

The Use of Hydrogen in the Production of Fuels and Additives for Internal Combustion Engines

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Currently, energy demand worldwide has inflated the prices of conventional fuels, so it is essential to identify alternative solutions. One such solution involves hydrogen (H₂), which can be used directly as a fuel or an additive for internal combustion engines (ICE). This work aims to review the hydrogen applications related to fuels and/or additives in ignition engines. For instance, hydrated vegetable oil (HVO) can be considered a possible substitute for biodiesel, while synthetic fuels involve a high cost, mainly due to the production process. Furthermore, using H₂ as an additive can offer benefits such as reducing pollutant emissions.

Keywords: Hydrogen. Hydrotreated Vegetable Oil. Diesel. Additive. Synthetic Fuels.

Introduction

The use of fuels to meet population demand across the planet has increased over the years [1]. Under this scenario, it is essential to identify alternative sources of energy for the most varied sectors of society, especially the transport sector. Fossil fuels are still widely used in ICE due to their availability and low cost compared to some biofuels. Nevertheless, fossil fuels also have drawbacks, such as the emission of pollutants and the concern of depletion, and therefore researchers are looking for other solutions [2]. Hydrogen has been indicated as a strategic solution for this scenario. Hydrogen has a higher calorific value, about 120 MJ/kg, than other fuels. Methane, gasoline, and diesel have, respectively, 50 MJ/kg, 44.5 MJ/kg, and 42.5 MJ/kg [3].

Hydrogen is crucial as it can be produced using both conventional and renewable energy sources. In addition, it has several applications in the transport sector (e.g., in fuel cells) and the industrial sector (in refining and product generation) [4].

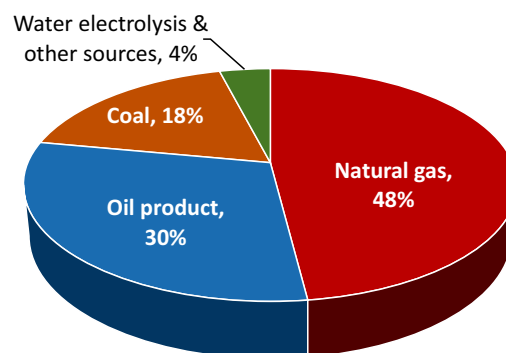
Based on the energy source used to produce hydrogen can be divided into three categories,

namely: green, blue, and gray [3]. Green hydrogen is considered the cleanest, given that renewable energy sources are used for production. On the other hand, blue and gray hydrogen have similar sources as they can produce hydrogen from fossil fuels. However, the process classified as gray hydrogen uses the capture and sequestration of the generated CO₂ to reduce the environmental impact.

From an environmental point of view, hydrogen should be produced from renewable energy sources, such as solar and wind energy [5]. However, those mentioned earlier have low competitiveness in terms of operating costs compared to extraction methods that use fossil fuels. Figure 1 represents a comparison between the methods commonly used to extract H₂.

The role played by H₂ in the transport sector has been reinforced because of the production of HVO. Furthermore, due to the hydrotreatment processes, this fuel can present better physicochemical

Figure 1. H₂ extraction methods [3].



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properties (e.g., calorific value, cetane number) when compared to biodiesel and Diesel. Furthermore, the search for new fuels has been reinforced as a result of the market oscillations of the oil price in recent years. Therefore, this work aims to present a literature review on the use of H₂ in the production of fuels or its application as a fuel additive in internal combustion engines.

Materials and Methods

The bibliographic search was carried out in July 2022 using the search engine Periódico CAPES, available at <https://www.periodicos.capes.gov.br>. The keywords used were: Hydrogen; Hydrotreated vegetable oil; Diesel; Additive; Synthetic fuels.

Articles from the last 10 years were selected so that each one presented contributions to the proposed theme, indicating that it was a literature review or experiments in English. In addition, some articles were selected regardless of publication date due to their scientific relevance to this work.

Results and Discussion

The transport sector is one of the biggest fuel consumers in the European Union and the rest of the world, presenting a higher consumption than the residential and industrial sectors [6].

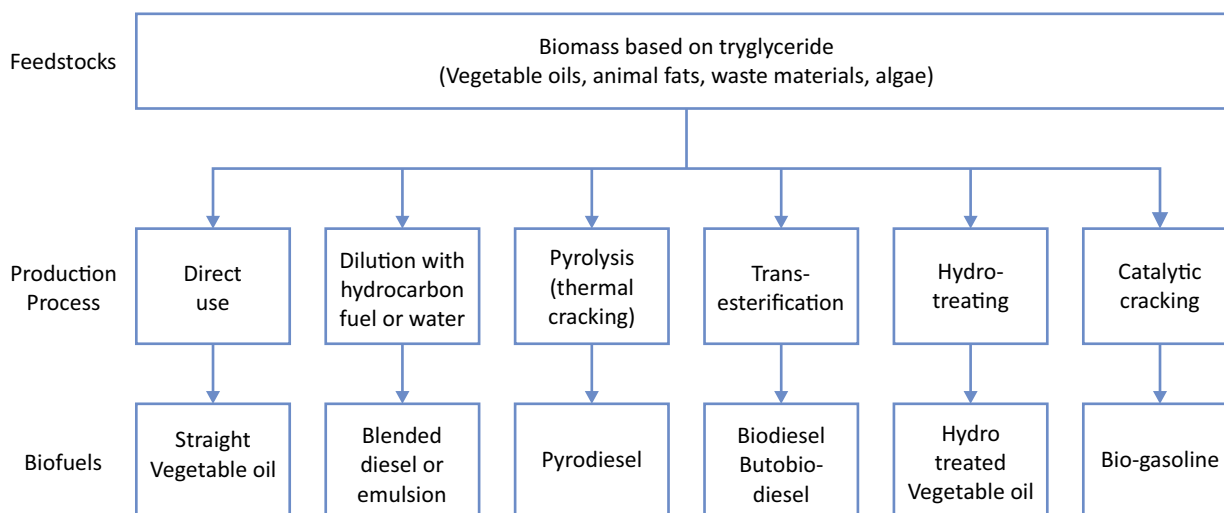
Although biofuels are used without engine modifications, they cost more than fossil fuels. The highest cost for biofuels refers to their raw material [7]. The cost of producing conventional biofuels ranges from US\$70 to US\$130 per barrel of oil equivalent (boe); while advanced biofuels cost range from US\$85 to US\$160 per boe [8]. The main biofuels used in compression ignition engines are 1st- and 2nd-generation biodiesel (Figure 2).

Hydrotreated Vegetable Oil

HVO is a bio-based liquid paraffinic fuel that can be used solely or blended in diesel engines [9]. The raw material used in the production process of biodiesel and HVO can be the same. For both processes, vegetable oils, and animal fat are commonly used. The difference in the production of each biofuel occurs in their chemical process. While HVO uses the hydrotreatment process, biodiesel is usually produced via transesterification.

Despite the more frequent use of biodiesel, HVO has advantages in its production. These advantages occur because there is no need to verify the degree of establishment of the raw material for HVO since hydroprocessing results in fully saturated paraffinic hydrocarbons and is not susceptible to oxidative

Figure 2. Production of liquid biofuels from biomass [9].



instability [10]. Moreover, the free fatty acids present in the raw material of HVO are converted into paraffin in the hydrotreatment process, while the transesterification process results in the formation of glycerin. From an economic point of view, paraffin is more attractive due to its ease of commercialization.

In the HVO hydrotreatment process, hydrogen acts by removing oxygen present in triglycerides at high pressure (approx 70 bar) and temperature (between 300 and 400 °C) [10,11].

The derivatives of the HVO production process are propane (from the hydrogenation of glycerol), water, and CO₂ [7]. The hydrogen used in the production process can be derived from propane or extracted from other sources, such as renewable and non-renewable resources, microbial production, electrolysis, and other thermochemical processes [3].

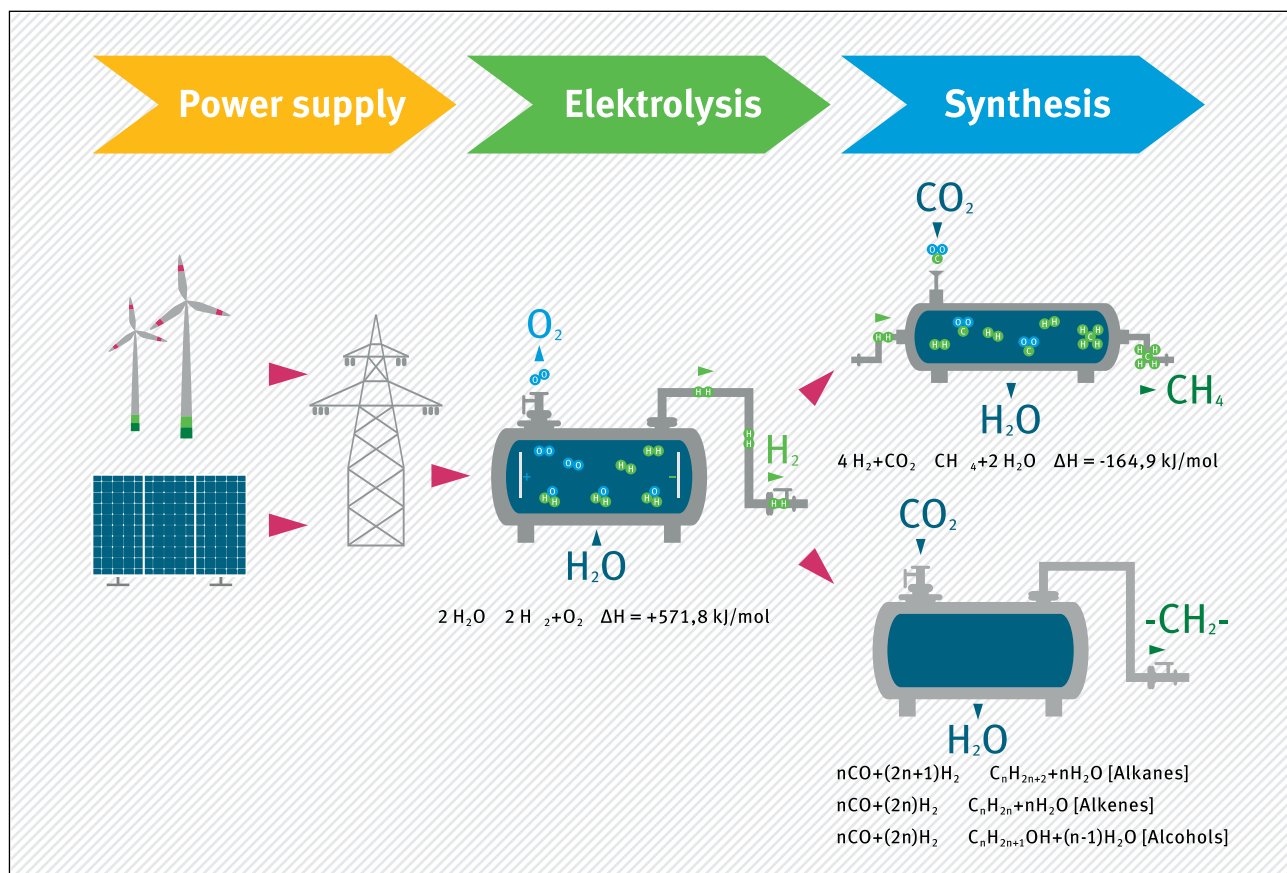
According to Waldheim [7], the total cost of producing HVO varies between 600 to 1,100 €/ton

(50 to 90 €/MWh). The use of different sources of hydrogen can have a direct effect on the final cost of HVO. Despite the higher value than other fuels, HVO has better physicochemical characteristics that enable better fuel combustion. The cetane number of HVO is higher than the other fuels evaluated (e.g., diesel, ethanol, biodiesel), and it presents good chemical stability in its storage. Other important characteristics are the absence of sulfur content, aromatic components, and ash. This combination of factors provides a complete combustion process and a more efficient catalytic after-treatment process [9].

Hydrogen in the Production of Synthetic Fuels

Synthetic fuels combine hydrogen, hydrocarbons, and an energy source. CO₂ and H₂ can be used to produce liquid fuels, which can be used in the transport sector [12]. This production process,

Figure 3. Simplified scheme of the Power-to-Liquid (PtL) process [13]



called Power-to-Liquid (PtL) (Figure 3), is initiated through the production of H₂, which will later be combined with CO₂, promoting the production of liquid hydrocarbons that can be refined to generate synthetic fuels (methanol, gasoline, and aviation fuel) and also can produce diesel through the Fischer-Tropsch process [13].

Hänggi and colleagues [14] discuss that one of the goals of synthetic fuels is to create a sustainable fuel. According to the source of hydrogen production, the process can present a high-energy loss, which reduces the overall energy efficiency [13]. Synthetic fuels are less effective in energy efficiency than fossil fuels; however, they are an exciting alternative to reducing atmospheric carbon.

Hydrogen as an Additive

The utilization of engines that operated only with hydrogen was tested in 1978, presenting limitations due to the high self-ignition resistance of the fuel [15]. The use of H₂ showed better results in tests on spark-ignition engines. Due to these limitations, several researchers have studied the addition of hydrogen as a fuel additive. The main advantages are the absence of carbon in

its molecules, the higher calorific value when compared to diesel fuel, and the reduction of exhaust gases to the environment when used in compression ignition engines. Kanth [16] evaluated the use of hydrogen in a mixture of rice biodiesel and Karanja biodiesel. The experimental setup (Figure 4) had hydrogen supply through a pressure cylinder regulated to enter the diesel engine at a pressure of 2 bar and 7 lpm (liters per minute). A 5.2 kW diesel engine was kept at a constant speed and variable load. They reported a reduction in the specific consumption of fuel, CO, and HC emitted by the engine due to better combustion from flame propagation caused by the presence of hydrogen. However, due to higher combustion pressure and temperatures, NO_x emission had slightly increased.

Barrios [17] evaluated the use of hydrogen in a blend of diesel and biodiesel. They reported a reduction in the concentration of fine PM particles emitted by the engine (Figure 5). This result was associated with increased particle oxidation. The latter resulted from higher combustion chamber temperatures and the formation of OH (hydroxyl) free radicals that react with unburned hydrocarbons.

Figure 4. Experimental scheme for hydrogen and biofuels [16].

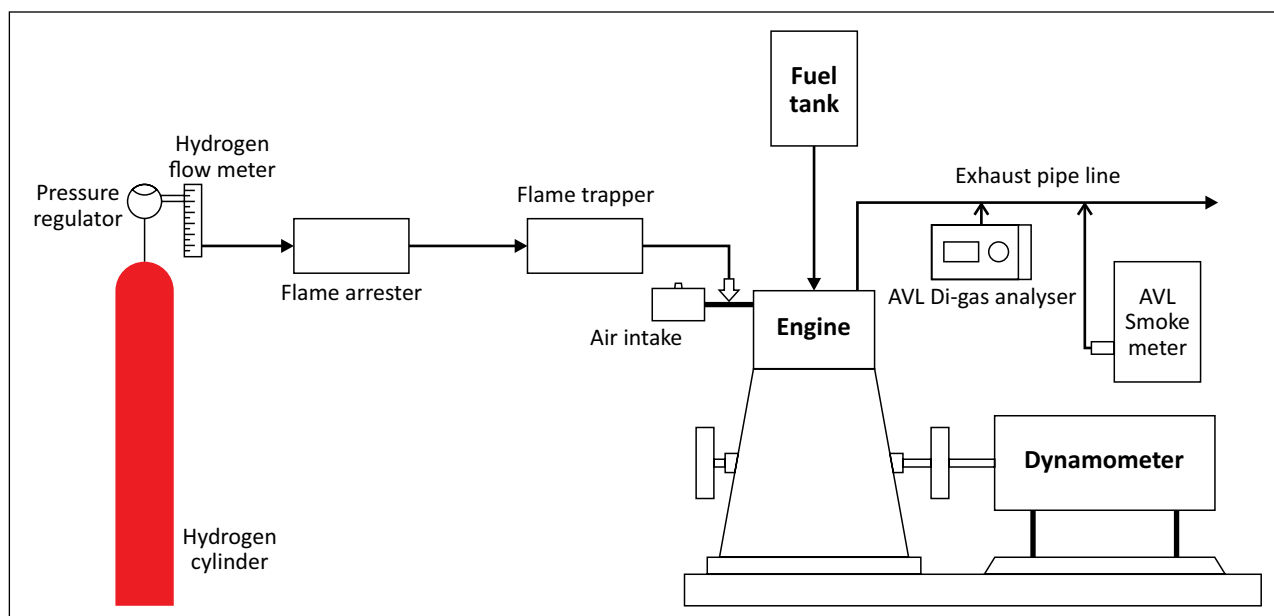
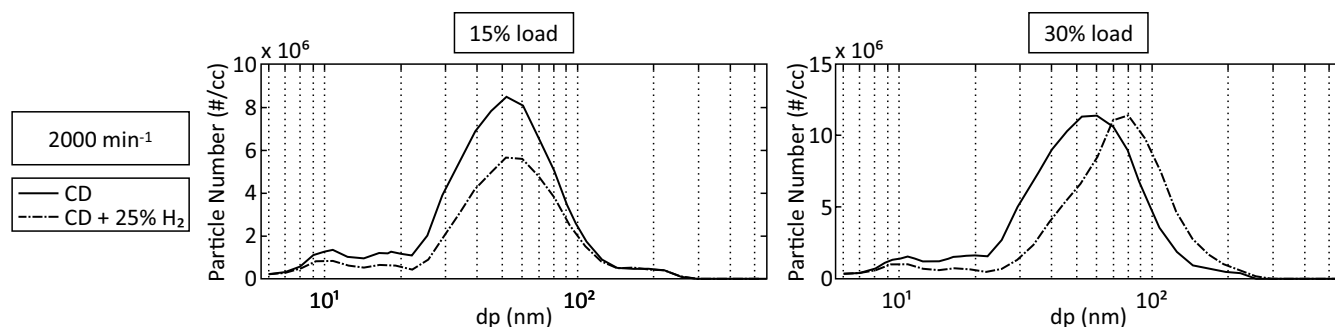


Figure 5. Particle distribution and concentration for blending diesel, biodiesel, and hydrogen [17].

Conclusion

Based on the literature review, one of the challenges for the coming years is the development of new processes and industries for producing biofuels on a global scale, in addition to the development of raw material supply chains for this production, such as biomass. Furthermore, hydrogen has been pointed out as a significant potential in the short- and medium-term scenario as an additive used in conventional fuels and for synthesizing new fuels.

Finally, we summarized the conclusion in topics as following:

- HVO is a possible substitute for biodiesel because it has better physicochemical characteristics that result in better combustion. Despite that, its production cost is a drawback since using hydrogen results in a more expensive fuel than transesterification (resulting in biodiesel) or the production of fossil diesel. Still, more research is regarding the engines' durability before considering a complete replacement of diesel fuel.
- Synthetic fuels are an alternative fuel option as they combine elements such as CO₂ and H₂ in the production process. The main product currently produced is methanol and synthetic gasoline. From an environmental point of view, this fuel presents advantages because of the CO₂ sequestration. On the other hand, it requires more significant investments and fuel production.
- The use of H₂ as an additive in engines was pointed as the lowest cost compared to the others. The use of H₂ can contribute to the

reduction of emission pollutants and reduce specific fuel consumption.

- The use of different hydrogen extraction methods has a direct impact on its final associated cost. Although those renewables can be considered to produce the so-called 'green hydrogen,' the H₂ extracted from fossil sources is still the one with the lowest value.

It is expected that in the future, the cost of sustainable fuels to decrease and that technological limitations to be overcome. This combination of factors could provide a cleaner and more affordable fuel.

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