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Energy Storage Development using Hydrogen and its Potential Application in Colombia

Adriana Rincón Montenegro*, Marco Sanjuan, Mauricio Carmona

Grupo de Investigación UREMA, Departamento de Ingeniería Mecánica, Universidad del Norte, Barranquilla, Colombia.
*Email: afrincon@uninorte.edu.co.

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ABSTRACT

With the increase in the world population, the needs for energy generation have increased, the biggest contribution for this production comes from fossil fuels, which causes significant negative impacts on the environment and sustainability, such as global warming and stock-outs. In this way, it is essential to develop renewable energy alternatives that gradually replace conventional sources. However, these kinds of sources mostly dependent on environmental conditions, so they have the disadvantage of being intermittent and fluctuating. It is considered that hydrogen can be an attractive option for energy storage maximizing the benefit of renewable energy sources. In the last decades, different technologies have been developed to the use of hydrogen as backup and a renewable energy source. This study provides an inspection of the hydrogen technologies that range from the ways to produce hydrogen from renewable energy sources to their different storage alternatives. It is also presented an outlook of available energy policies and development background in different Latin American countries for power generation using renewable sources. Finally, the analysis focuses its attention in the Colombian potential for several sources (solar, wind, biomass) combined with the use of production and storage technologies for hydrogen as an energy carrier.

Keywords: Hydrogen Energy Storage, Hydrogen Production, Renewable Energy, Power-to-Gas.
JEL Classifications: Q28, Q48, Q58

1. INTRODUCTION

The development of the generation of energy through renewable sources in order to replace fossil fuels has been increasing in recent years; reaching a generation of 2351 GW at the end of 2018, which represents approximately one third of the total installed electrical capacity (IRENA, 2019).

Renewable energy plants have different drawbacks due to their natural dispersion. Usually, these plants are far from energy demand place, and this difficult the transportation of the energy produced. Generation depends on the climatic conditions in its operation, the characteristic intermittency and fluctuation of these types of sources cause difficulties for predicting their power generation capacity, resulting in non-balance between power generation and load demand (Zhang et al., 2016). The most worked alternative to overcome these problems is the storage of energy. Research has shown that the use of hydrogen as a fuel and coupler in energy storage systems generates flexibility and support for power generation with renewable sources (Schiebahn et al., 2015).

Although the market for hydrogen is mainly based on industries such as oil, food, ammonia production, among others, different countries in the world as Brazil (Sacramento et al., 2013), Ecuador (Pelaez et al., 2014), China and Japan (Lee, 2014) have been working on the development of production, distribution and storage of hydrogen for energy purposes.

In this study, the use of hydrogen as a source of renewable energy is reviewed, starting with from the production of hydrogen from different renewable sources, different storage forms such as compressed gas, cryogenic liquid and through solid materials. Also, the available technologies for electrical generation using hydrogen are presented. Finally, the application landscape of hydrogen for Colombia is analyzed as a study case for developing countries.

2. WHY ENERGY STORAGE WITH HYDROGEN?

Due to the limited nature of fossil fuels and the environmental problems of today, renewable and clean energy sources are required to meet energy requirements. Despite the benefits of renewable sources such as wind and solar energies, some difficulties as their natural intermittency and dispersion avoid its extensive use, which increases the vulnerability of the existing electrical system. Furthermore, due to the lack of accurate predictive models for power generation using this type of energy, its integration to the current electricity grid could cause severe problems for final users, such as voltage drops, frequency variations, and low power factor, etc. (Albadi and El-Saadany, 2010). Energy storage would be a robust alternative to overcome most of these challenges (Aneke et al.,2016).

Hydrogen is considered as a potential energy source of energy (Kaur and Pal, 2019). Hydrogen has several advantages compared to other fuels. E.g. its high specific energy, the energy content of 9.5 kg of hydrogen and 25 kg of gasoline is equivalent (Das, 1996), since it is the lightest element, it can be easily transported and stored in different ways.

Hydrogen is a versatile energy carrier, which can be produced from different primary and secondary sources of different origins. Figure 1 shows a summary of the routes and processes involved depending on the generation source chosen for its production.

Hydrogen storage can help move from centralized to distributed generation, which offers benefits such as increasing access to energy and availability in remote areas, reliability, energy security, and improve the performances. Some benefits offered by hydrogen storage are listed in table 1 for different segments of the energy market.

3. CLEAN TECHNOLOGIES FOR THE PRODUCTION OF HYDROGEN

For hydrogen to be considered as a relevant source of energy to replace fossil fuels, it is required that its production comes from cheap and renewable sources some different things. There are different technological gaps that not allow the viability in some scales of the generation, storage, distribution and use of hydrogen; which have become opportunities for technical and innovation developments in different countries (Wen Li et al., 2016). Among the sources for the production of hydrogen is the use of different raw materials such as biomass, water, glycerol, and others, through thermochemical, electrolytic or photolytic processes (Niaz et al., 2015).

3.1. Biomass Processes

Generating hydrogen from renewable biomass has several advantages compared to fossil fuels, such as mitigating CO_2 emissions, increasing value in agricultural production, and being a renewable source (Kırtay, 2011). Different types of biomass can be transformed into hydrogen through thermochemical processes such as gasification, pyrolysis, and fermentation.

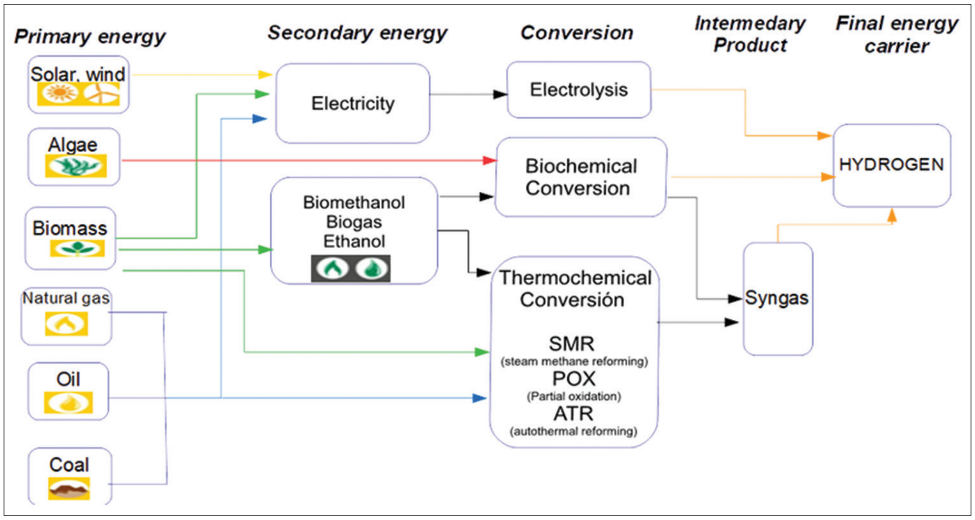
3.1.1. Gasification

It is a thermochemical process in which a gaseous fuel is produced from a solid fuel like biomass or solid waste obtaining a synthesis gas (a mixture of hydrogen and carbon monoxide). gasification process can be expressed by the following simplified net reaction (Zhang et al., 2016):

$$C_xH_y + xH_2O \rightarrow \left(\frac{y}{2}+x\right)H_2 + xCO \qquad (1)$$

The carbon monoxide produced from the process can be reacted to produce H_2 through the catalytic reaction of water-gas at a temperature lower than that of gasification. After that, the carbon dioxide can be separated and removed from the final H_2 product, along with any other remaining impurity (Wietschel and Ball. 2009.

Figure 1: Summary of the existing processes for the production of hydrogen



Adapted from: (Shell Deutschland oil GmbH, 2017)

Table 1: Benefits of storing hydrogen

Benefits to transmission y distribution companies	Benefits to electricity users	Benefits to renewable energy generators
Reduce the need for contingency reserves	Improved power quality and reliability, hence less process interruption and maintenance cost	Improved capacity utilization, reduction of grid non-availability hours
Ability to diversify generation resources	Ability to use higher onsite renewables.	Voltage and frequency regulation at the point of injection- avoidance of grid penalties
Grid voltage and frequency regulation	Overall lowered costs with price arbitrage/use of off-peak power of low cost	Load leveling and better ability to forecast, which modern grid system requires
Meeting off-grid mandates and demands		
Grid stability		

Source of data: Prepared by the authors based on data from: (ESA, 2019)

3.1.2. Pyrolysis

This technique consists on the rapid heating of the biomass at a high temperature in the absence of air (Jalan and Srivastava, 1999). The pyrolysis products are presented in gaseous, liquid, and solid phases, which are formed by:

- Gaseous products: hydrogen, methane, CO, CO_2, and some other gases.
- Liquid products: tar and oil that remains in the liquefied form at room temperature such as acetone, acetic acid, etc.
- Solid products: mainly includes coal, pure carbon, and some other inert materials.

3.1.3. Fermentation

This type of process consists of the production of hydrogen from biological methods, with the use of organic waste (Mohammadi et al., 2014; De Gioannis et al., 2013). The fermentation reaction is carried out by anaerobic microorganisms that convert the rich matter in carbohydrates, in hydrogen, CO_2 and other acid end products (Turner et al., 2008), the reaction can be expressed as:

$$C_6H_{12}O_6+2H_2O\rightarrow 2CH_3COOH+2CO_2+4H_2 \tag{2}$$

Biological methods have been considered a promising way to produce hydrogen with low contamination and high efficiency (Chaubey, 2003).

3.2. Water Electrolysis

Hydrogen can be produced by the electrochemical division of water in the presence of a continuous electrical current supplied by renewable energy sources (Kwak et al., 2014). An electrolyzer is a device that combines the oxidation and reduction reactions to produce hydrogen and oxygen gas. In principle, any source of electric power generation could be used, e.g. photovoltaic power plants, wind and other sources.

3.3. Photolytic Processes

The photolytic processes use the energy contained in the photons to carry out the electrolysis of water, which leads to the production of hydrogen. The photocatalytic division of water, the photoelectrochemical division of water and biophotolysis are examples of this kind of processes (Dincer and Acar, 2015).

3.3.1. Photocatalytic water separation

In this process, hydrogen is released from water when the molecules absorb energy at a rate of 285.57 kJ/mol of ultraviolet radiation (Kothari et al., 2008). Several supramolecular complexes, like TiO_2 with CuO, can be used to convert the energy of the photons to release the gases formed from the water. Two actions occur in this process: photo-reduction and photo-oxidation, which are represented by the following reactions (Zhang et al., 2016):

Photoreduction:

$$2H_2O+2e^-\rightarrow H_2+2OH^- \tag{3}$$

Photo-oxidation:

$$2H_2O\rightarrow 4H^++4e^-+O_2\ (g) \tag{4}$$

The separation of photocatalytic water is a direct method of hydrogen production from any water source. However, this method has low production efficiency (Kothari et al., 2008).

3.2.2. Photoelectrochemical separation of water

The photoelectrochemical division of water, also called photoelectrolysis, uses solar irradiation to generate an electric current that drives the water electrolysis process, that drives the water electrolysis process by using photoelectrochemical cells (PEC). One of the main characteristics of the PEC cell is its compact integration between the generation of solar energy and the electrolysis of water. Efficiencies of 18.3% have been achieved for a single band system in the laboratory, while conversion efficiency above 30% can be achieved for dual-band systems (Licht 2001).

4. TECHNOLOGIES FOR THE STORAGE OF HYDROGEN

Storage of hydrogen is a decisive factor in the economy of hydrogen. One of the most critical and challenging applications is to develop safe, reliable, efficient, and practical storage mechanisms. Hydrogen storage applications are summarized in Figure 2. These can be divided into fixed and mobile applications. The stationary storage methods are mainly for in situ storage at any point of production or use, and for the generation of stationary energy. Mobile applications are intended to transport small amounts of stored hydrogen, according to the needs of the vehicle, to be used on spot.

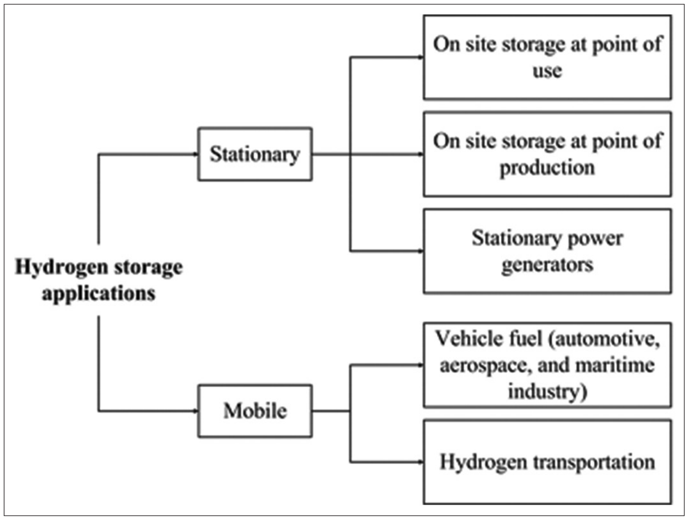
Hydrogen has a low energy density by volume compared to fossil fuels, which usually results in large storage vessels. Alternatives to store an appropiate amount of hydrogen include the use of high storage pressure, low storage temperature, or materials that attracts a large number of hydrogen molecules. Figure 3 shows the most common hydrogen storage technologies.

4.1. Physical Storage as Compressed Gas

Due to its characteristics, hydrogen needs to be stored under special conditions, the main drawback being the non-proportionality of the relationship between volumetric density and pressure (Stetson, NT, 2014), as a result, such storage is bulky and difficult to integrate for some applications. Reason why the alternative of storing hydrogen at high pressure offers simplicity of technology and fast filling speed.

After the compression of hydrogen storage is done in two ways: on the surface or under the ground. The alternative on the surface generates high investment costs for large storage scales. The below-ground alternative has been implemented in a wide range of hydrogen storage, saline cavities of Teesside, United Kingdom, and Texas, USA. UU (Kruck et al., 2013). Which demonstrates the applicability of the method (storage of electrochemical energy for renewable sources and grid balance, 2014).

Figure 2: Types of hydrogen storage applications



Source of data: Prepared by the authors based on data from: (Moradi and Groth, 2019)

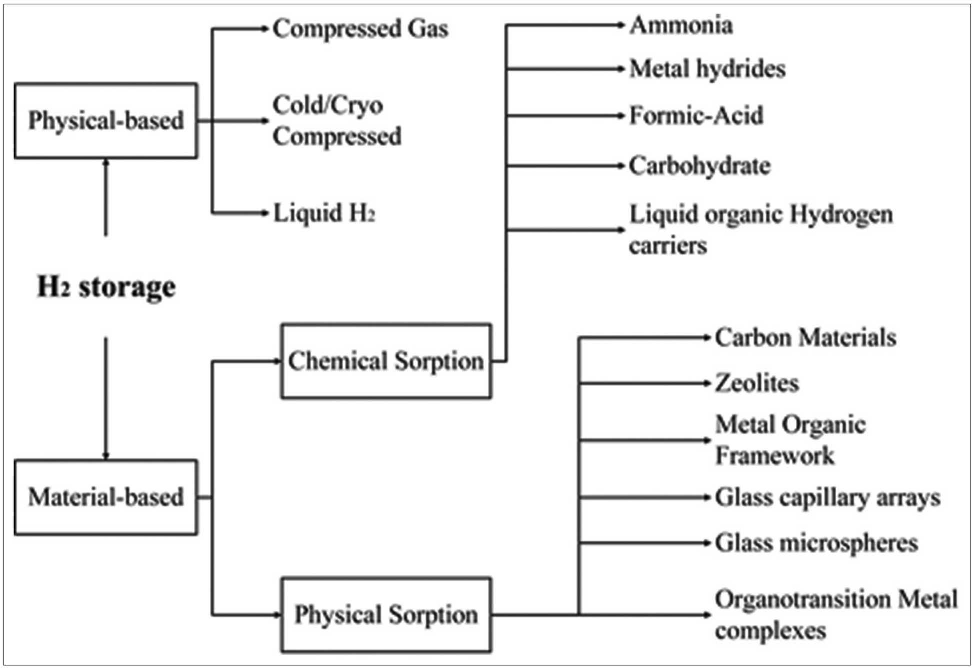
In Sweden, there is a large underground storage tank for natural gas in the form of a coated rock cavern. It consists of a steel cylinder within a surrounding rock formation that supports the primary structural load, while the steel coating simply acts as a permeability barrier; the space between the steel inner lining and the surrounding rock is filled with concrete, allowing a maximum storage pressure of 200 bar, this means that approximately 740 ton of hydrogen could be stored under similar conditions, although more research is needed (Tengborg et al., 2014).

However, these types of alternatives are not applicable to all lands; suitable geological conditions should be taken into account, away from aquifers or oil and gas reserves (Kruck et al., 2013).

The material and construction of the vessel determine the structural integrity and the maximum allowed storage pressure. If metal containers are chosen, the investment costs are increased, but the storage stability and the quality of the stored hydrogen is guaranteed, becoming an alternative applicable regardless of the location. On the other hand, it is recommended to bury the containers at low depths, which improves the distribution in less space, protection against physical impact, and insulating effect (Kruck et al., 2013).

In addition, different types of materials have been investigated for the manufacture of the storage tank, such as the use of low-cost carbon fiber that can meet the safety, strain and deformation specifications required for high pressure storage tanks, as well as the satisfaction of thickness restrictions of the tank to meet volumetric capacity

Figure 3: Hydrogen Storage methods



Source of data: Prepared by the authors based on data from: (Moradi and Groth, 2019) goals (Satyapal et al., 2007). Also, the use of cryo-tank compresses and conformable tanks has been investigated (Satyapal et al., 2007).

Another option with projection for the storage of hydrogen is the storage of pipes; this has been applied for the storage of natural gas since the 1980s, to manage the maximum demand of storage facilities with limited access to a natural gas network natural (Kruck et al., 2013). By making an analogy with the commonly available natural gas pipelines, approximately 12 tons of hydrogen per km of pipe could be stored (Kruck et al., 2013). Although the construction of natural gas pipelines is well known, there are technical obstacles to the construction of hydrogen pipe storage (Gillette and Kolpa, 2008, among the most relevant are the costs for the materials due to a phenomenon known as embrittlement by hydrogen that negatively affects the mechanical properties of steel materials over time, which requires higher quality standards that guarantee safety (Fekete et al., 2015).

4.2. Physical Storage as Liquid

One of the most important advantages of liquid hydrogen storage is that of achieving very high storage densities at low pressures (the density of saturated liquid hydrogen at 1 bar is 70 kg/m^3) (Godula et al., 2012). The main disadvantage of this method is the liquefaction process, which consumes a considerable amount of energy, due to the low point of liquefaction of hydrogen (-253 °C to 1 bar) and the fact that the hydrogen gas does not heat during the throttling processes (adiabatic) and isenthalpic expansion for temperatures below -73 °C, which requires a previous cooling in the liquefaction process, most of the times, by evaporation of liquid nitrogen (Valenti, 2015).

Despite this, hydrogen liquefaction is a well-established process. The global installed capacity of hydrogen liquefaction is around 355 ton per day (TPD), the largest trains are reported in the USA for liquefaction capacities of up 55 TPD (Cardella et al., 2017). The most modern hydrogen liquefaction plants have a specific energy demand of approximately 10 kWhel/kg in larger plants. However, a large part of the capital costs of a liquefaction plant is derived from the liquefaction process. Has been estimated that capital investment constitutes around 40-50% of the specific liquefaction costs for a new liquefaction plant of 100 TPD (Cardella et al., 2017).

Liquid hydrogen storage vessels are usually double-walled, with a high vacuum between the walls. Vacuum minimizes heat transfer through conduction and convection (Klell, 2010). Also, in this space between the walls is filled with additional materials, such as sheets of polyester coated with alumina; alternating layers of aluminum foil and fiberglass; or particles of aluminum, silica or perlite (Tietze et al., 2016). As a result of the high degree of isolation and the low surface-volume ratio, boiling rates are very low for large spherical tanks, generally below 0.1% per day (Amos, 1999).

At Cape Canaveral, USA, NASA operates liquid hydrogen storage vessels with a capacity of 230-270 ton (Tietze et al., 2016). The construction of this type of container has the potential to reach capacities higher than 900 ton (Amos, 1999). Despite the relative complexity on its construction, there are indications that liquid hydrogen storage tanks are less expensive by weight of stored hydrogen than containers for hydrogen gas under pressure at larger scales (Tietze et al., 2016).

4.3. Material-based Storage or Solid-state Storage

It is considered one of the most promising hydrogen storage methods, it is possible to store a large amount of hydrogen in small volumes, low pressure, and room temperature increasing safety. There are two underlying binding mechanisms for such solid-state storage based on materials:

Chemisorption (absorption): hydrogen molecules are dissociated into hydrogen atoms and are integrated into the network of materials. Physisorption (adsorption): hydrogen atoms or molecules are attached to the surface of materials. Table 2 shows examples of these two storage methods and their capacity.

4.3.1. Chemical storage

Technologies in which hydrogen is generated through a chemical reaction. The materials which store hydrogen through chemical storage are ammonia (NH_3), metal hydrides, formic acid, carbohydrates, and liquid organic hydrogen carriers (LOHC).

4.3.1.1. Ammonia

Ammonia (NH_3) allows storage in the liquid phase under mild conditions with a higher volumetric density of hydrogen than liquid H_2, which facilitates transport as well as storage. Because NH_3 is liquid at lower pressures and a higher temperature than H_2, liquefaction consumes less energy and requirements for containers are more achievable.

The process for storage and utilization of the H_2 from the stored NH_3 is schematized in Figure 4; the technologies for the storage and transport of NH_3 are commercial, like the storage, the compression and the use of H_2. Nevertheless, the technologies and the processes for decomposition of NH_3 and the separation and purification of H_2 for this application are in a development stage.

4.3.1.2. Metal hydride

Hydrogen can react with metals such as Li, Na, Mg, Ti alloy, or intermetallic compound (IMC) to form metal hydride (MH) (Jain et al., 2010). The reversible reaction of hydrogen gas to form metal hydride can be expressed as (Lototskyy et al., 2014):

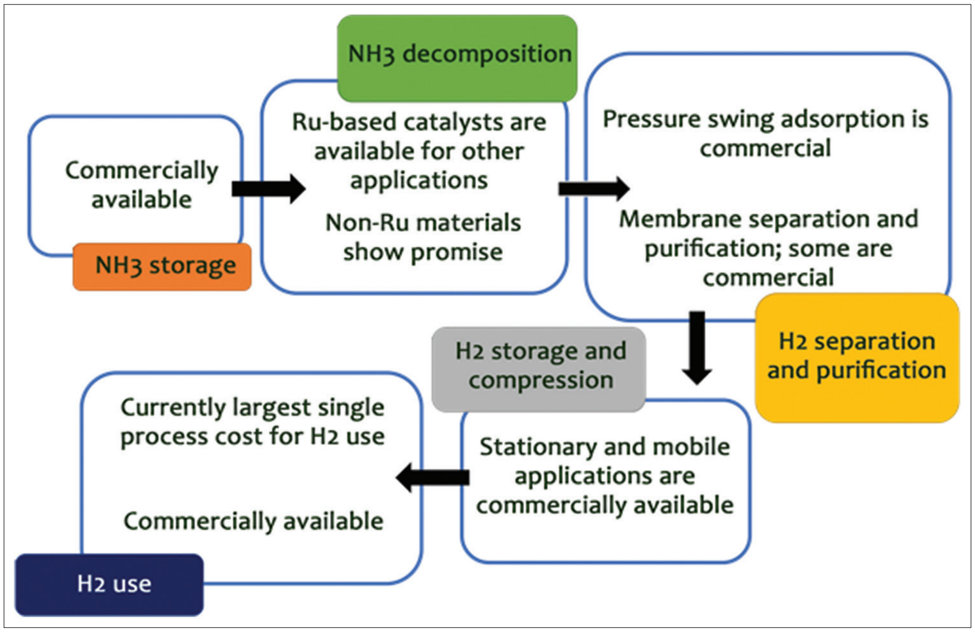
$$M(s) + \frac{x}{2} H_2(g) \leftrightarrow MH_x(s) + Q \tag{5}$$

Table 2: Maximum storage capacities (percentage of weight %wt) reported for several different physical and chemical hydrogen storage methods

Type of storage	Material-based storage method	Maximum reported storage capacity (%wt)
Chemical	Ammonia borane	19.4
	Metal hydrides	12.6
	Alanates	9.3
	Formic acid	4.4
	Carbohydrate	14.8
	Liquid organic hydrogen carriers	7.2
Physical	Carbon materials	8
	Zeolites	9.2
	Glass capillary arrays	10
	Glass microspheres	14

Source of data: Prepared by the authors based on data from: (Mah et al., 2019)

Figure 4: Process for storage and subsequent use of H_2 from NH_3 and the commercial availability of the technologies



Source of data: Prepared by the authors based on data from (Lamb et al., 2019)

Where M is a metal, an alloy or an IMC and Q is the heat generated during the formation of MH or the heat required to release hydrogen from MH. Table 3 shows the characteristics of some metal hydrides.

Although it presents an alternative of simple operation, low complexity of the devices that contain them, safety and the possibility of using residual industrial heat instead of electricity (Lototskyy et al., 2014), however, research has shown that MH it cannot offer a satisfactory performance for vehicle applications (Jain et al., 2010).

Complex metal hydrides are another type of light hydrogen storage material (Sakintuna et al., 2007). The main difference between complex and regular metal hydrides is the formation of an ionic or covalent compound during the absorption of hydrogen (Züttel, 2003). Table 4 shows some complex metal hydrides.

Its main advantage is the high ratio of hydrogen-metal atoms and low weight (Jain et al., 2010). The investigations under development are in low-weight complex hydrides, such as alanatos, amides, imides and borohydrides.

4.3.1.3. Formic acid

Formic acid has been studied as one of the most promising and safe materials for the storage of hydrogen due to its high content of hydrogen (4.4% by weight) in the liquid state at room temperature. Using this chemical compound for hydrogen storage technology requires to develop sustainable methods to synthesize and release H_2. Among the methods to perform the above processes is the direct hydrogenation of CO_2 and the development of catalysts, which could lead to large-scale production of formic acid.

There are two possible ways for the catalytic decomposition of formic acid, one is the evolution of hydrogen from the dehydrogenation of formic acid (FADH), and the other one is the generation of CO of FA dehydration. Equation 9 and 10 represent these two paths:

Table 3: Summary of metal hydride materials

Materials	Maximum hydrogen content (wt %)	Decomposition temperature (K)
NaH	4.2	698
MgH_2	7.6	603
LiH	12.6	~1000
CaH_2	4.8	873
AlH_3	10.0	423

Source of data: Prepared by the authors based on data from: (Song, 2013)

Table 4: Properties of various complex hydrides

Complex hydride	Maximum hydrogen content (wt%)	Decomposition temperature (K)
$LiBH_4$ nanocomposite	6.5	573
$LiBH_4$+$LiBH_{3.75}F_{0.25}$	9.6	373
$LiBH_4$+SiO_2	13.5	373
$NaAlH_4$+Porous carbon	7	673
$NaAlH_4$+Non-porous carbon	6.3	673

Source of data: Prepared by the authors based on data from: (Rusman and Dahari, 2016)

$$HCOOH \rightarrow H_2 + CO_2 \quad (6)$$

$$HCOOH \rightarrow H_2O + CO \quad (7)$$

In 2008, Loges (Loges et al., 2008) reported two excellent FADH results using Ru catalysts. Their catalysts could effectively produce H_2 without CO contamination at relatively low temperatures in aqueous solutions. Especially, Beller's report was significant from practical use because he developed fuel cells powered by H_2 from FA (Loges et al., 2008). Also, the generation of H_2 with a robust Ru catalyst in a large scale and for a long time was achieved by the continuous addition of FA through a pump (Sponholz et al., 2013). Following these results, the FA as storage of hydrogen again considered promising.

Recently, the reports on catalysts based on non-precious metals for FADH are increasing. Although performances of these catalysts were unsatisfied compared with those of precious metals such as Ru and Ir, they have still advantages, because these metals are earth-abundant and low cost.

4.3.1.4. Carbohydrate

Carbohydrates as a storage medium for hydrogen have several advantages over other alternatives such as hydrocarbons, ammonia, and formic acid. Table 5 shows a comparison between these alternatives and carbohydrates.

Its high availability in nature and easy removal of primary sources means that costs are low, it is estimated that around 150 billion gallons of gasoline can be replaced with hydrogen energy produced from 700 million ton of biomass through of SyPaB (Huang and Zhang, 2011).

Carbohydrates have a very high hydrogen storage density (see Figure 5). The carbohydrate (Polymeric $C_6H_{10}O_5$) is the most abundant renewable biological resource available, it has high storage densities of hydrogen as a liquid, less pressurization, does not require cryogenic process and it can also be stored as a solid powder. Recently, researchers have managed to produce about 12 mol of hydrogen per unit of glucose from cellulosic materials and water (Ye et al., 2009). Due to the complete conversion and modest reaction conditions, carbohydrates can act as high energy density hydrogen storage (14.8% by weight) (Zhang, 2009).

Carbohydrates are a source of carbon-neutral energy in terms of the entire life cycle. The amount of CO_2 released during the production of hydrogen from carbohydrates through SyPaB would be equal to CO_2 consumed by carbohydrates used (Kirk and Othmer, 2000). Due to the advantages above, carbohydrates could be the definitive solution for many energy sustainability challenges (Zhang, 2011).

4.3.1.5. Liquid organic hydrogen (LOHC)

An alternative method for hydrogen storage consists of using liquid organic hydrogen carriers (LOHC). Some studies indicate this could be a potentially cheap, safe, easy to use technology that allows long-term energy storage without boiloff losses (Niermann et al., 2019).

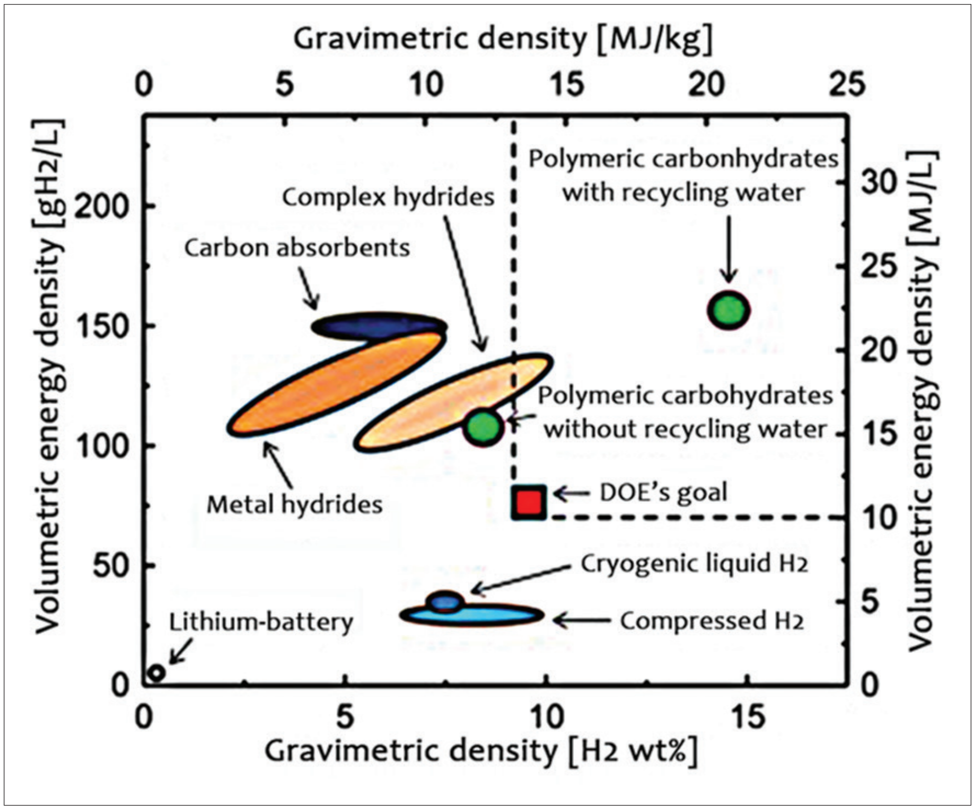
During the hydrogenation process, the double bonds between carbon atoms are broken down to allow hydrogen to occupy this

Table 5: Comparison of hydrogen storage

Type of storage	Temperature (°C)	Pressure (bar)	Costs	Purification needed
Hydrocarbons	≥700	10-40	Hight	Hight
Ammonia	300-700	-	Modest	Modest
Formic acid	30-50	~1	Modest	Low
Carbohydrates	30-80	~1	Low	No needed

Source of data: Prepared by the authors based on data from: (Kim and Percival, 2016)

Figure 5: Available hydrogen storage media



Source of data: Taken from: (Kim and Percival, 2016) place. It is an exothermic chemical reaction that typically takes place at high pressure and temperature. A distinctive characteristic is the ability of this process to re-released the hydrogen back to its pure form through a dehydrogenation reaction, that takes place mainly close to atmospheric pressure and high temperature.

Properties of LOHCs are typically similar to that derived from crude oil. Table 6 shows several chemical compounds that can be used as LOHC.

4.3.2. Physical storage

It is a process in which the H_2 molecules adsorb weakly on the surface of the material. The most widely studied materials are porous materials, such as carbon materials, zeolites, organic metal structures (MOF), and organotransition metals.

4.3.2.1. Carbon materials

Carbon materials can form C-H bonds with hydrogen, which makes hydrogen storage feasible in these materials. There are different types of carbon materials such as carbon nanotubes, graphene, etc., that can have viable hydrogen storage.

4.3.2.1.1. Nanotubes

Carbon nanotubes (CNT) are microscopic carbon tubes (Darkrim et al., 2002) that can store hydrogen in their microscopic pores or within the structures of the tubes. The nanotubes have a single, or multiple wall structure, multiple adsorption sites, high packing density, and have an estimated capacity of 6% by weight. CNT and buckyballs have been modified by transition metals or alkali metals to increase the binding of H_2 molecules to metal-CNT hybrids. Chen et al. (Chen, 1999) reported that multiple wall nanotubes (MWNT) doped with Li and Kopados show a catchment capacity of 20% by weight and 14% by weight, respectively. Among which the MWNTs with doping K are chemically unstable, while the Li Doped MWNTs are chemically stable but require high temperatures (473 to 673 K) for maximum adsorption and H_2 desorption.

4.3.2.1.2. Graphene

Hydrogen is stored between layers of graphite, which is later released by heating at a temperature higher than ~ 450 °C. Comparing to nanotubes, this material is cheaper, more efficient, safer and easier to manufacture (Zhou et al., 2009). The sorption process can be adjusted by modifying the distance between the adjacent layers, the adjustment of the curvature of the sheet or the chemical functionalization of the material.

Table 6: Possible LOHCs

LOHCs.	Reasons to take into account
N-ethylcarbazole	Well-studied nitrogenous LOHC
Dibenzyltoluene	Already existing application as LOHC; safe and convenient handling
1,2-dihydro-1,2-azaborine	Unique characteristics through the integration of boron and nitrogen
Methanol	Very high storage density
Naphthalene	Well-studied cycloalkane; high storage density
Toluene	Well-studied cycloalkane; planned application as LOHC

Source of data: Prepared by the authors based on data from: (Niermann et al., 2019)

4.3.2.2. Zeolites

Capturing the H_2 in the zeolite requires low temperatures and high pressures to induce a displacement inside the molecular sieve cavities. It is hold inside the porous medium at ambient conditions and can be released by raising the temperature. This material has been shown a hydrogen storage capacity of 2.07 wt% under 1.6 MPa (Dong et al., 2007), and it is known for its high thermal stability, low cost and adjustable composition (Langmi et al., 2005). Table 7 shows examples of zeolites with their storage capacity in the percentage of weight.

4.3.2.3. Organotransition metal complexes

The organotransition metal complexes are structures based on carbon and transition metals, which increases the hydrogen storage capacity of the complex. The complexes such as the Ti-polyacetylene complex (Yürüm et al., 2009), the ethylene and propane complexes based on scandium and vanadium (Wadnerkar et al., 2010), the alkane complexes (Kiran et al., 2006), the Sc and Ti atoms decorated in C60 and C48B12 (Deng et al., 2004), niobium-based ethene complex (Niaz et al., 2013), organosilica complexes doped with TM (Park and Lee, 2010), buckyballs decorated with metal and organometallic multi-decker complexes, are some of the known hydrogen storage complexes. These complexes hold not only high binding energy but also have accelerated hydrogen adsorption and desorption cycles.

5. TECHNOLOGIES IN ELECTRICAL GENERATION USING HYDROGEN

5.1. Fuel Cells (FC)

A fuel cell is a device that allows using hydrogen and oxygen to carry out electrochemical reactions to transform chemical energy into electricity. It is composed of an anode, a cathode, and an electrolyte. In the anode section, the oxidation takes place which allows the release of protons and electrons that are then transferred to the cathode through the electrolyte and an external circuit. Figure 6 shows the basic structure of a typical fuel cell.

The kind of electrolyte determines the operating conditions and the type of fuel cell. Primarily available devices are proton exchange membrane, alkaline, solid oxide, phosphoric acid, and molten carbonate fuel cells (Wilberforce et al., 2016). Applications that use fuel cells go from battery charging to complex space systems. Its advantages include high efficiency, allows using a different kind of fuels, is a clean technology, and is a reversible device. Fuel cells that use hydrogen include:

5.1.1. Proton exchange membrane fuel cell (PEMFC)

The compact structure, fast filling start time, and high energy density of these fuel cells make it fit to mobile and stationary applications (Iwan et al., 2015). The electrochemical reaction takes place through a solid polymer membrane that prevents corrosion inside it. Main challenges of this fuel cell involve high cost and insufficient durability, which makes them unreliable.

5.1.2. Phosphoric acid fuel cell (PAFC)

The electrolyte in this fuel cell consists of orthophosphoric acid bounded in a silicon carbide matrix. Its high reliability and low cost made it be the first commercial fuel cell (Yang et al., 2016).

Main applications include the generation of stationary energy using fuels directly, working with the presence of carbon monoxide, which is a compound not suitable for other types of fuel cells. Operation with pure hydrogen, despite possible, requires thermal management. Even though it lacks high electrical efficiency, an operation under higher heating conditions can improve this drawback.

5.1.3. Alkaline fuel cell (AFC)

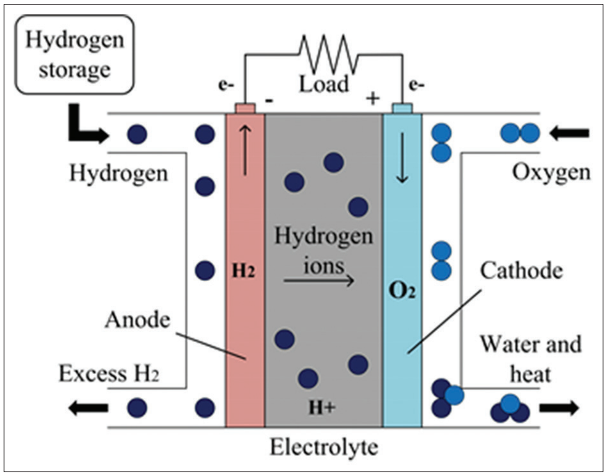
These fuel cells use an alkaline solution as the electrolyte, which provides sustained power generation at low cost and high-density. Alkaline fuel cells advantage includes improved kinetics of complex reactions inside the electrolyte (Barsuk et al., 2016). Table 8 shows the main specifications of these fuel cells.

Table 7: Types of zeolites

Types of zeolites	Wt (%)
IRMOF-1	1.3
MOF-177	7.5
IRMOF-20	6.5
Li-doped MOF-C-30	6
COF-102	9.95
COF-102-3	26.7
Clathrates	5

IRMOF: Isoreticular metal-organic frameworks, MOF: Metal-organic frameworks, COF: Covalent organic frameworks. Source of data: Prepared by the authors based on data from: (Niaz et al., 2015)

Figure 6: Basic structure of a fuel cell



Source: Created by the authors based on data from: (Inci and Türksoy, 2019)

5.2. Power to Gas

The concept of gas power consists in feeding electrolyzers with cheap surplus renewable electricity to produce hydrogen and inject it into the gas grid. Figure 7 shows a schematic of the gas energy process with hydrogen storage facilities. There are two ways to perform this process: direct injection and methanation.

5.2.1. Direct injection

It consists of the direct injection of hydrogen into the natural gas grid. It has the advantages of not requiring more investment; there is no losses of energy and does not require additional storage. Some studies mention that, at standard temperature and pressure, the gas grid can cope with up to 17% hydrogen by volume without any difficulty, there is also legislation in several countries that restricts the amount of hydrogen content in the natural gas grid. Injecting an amount of 1% by volume of hydrogen in natural gas distributed on an annual average basis, would consume more energy than the current installed capacity of combined wind and solar, which demonstrates a high possibility of mitigating the instability of production of large wind farms (Guandalini et al., 2015).

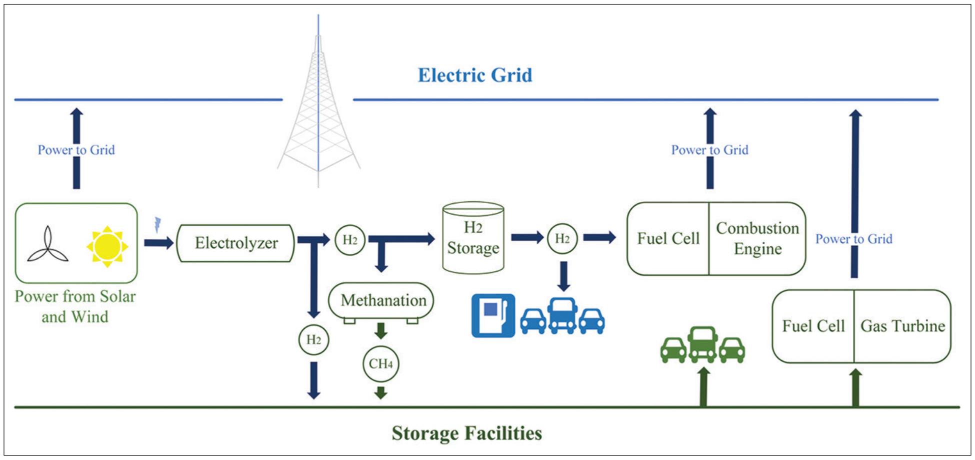
5.2.2. Methanation

Methanation process consists in the reaction of CO_2 with H_2 on a metal catalyst to produce methane. The reactions are expressed as:

$$CO_2+4H_2\rightarrow CH_4+2H_2O \tag{11}$$

The most significant advantage of hydrogen methanation is that the synthesized methane can be fed directly into the gas distribution grid without any limitation. Due to the need for CO_2, the methanation plants must be located near a source of CO_2, such as fossil fuel power plants, industrial or biomass plants to obtain access to a large amount of CO_2 with a low economic effort. Therefore, these systems can also recycle CO_2 emissions from existing CO_2 sources (Zhang et al., 2016).

Figure 7: Principle of power-to-gas technology



Source of data: Created by the authors based on data from: (Gondal, 2019)

Table 8: Specifications of fuel cells

Fuel cells type	T (°C)	Reactions	Efficiency (%)
Proton exchange membrane fuel cells	60-140	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ $\text{Cathode}: \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	55
Alkaline fuel cells	150-200	Anode: $H_2 + 2OH^- \rightarrow H_2O + 2e^-$ $\text{Cathode}: \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$	60
Phosphoric acid fuel cells	150-200	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ $\text{Cathode}: \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	>40

Source of data: Prepared by the authors based on data from: (Dincer and Zamfirescu, 2011)

6. APPLICATION POTENTIAL FOR THE ENERGY STORAGE WITH HYDROGEN, CASE STUDY IN COLOMBIA

Determining accurate applicability of hydrogen as an energy storage vector requires to consider different essential variables. These include the characteristics of the region's energy market to analyze, the installed capacity according to the opportunity, the feasibility of technological processes, and the availability of eco-friendly resources for energy generation. Among the restrictions, it can be outlined the availability of renewable sources for power generation, cost overruns in initial investments for the construction of systems due to technological gaps, lack of commercialization of available technologies, among others. The reason to carry out an in-depth analysis is to have an initial approximation of the energy market, e.g. in Latin American countries, power generation from renewable sources has an incipient growth, although there are many of the barriers imposed by the mentioned restrictions. Renewable energy sources that lead the region are biomass and hydropower.

Table 9 shows the general picture of the sources of energy generation in some Latin American countries and the trends towards the introduction of policies for generation through renewable sources, taking into account that the most used are water, followed by biomass (OLADE, 2019). Government and regional incentives work for the implementation of other renewable sources such as solar, in countries like Chile, this initiative is being tackled strongly. It is a composite introduction for the region as mentioned above for the variability of approaches necessary for the determination of the potential for production and use of hydrogen as a flexible energy vector, in general renewable generation is explored in order to obtain a closer view of the analysis of opportunities for the implementation of hydrogen technologies, the following subsections expose the specific case of Colombia and the opportunities for production and use based on its resources, technologies and energy reality.

6.1. The Energy Situation in Colombia

Currently, the generation of electricity in Colombia is led by hydroelectric technology with 67.14%, on the other hand thermal plants operated by fossil fuels such as coal, gas and liquid fuels (diesel), among others, represent 31.96% of the electricity generated (UPME, 2017). Concerning the generation of electricity from renewable energy sources, such as biomass and wind energy, it represents 0.57% and 0.11%, respectively (Garcia et al., 2017). It is clear Colombia's high dependence on hydroelectric resources, which represents a significant drawback due to meteorological events such as El Niño and La Niña (González et al., 2017). This situation triggers the establishment of power generation alternatives for electricity generation.

One of the structures that can retain large amounts of hydrogen at low pressure are carbon nanotubes. However, they have a high cost. Some studies have shown that chicken keratin by a heating process obtains properties similar to carbon nanotubes (He et al., 2010, Chen et al., 2011). In the poultry industry of Colombia, waste disposal processes represent a high cost. Given its availability, low cost and protein structure, it is proposed as an ecological and bio-renewable candidate as a storage medium for hydrogen due to its similarity to carbon nanotubes. Chicken feather rachis reaches can get a maximum capacity of 3.5% weight/weight, which is a desirable result due to the low cost of the material (Giraldo et al., 2013).

Another residue of high availability is the oil palm shell. Research has reported on the production of activated carbon from this waste and its subsequent use as hydrogen storage material (Dabrowski et al., 2005; Hameed et al., 2008 and El-Khaiary, 2008). Gonzales et al. (2014) shows thermochemical treatments with microwaves yielded good results obtaining a storage capacity of 6.5% by weight, demonstrating the oil palm shell becomes a material with potential for hydrogen storage. Colombia being the third-largest producer of African palm in the world, annually producing around 3 million tons per year.

Alternative use of biomass has also included different thermochemical projects such as gasification as it offers higher efficiency compared to combustion and pyrolysis (Sheth and Babu, 2009, Muellerlanger et al., 2007), and it is carried out to produce bioenergy for cities that are not connected to the interconnected national system. Considering the large production of farming crops in Colombia, the readily availability of organic waste opens a huge opportunity to pose renewable alternatives as a strong support to the energy pool of the country. Table 10 shows the amount of organic waste per year for main crops in Colombia (Escalante, 2011). At present, they are used directly in combustion processes in rural areas, this inappropriate use impacts on the increase in emissions, which is why different thermochemical and biochemical methods have been tested for the transformation of these wastes into bioenergy which has a high potential for the production of hydrogen (García et al., 2017).

Additionally, the by-products of the coffee sector, forest biomass of the Pinus Patula tree species distributed in Colombia

Table 9: Sources of energy generation in some Latin American countries and policy trends for renewable energies

Country	Power generation technology		Background	Renewable energy policy trends
	Renewable	No renewable		
Mexico	Hydro biofuels Wind Geothermal	Natural gas Oil Coal and peat Nuclear	Was an early adopter of renewable energy source through its explorations in geothermal energy, which can be traced back to the 1930s, the Comision Federal de Electricidad (Federal Electricity Commission), CFE, in 1937 and lead first explorations and potential studies and founded the Geothermal Energy Commission CFE is still the main generator with over 80% of installed capacity (EIA 2012)	In order to encourage the use of renewable energies, benefits were established through the Law for the Use of Renewable Energies and the Financing of the Energy Transition approved in November 2008, which also included the promotion and biofuel development and energy efficiency; The Mexican government will migrate from fuel oil to a cleaner and more available option such as natural gas and the stimulation for the adoption of renewable energies, such as wind, hydro, among others .
Colombia	Hydro Biomass Wind	Natural gas Oil Coal and peat	The Colombian electricity sector shows one of the most modern designs in Latin America. It bases its operation on trading companies and large consumers to acquire energy and power in a market of large energy blocks. It operates freely by the conditions of supply and demand. Moreover, it allows the participation of economic, public, and private agents to promote competition between generators. This system was a consequence of a high investment due to a major blackout that took place in 1992.	Law 1715 has been created to promote renewable energy projects It allows for reductions in income tax, accelerated depreciation of assets, exclusion of VAT on goods related to the project and exemption from customs duties. The UPME, Mining, and Energy Planning Unit has stated that efforts are aimed at reducing dependence on single sources of generation and that such planning is sustainable.
Brazil	Bioenergy Hydro Geothermal Solar Wind	Coal Crude oil, LNG & oil products Natural gas Nuclear	Brazil was a late adopter of market-oriented reform. The emphasis of the reform was the privatization of existing assets and capital attraction for greenfield projects. However, due to incomplete institutional change, Brazil drives away investments up to early 2000s which led to a significant crisis due to the nation's largest drought in 2001-2002. The response was a thorough revision of the existing electricity sector. Nevertheless, a relatively small private penetration in the generation and transmission sector was achieved due to the early ceased of the first wave of privatization.	Brazil´s policy framework, announced on December 2015, of renewable energy, today is the Nationally Determined Contribution (NDC) which aims the objective of the United Nations framework convention on climate change. This document gives a broad perspective of the Brazilian energy trends for the next years and provides orientation for the main energy planning. Brazil intends to adopt additional measures that are consistent with the international objective of detention in temperature increasing, in particular: (1) increasing the share of sustainable bioenergy, (2) in land-use change and forests, (3) achieving 45% of renewables in the energy mix by 2030. (IEA Bioenergy. 2018)
Chile	Hydro Biomass Wind Solar	Coal Natural gas Diesel	The energy sector in Chile emphasizes decentralization, efficiency, competitiveness to attract private capital attraction. There are three markets: a long-term auction market, a bilateral contract market between free customers (over 2 MW of capacity), and a short-term spot market. This structure is complemented by a Ministry of Energy, in charge of strategic overview of the sector and policy design, a regulator in charge of carrying tariff processes, and a superintendent that enforces law and issues fines. (Vásquez et al., 2018)	By 2015 in Chile was created a National Energy Policy 2050 to promote the country as a world-class destination for solar and wind energy developers. This policy allowed the creation of a consultative committee formed by representatives from different sectors, which had as a primary result 20 principal energy goals, ten by 2035 and ten by 2050. These are based on the following four pillars: (1) Quality and security of supply, (2) Energy as a driving force for development, (3) Environmentally friendly energy, (4) Energy efficiency and energy education. (IEA. Energy Policies. 2018)

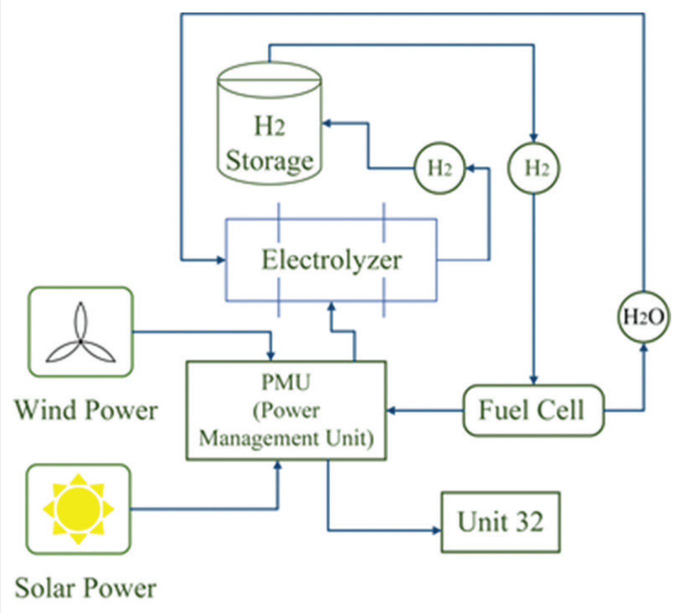
Source: Based on data from Bodelón, 2016

for reforestation programs can be used to produce hydrogen through technologies such as direct gasification. Other abundant product in Colombia is rice husk biomass (approximately 500000 tons/year). Rice husk has been widely used for the production of electricity through combustion (Armesto et al., 2002). Research points out that the gasification process for hydrogen production is more efficient than direct combustion (Werther et al., 2000).

Table 10: Energetic potential for different types of biomass produced in Colombia (Escalante, 2011)

Crop	Main product (ton/year)	Waste (ton/year)	Potencial Energy production (TJ/year)
Oil palm	872117	1660073	16013.64
Sugar cane	2615251	15534591	118578.87
Panela cane	1514878	9513430	81054.57
Coffee	942327	5051248	49106.88
Corn	1368996	1937129	20802.79
Rice	2463689	6282407	27805.94
Banana	1878194	11550891	6595.92
Plantain	3319357	20414043	11657.07

Figure 8: Schematic of the hybrid renewable energy with the hydrogen storage system



6.3. Solar and Wind Energy Resources in Colombia

According to the Atlas of solar radiation of the UPME, regions such as La Guajira, part of the Atlantic Coast and other specific areas of the departments of Arauca, Casanare, Vichada and Meta, among others, have radiation levels above the national average that can reach the order of 6.0 kWh/m^2, which is one of the best indices in the world.

In the case of wind, Colombia also has several regions with a significant amount of resources available for wind power generation. The specific case of La Guajira is considered the best in Latin America (UPME, 2019) with an average wind speed close to 9.8 m/s (Huertas and Pinilla, 2007). Nowadays the installed wind power is 19.5 MW, which represents 0.4% of the total technical potential (Edsand, 2017). From the financial point of view, projects around wind energy in Colombia need to be above the capacity of 1000 kW to make the lifecycle time into the business case to be lower than 20 years (Jimenez, 2012). Although, it is also crucial to consider the topological conditions where massive mountains and steep terrain are included, it makes any economic investment in infrastructure expensive (Dekker et al., 2012), it could be the case at locations such as Gachaneca in Boyaca where there exists a high technical potential for wind power (Jimenez, 2012).

In Colombia, the inclusion policies for non-conventional renewable technologies point to the exploration of alternatives such as photovoltaic and wind solar, being promising options to meet the electricity demand despite its natural variability due to atmospheric conditions and the need to storage systems. Currently, batteries are the leading technology used to cope with the inherent variation of renewable sources (Nair and Garimella, 2010). However, its high cost and limitations in load ranges greater than 1 MW open the window to the exploration of hydrogen as an energy vector.

Within the framework of the Horizon 2020, the European Union created the EU.3.3.8.3 program whose purpose is to demonstrate on a large scale the possibility of using hydrogen to support the integration of renewable energy sources in energy systems (Sumper et al.,2016), including their use as a storing competitive energy for electricity produced from renewable energy sources, which cover different needs in production, storage and energy sustainability. In Colombia, Law 1715 of 2014 defines the integration of non-conventional renewable energies (NCRE) into the National Energy System, with the objective of promoting the development and use of unconventional energy sources, mainly those of a renewable nature. Although the law is a progress towards the integration of the ERNC into the National Electric System, more policies and developments are required to promote the installed generation capabilities based on the ERNC.

Figure 8 shows a diagram of a hybrid photovoltaic/wind energy system with hydrogen storage. In the PUM (power management unit) is a power management unit from photovoltaic and wind sources. When these sources are not available, the storage system will supply power. If the total energy produced by renewable energy sources is greater than the unit's energy demand, the electrolyser uses the excess electrical energy to produce hydrogen and store it in hydrogen tanks, resulting in a sustainable renewable energy system and flexible (Khosravi et al., 2018).

Arguments such as those described above indicate potential for the use of hydrogen as an energy carrier in different perspectives of the Colombian energy market, as well as an integrator in a solar and wind energy storage system, reducing the intermittent nature of this type of energy, or with Energy production through biomass.

7. CONCLUSIONS

Despite the growth in the generation of renewable energy, there are still difficulties due to their intermittent nature, fluctuations and the difficulty of predicting the amount of energy that can be produced, which has caused limitations for their connection to existing power grids. Energy storage can be a solution to minimize these problems and provide a better connection between the demand and supply of renewable energy generation. Among available alternatives, hydrogen has been considered a promising means of storage.

There are different mechanisms to produce hydrogen from renewable sources, either from biomass, water or any source of renewable electricity, using different processes such as gasification, pyrolysis, fermentation, photolytic processes and electrolysis.

One of the most adopted alternative for the storage of the hydrogen produced is the compressed gas. However, material-based storage has aroused great interest, due to its ability to store a large amount of hydrogen in a relatively small volume and improved security. Materials such as alloys, carbonaceous materials and microspheres are used in this storage method, in which the atoms or hydrogen molecules can be attached to the surface of the materials or the atoms can be integrated into the network of materials. Therefore, a large amount of hydrogen can be stored and released at a constant temperature and pressure.

At the time of using it as a source of electric power generation, hydrogen can be used by fuel cells without produce any pollutants. Through mixtures with natural gas, their range of action can be expanding with the use of networks of distribution, providing a link between electricity generation and providing additional energy storage capacity to relieve the infrastructure of the electricity grid, that generally has lower capacity and high cost compared to the natural gas network. Hydrogen is a versatile energy carrier, which can be produced from different primary and secondary sources of different origins. Its flexibility comes from the fact that can be used to store, distribute and transport energy to integrate a wide variety of technologies.

Even though in Latin American countries there are many of the barriers imposed by some constraints, such as availability of sources for power generation, capital expenditure investments, and lack of commercialization of available technologies, an initial overview of the energy market in the region shows that power generation from renewable sources has an incipient growth. Renewable sources of energy that lead the region are biomass and hydropower.

The Colombian landscape has a great variety for the generation, use and exploitation of hydrogen from different renewable sources in different alternative processes, among them is biomass with potential for storage and production of hydrogen from products with high availability that generate a large amount of residues that can be used for such processes such as oil palm are and with a hydrogen storage capacity of 3.5% and 6.5% by weight, other sources of biomass are also available in the country such as coffee waste, banana among others, forest residues of Patula pine species and rice husks, which have proven to be a potential form of hydrogen production through the gasification process. In addition to the above, Colombia has an incipient potential in other renewable energy sources, such as photovoltaic and wind energy, which combined with hydrogen storage technologies would improve access to electricity in remote areas, since they would minimize their dependence on the climatic conditions, making these technologies more attractive.

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