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Abstract

Hydrogen is the lightest chemical element in the periodic table, with a high calorific value, much higher than that of methane, gasoline, diesel, and methanol. Its combustion releases a large amount of energy and water as a product. The major part of the world's production of hydrogen comes from natural gas, through Synthesis Gas production, which can also be produced from alternative renewable sources or even water. Synthesis gas is an intermediate product of great importance for the industry, as it is possible to produce hydrogen from it, but, among other products, ammonia is one of the most important products as is used mainly to produce fertilizers. This paper resume the importance of syngas and hydrogen, its ways of production, classifications, scientific production around the world in this field, and their relation to the current economical problems such as food shortages and energy crisis specifically in Brazil.

Keyword: Hydrogen, Syngas, economical problems, energy, food, Brazil.

Hydrogen as an energy alternative

Hydrogen (H) is the lightest chemical element in the periodic table, with a molar mass equal to 1 gram per mol ($g.mol^{-1}$). Under ambient conditions it is an odorless, colorless gas, less dense than air; has a high calorific value (amount of energy per unit mass released by a substance by combustion) equal to 141.4 $kJ.g^{-1}$, much higher than that of methane (55.5 $kJ.g^{-1}$), gasoline (47.5 $kJ.g^{-1}$), diesel (44.8 $kJ.g^{-1}$) and methanol (20 $kJ.g^{-1}$). [Dincer, 2012]. Hydrogen is a potentially explosive gas and special conditions are required for its handling and storage. The difference between the aforementioned fossil fuels is that, when they burn, they produce carbon dioxide (CO_2), one of the main greenhouse gases, and water (H_2O). The combustion of hydrogen releases a large amount of energy and water as a product (Reaction 1). [Asencios et al. 2022[a,b]]

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(v)} \quad \Delta H^{o}_{298K} = -286\ kJ.mol^{-1} \quad \text{- (Reação 1)}$$

Hydrogen is the most abundant chemical element in the universe. It is abundant on the earth's surface, as it forms part of water molecules (H_2O), it is also found in hydrocarbon molecules, for example, in petroleum, and many other organic substances. However, because hydrogen is not found in an isolated form on our planet, chemical processes are necessary to extract it. Nowadays, with scientific advances, it is possible to extract hydrogen from different sources, for example, water, oil (and derivatives), natural gas, ethanol, methanol, biomass, biogas, algae, glycerol, etc. Each source follows a specific process to produce hydrogen. Furthermore, Syngas can be produced from pre-treated biogas [Asencios et al. 2014, Asencios et al. 2022[a]], biomethane [Asencios et al. 2022[b]], bioethanol [Carvalho, et al. 2016] among other sources. However, most of these procedures are still at a laboratory scale or exist only in pilot-level studies.

Green hydrogen and gray hydrogen

Hydrogen produced from fossil fuels is known as **gray hydrogen.** Although hydrogen has no color, this is a way of naming its origin. Currently, the world production of hydrogen comes from synthesis gas, which is a gaseous mixture formed by carbon monoxide (CO) and hydrogen (H_2), also called Syngas (Synthesis-Gas), produced from fossil fuels, mainly natural gas, through a process called Methane Steam Reform (RVM, Reaction 2).

Synthesis gas can also be produced from other sources that do not depend on fossil fuels, such as biogas, bioethanol, glycerol, bio-oil, among others. Synthesis gas is a raw material of great importance for the chemical and petrochemical industry, as it is possible to produce hydrogen from it, through a purification process called Water-Gas Shift Reaction (WGSR), as well as other compounds of high industrial value such as methanol (used as a solvent, fuel, etc.), dimethyl ether (DME, also used as a fuel with similar properties to diesel), Fischer-Tropsch liquid fuels, and ammonia (NH_3), used mainly to produce fertilizers. Synthesis gas can also be used in direct combustion. [Asencios et al. 2022, Morales Udaeta et al. 2022]

Most of the hydrogen and synthesis gas produced in the world is used in the production of fertilizers, petroleum refining, and the petrochemical industry. Recently, hydrogen has been seen as a promising source of clean energy. Its use as fuel in cars takes place through devices called fuel cells, whose technology is accessible in European, North America, and other countries, such as Japan, South-Korea, among others, for now. There is the possibility of using hydrogen by direct combustion, as shown by some recent studies, for example, in turbines. [Vieira da Rosa and Ordóñez, 2022].

Hydrogen can also be produced by the electrolysis of water (Reaction 3). In this case, it does not require fossil fuels, the electrolysis of water is widely known. It is a process that needs water, electricity, and electrodes to happen. Electric energy can come from renewable sources, for example, renewable energy plants, such as wind, solar, hydroelectric, etc., and supply this energy needed to obtain hydrogen. Hydrogen produced from the electrolysis of water and electricity from renewable energy is known as **green hydrogen.**

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2 \quad (\Delta H_{298K} = 285{,}8\ kJ.mol^{-1},\ \Delta G_{298K} = 1{,}23\ v) \text{ - (Reação 3)}$$

Using seawater in this process would be wonderful, especially due to the large amount of seawater available on our planet, however, its use presents some problems due to the amount of salts it has, which makes the process difficult and also causes an abundance of by-products/waste, such as brine, which needs to be treated before being dumped into the sea, as the absence of the process can change the environment and influence the marine flora and fauna. Its disposal is something that should be analyzed with caution [Gao et al. 2022]. The industrial use of brine is still not very diverse. It is currently possible to use it in the food industry and to produce chlorine gas and sodium, both of industrial value. However, the production of the latter, coupled with a green hydrogen production system, is a topic that needs to be evaluated globally and overcome economic, logistical, and environmental barriers.

In the case of Brazil, technology based on electrolysis is very attractive, mainly due to the existence of large natural resources and the various hydroelectric plants spread across the country, since 87% of the Brazilian energy matrix comes from renewable energies in 2021 (and in the rest of the world this value was 27% in 2019), and

65.2% of this value comes from hydroelectric plants, according to data from the Energy Research Company of Brazil [2021]. Electrolytic processes are well known and easily scalable, therefore, such technology is the most coherent in the short term.

Still, concerning hydrogen, it is important to mention that the chemical element can also be obtained through photocatalytic processes, using solar energy and water, when performing the separation of water with a semiconductor catalyst. [Asencios and Machado, 2022].

The use of hydrogen as a source of energy requires electrochemical devices called fuel cells (which convert chemical energy into electrical energy, through oxidation and reduction reactions of hydrogen and oxygen, respectively, producing water and electrical energy) and special cylinders for their storage and adequacy of an entire supply chain to the final consumer, in addition to local legislation. These are all challenges to achieving an economy that revolves around hydrogen rather than oil. This is not so close to the reality of developing countries. Other alternatives are closer to being developed, such as bioenergy and renewable energies.

There are other definitions of hydrogen, such as blue hydrogen, which refers to the element obtained from the burning of fossil fuels, followed by the capture and storage of carbon dioxide emitted in the process. Turquoise hydrogen is produced by breaking down the methane molecule through pyrolysis. Natural gas pyrolysis is a process that requires thermal (endothermic) energy to convert methane into hydrogen and solid carbon. . [Energy Research Company of Brazil, 2022]

Hydrogen as a source of energy storage and its relationship with renewable energies.

The use of renewable energies is extremely necessary in today's times to avoid the emission of greenhouse gases and the consequences of the increase in the planet's temperature and to guarantee a sustainable future that lasts for generations to come. However, the dependence of these energies on the climate makes it an intermittent source of energy, as they jeopardize the continuous production of energy in the absence of favorable climatic conditions, for example, at night, when there is no sunlight. Therefore, together with renewable energy systems, it is necessary to store electrical energy, which is currently done through batteries, which can be lead-acid, nickel-cadmium, or Li-Ion. However, energy storage in batteries is still expensive and inefficient. High-performance batteries are still a challenge (high performance in terms of maximum energy storage capacity, low weight, small space, and low cost). An alternative to this is to store energy in the form of hydrogen, using excess renewable energy to produce it, due to the characteristics of this chemical element mentioned earlier.

The role of hydrogen in achieving international agreements.

In a joint effort of the United Nations Framework Convention on Climate Change (UNFCCC), the Paris Protocol was created, an agreement that has as its main objective to mitigate climate change and bring global temperatures well below 2, compared to pre-industrial levels (UNFCC, 2020), in addition to accelerating investments and actions for a more sustainable future. Brazil has committed to reducing greenhouse gas emissions by 37% below 2005 levels by 2025 and, consequently, by 43% below 2005 levels by 2030, according to data from the Ministry of the Environment released in 2020. To meet the deadlines established by the Paris Protocol, new sustainable measures are being designed by the signatory countries of said agreement, to mitigate the impacts of the use of fossil fuels on the planet. There are strong reasons for the development of hydrogen technology in Brazil, among them we can mention:

1) Reduce climate change and the emission of greenhouse gases;

2) Combat high dependence on fossil fuels. Brazil still depends on fossil fuels (mainly concentrated in means of transport that use automotive fuel). Despite this, Brazil has one of the cleanest electrical matrices in the world, with a share of 70% of renewable energies in the national electrical matrix. However, these are weather-dependent (disadvantages were mentioned earlier). In addition, 60% of this share comes from hydroelectric plants, which are highly dependent on rainfall and are more sensitive to climate change and the Amazon rainforest. A more diverse electrical matrix is needed and 30% of the energy still comes from fossil fuels;

3) Oil price variation. The value of the price of oil follows a complex formula that goes beyond the objectives of this article, as it depends on many variables, such as global supply and demand, the price in the international market, the price of the dollar, the internal policy of each country and the geopolitics. It is worth remembering that at the beginning of the pandemic we saw the price of a barrel of oil fall to negative values and soar its value over the last few months due to the war between Ukraine and Russia. Achieving energy independence from oil and energy security are goals that every country aspires to;

4) The challenges of controlling uncertain oil reserves;

5) The growing world energy demand.

Developing countries, such as those in South America, have enormous potential for generating solar, wind, hydroelectric, and bioenergy. All of them are promising. A not-so-favorable scenario is seen in developed countries, for example, those that make up the European Union and the US, where the use of hydrogen as a fuel seems to be a quick alternative to comply with the Paris Agreement. Brazil has the potential to become a major exporter of hydrogen, which would generate many jobs and demand qualified labor.

Synthesis gas and food security in Brazil

Plants need NPK macronutrients (symbols for the chemical elements nitrogen-phosphorus-potassium, respectively), in addition to sun and water, of course, in order to survive and grow. Fertilizers contain these macronutrients. In the case of nitrogen-based fertilizers, they are made from NH_3. Although nitrogen is an element in abundance on planet Earth, as it is found in atmospheric air at a composition of 79% by volume, plants need to absorb it through the roots (in the form of NO_3^- or NH_4^+), with the use of fertilizers when the soil does not have this nutrient in abundance. A way to fix atmospheric nitrogen was discovered over 100 years ago, just before 1st World War, in Germany, by the chemist Fritz Harber, who discovered the synthesis of ammonia using nitrogen from air and hydrogen (over iron catalyst). The industrialization of the process was carried out later by Carlos Bosch. These discoveries led to both winning the Nobel Prize in Chemistry in the years 1918 and 1931, respectively. The process is better known as Harber-Bosch is still used today (Reaction 4). This process uses hydrogen, obtained from natural gas, nitrogen, and Fe catalysts.

$$N_2(g) + 3\ H_2\ (g) \leftrightarrow 2\ NH_3\ (g)\ \Delta H_{298K} = -92.22\ kJ.mol^{-1} \text{ - (Reaction 4)}$$

Brazil exports food to supply the demand of almost one billion people in the world; around a sixth of the planet's population [Senra 2020]. Contrary to this, it has recently been reported that 33 million people in Brazil do not have what to eat [Silveira 2022, Andrade 2022]. There are several reasons for this food shortage, and one of them is related to the high price of fertilizers, which makes food prices more expensive.

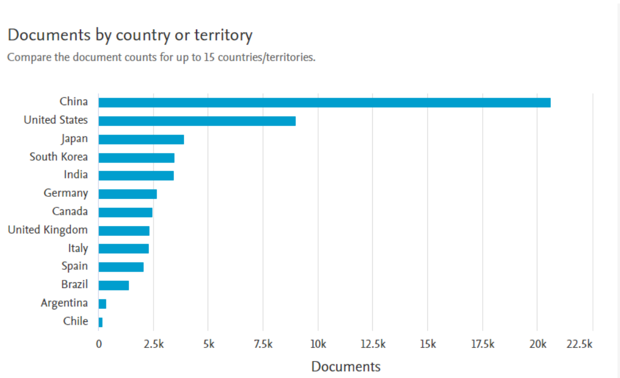
Brazil is the fourth largest consumer of fertilizers in the world, preceded by China, India, and the United States, and is the world's largest importer of these inputs. Just to give you an idea, in 2021 Brazil consumed more than 40 million tons of fertilizers, 85% were imported. The biggest NPK exporter on the planet is Russia. The hydrogen needed for the synthesis of ammonia (Reaction 4) comes from natural gas, which is transformed into synthesis gas through Reaction 2, seen above, a fuel of which Russia is the second-largest producer in the world and the largest exporter. Ammonia is the raw material for the production of fertilizers, for example, urea and ammonium nitrate. Russia and the Middle East (Saudi Arabia, Qatar, and Iran - major producers of oil and natural gas) - are the biggest exporters. [Frost 2022]

The intensification of hydrogen production in Brazil would, consequently, help the local production of ammonia and, with it, the production of nitrogen fertilizers. This would bring benefits to the country's economy and also help to reduce this food insecurity.

Research metrics in the world

According to one of the most important databases of scientific articles, Scopus, research in the world on Hydrogen and Synthesis Gas (Syngas) began to gain more interest in 2004 with enormous growth since then, resulting in 62,292 articles published between 1964 and 2022. Research is led by countries such as China, the United States, Japan, South Korea, India, and Germany, among others. And in the regional scenario, Brazil stands out in Latin America. Many of the works in Brazil focus on the production of hydrogen/synthesis gas from bioproducts, such as sugarcane ethanol, glycerol, bio-oil, and biogas, it is important to mention that Brazil is a world power in biofuels. The data can be found in Figure 1.

Although these processes are still at a laboratory scale, the results are very promising, even more so considering the current global scenario.



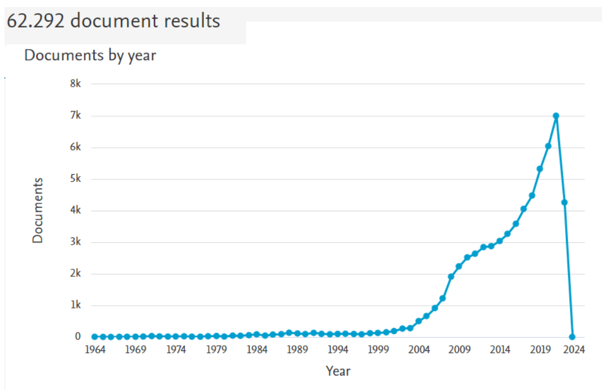


Figure 1. Search results on the Scopus platform using the keywords hydrogen and production. Available at: < https://www.scopus.com/search/form.uri?display=basic#basic>. Accessed on: 26 jun. 2022.

The implementation of technology to produce hydrogen and support for science and universities in Brazil would facilitate the construction of a project for the energy future of Brazil, and with this, it would achieve energy and nitrogen fertilizer independence. This would also help create demand for skilled labor and heat the economy.

Final considerations:

- More investment should be addressed in the development of the production of hydrogen technologies from renewable sources, including water.
- A lot of studies have been reported about Syngas and hydrogen production, however, it's the perfect time to scale up hydrogen production from renewable sources.
- The production of Syngas to produce ammonia must catch more attention, owing to the current global economic crisis of food.
- Hydrogen is promissory for fuels and for other uses such as ammonia, however, the current scenario demonstrates that its use as fuel is more close to the reality of developed countries. Brazil and Latin America in conjunction have a lot of potentials to be hydrogen suppliers for the world (if produced from renewable sources). This technology would favor the economy of Latin America and the demand for skilled workers.

Conflicts of interest

The Author declares that there is not any conflic of interest.

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