenges include the construction of transmission lines to enable off-grid setups, the environmental impact analysis, and rights-of-way issues.

Hydrogen production, transportation, and storage face significant challenges in terms of developing the market. Long-term demand uncertainties, both in terms of volume and prices, pose risks for investors, potentially inhibiting the funding of large projects. Regulatory challenges also exist, for example determining which government agency will take on regulatory functions and establishing regulations governing the use of hydrogen. Technical standards for hydrogen facilities and transportation must be developed, such as when adding hydrogen to natural gas flowing in pipelines. Concerning the end-use of GH_2 and its derivatives, the primary challenges lie in certification trends. In international markets, the requirement that only wind and solar energy be used may limit the use of the cleanly integrated grid that exists in Brazil, which constitutes a significant competitive advantage. Internally, regulations to support other sources of energy and the non-existence of carbon pricing make traditional solutions more competitive in the short term, delaying the domestic adoption of hydrogen [4,53].

Analyzing the technological strategy, the expanding generation will require doubling or at least reinforcing the current transmission infrastructure. In Figure 1 it can observe the perspective for the technology to Brazil with the following

proposal tree steps to materialize 2050 goals: short-term (2025-2040), medium-term (2040-2050) e long-term (from 2050 on). First, the focus for short-term in Brazil should ensure the effective implementation of the first projects and associated infrastructure. This first time will create the infrastructure to value chain hydrogen, so it is necessary to develop the pilot plants related to the entire hydrogen chain, such as renewable energies, electrolyzes, transmission, storage, and transport, in addition to initiating upgrades in ports and terminals [53].

From the point of view of technology for mobility, the vehicle-based fuel hydrogen not being the focus for Brazil, due to the difficulty to change the fueling infrastructure and territorial extension of the country, mainly to passenger car fleet. However, it is necessary to develop a basic infrastructure to support the future fueling stations. For the heavy fleet, the application is a possibility due to high-efficiency technology-based hydrogen. According to a report, by CNI (2022) [53] hydrogen fuel cell technology has the potential to revolutionize mobility in heavy-duty trucks, buses, trains, and forklift fleets, offering a more economical option even without carbon pricing. In addition to contributing to mobility decarbonization, these applications can also significantly improve the quality of life in large cities, reducing pollution and associated health problems. In Brazil, the transportation sector was responsible for 14.2% of all greenhouse gases emissions in the country in 2016, making it a priority sector for reducing anthropogenic carbon emissions. Urban public transportation by bus is the most important mode of daily commuting in the country, with some prototype projects already executed since the year 2000. It is worth noting that, given Brazil's leadership in bus manufacturing, with an annual production of about 30,000 units, the country already has a solid foundation for the development of a national hydrogen fuel cell bus industry. Another interesting market to Brazil and important for the hydrogen application chain is equipment and tolerant components of this fuel. This time the expectation for prices to end consumer in the fueling station scenarios is 4.9 USD/kgH_2 [4].

Medium-term (2040-2050), the main goal is to consolidate Brazil as a global industry leader by continuously evolving regulations, promoting the use of GH_2 in new applications, and capturing synergies of scale, preparing for an industry free of incentives. During this period, the infrastructure created both on an industrial scale and for mobility will be consolidated. By 2050, long term, this technology will be fully consolidated, Brazil will be a reference in the distribution of hydrogen and renewable energy. At this time, the expectation for prices to end consumer in the fueling station scenarios is 4.2 USD/kgH_2 [4,53]. Regarding the GH_2 price, the report emphasizes that it is currently more expensive than other conventional energy sources. However, as GH_2 demand increases and production and storage technologies are improved, costs are expected to

decrease significantly. Additionally, the report suggests that GH_2 may become more competitive compared to other energy sources, especially in sectors that are difficult to electrify, such as heavy industry and long-distance transportation. Brazil can use its natural resources sustainably and become one of the global leaders in GH_2, stimulating the growth of numerous industries that will be driven by this new commodity. To enable this, we must start acting now.

Discussing the moss hydrogen technological roadmap, due to the ethanol industry experience as given the prevalence of flex (gasoline/ethanol) engines in Brazil and the expectation that ethanol prices will continue to remain around 70% of gasoline prices, it is likely that moss hydrogen will face limited competition. Nonetheless, in areas where ethanol production is abundant, this alternative could potentially secure a notable portion of the energy mix, by converting ethanol to hydrogen at fueling stations. In essence, the biofuel market could facilitate the growth of the hydrogen industry as emerging technologies advance. Brazil's established infrastructure for manufacturing, distributing, and storing ethanol, it's worth considering that this industry may also explore opportunities in the hydrogen market. While we anticipate passenger vehicles will eventually transition to electric power in the distant future, heavier vehicles like buses and trucks are more inclined to rely on hydrogen fuel cells to achieve decarbonization.

Furthermore, the roadmap for ethanol reform involves the production of GH2 from ethanol. This technology has the potential to significantly reduce greenhouse gas emissions from the transportation sector, which is currently responsible for a relevant portion of global emissions. Furthermore, the roadmap for ethanol reform involves the production of GH2 from ethanol. This technology has the potential to significantly reduce greenhouse gas emissions from the transportation sector, which is currently responsible for a relevant portion of global emissions. The roadmap for the application of ethanol reforming in Brazil consists of strategic planning for the development of technologies and infrastructure for hydrogen production from ethanol. Brazil is one of the world's largest ethanol producers, and ethanol reforming can be a promising alternative for hydrogen production, given that the country already has a well- developed ethanol distribution network. In the roadmap for the application of ethanol reforming in Brazil, it is important to consider the main challenges to be faced, such as the optimization of the reforming process to maximize energy efficiency and reduce greenhouse gas emissions, the adaptation of fuel cell and infrastructure for the use of hydrogen as fuel, and the creation of policies and incentives to stimulate investment in research, development, and implementation of the technology.

According to Figure 5, the future scenarios forecasts that through technology innovation and increase deployment of hydrogen production in regions with excellent renewable resources, will be comparable with the cost of hydrogen from natural gas with CCUS, close to 1,3-3,5 USD/kg, being more competitive in 2030 [11]. Regarding ethanol reforming, the short-term forecast is that it will occur investment in research, mainly in scaling up the production of moss hydrogen and use cases as onboard vehicle applications.

Figure 5. Technologic roadmap green and moss hydrogen: short, medium, and long term.
Source: Adapted McKinsey(2021) [4] and CNI (2022)[53]

At this time, the price of moss hydrogen will be in the range of 4.6 – 7.5 USD/H2kg. The medium-term will have a scale pilot of the application of ethanol reforming to vehicles and promotion of the stationary production of moss H2. The third period will have the infrastructure for moss H2 production already consolidated, so the technology will be utilized in high demand for the H2 distribution and onboard on vehicles. At this time, the price of moss hydrogen will be in the range of 4.2 – 7.0 USD/H2kg.

It is important to point out that this paper is a prediction based on market studies. Much effort by both private and public sectors is important to materialize this scenario. But the use of hydrogen as a fuel has the potential to reduce the dependence on fossil fuels, reducing the CO2 and polluting gases emission, contributing to the energy transition towards a more sustainable and cleaner model. Moreover, hydrogen can be used in various applications, such as electricity generation, transportation, and the chemical industry, among others. Therefore, the roadmap for the application of ethanol reforming in Brazil is essential to guide public policies, investments, and research aimed at hydrogen production from ethanol, aiming to contribute to the sustainable development of the country and the reduction of greenhouse gas emissions.

6. CONCLUSIONS

In conclusion, ethanol reforming is a conventional process heterogeny catalyst, using fixed bed catalysis reactor. This is a well-developed and polished technology with a defined operational parameter proving its efficiency. However, challenges remain in scaling up the technology and maintaining a dynamic and efficient operation. Investments in research and development is crucial for the implementation of this technology in medium-term. The potential benefits of this process, such as improved efficiency and reduced environmental impact, make it a worthwhile area for continued investment and development.

7. ACKNOWLEDGMENTS

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