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REVIEW ARTICLE

Storage of Hydrogen by Liquefaction and Use in Internal Combustion Engines

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ABSTRACT

Alternative fuel research has become widespread due to climate crises. Unlike fossil fuels, hydrogen does not release toxic gases such as HC (hydrocarbon) and CO (carbon monoxide) during combustion, and this makes it a prominent feature in alternative fuel research. This article is about the methods of storing hydrogen by liquefaction and the details of its use in internal combustion engines. To begin with, the properties of hydrogen which makes it convenient to consider it as a fuel will be explained. After that, the hydrogen usage in engine types will be evaluated. To conclude, storage methods by liquefication and their effectiveness will be discussed.

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1. Introduction

As the effects of climate crises due to the greenhouse effect increase worldwide, incentives and efforts to prevent the release of gases that cause the greenhouse effect are increasing also. A study conducted in 2019 revealed that approximately 33 Gr-CO2 emission was generated by the energy production sector and it has been observed that this emission is equivalent to 87% of the worldwide CO2 emission (Aziz, 2021). For this reason, the European Parliament and the Council published the Euro 7 regulation in 2024. With this regulation, the exhaust-sourced CO emission limit for compression internal combustion engines in M1 class vehicles was reduced to 500 mg/km, while the exhaust-sourced CO emission limit for injection internal combustion engines was reduced to 1000 mg/km (EU, 2024). According to Green Deal Program proposal, the European Union have a target to reach zero net greenhouse gas emission by 2050 and they aim to reduce GHG by %55 with respect to 1990 by 2030 (Stępień, 2021).

One of the most important reasons for researching hydrogen as a fuel is that the net thermal energy released after the combustion of hydrogen is more than fossil fuels. Moreover, hydrogen has a 6 times higher combustion velocity than petrol and it has a wide flammability limit which leads lean air-fuel mixtures (Stępień, 2021). The only product that comes out after the combustion of hydrogen with oxygen is water and that the CO and HC production is not observed in fossil fuels allows hydrogen to be considered as a green fuel (College of the

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Desert, 2001). This is the main reason why hydrogen is considered in the green fuel category compared to fossil fuels. In addition to these properties, hydrogen is found in nature as water and can be separated by various methods (Aziz, 2021). For this reason, it can be said that hydrogen is a promising renewable energy source. In this article, favorable and unfavorable properties of hydrogen to use in internal combustion engines will be examined.

One of the important issues that will affect the widespread use of hydrogen is the storage and transportation of hydrogen. Complex systems and methods are used in hydrogen storage and transportation. Pressurizing and storing in tanks with the use of multi-stage compressors or liquefying and transporting by performing phase change with temperature control can be given as examples of these methods (Kharea & Bhatiab, 2025). A significant disadvantage is that hydrogen is in gas phase at room temperature and its energy/volume ratio is low compared to fossil fuels (Tamarona et al., 2024). Transporting and storing hydrogen by liquefaction allows this disadvantage to be eliminated and make it more efficient. Liquid hydrogen has 2,8 times higher density than gas hydrogen at 35 Mpa, and 1,7 times higher density than gas hydrogen at 70 Mpa (Liu et al., 2024). For this reason, this article will examine the methods of storing hydrogen by liquefaction.

2. Use of Hydrogen in Internal Combustion Engines

2.1. Properties of Hydrogen

Many properties of hydrogen allow it to be used in internal combustion engines. One of the major properties of the hydrogen is that hydrogen has a wider flammability limits and the wider flammability limits allows for a leaner mixture to be obtained (College of the Desert, 2001). A leaner mixture means that the fuel ratio used can be less than the stoichiometric or chemically ideal amount compared to the amount of air required for combustion (Taha et al., 2013). This allows for more complete combustion, reducing fuel consumption, while also reducing combustion chamber temperature and resulting in lower emissions (Stępień, 2021).

Another important point in using hydrogen as a fuel is that hydrogen has a high flame velocity. The flame velocity of hydrogen is higher than that of gasoline in the stoichiometric mixture (College of the Desert, 2001). For this reason, combustion occurs at almost constant volume, thus approaching the thermodynamically ideal combustion cycle (Fırat et al., 2017).

The other reason to use hydrogen as a fuel is that hydrogen has high autoignition temperatures. Therefore, hydrogen air mixture can be compressed more than other air-fuel mixture without causing unwanted premature ignition. This higher compression ratio leads to generating more thermal power (Fırat et al., 2017).

Final advantage of hydrogen to be preferred as fuel among other alternative fuel options is that hydrogen has higher diffusivity rate. This feature helps hydrogen to diffuse into the air easily and it allows us to obtain more homogeneous air fuel mixture (Stępień, 2021). In addition, the fact that hydrogen diffuses quickly into the air in the case of leakage makes it a safer alternative fuel option (Fırat et al., 2017).

These mentioned features make it easier to choose hydrogen as a fuel, but it also has features that make it difficult to use in internal combustion engines. One of the most effective features is the low thermal energy required for the ignition of hydrogen. The energy required to ignite a hydrogen-air mixture is approximately 0.02 mJ, while the thermal energy required to ignite a petroleum-air mixture is approximately 0.24 mJ (Stępień, 2021; Taha et al., 2013). As a result of this difference, unwanted ignitions may occur in the hot zones formed as a result of the combustion of the hydrogen-air mixture (College of the Desert, 2001).

Another disadvantage that causes unwanted ignitions is its shorter extinguishing range compared to fossil fuels. This feature also has a negative impact on hydrogen's evaluation as an alternative fuel. The quenching distance is defined as the distance between the walls of the combustion chamber and the flame is extinguished, and this distance is 2.0 mm for gasoline and 0.6 mm for hydrogen. This allows the hydrogen-air mixture flame to pass close to the cylinder walls and the intake manifold, thus causing undesirable ignition (Taha et al., 2013). These values that reflect disadvantage and advantages of hydrogen usage as a fuel and their comparison with diesel and gasoline are summarized in Table 1.

Table 1. Properties of hydrogen and comparison with diesel and gasoline (Ciniviz & Köse, 2012; Stępień, 2021).

Properties	**Diesel**	**Gasoline**	**Hydrogen**
Formula	CnH1.8n	CnH1.87n	-
Auto-ignition temperature (K)	530	533-733	858
Minimum ignition energy (at 1 bar and at stoichiometry, mJ)	-	0.24	0.02
Stoichiometric Ratio	14.5	14.6	34.3
Specific gravity (at 16 ^{o}C temperature and atmospheric pressure) (kg/m3)	833-881	721-785	0.0838
Lower Heating Value (MJ/kg)	42.5	43.9	119.93
Flame Speed (cm/s)	30	37-43	265-325
Octane Rating	-	92-98	130

2.2. Use of Hydrogen in Diesel and Gasoline Engines

After discussing combustion characteristics of the hydrogen, it is essential to corelate these properties with engine types. Under the previous heading, it was mentioned that hydrogen has a high self-ignition temperature. This makes it difficult to use hydrogen in diesel engines. However, it is preferable to use hydrogen in diesel engines with a dual fuel system using a hydrogen-diesel fuel mixture (Taha et al., 2013). In studies conducted with diesel engines where hydrogen is used as a second fuel, it has been observed that CO and CO2 emissions decrease. The reason for this is that, thanks to the hydrogen additive, combustion can be achieved with leaner mixtures, the high combustion speed of hydrogen accelerates combustion and the amount of unburned fuel decreases (Fırat et al., 2017). However, hydrogen addition also increases NOx emissions. It is possible to reduce NOx emissions by leaning the mixtures and reducing the oxygen concentration in the combustion chamber with the EGR system. On the other hand, the EGR system increases the level of particulate emissions. For this reason, another preferred method of reducing NOx emissions is the addition of water. Adding water can also cause a cooling effect but reduces volumetric efficiency (Ciniviz & Köse, 2012; Stępień, 2021).

It is possible to use hydrogen as the main fuel in gasoline engines. The fact that hydrogen requires low thermal energy and has a wide flammability limit provides advantages for its use in gasoline engines. While combustion at wider fuel-air ratios allows leaner fuel mixtures to be obtained, reducing the fuel ratio also contributes to lowering the ignition temperature. Thanks to this, NOx emissions can be reduced (College of the Desert, 2001).

To summarize, the high self-ignition temperature of hydrogen prevents its use as the main fuel in diesel engines. However, the fact that low thermal energy is sufficient for the combustion of hydrogen, that combustion can occur with high combustion speed and lean fuel mixtures make it easier to use hydrogen in gasoline engines. For this reason, hydrogen studies are focused on the use in gasoline engines.

3. Storage of Hydrogen by Liquefaction

Hydrogen is the lightest element and therefore has one of the highest energy-to-mass ratios. However, its low energy-to-volume ratio poses an obstacle to its usege as an alternative fuel. For this reason, hydrogen is generally stored in pressurized cylinders reaching 700 bar or by liquefaction. The critical temperature of hydrogen is -240.01 ^{o}C and its condensation temperature at atmospheric pressure is -253 ^{o}C. Various methods are used to reduce hydrogen to such low temperatures. These methods will be explained in this part of the article

3.1. Linde-Hampson Liquefaction Cycle

The Linde-Hampson cycle is considered the most basic cycle used in the liquefaction of gases. In this cycle, the gas that is to be liquefied is first compressed until high pressure values are reached. Afterwards, the compressed high-pressure gas is cooled by the gas returning from the cycle in the main heat exchanger. Finally, the cooled gas is expanded at room temperature in the thermal expansion valve called the Joule Thompson valve, resulting in a phase change. The gas, that does not pass into the liquid phase, is used as a cooling gas by returning it to the heat exchanger in the thermal valve (Aziz, 2021). Schematic diagram of Linde-Hampson cycle is illustrated in Figure 1. Joule Tompson valve utilizes Joule Thompson effect. Joule Thompson effect is explained as that temperature change of a high-pressure gas occurs while it is passing through an expansion throttle. However, this temperature change can be positive or negative which means that temperature of gas can increases while pressure of this gas is decreasing or opposite situation can be observed (Yang et al., 2025). Therefore, this cycle can be used for gases such as nitrogen, which can cool while expanding at room temperature. But hydrogen heats up as it expands at room temperature for this reason, hydrogen must be cooled by adding an external cooler to this cycle with a pre-cooling process. Liquid nitrogen is generally preferred as the external cooling source. Thanks to the Linde-Hampson cycle applied to hydrogen cooled with liquid nitrogen, it is possible to liquefy 1 kg of hydrogen with a specific energy consumption of approximately 72.8–79.8 kWh (Zhang et al., 2023).

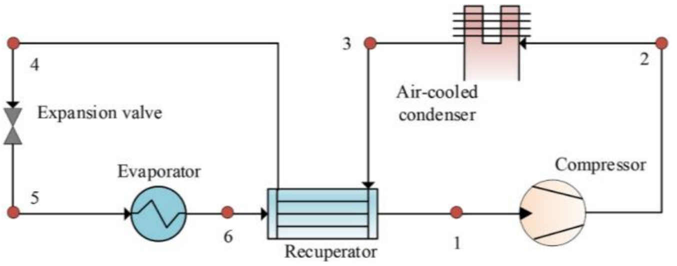

Figure 1. Schematic diagram of Linde-Hampson Cycle (Qin et al., 2023).

3.2. Claude Liquefaction Cycle

To put it simply, the Claude cycle is the liquefaction cycle formed by adding the isentropic expansion process to the Linde-Hampson cycle. Only the Joule Thomson adiabatic expansion valve is used in the Linde-Hampson cycle, which causes the efficiency of the system to decrease. However, in the Claude cycle, an expansion machine that can provide isentropic expansion is used, thus increasing efficiency. In addition, while pre-cooling must be added to the Linde-Hampson cycle to liquefy hydrogen, hydrogen can be liquefied using the Claude cycle without any additional processes (Zhang et al., 2023). On the other hand, specific energy consumption of Claude cycle with liquid nitrogen pre-cooling was achieved to reduce even more to the range of 11,9-13,6 kWh/kg LH2 in the Ingolstadt liquefaction plant in Germany (Liu et al., 2024; Xue & Boukadi, 2025).

In the Claude cycle, some of the compressed gas is sent directly to the heat exchanger, while some is directed to the expansion machine. Afterwards, the gas cooled in the expansion machine is returned to the heat exchanger to cool the compressed gas. Since the expansion machine will be damaged if there is liquid present, it is not possible to liquefy a gas directly with the expansion machine. However, the expansion machine ensures that the gas cools down before the Joule Thomson expansion valve, thus ensuring that the hydrogen is liquefied at the end of the cycle (Aziz, 2021).

3.3. Helium Brayton Cycle

The Joule Thomson expansion valve is not used in the helium Brayton cycle, a heat exchanger is used instead. The hydrogen compressed in the compressor is cooled firstly with liquid nitrogen in the first-stage heat exchanger meanwhile, helium gas is compressed by the compressor. Afterwards, the compressed helium gas is expanded and cooled by an isentropic expansion machine. The cooled helium gas is used as a refrigerant in the second stage heat exchanger to condense the hydrogen (Aziz, 2021). A more efficient liquefaction process can be achieved by increasing the number of Brayton cycles or by using a refrigerant mixture instead of a single gas. It has been observed that the specific energy required to liquefy 1 kg of hydrogen with the help of a four Brayton cycle using a refrigerant gas consisting of a mixture of 4% hydrogen, 18% nitrogen, 24% methane, 28% ethane and 26% butane is approximately 5.91 kWh (Zhang et al., 2023).

3.4. Magnetic Liquefaction

Magnetic liquefaction is the one of the promising liquefication process, but it is currently in experimental stage. The process is carried out using the magnetocaloric effect of magnetic materials. This effect occurs because the magnetic material absorbs heat when the entropy increases (Zhang et al., 2023). This process consists of four steps. First, the magnetic material is exposed to a magnetic field in an adiabatic environment. During this time, the dipoles align and reduce entropy. Heat is released as entropy decreases. Afterwards, the magnetic field is kept constant by isothermal magnetization, and the released heat is absorbed by another liquid. This prevents the temperature of the dipoles from increasing. Then, demagnetization is applied to magnetic material in an environment where heat exchange with the environment is prevented. By this process, heat is consumed in the movement of magnetic dipoles and thus the magnetic material cools down. Finally, the magnetic field is kept constant by applying the isothermal magnetization process. During this time, hydrogen encounters magnetic material and the hydrogen cools and becomes liquid (Aziz, 2021).

3.5. Storage of Liquid Hydrogen

Since the temperature of liquid hydrogen is much lower than ambient temperature, any increase in temperature will cause the hydrogen to vaporize. The causes of evaporation can be listed as ortho-para hydrogen conversion, heat exchange with the surrounding elements, agitation, heat generated during tank filling, thermal overfilling and thermal stratification. Hydrogen has two isomers: ortho hydrogen and para hydrogen. Ortho hydrogen is the isomer of hydrogen in which the hydrogen atoms rotate in the same direction, and para hydrogen is the isomer of hydrogen in which the hydrogen atoms rotate in opposite directions. For this reason, ortho hydrogen is in an unstable structure, para hydrogen is in a stable structure. This causes the unstable ortho hydrogen to transform into stable para hydrogen and heat to be released during this transformation (Zhang et al., 2023). This heat causes the hydrogen to evaporate. Another cause of evaporation is the shaking movement of the hydrogen in the tank. This agitation during transportation causes the kinetic energy of hydrogen to increase and this kinetic energy to be converted into thermal energy and transmitted to the tank walls. Evaporation of hydrogen is also observed during hydrogen filling. When hydrogen is transferred from a high-pressure tank to a low-pressure tank, some of the hydrogen vaporizes due to the pressure difference. A similar pressure difference also occurs in the layer between the vaporized hydrogen gas and liquid hydrogen due to thermal leakage. This pressure difference allows more hydrogen to evaporate. The last cause of evaporation to be mentioned is thermal overfilling of the tank (Aziz, 2021). This occurs when the saturation pressure of hydrogen exceeds the maximum working pressure of the hydrogen tank. Therefore, some of the liquid hydrogen vaporizes until the system pressure reaches equilibrium. Therefore, some of the liquid hydrogen vaporizes until the system pressure reaches equilibrium. In order to prevent the hydrogen gas formed when liquid hydrogen evaporates from increasing the pressure of the tank and causing deformation or explosion, the hydrogen gas in the tank is removed from the tank by valves with temperature or pressure sensors.

Liquid hydrogen is stored in cryogenic tanks. Two important elements are taken into consideration in cryogenic tank design. When hydrogen encounters metal, it causes microscopic cracks in the metal. This situation occurs to a lesser extent with liquid hydrogen, but it is still a serious risk that microcracks will turn into macrocracks over time under the influence of pressure and temperature. To reduce this risk, stainless steel is preferred in cryogenic tank production. The other element is to prevent liquid hydrogen from evaporating due to heat exchange with the external environment mentioned in the previous paragraph. For this reason, cryogenic tanks consist of several layers. The first step of insulation is provided by applying materials with low heat conduction coefficients on the stainless steel in the innermost layer. A vacuumed area is created in the middle layer, thus preventing heat conduction. Reflective materials are preferred on the outermost surface to prevent radiation (Zhang et al., 2023).

4. Conclusion

Hydrogen is an element that has been researched as an alternative fuel for many years. The main reason why it is considered as an alternative fuel is that it does not release CO or CO2 after combustion. However, NOx is released after the combustion of hydrogen, but the NOx level can be significantly reduced by using a lean fuel-air mixture and an EGR system. In addition to these properties, hydrogen's high burning rate and self-ignition temperature, wide burning range, and high diffusion rate make it easier to consider hydrogen as an alternative fuel. However, it also has features such as requiring low energy for combustion and having a low energy volume ratio, which reduces its preferability as an alternative fuel. For this reason, efforts are being made to reduce the impact of these disadvantages.

The most promising study to increase the energy volume ratio of hydrogen is the liquefaction of hydrogen. Over the years, many techniques have been used to liquefy hydrogen, such as compressing it with a compressor and expanding it in an expansion valve. It increases the efficiency of the use of refrigerants such as pre-cooling and nitrogen in liquefaction cycles. In this way, the specific energy required to produce 1 kg of liquid hydrogen has been reduced from approximately 79.8 kWh to 5.91 kWh. However, the large size and cost of the machines and equipment used in these liquefaction cycles create disadvantages. Therefore, studies are continuing alternative methods such as using magnetic effect as a liquefaction method. It is also important to store hydrogen by preserving its liquid phase after liquefaction. For this reason, phase change is tried to be prevented by using vacuum method and materials with low heat conduction coefficient in the design of cryogenic tanks.

Conflict of Interest

The author has no conflict of interest to declare.

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