Review

HYDROGEN COMBUSTION IN INTERNAL COMBUSTION ENGINES

Rauker, J.[1], **Šaban, A.**[1]

[1]University of Applied Sciences Velika Gorica,

ABSTRACT

Reducing carbon dioxide emissions, as well as other harmful gases generated by the combustion of fossil fuels, is one of today's main priorities. Hydrogen economy is one step in that direction. The basic idea is to replace fossil fuels with hydrogen obtained through environmentally friendly methods. When it comes to motor vehicles, there are two main ways of using hydrogen for propulsion: in fuel cells or by combustion in internal combustion engines. Due to the relatively high cost of fuel cells, some vehicle manufacturers have begun developing hydrogen-powered internal combustion engines. Current research focusing on hydrogen-burning engines shows promising results, although there are still a number of issues that need to be addressed before such engines are ready for the market. Issues mostly arise from hydrogen's low density which makes it problematic for storage, especially in motor vehicles. Premature ignition and detonations were solved using lean mixtures and direct injection.
Keywords: *hydrogen, combustion, internal combustion engines*

1. INTRODUCTION

Aim of this paper is to show the current development of hydrogen powered internal combustion engines. This paper will not focus on problems with hydrogen storage in personal vehicles, but will focus mainly on fuel mixture preparation and combustion of hydrogen in internal combustion engines. The research was done using scientific papers that are focused on using hydrogen as fuel in internal combustion engines.
Today's strict and future even stricter environmental standards are forcing vehicle manufacturers to continually search for efficient propulsion systems with the lowest possible emissions of harmful gases.
One option is hybrid vehicles, which are now produced by almost all personal vehicle manufacturers. Hybrid vehicles do not completely solve the problem of harmful exhaust gases but, through the efficient interaction of the electric motor and the internal combustion engine, they achieve savings in fuel consumption, and consequently reduce the harmful emissions.
In this regard, electric vehicles are ideal, but due to the high production costs, primarily of batteries, insufficient charging infrastructure, the time required for charging, and their shorter range compared to internal combustion engine vehicles, they still cannot fully compete with conventional vehicles. Additionally, the method of generating electricity can sometimes be more harmful to the environment than internal combustion engines equipped with modern

exhaust purification systems. Batteries have a relatively low energy density, are complex, and require expensive and rare metals for production. They also have a limited lifespan, measured in charge and discharge cycles.

Hydrogen represents a relatively simple way to store large amounts of energy. However, there is still no adequate technical solution for storing sufficient quantities of hydrogen for the average range of a vehicle. Hydrogen has a relatively high energy density by mass, but due to its low density, it requires large storage volumes or high-pressure storage. Methods like cryogenic cooling for liquefaction and some chemical binding methods are also used. All these methods of storing hydrogen are not yet optimal for use in motor vehicles.

Hydrogen can be used in two ways to power motor vehicles: in fuel cells to generate electricity to drive an electric motor or through direct combustion of hydrogen in an internal combustion engine. In both types of propulsion, energy is obtained by the oxidation of hydrogen, and in both cases, the final byproduct is water. The cost of fuel cells is still high, preventing their widespread use in motor vehicles. Direct combustion of hydrogen in internal combustion engines offers a potentially cheaper alternative to fuel cells.

2. METHODS

This paper was written using all the available sources for relevant research papers that deal with the problem of hydrogen combustion in internal combustion engines. Chosen sources deal mostly with hydrogen combustion in spark ignition and compression ignition engines and problems which arise from different types of ignition. Sources dealing with chemical and physical properties of hydrogen, as well as sources that compare properties of hydrogen to other fuels used in internal combustion engines were also chosen in order to demonstrate the influence of these properties to combustion behavior of hydrogen in internal combustion engines

3. HYDROGEN AS FUEL FOR INTERNAL COMBUSTION ENGINES

Hydrogen is the most abundant chemical element in the universe. It is the lightest chemical element and exists in a gaseous state under standard atmospheric conditions. On Earth, hydrogen is commonly found bonded in chemical compounds such as hydrocarbons or water. Today, most elemental hydrogen is produced from natural gas through processes like steam reforming, partial oxidation, or autothermal reforming, as well as coal gasification. A smaller portion of hydrogen is produced via electrolysis and biomass gasification (U.S. Department of energy, 2024).Extracting hydrogen from hydrocarbons (natural gas or coal) results in varying emissions of carbon dioxide. Based on the environmental friendliness of its production, hydrogen is categorized into grey, blue, and green hydrogen (Šarčević, 2023).

Hydrogen derived from hydrocarbons (fossil fuels) is termed grey hydrogen because its production emits carbon dioxide. If the hydrogen production facility is equipped with carbon capture and storage systems, the hydrogen produced is considered blue. Green hydrogen is produced through processes that rely exclusively on renewable energy sources (Šarčević, 2023). The primary method for producing green hydrogen is water electrolysis, which generates pure oxygen as the only byproduct.

Combustion or oxidation of hydrogen is the fundamental chemical process for extracting energy from hydrogen. The oxidation of hydrogen results in water, producing no greenhouse gases or

other toxic compounds typically generated from fossil fuel combustion. Green hydrogen would be a fuel with minimal negative environmental impact throughout its lifecycle.
Hydrogen has a lower heating value of 119.7 MJ/kg (Karim, 2003), much higher than the lower heating values of gasoline (43.9 MJ/kg), diesel (42 MJ/kg), propane (46.34 MJ/kg), or butane (45.71 MJ/kg) (Šilić, Stojković, & Mikulić, 2012). Since liquids have a higher density than gases, they require much less volume to store the same mass of fuel. This is why liquefied petroleum gas (propane-butane) is stored in liquid form in vehicle tanks, reducing its volume by 260-270 times. Liquefied petroleum gas can be easily liquefied at a pressure of 1.7 bars at ambient temperature. Natural gas is more challenging to liquefy, requiring a temperature of -167°C at normal atmospheric pressure for liquefaction. In motor vehicles, achieving and maintaining such a low temperature is impractical, so natural gas is compressed to 200 bars and remains in a gaseous state (Šilić, Stojković, & Mikulić, 2012).
Liquefying hydrogen also requires an extremely low temperature of -253°C at normal pressure, which is similarly impractical for storage in motor vehicles. To store a sufficient quantity of hydrogen in a volume that can be integrated into a vehicle, hydrogen needs to be compressed to 350 - 700 bars. An average fuel tank in vehicles using liquid fuels has a volume of 50 liters. The lower heating value of gasoline is approximately 32.5 MJ/dm^3, and diesel is 35.7 MJ/dm^3 (Šilić, Stojković, & Mikulić, 2012). From these values, it can be calculated that an average gasoline tank contains 1625 MJ of energy, while an average diesel tank contains 1785 MJ of energy. A 50-liter tank with hydrogen at 350 bars contains 1.55 kg of hydrogen or 3.1 kg at 700 bars. This means that the energy content of such a tank would be 185 MJ at 350 bars or 371.07 MJ at 700 bars. The energy content of a hydrogen tank at 700 bars is about 4 to 5 times lower than that of an average gasoline or diesel tank. Efficiently storing larger amounts of hydrogen in motor vehicles is still a subject of research and represents one of many technical challenges hindering the wider use of hydrogen in motor vehicles.
The autoignition temperature of hydrogen is 585°C, which is higher than that of gasoline (260°C to 460°C) and diesel (180°C to 320°C) (Akal, Oztuna, & Buyukakin Kemalettin, 2020). A lower autoignition temperature is advantageous in engines where the mixture self-ignites (Diesel engines), while a higher autoignition temperature is preferable for Otto engines as it reduces the likelihood of premature self-ignition of the fuel mixture and the occurrence of abnormal combustion modes. The high autoignition temperature of hydrogen makes it more suitable for use in Otto engines, but there are also HCCI (Homogeneous Charge Compression Ignition) versions where the hydrogen and oxygen mixture ignites through compression (Gomes, Mikalsen, & Roskilly, 2008).
Otto engines are more prone to knocking than Diesel engines. Knocking is a type of abnormal combustion in the engine, resulting in elevated pressures and temperatures that can damage the engine. In Otto engines, knocking occurs after the spark ignites the mixture if the pressure wave becomes faster than the flame front (usually with a lean mixture), compressing the mixture ahead of the flame front, causing it to self-ignite. The causes of knocking in Otto engines can vary but are often due to poor maintenance, old engines, poor combustion chamber design, or low octane fuel. The octane number of fuel indicates its resistance to knocking. A higher autoignition temperature results in a higher octane number, meaning greater resistance to knocking. Therefore, hydrogen should have a higher octane number than gasoline and be more resistant to knocking. Current literature offers divided opinions on the octane number of

hydrogen, with research octane numbers (RON) ranging from 60 to over 130 (Poursadegh F. , Brear, Hayward, & Yang, 2023). Some authors believe that hydrogen combustion does not lead to knocking but that surface ignition is the primary cause of abnormal hydrogen combustion. Tests on an engine with variable compression ratio have shown that increasing the compression ratio does not lead to knocking (X Tang, 2002). Testing the research octane number of hydrogen on a CFR engine showed that under standard test conditions, the octane number of hydrogen is 63, but it significantly increases if the mixture is lean, with a lean mixture of λ=2 having an octane number greater than 120 (Poursadegh F. , Brear, Hayward, & Yang, 2023).
The stoichiometric ratio of hydrogen to air is 1:34 (Karim, 2003), whereas the stoichiometric ratio for gasoline and diesel is approximately the same at around 1:14.7 (Šilić, Stojković, & Mikulić, 2012). This means that twice as much air is required to completely burn 1 kg of hydrogen compared to 1 kg of gasoline or diesel. This results in lower volumetric efficiency of the engine, especially in engines with external mixture formation (Verhelst & Sierens, 2006).
Unlike fossil fuels used to power motor vehicles, hydrogen has a very wide flammability range, being flammable in volumetric concentrations from 4% to 75%, while the flammability range for gasoline is 1.2% to 6% (Karim, 2003). Such a wide flammability range for hydrogen means that the engine can operate with both very rich and very lean mixtures.

4. AIR FUEL MIXTURE PREPARATION

Internal combustion engines typically employ two methods for preparing the air-fuel mixture: external and internal mixture preparation. External mixture preparation is used in Otto engines with fuel injection into the intake manifold. The advantage of this method is better mixing of fuel and air, resulting in a homogeneous mixture. It also provides a longer time for fuel evaporation, which further contributes to the homogeneity of the mixture and results in lower soot content in the exhaust. These advantages are significant for Otto engines running on liquid fuels, whereas gaseous fuels do not need to evaporate or, in the case of LPG (liquefied petroleum gas), evaporate in the vaporizer before injection, allowing them to form a homogeneous mixture with air more easily and quickly.
Due to the wide flammability range of hydrogen, external mixture formation poses a risk of ignition of the fuel mixture in the intake system or during the intake stroke. This can occur as a result of surface ignition, where a hot surface in the intake or cylinder, such as the electrode of a spark plug, the exhaust valve, or residual combustion gases, ignites the mixture. Although hydrogen has a high ignition temperature, it also has a very low ignition energy of just 0.02 mJ, compared to gasoline’s 0.25 mJ (Karim, 2003). This low ignition energy, combined with the wide flammability range of hydrogen, makes it easily combustible, leading to frequent occurrences of abnormal combustion modes such as knocking or surface ignition. Some authors argue that the low ignition energy does not influence the risk of surface ignition because surface ignition is related to the ignition temperature rather than the ignition energy (Verhelst & Sierens, 2006).
The literature describes several methods for external mixture preparation, including external mixture formation using carburators, parallel hydrogen induction, a combination of carburator

and water injection, and port fuel injection (Verhelst & Sierens, 2006). All these external mixture preparation methods have been tested to address the issue of premature ignition. In the parallel hydrogen feed method (Figure 1), hydrogen is supplied through a separate line to the intake valve, where it mixes with air. This way, the mixture is formed inside the cylinder, preventing the hydrogen from igniting in the intake manifold.

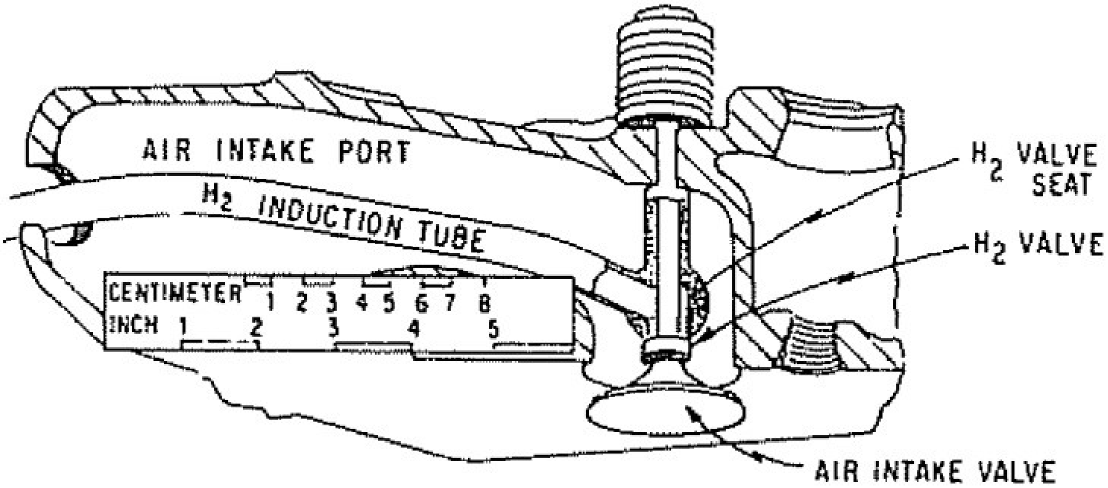

Figure 1. Parallel hydrogen intake (Olavson, Baker, Lynch, & L.C, 1984)

In the method combining carburetion and water injection, the mixture is formed in the intake manifold, and water is injected to cool the system. This prevents premature ignition. Over the past decade, engines running on hydrogen with external mixture preparation mainly use hydrogen injection through nozzles into the intake manifold. External mixture preparation by injecting hydrogen increases engine efficiency and reduces nitrogen oxide emissions compared to direct injection (Yi & Kim, 2000). A further advantage of external mixture formation is cost, as these systems are cheaper than direct injection systems.

Aside from the risk of premature ignition, another significant drawback of external mixture preparation is reduced volumetric efficiency. Hydrogen requires more than twice the mass of air to form a stoichiometric mixture compared to traditional fuels. Furthermore, hydrogen occupies a relatively large volume relative to its mass. In a stoichiometric mixture, hydrogen occupies 29.5% of the volume. Consequently, this results in an 18% lower volumetric energy content for hydrogen-air mixtures compared to gasoline-air mixtures, leading to reduced overall engine power (Verhelst & Sierens, 2006).
Internal mixture preparation is used in engines with direct injection, which includes all modern Diesel engines and some types of Otto engines. Given the problem of premature ignition in hydrogen-fueled engines, direct hydrogen injection has proven to be a more effective method of mixture preparation. Additionally, hydrogen combustion often faces the issue of premature ignition during the compression stroke. This increases the temperature in the combustion

chamber and heats the chamber surfaces, which further raises the risk of surface ignition (Verhelst & Sierens, 2006). Injecting hydrogen during the intake stroke can cause early ignition of the mixture, so hydrogen is injected later, towards the end of the compression stroke. Injection during compression requires high injection pressures to ensure sufficient hydrogen for forming a stoichiometric mixture.

Direct hydrogen injection improves the engine's volumetric efficiency compared to external mixture preparation. This is achieved through higher injection pressures, allowing the formation of richer mixtures compared to engines with external mixture preparation. To achieve the necessary high injection pressures, hydrogen must be stored appropriately. High injection pressures required for direct injection systems require storing hydrogen in liquid state, as this is the only way to ensure injection of a sufficient amount of fuel. When storing compressed hydrogen in gaseous state, the pressure in the hydrogen tank must always be higher than the injection pressure, which ultimately results in reduced vehicle range because the tank can only be partially emptied. This can be addressed by installing an additional compressor in the fuel supply system, but compressors can demand significant amounts of energy (Verhelst & Sierens, 2006).

Figure 2 illustrates the comparison of volumetric efficiency for engines powered by hydrogen, depending on the mixture preparation method. It can be seen that direct injection of compressed hydrogen provides the highest volumetric efficiency, while injection of liquid hydrogen is slightly less efficient. Storing liquid hydrogen in motor vehicles is too complex due to the need to maintain hydrogen at extremely low temperatures (below -200 °C).

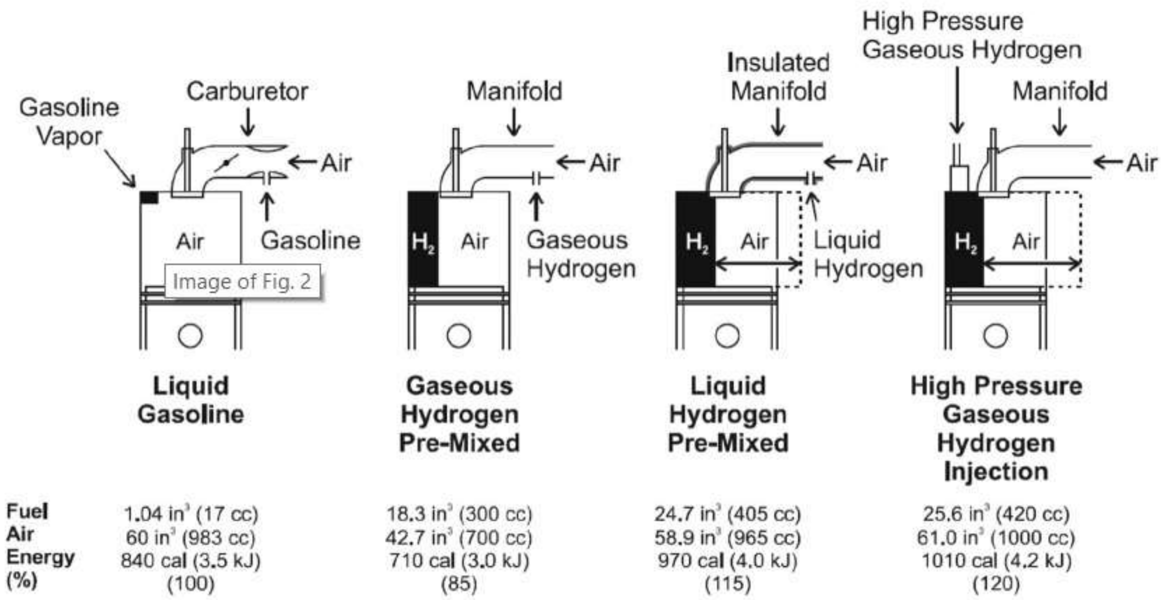

Figure 2. Energy and volumetric efficiency comparison between different mixture preparation methods (Akal, Oztuna, & Buyukakin Kemalettin, 2020)

5. IGNITION AND COMBUSTION OF AIR FUEL MIXTURE

There are two primary ways to ignite the mixture in internal combustion engines: ignition of the mixture by an external energy source (Otto engine) and compression ignition using air heated above the fuel's ignition temperature (Diesel engine). Based on these differences in ignition, fuels for these engines need to have different properties. In compression ignition engines, it is crucial to have a fuel with a lower ignition temperature to ensure the mixture ignites even under colder atmospheric conditions. Conversely, Otto engines require fuel with a higher ignition temperature to prevent premature ignition and detonation, which reduces engine efficiency and can cause damage.

Hydrogen, due to its high ignition temperature, is more suitable as fuel for Otto engines, although there are also compression ignition engines using hydrogen. The main advantage of hydrogen compared to gasoline is its wide flammability range. For a gasoline-air mixture to ignite, it must be stoichiometric or rich around the spark plug; lean mixtures are difficult to ignite with a spark plug. Hydrogen, on the other hand, can operate with leaner mixtures than gasoline because of its broad flammability range (4-75%) and low energy required for ignition. Hydrogen combustion is faster than gasoline and involves fewer heat losses, as hydrogen combustion is simpler compared to the complex hydrocarbons' combustion, which involves molecule splitting before combustion, a process that is endothermic and consumes some of the heat generated by combustion. The faster combustion is beneficial because of the reduced heat losses, but it can cause abnormal combustion modes like detonation. Additionally, faster combustion is advantageous for achieving higher engine rotation speeds. Ignition angles are smaller for hydrogen than for gasoline due to hydrogen’s faster combustion (Karim, 2003). Adjusting the ignition angle is an effective method for preventing detonation in Otto engines.

Laser ignition of the mixture is an old idea researched since the late 1970s (Dale, Smy, & Clements, 1978). One reason for developing a new ignition system is the issue of igniting lean mixtures, which have a lower flame front propagation speed. One way to increase the flame front propagation speed is to optimize the spark plug position or increase the number of spark plugs in the cylinder. Both solutions have drawbacks, primarily the limited space within the cylinder. Using a laser to ignite the mixture allows changing the ignition point by altering the laser's focus point. This increases the combustion speed and reduces heat losses. An additional advantage of laser ignition is the reduction of the required ignition energy as the cylinder pressure increases, while a spark plug requires more energy with increasing pressure (Srivastava & Agarwal, 2014).

Removing the spark plug eliminates one of the causes of hydrogen's autoignition. The spark plug heats the mixture between the electrodes to a high temperature (around 10^4 K) through spark discharge, while laser ignition achieves higher temperatures (10^6 K), resulting in shorter ignition delays and faster combustion speeds for laser-ignited mixtures. Results have shown that maximum power and pressure rise rates during fuel ignition are higher with laser ignition, while effective consumption and nitrogen oxide emissions are slightly lower (Pal & Agarwal, 2015).

The main disadvantage of laser ignition is the relatively high cost and complexity of the entire system. Although laser prices have significantly dropped in recent years, they are still not low enough for large-scale use needed by the automotive industry (Morsy, 2012).

Due to its relatively high autoignition temperature, hydrogen is not very suitable for compression ignition engines. Experiments with hydrogen compression ignition have shown that high compression ratios are needed for hydrogen to autoignite. In the case of lower compression ratios, the air must be preheated to achieve a sufficiently high temperature during compression for hydrogen autoignition (Gomes, Mikalsen, & Roskilly, 2008). Figure 3 shows the dependency between intake air temperature and the compression ratio required for hydrogen autoignition. It can be seen that compression ratios higher than 25 are necessary to ensure hydrogen autoignition without preheating the air. The diagram indicates that colder weather conditions would certainly require air preheating for compression ignition engines running on hydrogen.

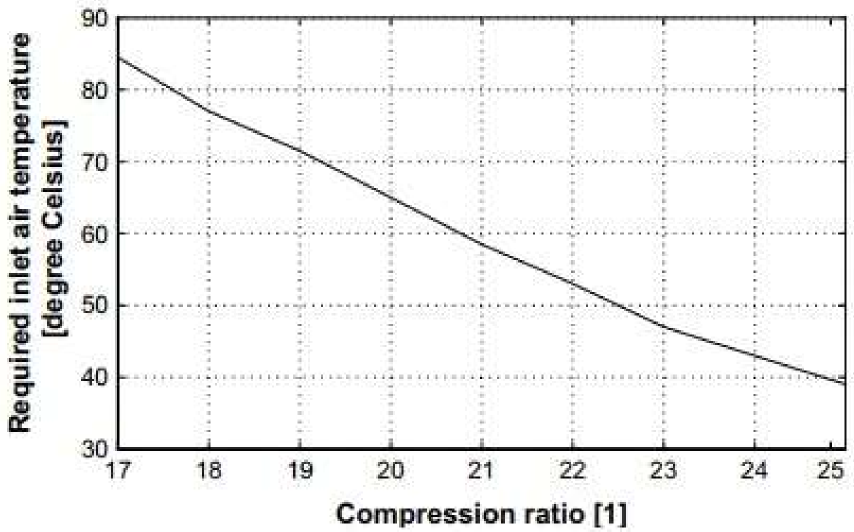

Figure 3. Preheated air temperature in relation with compression ratio (Gomes, Mikalsen, & Roskilly, 2008)

Tests have also been conducted on HCCI (Homogeneous Charge Compression Ignition) engines. These engines use external mixture preparation and compression ignition. Such engines operate with lean to stoichiometric mixtures. HCCI engines running on hydrogen can operate with very lean mixtures, even up to λ=6 (Gomes, Mikalsen, & Roskilly, 2008). Figure 4 shows the dependence of efficiency on the mixture composition, illustrating that the thermal efficiency remains above 34% even with very lean mixtures of λ=6.

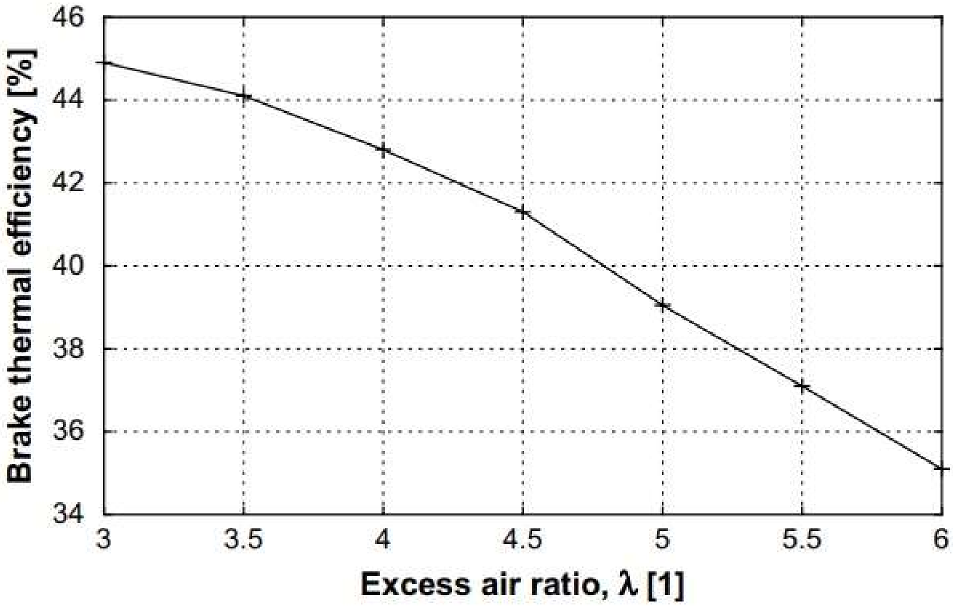

Figure 4. Dependence of thermal efficiency on mixture composition (Gomes, Mikalsen, & Roskilly, 2008)

In compression ignition engines, the injection timing is used to control the start of combustion and is adjusted with the engine speed to ensure that the maximum pressure occurs at the optimal moment (around 10°-15° after TDC) (Hnatko, 2016). The pressure gradient is higher for hydrogen compared to diesel fuel. Consequently, with the same injection timing, the peak cylinder pressure occurs earlier in hydrogen-powered engines than in those powered by diesel. The maximum pressure is 40% higher for hydrogen (Gomes, Mikalsen, & Roskilly, 2008).

In Diesel engines, the timing of peak pressure in the cylinder in relation to the crankshaft angle is regulated solely by the injection timing. Given hydrogen's high resistance to autoignition and the need for preheating the air, it has been observed that the intake air temperature influences the timing of fuel ignition.

Figure 5 illustrates the relationship between the ignition timing and the temperature of intake air.

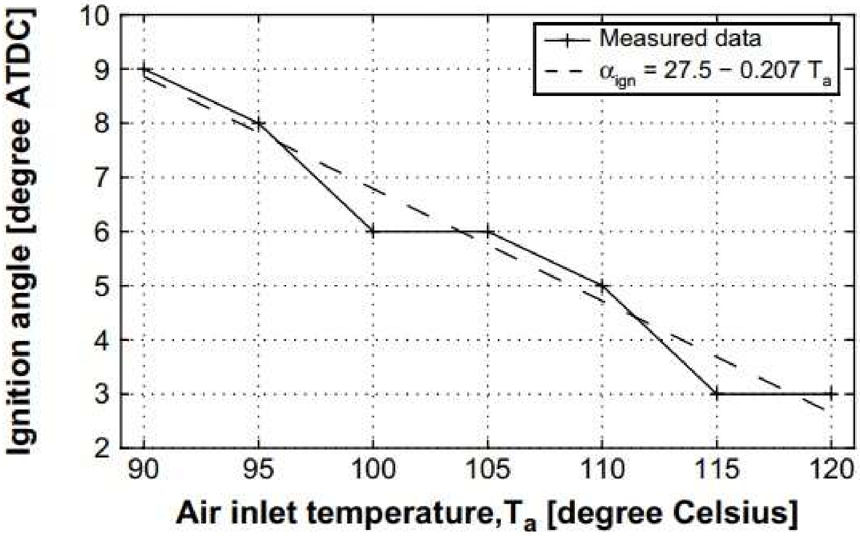

Figure 5. Ignition angle dependency on inlet air temperature (Gomes, Mikalsen, & Roskilly, 2008)

6. DISCUSSION

Using hydrogen as a fuel in internal combustion engines significantly reduces their environmental impact. Hydrogen combustion produces only water vapor and nitrous oxides. Because of abnormal combustion modes like detonation and premature ignition, hydrogen-air mixture must be lean. Lean mixtures result in the formation of nitrogen oxides in the exhaust, but their concentration can be kept below legally permissible levels using exhaust gas recirculation (EGR).

By optimizing mixture preparation and ignition timing, it is possible to use hydrogen at higher compression ratios. This is due to hydrogen's relatively high autoignition temperature, which increases engine efficiency. Additionally, hydrogen burns faster than gasoline, resulting in lower heat losses and greater thermal efficiency even at the same compression ratios as gasoline engines.

The biggest problem with hydrogen as a fuel is its storage. Using liquid hydrogen is impractical for road vehicles because of the low temperature required to liquefy hydrogen. Due to hydrogen's low density in its gaseous state, it must be compressed to pressures over 300 bar in order to store a sufficient amount of hydrogen for a range of 300-400 km.

7. CONCLUSION

Piston engines with internal combustion have been developed for over a century and are a reliable way to power a wide range of different vehicles, from road vehicles, rail vehicles, smaller aircraft, and ships. Besides their relatively low efficiency, their primary disadvantage is their harmful impact on the environment and human health due to the emission of harmful gases.

Internal combustion engines running on hydrogen represent a cheaper alternative to fuel cells, but further research and innovation in hydrogen storage are needed for such engines to be viable for market introduction.

Table of figures

Bibliography

Akal, D., Oztuna, S., & Buyukakin Kemalettin, M. (2020). A review of hydrogen usage in internal combustion engines (gasoline-LPG-Diesel) from combustion performance aspect. *Internationa Journal of Hydrogen Energy, 45*(60), 35257-35268.

Dale, J., Smy, P., & Clements, R. (1978). Laser ignited internal combustion engine - a comparative study. *SAE Paper 780329*.

Gomes, A., Mikalsen, R., & Roskilly, A. (2008). An investigation of hydrogen fueled HCCI engine performance and operation. *Journal of Hydrogen Energy, 33*, 5823-5828.

Hnatko, E. (2016). *Motori.* Velika Gorica: Veleučiište Velika Gorica.

Karim, G. (2003). Hydrogen as spark ignition engine fuel. *International Journal of Hydrogen Energy, 28*(5), 569-577.

Li, H., & Karim, G. (2004). Knock in spark ingnition hydrogen engines. *Internationa Journal of Hydrogen energy, 29*, 859-865.

Morsy, M. (2012). Review and recent developments of laser ignition for internal combustion engines applications. *Renewable and Sustainable Energy Rewievs*, 4849-4875.

Olavson, L., Baker, N., Lynch, F., & L.C, M. (1984). Hydrogen fuel for undergroung mining machines. *SAE, 840233*.

Pal, A., & Agarwal, A. (2015). Comparative study of laser ignition and conventional electric spark ignition systems in a hydrogen fuelled engine. *International Journal of Hydrogen Energy, 40*(5), 2386-2395.

Poursadegh, F., Brear, M., Hayward, B., & Yang, Y. (2023). Autoignition, knock ,detonation and ocatane rating of hydrogen. *Fuel, 332*.

Srivastava, D., & Agarwal, A. (2014). Comparative experimental evaluation of performance, combustion and emissions of laser ignition with conventional spark plug in a compressed natural gas fuelled single cylinder engine. *Fuel*.

Šaban, A., Rauker, J., & Susak, N. (2023). Vodikova ekonomija u cestovnom prometu. *Dani kriznog upravljanja* (pp. 191-205). Velika Gorica: Veleučilište Velika Gorica.

Šarčević, F. S. (2023). Mogućnosti korištenja vodika kao goriva. *Nafta i plin*.

Šilić, Đ., Stojković, V., & Mikulić, D. (2012). *Pogonska goriva i maziva.* Velika Gorica: Veleučilište Velika Gorica.

Tang, X., Kabat, D., Natkin, R., Stockhausen, W., & Heffel, J. (2002). Ford P2000 hydrogen engine dynamometer development. *SAE World congress.* Detroit.

U.S. Department of energy. (2024, 3 21). Retrieved from Alternative fuels data center: https://afdc.energy.gov/fuels/hydrogen_production.html

Verhelst, S., & Sierens, R. (2006). A critical review of experimental research on hydrogen fueled SI engines. *SAE world congerss.* Detroit.

X Tang, D. K. (2002). Ford P2000 Hydrogen Engine Dynamometer Development. *SAE paper no 2002-01-0242*.

Yi, H., & Kim, E. (2000). The optimised mixture formation for hydrogen fueled engines. *Internationa Journal of Hydrogen Energy, 25*, 685-690.