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Review

Is Hydrogen Indispensable for a Sustainable World? A Review of H_2 Applications and Perspectives for the Next Years

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Hydrogen (H_2) was one of the first molecules discovered by our society, being the most abundant element in the whole universe. Thus, H_2 has gained a lot of attention throughout the years, and it has lots of applications in different areas, especially since it offers ways to decarbonize a lot of sectors, mainly the ones where it has been proved to be very difficult to meaningfully reduce those carbon emissions. Herein, the main aspects of the hydrogen economy and its main applications for energy, transportation and industries are described. These main areas outline how important is H_2 for our society highlighting how H_2 can make those well-known processes more sustainable and greener. By the end, a brief discussion on these applications with future perspectives is presented.

Keywords: hydrogen, hydrogen applications, sustainability, green chemistry

1. Introduction

It was not by accident that hydrogen was one of the first molecules discovered by our society.[1] After all, it is the most abundant element in the whole universe. Hydrogen is present in our atmosphere, in water, in several chemical compounds and in almost every organic molecule.

Mankind progressively learned how to produce hydrogen and use it. Nowadays, hydrogen is a symbol of sustainability and runs through all the production chain including several applications,[2-4] as presented in Figure 1.

Hydrogen has been involved in the petrochemical, fertilizers, clean processes, and energy sectors. Thus, hydrogen is attracting vigorous interest of several groups from governments to companies as it offers ways to decarbonize a lot of sectors, especially those that have been proved to be difficult to meaningfully reduce emissions.[5] Moreover, in the industry, hydrogen has had an increasingly important role along the chain of production in the last years.

Investments in hydrogen science can help emergent technologies and new sustainable industrial processes around the world. After all, hydrogen is an integral part of many chemicals, being the reactant, part of the products, or participating in processes to achieve the desired product, such as catalytic hydrogenation and hydrogenolysis.

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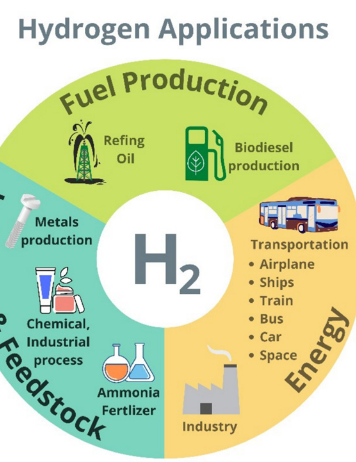

Figure 1. An overview of the applications of hydrogen.

Thus, hydrogen proves to be an essential compound for green chemistry, not only as an energy source but as an important feedstock to many processes. There are many examples that showed how hydrogen can be applied to turn industrials processes more environmentally friendly, mainly as feedstocks production of pharmaceuticals,[6,7] cosmetics[8,9] and food.[10,11]

In this review, the way by which hydrogen is an important solution to achieve a more sustainable industrial production will be presented, besides, we highlight the main applications in the energy field. Firstly, it will be present what is the hydrogen economy. Then, it will be discussed how H_2 is used in the petrochemical industry in different parts of the process of oil refining. In addition, some examples of hydrogen application in the chemical industry will be illustrated and commented. Then, the fuel cell technologies will be shown. Finally, it will be discussed the environmental benefits of the H_2 and its challenges and perspectives.

2. Hydrogen Economy

The hydrogen economy has been associated with a new paradigm where fossil fuels are being replaced by sustainable sources of energy with zero carbon emissions, like H_2. However, the concept of the hydrogen economy may be broader and more elaborated than it looks.

Hydrogen economy may be understood as the whole chain that hydrogen goes through, from its production to the end-users. Thus, hydrogen economy encompasses the hydrogen production, its purification, storage, distribution, quality control to ensure the safety to the users, and then, how it will be applied by the end users. An illustrative scheme to summarize this concept is found in Figure 2.

2.1. From the production to end users

The hydrogen economy introduces a more sustainable processes in the chemical industry and is closely linked to the production of clean energy from H_2. Furthermore, H_2 is considered the starting point for the sustainable designs. The cleanliness of the processes involving the synthesis of H_2 is associated with the greenhouse gases produced during its production. Besides, for the energy or chemical chain to be sustainable, it also depends on the energetic input, the type of raw material, the design of the industrial process, and the quantity of CO_2 emissions.[2]

Nowadays, hydrogen is mainly produced from fossil fuels[12] in typical reforming processes, where natural gas is the most important reagent, and a small fraction of hydrogen comes from water electrolysis (about 5% is produced from water electrolysis). Fortunately, different ways to produce H_2 have been studied in recent decades, as was discussed in our recent review.[2] In this work, the hydrogen production was classified using a color code (see Figure 3) according to the greenhouse gases emission, environmental benefits, and cleanliness of all processes.[2] The set of colors are meant to help consumers and companies to understand about the provenance of the hydrogen they may acquire.

In this classification, the grey, blue, and green colors are the most relevant for the global scenario. Grey hydrogen, for example, is produced from the steam reforming process and uses fossil fuels (natural gas) as raw material; this is the most important industrial process for H_2 production. In the same way, blue hydrogen also has fossil fuels as feedstock, nonetheless, the produced carbon is captured and stored, resulting in lower CO_2 emission. Finally, the green hydrogen comes from renewable energy through electrolytic process, and it has zero carbon emission.[2,4,13,14]

Currently, almost all hydrogen in the world is produced by a "grey" route, which applies fossil fuels, such as natural gas, as reagents. Therefore, it is important that the sustained development and improvements in hydrogen production be made, once a greener society is pretended. In this way, production costs will decrease over time and, as a result, green hydrogen will become more economical. Decreasing green H_2 costs will increase the hydrogen potential. Ultimately, if solar and wind costs become cheaper, the primary energy will be a mixture of renewable sources. The European Union objective of reducing emissions by 80-95% by 2050 compared to 1990 levels, means an almost complete decarbonisation of power generation and high levels of variable renewables.[5]

After the production, hydrogen needs to go through some steps herein described:

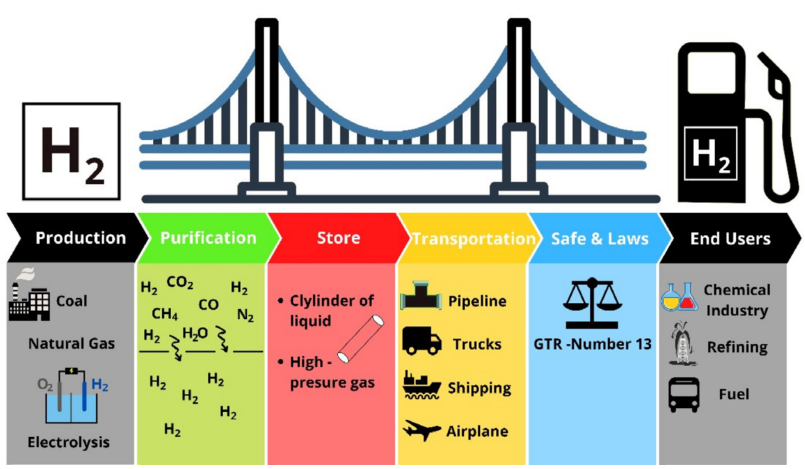

Figure 2. Hydrogen economy is the bridge between the producers and end users of hydrogen.

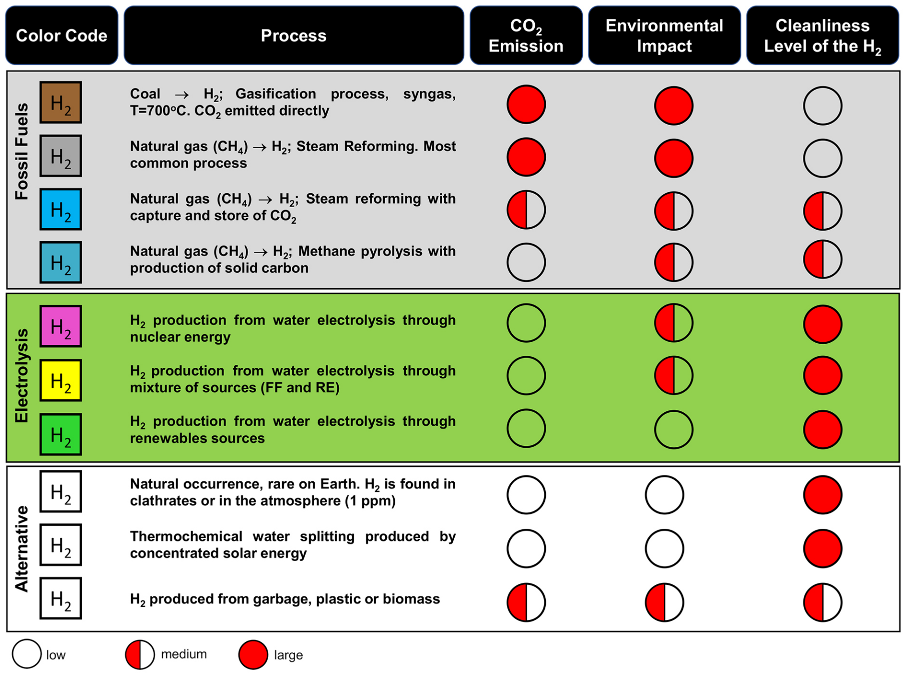

Figure 3. Color classification of hydrogen production processes according to environmental criteria (figure from reference 2 with CC-BY attribution). FFs: fossil fuels and RE: renewable energy.

Purification

After the production, the purification process of the final H_2 will direct its use in the industries. This means that the prices of the processes can be different. The reforming processes, for example, produce H_2 with a purity between 87 to 95%. On the other hand, the electrolysis of water delivers H_2 with purity superior to 99.9%.[13] Vehicles powered by fuel cells require high purity H_2 to avoid the poisoning of the catalyst. Some forms to hydrogen purification are pressure swing adsorption,[15] cryogenic distillation[16] and membrane separation.[17]

Storage

The storage of hydrogen is an important step, not only for its safety, but also for its transport. Normally, hydrogen is stored in cylinders of liquid and high-pressure gas. However, due to its low energy density, storage becomes challenging.[18] Around 40% of its energy content can be lost to liquefaction[19] when hydrogen is stored as liquid H_2. Furthermore, hydrogen must be stored in a special container due to its reactivity with various metals and metal alloys.[20]

Transportation

Hydrogen can be distributed by pipeline, the same used for natural gas,[21] or can be transported by trucks, rail, airplanes and ships, to other parts of the planet. To accommodate high volumetric efficiency, hydrogen is stored at high pressure (> 700 bar) and low temperature (20 K).[22] The cost of storage and transport is a very important part of the cost of the delivered product.[23]

Safe and laws

Hydrogen has special properties that demand specific conditions, as the storage at high pressure or at extremely low temperatures. For a safe use, it is essential to regulate its management.[22] Consequently, regulations have been created, as the United Nations Economic Commission for Europe Global Technical Regulation (GTR) Number 13 (Global Technical Regulation on Hydrogen and Fuel Cell Vehicles) that regulated safety requirement in hydrogen vehicles. This document specifies hydrogen levels allowed in vehicles during in-use and post-crash conditions. Also, it determines acceptable hydrogen emissions levels in vehicle exhaust.[24]

In all these steps, there are several processes still needing improvement. In this scenario, studies to develop the hydrogen economy must progress and the biggest challenge is always focusing on the hydrogen applications. The final use of hydrogen is what will determine how its purification, storage, transportation, and quality must be.

2.2. The hydrogen economy will keep growing

Hydrogen has been drawing a lot of international interest, and the amount of countries that directly support investment in hydrogen technologies is increasing. Since the Sustainable Development Goals were adopted in 2015, governments have invested to reach the goals.[5,25,26] In 2019, the number of targets, mandates and policy incentives was around 50 actions, several policies that directly support the hydrogen application had been made, by countries of G20 and the European Union.[5]

As presented in Figure 4, in the last decades, the demand for hydrogen has been growing and will keep the pace until 2050.[2] Particularly in the Latin America, it is expected an increase of 67% in the hydrogen demand until 2030, to apply in the sector of iron, steel, ammonia, cement and methanol production, refining and transport.[27] With the perspective of increasing the hydrogen production, combined with a more sustainable production pathway, the prospect for the next decades is a decreasing in the price of green H_2.[2,4,28]

Apart from the interest in hydrogen with climate change ambition, there are other policy objectives to which hydrogen can contribute, as the energy security, local air pollution, economic development, and energy access. If the hydrogen is deployed alongside electricity infrastructure, electricity can be converted to hydrogen and *vice versa*, or also converted to other fuels, making the countries less dependent on specific energy resources and increasing the independence of energy supplies as a nation.[5]

Hydrogen produced from fossil fuels with carbon capture, utilization and storage (CCUS) or from biomass can also increase the diversity of energy sources.[29] Depending on how the infrastructure is developed, in the future, the countries may use it to diversify their economies, via the exporting low-carbon energy in the form of hydrogen and hydrogen-based fuels. In addition, from an optimistic perspective, in a low-carbon context, the hydrogen trade would enable trade and storage of wind and sunshine between different regions to solve seasonal differences.[5]

Currently, there are many private groups in favor of hydrogen. Among them are the renewable electricity suppliers, industrial gas producers, electricity and gas utilities, automakers, oil and gas companies, major engineering firms and the governments of most of the world's largest economies and those who use, or could use, hydrogen as a feedstock for industrial production, not just energy.[5]

With the growth of concern for the sustainability of production by the society, the advantages for the companies in using clean energy are also based on the green approach. Thus, in the field of industrial feedstock, for example, it is more difficult to be economically competitive using green hydrogen because of distance to the end consumer, while in the consumer goods industry the companies can directly benefit from switching to hydrogen-based raw material.

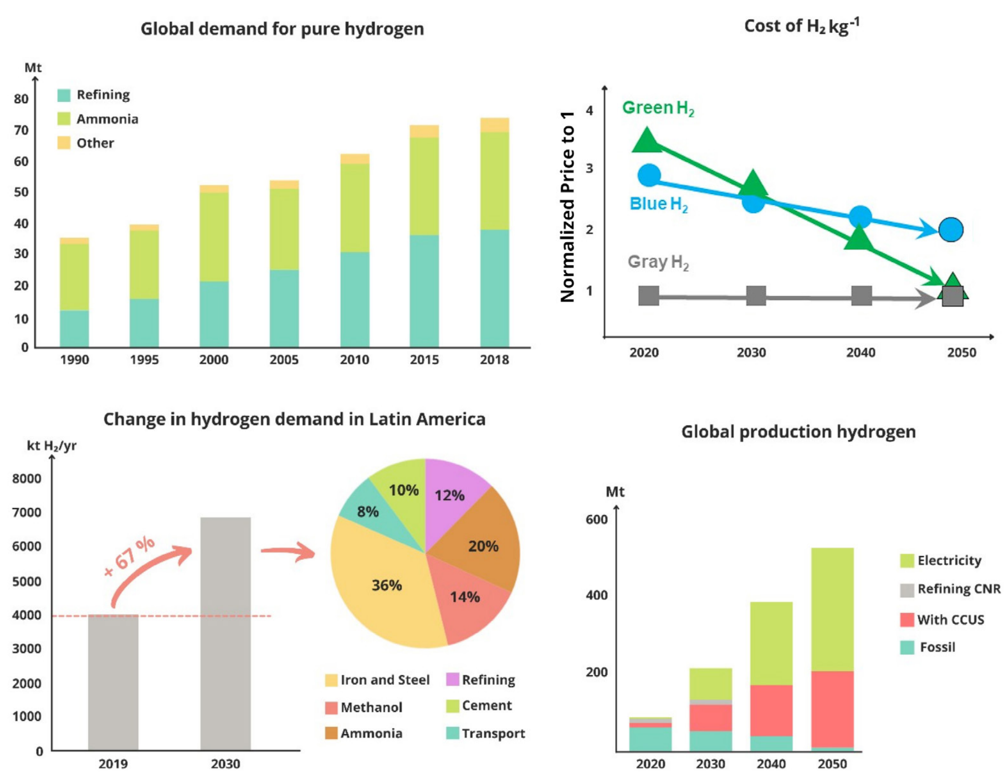

Figure 4. The chart describing the global demand for pure hydrogen (1990-2018), the cost of H_2 kg^{-1}, the change in hydrogen demand in Latin America (2019-2030) and the global production hydrogen (2020, 2030, 2040, 2050)[2,5,21,27] (adapted from Germscheidt *et al.*[2]).

3. Hydrogen in the Petrochemical Industry

Hydrogen is a fundamental feedstock in the petrochemical industry, and oil refineries are the largest consumer of H_2 worldwide, being responsible for approximately 52% of the overall consumption of molecular hydrogen, according to the International Energy Agency (IEA).[5] H_2 is used for the processing of intermediate oil products through hydrogenation reactions as well as for the processing of crude oil into refined fuels (diesel, gasoline, and jet fuel) by hydrocracking and hydrodesulfurization.[3,30] An important point is that the use of grey hydrogen (produced from methane-95% of the total of produced H_2) is responsible for around 20% of total refinery emissions, which produce around 230 Mt of CO_2 *per* year. In addition, the refineries are demanding a large amount of H_2 and it is growing as regulations for a decrease of the sulfur content of oil products tighten.[5] As a consequence, there is a huge market to be explored by the green hydrogen.[2]

The main applications of H_2 focusing on the petrochemical area are presented ahead. Also, we will discuss the principal features, advantages, disadvantages, and economical value of them. The four main processes that will be discussed in the next sections are hydrodesulfurization, hydroisomerization, dearomatization and hydrocracking.

3.1. Hydrodesulfurization (HDS)

The current international environmental legislations have been stringent regarding quality specifications of sulfur content in fuels, imposing ultra-low sulfur (S) concentrations (10 ppm or less) in motorized vehicles. On the other hand, the oil demand is set to grow in an opposite trend, as is shown in Figure 5. S-impurities in fuels are converted into SOx during the burning and they are one of the major causes of acid rain.[31,32] Also, sulfur-containing solid particles cause air pollution, such as haze, which could affect directly human daily life and jeopardize human health.[33] Therefore, it is crucial to find ways of eliminating or reducing sulfur-containing molecules amount in fuels to a better and sustainable life in the future to become possible. In view of that, the production of ultra-low sulfur fuel is essential for the environment and for a sustainable life in the next years.

Faced with this problem, hydrodesulfurization, a process in which hydrogen reacts with sulfur compounds, is an important alternative. This technique involves the removal of around 70% of sulfur compounds from oil fractions in presence of an appropriate catalyst. In this process, the sulfur-containing organic molecules react with H_2 at high pressures (10^7 Pa) to produce H_2S and desulfurized

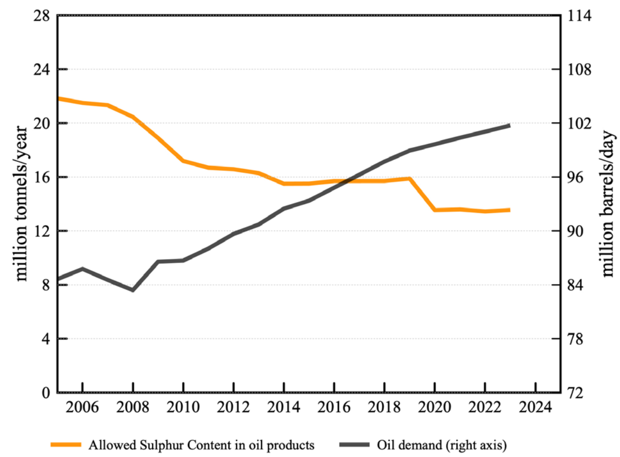

Figure 5. The relationship of allowed sulfur content and oil demand trends over the years. Due do strict limitations, sulfur content in oil products is decreasing while the energetic/oil demand is increasing (adapted from reference 5).

organic products. Sulfur compounds present in fuels are mainly classified into mercaptan, sulfides, disulfides, and thiophenes.[34-36] Such compounds as dibenzothiophene and 4,6-dimethylbenzothiophene, (Figure 6) are some of the most difficult to remove due to its aromatic structures and steric hindrance.

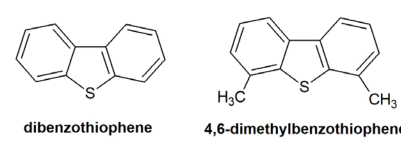

Figure 6. The structures of dibenzothiophene and 4,6-dimethylbenzothiophene, the most unreactive sulfur-compounds present in oil.

It is worth mentioning that after HDS reaction, the sulfur is present in the form of H_2S, which will be recovered and converted into S via Claus process.[37,38] The process consists of partial combustion of H_2S-rich gas and reacting the resulting SO_2 and unburned H_2S in the presence of an activated alumina catalyst to produce elemental sulfur. The global reaction of this process is shown below:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad \Delta H^0 = -442 \text{ kJ mol}^{-1} \quad (1)$$

where ΔH° is the standard enthalpy of reaction.

Claus processes plants are mandatory adjuncts to the gas-desulfurization chain. In addition, the Claus process yields sulfur of extremely good quality and thus is a source of a valuable basic chemical.[37,38] Approximately 60 million tons of elemental sulfur are produced annually, the majority coming from hydrodesulfurization.[39] Elemental sulfur has a great economical value, and can be used for the production of commodity chemicals such as sulfuric acid. Another application for elemental sulfur is the preparation of novel polymers and nanocomposites, which offers a great new direction in chemistry, material science and chemical engineering to create innovative materials from an alternative feedstock.

3.2. Hydroisomerization

In the modern petroleum refining industry, the linear paraffin content is usually reduced in hydrocarbon mixtures by a well-known hydroisomerization process (HIP), which is used to convert saturated hydrocarbon chains into branched ones with the same carbon number, increasing the quality of hydrocarbons.[36,40] This process is usually carried out in the presence of hydrogen to prevent the deactivation of catalysts and the formation of unsaturated hydrocarbons.[41] Moreover, this technique has been identified as one of the main technologies for producing high-quality gasoline blending components and low-pour-point diesel as well as for improving viscosity properties of waxy feedstocks such as slack waxes.[40] Thus, HIP of C_4-C_7 alkanes is performed to produce high octane number gasoline and C_7-C_{15} to obtain diesel fuel with high cetane index and good cold flow properties due to reduction of viscosity as well as freezing point.[42,43] This occurs mainly because the isomerized gasoline with high octane number is free of olefin, aromatic compounds and sulfur impurities, which are limited due to gasoline regulations, as discussed before.[41]

A key challenge of the HIP is the development of efficient catalysts with high alkanes conversion and multi-branched isomers selectivity.[44] At present, the procedure runs over a bifunctional catalyst, with a metal (such as Pd or Pt) loaded onto acidic support (such as aluminosilicate zeolites or silicoaluminophosphate molecular sieves). The metal provides a dehydrogenation-hydrogenation ability, and the acidic support offers a skeleton isomerization function.[41] However, some undesired by-products could be formed via conversion of reactant or intermediate into shorter hydrocarbons chains over the acid sites giving rise to catalyst deactivation, which is known as cracking, that will be discussed in the next sections. In general, catalysts with a high hydrogenation activity and a low degree of acidity are favorable for maximizing hydroisomerization against hydrocracking, once a strong hydrogenation activity limits the degree of branching by hydrogenating primary isomerization products.[42,43]

It is important to highlight that the best catalysts for HIP of *n*-paraffins must have a relatively high hydrogenation activity and a low acidity to achieve maximal hydroisomerization *versus* hydrocracking, once cracking always accompanies hydroisomerization.[43] The hydrocracking reaction may cause degradation of the *n*-paraffins to less valuable and lighter products. Therefore, catalysts based on zeolites, other moderate acidic materials and their composites with various mesoporous materials are the most suitable catalysts for HIP.[44]

3.3. Dearomatization

Aromatic compounds are characterized by unique chemical properties and reactivities, which are widely explored in the pharmaceutical and materials chemistry industries since aromatic molecules can be used as sources of synthetic building blocks.[45-48] An interesting feature of particular interest for synthetic organic chemists is that dearomatization processes, usually carried in the presence of H_2, can transform the aromatic π system, generating unsaturated, and often functionalized structures.[46] When arenes are chosen to be the starting materials, dearomative strategies offer rapid access to complex, value-added and synthetically versatile intermediates from readily available sources of hydrocarbons.[49]

The dearomative reduction field has seen major developments in recent years in terms of both heterogenous and homogeneous catalysis. Moreover, arene hydrogenation catalysis is present in lots of important reactions, with applications varying from small scale synthesis to industrial process, for example the synthesis of cyclohexene (Figure 7), which is a precursor to adipic acid used to produce nylon, and other reactions used in the oil industry and in paper production.[48]

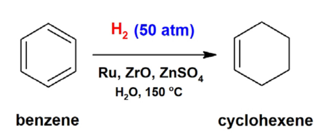

Figure 7. Chemoselective hydrogenation of benzene, a typical dearomatization reaction. Ciclohexene could be converted in adipic acid, which is used in important industrial processes.

3.4. Hydrocracking

Hydrocracking is a process by which heavy petroleum products (larger carbon number) are converted into lighter (small carbon number) and higher-value oil products with lower boiling point, in the presence of hydrogen and a suitable catalyst.[5,50,51] It occurs via carbon-carbon bond cleavage together with simultaneous or successive hydrogenation of unsaturated molecules formed during the process.[52,53] Hydrocracking allows the conversion of heavy and highly aromatic streams into middle distillates and naphtha, with a suitable composition for their integration into the corresponding refinery pools. Moreover, hydrocracking produces highly isomerized products of reduced molecular weight, which impart many of the properties of fuels and lubricants.[54]

Even though this technology is major used in petroleum refining, the fast development of nanotechnology in recent years opened the possibility of new applications for hydrocracking, such as biofuel production from vegetable oils, biomass and municipal wastes containing significant amount of hydrocarbons originating from food leftovers and plastics.[50] In this manner, the presence of hydrogen results in the removal of heteroatoms such as chlorine, bromine, and fluorine, which might exist in waste plastic. Also, compared to thermal cracking, hydrocracking is performed at relatively low temperatures and has better catalytic activity, which facilitates the conversion of fuels into high-quality products with high hydrogen to carbon ratio and low impurities.[55,56] Therefore, the post-treatment processes required in thermal cracking, for example, are not necessary, which reduces the total processing cost significantly, making it an interesting procedure from an economical and industrial point of view.

Due to the variety of feedstock possibilities for hydrocracking, the process can vary considerably, and thus, operating conditions (e.g., temperature, hydrogen partial pressure, hourly feed velocity, etc.) widely differ depending on the chosen feed and desired products. Regardless of the system environment and the feed applied, the performance of hydrocracking process depends on the presence of a catalyst. It is important to highlight that either hydroisomerization and hydrocracking processes occurs through a carbenium intermediate formation and thus are always present in the same systems.[57] In view of that, a selective catalyst for each process is of vital importance to avoid production of undesired species in both cases. Among all bi-functional catalysts studied, amorphous silica-alumina, as well as conventional and hierarchical zeolites, are two of great potential acidic supports for noble metals and non-noble metals.[50] However, zeolite-based catalysts for hydrocracking have shown to be superior to the conventional amorphous catalysts due to their strong acidity, higher thermal and hydro-thermal stability, higher resistance to sulfur and nitrogen compounds, which make them resistant to poisons and reduce coke formation. Additionally, the porosity of zeolites promotes a unique shape selectivity characteristic, favoring specific reactions, while suppressing others due to low accessibility of reactants to reaction sites.

4. Fine Chemicals and Hydrogen

Another fundamental use of hydrogen is in the fine chemical industry. Fine chemicals are the products of a chemical transformation for a specific purpose (feedstocks for pharmaceuticals, agrochemicals, food additives, fragrances, cosmetics, etc.). In general, fine chemicals are obtained from simpler, cheaper, and abundant chemicals compounds. The synthesis of these sophisticated compounds includes several steps resulting in significant value-added products.[58] Thus, the fine chemical industry is positioned between the commodity (suppliers) and specialty chemical industries (customers).[59]

Since the beginning, the industrial process of the fine chemicals had to worry with the social and environmental problems.[60] And nowadays, the industry is continuously concerned with safe chemical reactions. Normally, the synthesis of complex fine chemicals results in large amounts of by-products (0.5% to < 10% of product).[58] This amount of waste is an economic and environmental problem. Therefore, green chemistry is very important in the fine chemicals field. To harness greener chemistry methods, the fine chemical synthesis can take advantage of a novel catalytic reaction instead of more laborious methods of classic organic synthesis. Some reaction steps can be reduced; consequently, a significant waste and cost reduction is possible.

With the aim of improving the synthesis process of the fine chemical industry, from both economic and environmental points of view, H_2 can be effectively used for applications comprising industrial processes, such as catalytic hydrogenation or hydrogenolysis. Thus, in fine chemical synthesis, hydrogen is applied to turn some synthesis more conducive to green chemistry, as it will be present in this review.

Catalytic hydrogenation and hydrogenolysis are catalytic chemical reactions in organic molecules in the presence of a catalyst, as it is presented in Figure 8. In catalytic hydrogenation, there is the addition of hydrogen to a double or triple bond. The two hydrogen atoms are added to the same face of the bond (syn addition), and the product is the reduced organic molecule. Whereas in hydrogenolysis a carbon-carbon or a carbon-heteroatom single bond is cleaved by hydrogen with the simultaneous addition of a hydrogen atom to the resulting molecular fragments.

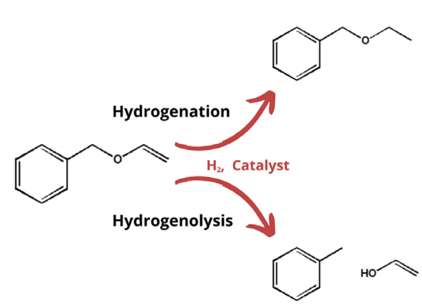

Figure 8. Scheme of catalytic hydrogenation and hydrogenolysis.

In this section, it will be presented examples of application of the hydrogen in the industry to produce raw material.

4.1. Synthesis of drugs

Sertraline hydrochloride ((1*S*-*cis*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-*N*-methyl-1-nanphthalenamine hydrochloride) is a famous example of fine chemical product that utilizes the hydrogenation in numerous steps of its synthesis. It is the most used pharmaceutical agent of a class of drugs known as selective serotonin reuptake inhibitors (SSRIs) that bring relief to the symptoms caused by changes in the serotonin neurotransmitter that precipitate psychiatric disorders like depression, schizophrenia, suicide and aggression.[61]

The challenge related to the production of sertraline is that its activity is stereospecific, being restrict to the *cis*-(1*S*,4*S*). Therefore, substantial research is devoted to design new routes to obtain purified products or to the challenge of stereoselective separation. Since the beginning of the sertraline synthesis,[7] hydrogenation was applied to control the stereochemical of the reaction for the two carbons of cyclohexane. In 2004, Taber *et al.*[7] published an article comparing the old and new commercial synthesis of sertraline.[7]

In the two routes, the stereocenter of the amine was achieved by the metal catalytic hydrogenation resulting in a mixture with different proportion of the species *cis* and *trans*, as it can be seen in Figure 9. After that, for both cases, sertraline was obtained by purification of the mixture with ethanol and (*D*)-mandelic acid.

In the new route, the most important difference is that the catalytic hydrogenation was carried by Pd/$CaCO_3$ as the metal catalyst and ethanol as the solvent. The effect of this change was an improvement on the diastereoselectivity, considering that the proportion of the species *cis* to *trans* increased more than three times (6/1 to > 20/1). Thus, on a commercial scale, the process became more efficient, easily purified, and cheaper. In 2019, another example of the application of hydrogenation in the synthesis of sertraline was proposed by Zheng *et al.*[62] To obtain the right stereochemical, the paper describes a strategy that enables to chiral alkanes via enantioconvergent formal deoxygenation of racemic alcohols.

With the catalyst, it will occur a deoxygenation, forming an alkene. Thus, a hydrogenation will lead to the formation of 98% of *S* product. In this article,[62] there is a study that related the organic structure and the enantioselectivity of the product. As it can be seen in Figure 10, the phenyl group favors the enantioselectivity required. Equivalently, the framework dichlorophenyl in sertraline probably benefits the enantioselectivity for the route proposed.

In the same way as sertraline, hydrogenation is also applied in synthesis of another mental drugs, as venlafaxine.[63] In the synthesis of fine chemicals related

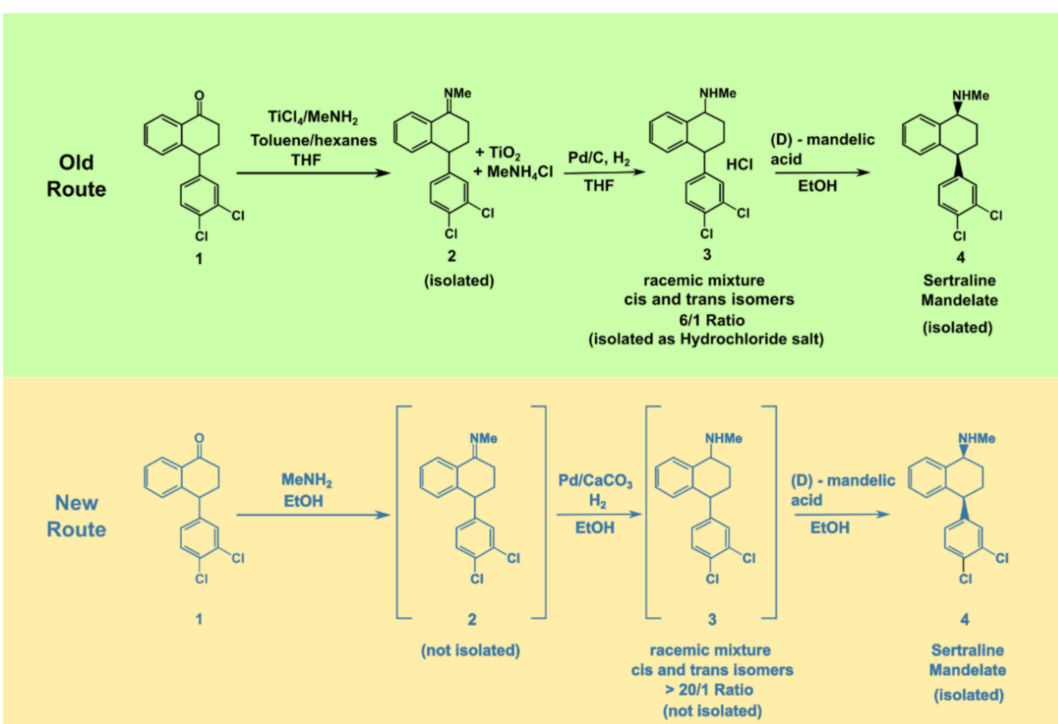

Figure 9. Route comparison between the old and new commercial synthesis of sertraline (adapted from reference 7).

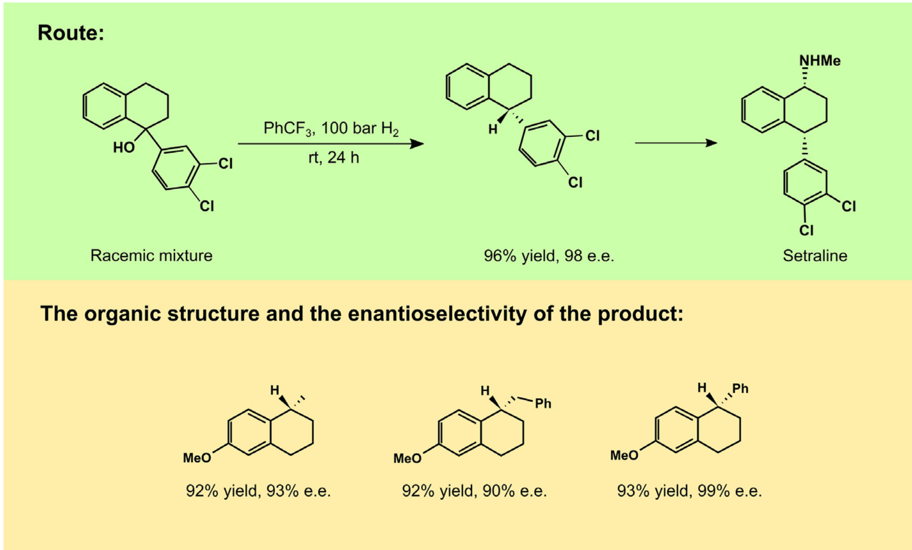

Figure 10. Synthesis of a sertraline intermediate and the relation between the organic structure and the enantioselectivity of the product (adapted from reference 62).

to health, the process of catalytic hydrogenation appears in literature for a series of examples, such as vitamin A,[64] anticancer drugs,[65-67] vaccine against bacterial pneumonia[68] and hydrocinamaldehyde's synthesis, that is applied in human immunodeficiency virus (HIV) treatment.[69] Thus, the catalytic hydrogenation is an important form that hydrogen contributes to the development of new and greener processes in the industry. Beside the catalytical process, hydrogen also acts as a reagent in the industry, as it will be show in next section.

4.2. Hydrogen for Fe and steel production

Global industrial CO_2 emissions account for 31% of the total, while steel is known as the largest single contributor, accounting for almost 7% of the total emissions.[70-72] Steel production generally happens through two main process routes, the integrated route and EAF (electric arc furnace). The integrated route is based on the production of iron from iron ore and coke, and steel from BOF (basic oxygen furnace) steelmaking, while the EAF route uses scrap as the main raw material, however, the energy consumption using these processes is very high.[70,73-75] Although these metallurgic industries are very important for our society nowadays, being the primary industry for various other processes, their high rate of greenhouse gases (GHG) emissions and energy consumption are the main drawbacks in the pursuit of a "greener" industry.[73,76,77]

Aiming to obtain "green steel", the use of H_2 for ironmaking has gained attention in the past few years, as an attempt to develop an entire fossil-free value chain for primary steel.[70,77,78] Thus, besides using H_2 and fuel cells to provide the required energy for the processes to take place, the hydrogen direct reduction (H-DR) process can also be used to produce direct reduced iron, and then, converting it into steel in an EAF. Using this approach, hydrogen can be used for both processes, replacing fossil fuels. Furthermore, this H_2 is expected to be produced on-site, through water electrolysis.[70,72,74,76,79]

In this system, the inputs are usually iron ore pellets, carbon, lime, and scrap, while the main output is liquid steel, containing only iron, also slag (containing other elements) and oxygen are part of the output. The iron ore pellets usually contain 95% hematite (Fe_2O_3) and 5% inert substances. Scrap charged to the EAF contains 95% iron and 5% inert substances. Besides, water is also split into O_2 and H_2 in an electrolyzer the whole time, to supply the H_2 consumption.[70,73,75] The reactions happening in the electrolyzer and the reduction shaft are presented on equations 2-4.

$$2H_2O \rightarrow O_2 + 2H_2 \quad (2)$$
$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \quad (3)$$
$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O \quad (4)$$

The literature shows that the total energy demand for H-DR is very similar to the traditional steelmaking processes, however, the latest uses coal and coke to obtain energy, while the H-DR relies on renewable energy sources. In terms of the cost of steel production, the H-DR pathway cost depends on the cost of H_2 production, which varies depending on its source. Nonetheless, as the cost of H_2 from renewable sources is still high, it reflects in the overall cost of H-DR process, which makes H-DR more expensive than traditional methods. Hence, decreasing the price to obtain sustainable hydrogen will further result in a more economically competitive process, allowing H-DR method to become the main plants for steel production in the next few years.[70,71,74,76,77,79]

Since this technology using H_2 to produce the "green steel" presents great perspectives, various countries, mainly in the European Union, have already started to adapt their plants to H-DR, also using some hybrid pathways, that can work with both H_2 and fossil fuels. Countries such as Germany, Sweden and Austria are examples that have been changing since 2016-2017 and are satisfactory outcomes from these changes.[75,78,79] It is believed that by 2050 more countries will adopt these changes and "green steel" will be produced at a high rate around the world, reaching a more sustainable society with the help of hydrogen.

4.3. From Haber-Bosch to a scaled up green ammonia production

The hydrogen application in the synthesis of ammonia through the Haber-Bosch process had been a game-changer in human story.[80] Developed by Fritz Haber and scaled up later by Carl Bosch (both won the Nobel Prize in Chemistry in 1918 and 1931, respectively), the production of ammonia on a large scale became possible through the reaction of nitrogen, obtained from the air, with hydrogen (equation 5) over an iron-based catalyst at elevated temperatures of 300-500 ºC (to increase the kinetics) and pressures of 150-200 atm (to shift the reaction equilibrium in the direction of the ammonia formation).[81,82]

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \qquad \Delta H^0 = -45.9 \text{ kJ mol}^{-1} \quad (5)$$

Around 85% of the total ammonia manufactured globally is converted into synthetic fertilizer which considerably supports the global food production.[81,82] While the remaining 15% is mainly used for explosives, pharmaceuticals, plastics and essential chemicals and products.

The Haber-Bosch process resulted in a remarkable progress on the agricultural productivity over the world. In current numbers, it is estimated that nitrogen fertilizers are accountable for feeding ca. 50% of world's population.[83] On the other hand, this process has also provided the feedstock to produce chemical weapons and war's munitions, which have been responsible for millions of deaths over the history.[80]

The main challenges for the reaction between nitrogen and hydrogen are energy consumption and greenhouse gases emission. Firstly, N_2 is one of the most inert molecules in nature, being one of the more abundant ones though. On the other hand, H_2 is more reactive than N_2 but it needs to be produced by industrial processes and about 42% of the hydrogen produced worldwide is applied in the ammonia synthesis.[2,84] An important point to be highlighted is that 95% of the hydrogen produced in the world is obtained from fossil fuel methods. Consequently, a high energy consumption and high CO_2 emissions are observed,[2] thus the Haber-Bosch process represents about 1.5% of the anthropogenic CO_2 emissions.[82,85] According to the literature,[81,86] on average for each ton of ammonia synthesized by the Haber-Bosch process is generated 2.86 tons of CO_2, while the modern and most efficient plants generate 1.6 tons of CO_2. In addition, the overall Haber-Bosch process corresponds to more than 1% of the world energy consumption, mainly due to the operational conditions (elevated pressure and temperature) coupled with the production of hydrogen.[82]

As the food demand grows according to global population growth, the ammonia production must be strictly aligned to provide an affordable food supply. Given this scenario, there is a need to develop sustainable routes to produce green ammonia on large scale and with more energy efficiency. Like hydrogen, synthetic ammonia can be labeled as brown, blue and green, according to the carbon footprint generated on its synthesis. Green ammonia refers to zero carbon footprint.[87] Besides, there are a few sustainable pathways to produce green ammonia through biological, non-thermal plasma, and photo/electrochemical approaches.[86,88,89]

It is worth mentioning that the search for sustainable industrial processes is introducing clean electrochemical methods. These methods range from producing green hydrogen and green ammonia to obtaining molecules of industrial interest. An example of the conceptual changes in the productive systems was explored by Marnellos and Stoukides,[90] which first demonstrated an electrochemical ammonia production from its elements (nitrogen and hydrogen) at atmospheric pressure. Electrochemical dinitrogen reduction reaction (E-N2RR) performed in ambient conditions emerges as a noteworthy approach to replace the traditional thermochemical method, mainly due to the possibility of switching the thermodynamic driving force, temperature and pressure, to electric power that can be generated from renewable sources.

Figure 11 shows a simple schematic set view of a world based on renewable energy sources integrated with all E-N2RR processes. Besides the environment benefits related to the decoupled from fossil fuels on the hydrogen production, the E-N2RR approach has, additionally, three more major advantages over the traditional Haber-Bosch process, as following described: (*i*) the N2RR is predicted to be by about 20% higher in energy efficiency, which implies in low energy consumption; (*ii*) mild operational conditions (it may proceed in ambient conditions) and (*iii*) scalability, since smaller-scale plants would be economically viable, it also would facilitate the decentralization of ammonia production and the logistic distribution. Differently from the Haber-Bosch plants that are only profitable at considerable scale, which implies in billions of dollars of investment capital and centralized manufacturing.[81,82,85,88] A question emerges from this analysis, what will be the sustainable process to produce ammonia in the future?

Despite the attractiveness of the E-N_2RR method, it has a long journey and challenges to overcome, in order to be scaled-up and profitable, as its current energy cost is twice more expensive than the conventional Haber-Bosch.[86] Moreover, the possibility of scale up E-N_2RR into a real application has been extremely restricted by limited Faradaic efficiency (most of the studied electrocatalysts that have shown efficiencies greater than 30% need elevated temperatures and exhibit short lifetime), which leads to low yield rates of ammonia.[82,85] The low Faradaic efficiency is primarily related to the competitive reaction between nitrogen reduction reaction and hydrogen evolution reaction (HER) at the cathode, since both reactions exhibit very close potential, but HER is kinetically favorable, leading to undesired hydrogen generation.[81,82,85] Therefore, the development of high selective electrocatalyst can suppress HER and maximize ammonia production, nonetheless this field remains extremely challenging. In conclusion, the replacement of the traditional Haber-Bosch process into a sustainable E-N_2RR production has major obstacles to be circumvented, but clearly dependent on two areas, the cheapening of green hydrogen production, we believe that water splitting is the most suitable way, and the development of a cost effective, stable and highly selective electrocatalyst toward ammonia production. In a view of that, this opens up a new pathway for a great business opportunity, that can be stated as the second ammonia revolution, as ammonia has also been increasingly recognized as a future energy carrier, owing to its high energy density, hydrogen storage molecule and established storage/transportation.[82,91]

5. H_2 as a Renewable Fuel

One of the most important promises for hydrogen use is in energy and energy conversion/storage since it can change the fuels uses all over the world and start a greener and more sustainable approach. Hydrogen combustion can easily be achieved, with a high energy *per* unit mass (kJ kg^{-1}), around 141.10 kJ kg^{-1}, which is almost 3 times higher than for fossil fuels, such as gasoline and methane.[92] However, the use of hydrogen in internal combustion engines can be dangerous due to its fast and powerful combustion, therefore, a very complex system must be designed in order to prevent further issues, a fact that can increase the cost of using H_2 in combustion.[93] Aiming to lower these issues and decrease the cost of H_2 combustion, studies[93,94] have proposed the use of a blend of methane (CH_4) and hydrogen, called hydrane. The use of hydrane can bring benefits for both H_2 and CH_4 systems. Studies show that the use of hydrane could improve the efficiency of natural gas internal combustion engines, since H_2 has a flame speed is way higher than CH_4 in natural conditions (2 cm s^{-1} for CH_4 and 230 cm s^{-1} for H_2).[95,96] Besides, it was shown that the addition of H_2 into the CH_4 lowers the GHG emissions, creating a cleaner process. The use of hydrane also decreases the risk of explosion present when using H_2 alone, and studies suggest that blends containing around 5 to 20% of H_2 can lower the emissions, without bringing bigger risks to a CH_4 system. Thus, no changes that could increase the system cost need to be done.[93] There are a few projects and companies that have been trying to implement the use of hydrane in a few countries, especially in the United States and Netherlands.[97]

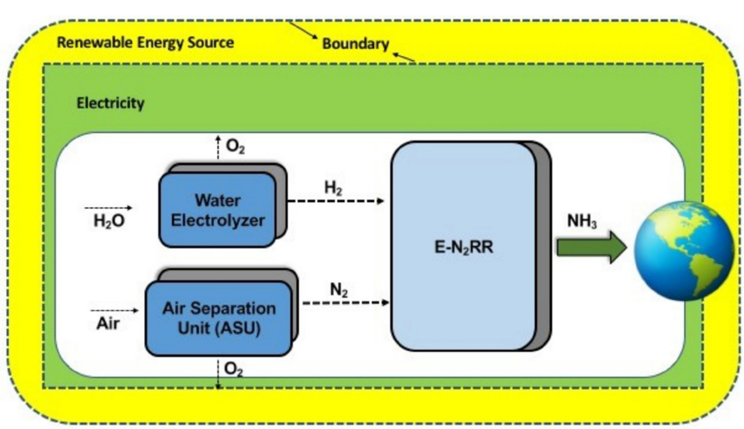

Figure 11. Simple schematic view of the E-N_2RR process completely integrated with renewable energy sources.

Although the use of hydrane can bring advantages, the GHG emissions are still high, and the main goal is to eradicate these emissions, thus making hydrane only a back-up plan, not a real green alternative. Some European authors,[98,99] where the use of hydrane for transportation vehicles has been tested, claim that it is better to invest time on the research of pure hydrogen transportation systems and fuel cells vehicles and how to improve them to reduce their overall cost, than spending time trying to improve the "back-up plan". Since the use of fuel cells could truly bring an enormous benefit for the environment, it is considered a green and renewable alternative, eradicating the carbon emission rates.[98,99]

5.1. Fuel cell

As mentioned before, fuel cell technologies are a huge area of study for using hydrogen to produce electricity. In its principle, fuel cell is an electrochemical cell that can convert chemical energy directly into electricity, without any other energy intermediate forms, using only H_2 and O_2 and producing only water and electricity.

After years of research, the general structure of a fuel cell (FC) nowadays consists in an electrolyte layer, which can be different for the different types of FC, however, a typical FC contains an anode, where the fuel is oxidized and a cathode, where an oxidant (e.g., oxygen from air) is reduced, generating electric power.[100,101] For typical FC, the fuel can be hydrogen or even light hydrocarbons and alcohol fuels, however, the application of hydrocarbons requires a fuel processor to be included into the system, making it more complex and with a lower efficiency. Thus, the use of hydrogen as the fuel source is the best option for FCs, besides making it more sustainable, following the general reaction presented on equations 6-8, in which equation 6 is the anodic reaction, 7 is the cathodic one and equation 8 represents the overall cell reaction.[102-104]

$$H_2 \rightarrow 2H^+ + 2e^- \quad (6)$$

$$2H^+ + {}^1/_2O_2 + 2e^- \rightarrow H_2O \quad (7)$$

$$H_2 + {}^1/_2O_2 \rightarrow H_2O + \text{heat} + \text{power} \quad (8)$$

When talking about FCs, it is important to bear in mind that although they have components and characteristics like batteries, they do not operate in the same way. Batteries can be classified as energy storage devices, and have their available energy determined by the number of chemical reactants stored, stopping to work as soon as the reactants are consumed. On the other hand, FCs are classified as an energy conversion device, and when not limited by an external issue (e.g., corrosion, catalyst stability and material malfunction), they can keep working as long as hydrogen and oxygen are being supplied.[100-102,104]

Besides the advantage of being an energy conversion device that can keep working as long as fuel is being supplied, FC have multiple advantages, which make them a goal for the research.[101,105] Among the numerous advantages, it is possible to highlight the main ones, as following:

(*i*) High efficiency: FCs efficiency can archive values up to 90% (with up to 30-40% of heat recovery), while other methods can only get maximum up to 35%. This happens because FCs produce electricity through a direct process from fuel, removing, therefore, the limitations from the Carnot Cycle, that can be observed in the other methods.[100,105]

(*ii*) Eco-friendly: the use of FCs reduces or even eradicate the emission of GHG, especially using H_2 as the fuel, in which the only product would be water and electricity. Some studies[105,106] show they can reduce carbon dioxide emissions by more than 2 million kg *per* year.

(*iii*) Low operation cost: due to the system's simplicity and the high efficiency, the operation costs such as installation and maintenance, can be quite reduced, which can compensate the high capital cost for FCs.

(*iv*) Quiet operation: the FCs system are noiseless, which allow an easy indoors installation, without the need for sound-proofing the location or even the utilization of noise cancelation technologies.

Besides, these cells have a great modularity and fuel flexibility, allowing a fast and easy assembling in different areas. Additionally, since it possibilities the use of different fuels, from heavy hydrocarbons to sustainable and green hydrogen, their use and implementation is suitable and simple.

Nonetheless, despite of all these outstanding advantages, the cost of stationary electric generation (€ Wh^{-1}) is still too high, and their degradation time remains unknown, which makes FC unsuitable for commercial and large-scale applications. As a result of that, in the past years, a huge effort has been made on the research of FCs technologies and how to improve them.[100-102,104,105] Different types of FCs were developed, and the main ones are: polymeric electrolyte membrane fuel cells (PEMFC), alkaline fuel cells (AFC), solid oxide fuel cell (SOFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and direct methanol fuel cell (DMFC). They will differ in terms of operating temperature, materials, electrolytes and efficiency, but besides that, they all work with H_2 and can produce energy and be used for different applications, that will be discussed further.[100,101,105]

Besides, it is important to highlight that fuel cells are only good and sustainable if the hydrogen used for the power generation is also being produced via a green pathway, as it was recently discussed in our last review.[2]

5.1.1. Fuel cells applications

One of the greatest advantages for the use of FCs are their wide range of applications in different areas and with great advantages, specially related to sustainability and lower GHG emissions. The main applications will be discussed during this section.

5.1.1.1. Stationary applications

One important use of FCs is that they can be used for stationary applications with a high-power reliability, with a possibility for distributed power generation using H_2 as the main fuel. These cells, both high and low temperature, can be used to power residential locations, emergency services such as hospital, industries, computer facilities, call centers, communication facilities, data processing centers and high technology manufacturing facilities, in which a FCs with a good stability can provide a reliable and green power source.[105,107-109] Besides, since this is a low noise technology, it can be installed inside homes or neighborhoods, without any further disturbing, which decrease the energy cost by eradicating costs with long power line transportation.[101,104] FCs can also be used for distributed power generation, for both small and large scales. This can be very useful in remote and rural areas, where the access to energy power is scarce and hard, thus, the use of FCs to generate a green and reliable energy power, with a low cost, can bring innumerous benefits for these areas.[110] In a view of that, remote areas can also be benefited from the use of microbiological fuel cells (MFC). These cells have the ability of generating energy power, coupled with wastewater treatment. Therefore, the communities can have access to in-site power generation and treated water resources.[105,110,111] Thus, the 3 main FCs technologies, alongside MFCs, have been extensively studied to have its efficiency and activity enhanced, and become suitable for this applications that can bring outstanding benefits for communities and the environment.

5.1.1.2. Transportation applications

The greatest concentration of research in FCs is mainly focused on transportation applications. Since transportation vehicles are responsible for 23% of greenhouse gases emissions and currently relies on hydrocarbons for 92% of its energy,[112] the use of hydrogen fuel cells vehicle (HFCEV) can contribute with the decrease of these emissions and create a culture of green vehicles. Fuel cell vehicles (FCVs) need to have a fast response and start-up times, in this way, high temperature FC are not the best option for these applications.[105,109] They can be used for any kind of transportation vehicles, since personal motorcycles and small cars, to buses, airplanes, and some spacecrafts. However, bigger and more complex vehicles require a more robust and developed FCs alongside with a sophisticated system that will power the vehicle. HFCEV are designed to replace conventional internal combustion engine vehicles, and although the primary energy source comes from the FCs, the overall system configuration also includes a battery, a supercapacitor, AC/DC convertors, three-phase traction motor, auxiliary devices, DC-bus and energy storage systems that will be part of the vehicle powering process (Figure 12).[113-115]

Although these cells have been extensively studied and some countries are already using some HFCEV, their lower power density and slower power response are the main drawbacks for a suitable HFCEV be

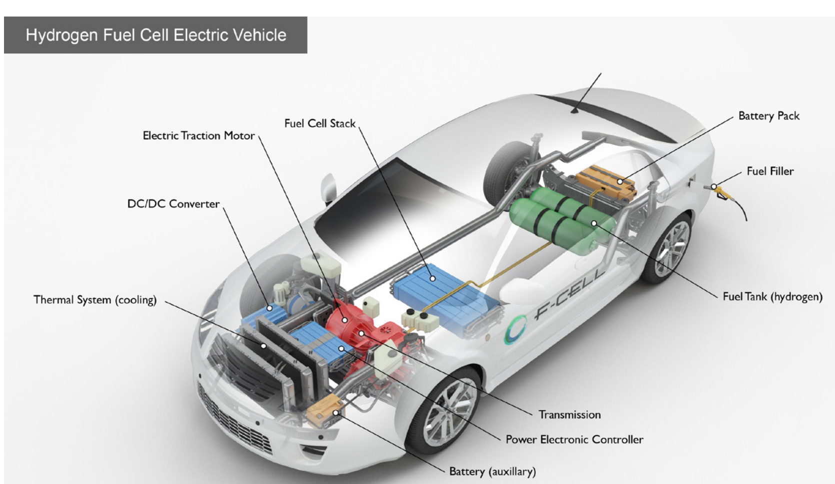

Figure 12. A general scheme of a hydrogen fuel cell electric vehicle (reproduced from reference 114 with copyright permission 2021 from AFDC, US Department of Energy).

commercially available. Besides, the main advantages for HFCEV rely on a green hydrogen production, such as water splitting, which also need to be powered by a green energy source. Nevertheless, HFCEV present great perspective for the future of transportation, helping to reduce, even to eradicate GHG emissions, yet further research is still needed to make this technology suitable and provide its advantages in a state of art and low-cost prototype.[101,105,109,112,116]

Lots of companies in different countries around the world are investing in fuel-cell cars, using H_2 as the main fuel. Recently (August 2021), a Chinese company delivered a fleet of 100 hydrogen-powered trucks, as an attempt to promote a green hydrogen transportation network nationwide.[117-119] Earlier this year (February 2021), a Canadian leading company in energy industries, announced purchase orders to power 10 fuel cell electric buses (FCEBs) in the Netherlands, and they are planning to ship the modules later in 2021, contributing and investing in a cleaner public transportation in Europe.[120,121] Besides, there are other important companies and industries investing and researching fuel cell cars and other transportation vehicles in different countries around the world, such as USA and the UK. Additionally, to invest in transportation vehicles, these companies also have to invest in the construction of H_2 gas station, to make it easier and faster filling up HFCEV.[122-124] Besides, it is important to highlight that heavy transportation vehicles like buses, trains and trucks will be the first to benefit from H_2 as a fuel, since it can help with the increasing in the use of H_2 for transportation.

They can also be used and applied in spacecrafts and any space module used for close or deep space exploration. The use of FCs is preferred for manned missions since such missions require a primary energy storage with longer discharge times and higher power levels, thus, these requirements can be met in a better way by FCs, instead of batteries or other energy power source or storage.[105,125] Besides, another important advantage for the use of this technology in space is that this process generates water, which can be used for crew drinking and spacecraft cooling during the missions. Therefore, alongside with the power generation, they can also have access to clean drinking water.[125,126] Thus, using H_2 in fuel cells can help a lot with space exploration as well, making the fuel cells even more important for transportation.

5.2. Combining CO_2 and H_2 to produce fuel

The global current consumption of methanol is over 98 million tons *per* annum, which has keep growing, as two-folded on the last decade.[127,128] Methanol is one of the most important chemicals as a feedstock in the chemical industry. Its largest applications are to obtain its oxidized species formaldehyde, acetic acid and as a C1 building block for synthesize other chemicals (dimethyl ether, methyl *tert*-butyl ether, synthetic hydrocarbons and so on). Among several uses, noteworthy as a solvent, methanol is used in transportation field, directly in a fuel cell or blended with gasoline or diesel, to increase octane ratings and reduce carbon emissions.[84,129] Around 5% of the H_2 produced worldwide is used for methanol production, by the catalytic hydrogenation of carbon oxides, according to equations 9 and 10, while the reverse water-gas-shift (WGS) reaction, equation 11, occurs in parallel.[129]

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H^0 = -49.8 \text{ kJ mol}^{-1} \quad (9)$$
$$CO + 2H_2 \rightleftarrows CH_3OH \quad \Delta H^0 = -91.0 \text{ kJ mol}^{-1} \quad (10)$$
$$CO_2 + 2H_2 \rightleftarrows CO + H_2O \quad \Delta H^0 = +41.2 \text{ kJ mol}^{-1} \quad (11)$$

In the above reversible reactions that methanol is produced, equations 9 and 10, both exothermic, considerable cooling is used to shift the reaction in methanol favor. Nevertheless, low temperatures slow down the reaction kinetic. Conventionally, to optimize methanol production, the industrial process is performed adiabatically in a gas-solid reactor over the $Cu/ZnO/Al_2O_3$ catalyst at 250-300 ºC and 50-100 bar.[129-131] The step described before equations 9-11 includes the synthesis of syngas, a mixture of H_2, CO and CO_2 that is mainly produced by steam methane reforming (SMR) and autothermal reforming (ATR).[5,132,133] In a brief description, the methanol synthesis consists in: (*i*) synthesis of syngas; (*ii*) methanol production; (*iii*) gas separation and product purification. Despite the consolidated technology, the overall process exhibits key aspects that could be further enhanced/changed to improve the production. As reactants are produced from the syngas synthesis, which requires significant amount of energy to reach high temperatures (800-900 ºC for SR and 3000 ºC for ATR) and release partly of the mixture to the atmosphere.[130,133] An alternative and green way to circumvent that issue is the application of the carbon capture and utilization (CCU) technology, where the carbon feedstock could be the CO_2 already present in the atmosphere or from the exhaust gases of carbon emission industries (such as cement plant, steel industry and so on). There has been considerable effort to develop methanol synthesis free of fossil fuel combined with green hydrogen.[134] Besides the scope of this review, which is mainly focused on hydrogen applications, a cost-effective and environmentally friendly methanol production that has attracted considerable attention is the photocatalytic conversion of methane into methanol with water under ambient conditions, but still at a lab scale.[135]

However, the global production of methanol currently generates 2.3 tons of CO_2 *per* year, which contributes to the increase amount of GHG in our atmosphere. While its global market keeps growing, accompanied of its industrial applications. Thus, to supply the current and future demand, it is environmentally imperative the development of sustainable pathways to achieve a clean and profitable methanol production, so these ones may must gradually replace the state-of-art methods available in the market. The nature of the feedstocks plays a pivotal role on the sustainability and cost of the overall process. On this way, the key parameters to be intensively developed, in order to become sustainable and economically competitive, are the use of CO_2 feedstock, through CCU technology, provided by the anthropogenic activity and the green hydrogen supply. Despite both technologies are still away to be competitive with the fossil fuel-based methods, several progresses have been achieved on both sides. Since it is already a reality of pilot plants, in Japan and Iceland, that produce methanol from green hydrogen and captured CO_2.[128]

5.3. The precursors of biodiesel

An alternative fuel with wide acceptance because of its reduction of most exhaust emissions, improved biodegradability and reduced toxicity over conventional diesel fuel is the biodiesel.[136] Also, with the urgent need to explore sustainable resources, that are low-cost, abundant and renewable, biomass is a good alternative, which has received widespread attention in recent years.[29]

Biodiesel is usually produced by the process of transesterification of the animal fat or vegetable oil with an alcohol, producing methyl esters (biodiesel) and glycerol.[136] The properties of biodiesel depend greatly on the various methyl esters that are formed. As well as the structure of the fatty acid, the ester moiety from the alcohol can influence the fuel properties of biodiesel. These structural features encompass chain length, branching of the chain, and degree of unsaturation of the fatty acid that is the most important factor.[136,137]

The goal to reach a higher quality of biodiesel can limit the use of alternative raw materials. In the way of find other feedstock to biodiesel production, processes with hydrogen are important to achieve news feedstocks. In this sense, Yang *et al.*[136] presented a one-pot process combining transesterification and selective hydrogenation for biodiesel production from the highly poly-unsaturated oil of hempseed. From the hempseed can be obtained the hempseed oil as raw material for biodiesel. This oil is highly polyunsaturated and passing through the transesterification combining with a selective hydrogenation, achieving the biodiesel within the quality standards set. This kind of work is an important initiative of new ways to find feedstock to biodiesel production. As well as the by-product of the hemp fibers is not a problem, but a solution, the by-products of biodiesel production also are very useful.

5.3.1. Glycerol, more than a biodiesel by-product

Glycerol was discovered in 1779 by Scheele and today it still has many applications because of its particular combination of chemical and physical properties.[138] It is a sweet-tasting liquid, transparent and odorless. At room temperature, it is viscous. Moreover, it absorbs and retains water, has plasticizer properties, it is non-toxic and easily biodegradable, has antioxidation properties and protects against fermentation processes.[138]

The Chemical Economics Handbook published in 2018 points that the market of "personal care and cosmetics" represented 30% of the global application of glycerol in that year.[139] In this field, glycerol is mainly used for its chemical properties: formation of esters that serve as emulsifiers or conditioners, moisturizing and conditioning properties. Thus, it is present in different products, such as creams, lotions, hair care and toothpastes. Also, it is one of the most important building block chemicals that can be converted to value-added products,[140] like 1,2-PDO (1,2-propanediol), 1,3-PDO (1,3-propanediol), allyl alcohol, 1-propanol, and propylene.[141] Some of these derivatives have similar characteristics to glycerol, consequently, they can be used in cosmetics products because of its physical properties. Mostly in creams, sunscreens, and even hand sanitizer that are widely used to prevent coronavirus disease (COVID-19), have in composition 1,2-PDO, also known as propylene glycol.

In current industrial routes, 1,2-PDO is produced by a petrochemical approach, which is an environmentally unfriendly and expensive process. Therefore, 1,2-PDO synthesis by the selective hydrogenolysis of glycerol is an economically competitive, environmentally friendly, and highly sustainable route. Zhang and co-workers[142,143] have published two papers about the transformation of glycerol into 1,2-PDO. Both articles described examples of how hydrogen by hydrogenolysis can improve a selective catalysis showing once again that beyond of energy production, hydrogen is useful in all the chain production.

6. Challenges and Perspectives for Sustainable Use of H_2

As shown throughout the text, hydrogen is a key chemical for sustainability and to achieve greener processes in the chemical industry. In the petrochemical industry, hydrogen contributes to a greener hydrodesulfurization and hydroisomerization processes. In the fine chemical industry, H_2 improves the production from both economic and environmental points of view, from the catalytic hydrogenation and hydrogenolysis. It is also used in Fe and steel production to produce the “green steel”. Moreover, as presented in this review, hydrogen can also be used in energy and energy conversion/storage since it can change the fuels uses and start a greener and more sustainable approach.

However, all environmental gains depend on the process of obtaining hydrogen. Thus, the production of green hydrogen (produced from water and electricity from renewable sources) is essential for this. Large investments in fundamental research and scale-up strategies should guide the scenarios in the coming years. And as fast as the prices of sustainable products gain competitiveness, the companies will redraw their processes and will open the doors to green and sustainable chemistry. Therefore, we believe hydrogen will be essential in the next decades as a key chemical to make the industrial processes greener, walking towards a more sustainable world.

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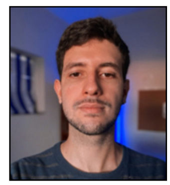

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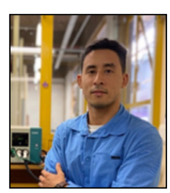

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