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Application and Characteristics of Hydrogen in Alternative Fuels for Internal Combustion Engines

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Petroleum has been used as the power source for internal combustion engines for hundreds of years. Nowadays, the problems of fossil energy shortage and environmental pollution are becoming increasingly serious. In response to China's carbon neutrality strategy, it is urgent to seek alternative fuels that can replace petroleum as the power source of internal combustion engines. The challenges of alternative fuels include reducing post-combustion pollutant emissions and being able to recycle them while maintaining the original engine performance. Using hydrogen as fuel can reduce automobile exhaust emissions, promote the development of hydrogen internal combustion engines, and achieve sustainable social and economic development. This article reviews the ideality of hydrogen as an alternative fuel for internal combustion engines and the combustion characteristics of hydrogen internal combustion engines. The bottleneck problems (such as abnormal combustion, NO_x emission control and power recovery) that need to be solved urgently in the development of hydrogen internal combustion engines are pointed out. It's found that these problems can be solved by the combination of software simulation and experimental verification in practice.

Keywords: Hydrogen energy; Internal combustion engine; Substitute fuels; Combustion characteristics; Emission characteristics

Introduction

China is a country rich in coal but poor in oil, and also a country with an increasing number of motor vehicles. With the rapid development of the automobile industry and the widespread use of internal combustion engines, fossil fuels have been consumed in large quantities, and the world is facing serious energy shortages and environmental pollution problems. China is in a period of rapid economic development, and the automobile industry, as a strong industry driving China's economic growth, is developing particularly rapidly. However, traditional cars mainly use gasoline, diesel and other fossil fuels, which greatly increases China's oil consumption [1]. While consuming a large amount of oil resources, it also emits a large amount of harmful substances such as carbon monoxide, nitrogen oxides, and hydrides, seriously polluting the environment. To meet the needs of the energy sector and reduce pollution, China's carbon neutrality strategic goal is to peak carbon dioxide emissions before 2030 and achieve carbon neutrality before 2060. Researchers from all over the world are actively looking for substitutes for oil, and the development and utilization of alternative fuels has become a research hotspot. In order to alleviate the contradiction between the shortage of oil

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resources and the growing demand for internal combustion engines and to ensure the long-term stable and sustainable development of China and the world's economy, it is necessary to find clean alternative fuels for internal combustion engines to replace petroleum-based fuels.

Alternative fuels must meet the requirements of high efficiency, cleanliness, low environmental impact, and recyclability. Hydrogen has become one of the ideal alternative fuels for internal combustion engines due to its clean, efficient combustion and almost zero emissions [2].

Physicochemical Properties of Hydrogen

Hydrogen is easy to diffuse and burn. The hydrogen diffusion in air is in the range of 0.756~1.747 $\times 10^{-4}$ m^2/s and the lower calorific value of combustion is about 120 MJ/kg. The minimum ignition energy (MIE) of hydrogen is only 0.02 mJ, the spontaneous combustion temperature is 858 K, the octane number is 130, the ignition limit range is 4~75 %, and the flame propagation speed is extremely fast which is about 1.85 m/s. At room temperature, hydrogen is very stable. Hydrogen generally does not react easily with other substances unless conditions are changed, such as ignition, heating, use of catalysts, etc. Since hydrogen is gaseous at room temperature, its portability and safety are poor. Hydrogen becomes highly reactive when adsorbed by metals such as palladium or platinum. Although hydrogen is non-toxic and physiologically inert to the human body, if the hydrogen content in the air increases, it will cause hypoxic asphyxia. As with all cryogenic liquids, direct contact with liquid hydrogen can cause frostbite. Hydrogen burns completely in oxygen to produce water, with almost no impact on the environment. There are many ways to produce hydrogen, including water electrolysis, natural gas reforming, biohydrogen, solar energy, wind energy, etc. It has a wide range of sources and meets the requirements for sustainable regeneration of alternative fuels for vehicles [3].

Hydrogen has extremely high requirements for sealing during its production, transportation and storage, and faces great safety challenges during its use. Many scholars have conducted in-depth research on its safety. Shivaprasad *et al.* [4] tested the performance and emission characteristics of a high-speed single-cylinder SI engine using different hydrogen-gasoline blends. They selected different hydrogen enrichment levels to study the effect of hydrogen addition on the engine brake mean effective pressure (BMEP), brake thermal efficiency, volumetric efficiency and emission characteristics. The results indicated that hydrogen enrichment improved combustion performance, fuel consumption, and brake mean effective pressure. The experimental results also showed that the brake thermal efficiency was higher than that of the pure gasoline condition. Additionally, the emissions of HC and CO were reduced with hydrogen enrichment.

When the engine uses hydrogen, only NO and H_2O are produced. In spark-ignition engines, hydrogen has the following outstanding physical and chemical properties compared to the 7-H gasoline used: First, the octane number is high. Hydrogen can achieve a larger ignition advance angle at low load, which is beneficial to improving the compression ratio and thermal efficiency. Second, the flame speed is high and flows horizontally, hydrogen and air mix faster and have higher thermal efficiency. Third, the ignition energy is low, hydrogen is not easy to ignite, and it is easy to achieve lean combustion, improve thermal efficiency, and reduce emissions. Fourth, wide ignition limit and wide hydrogen ignition range, which is conducive to working under partial load. Fifth, the high spontaneous combustion temperature of hydrogen is high, which is 1.6 times that of gasoline, and it is not easy to cause explosion hazards.

Combustion Characteristics of Hydrogen

Hydrogen is colorless and odorless, and its flame is transparent when it burns, so its presence is not easily detected by the senses. Generally, ethyl mercaptan is added to hydrogen for sensory detection and coloration of the flame. Hydrogen has strong self-ignition properties and the spontaneous combustion temperature is 850K under standard atmospheric pressure. It is easy to ignite, has excellent flame propagation characteristics, and can easily achieve lean combustion. Hydrogen can be mixed with air quickly to form a homogeneous mixture.

The chemical equation of hydrogen and air mixed combustion is

$$2H_2 + O_2 \rightarrow 2H_2O$$

A large amount of heat is released during this combustion process, which is three times that of gasoline combustion. Hydrogen is a high-energy fuel. Although the product of hydrogen-air mixed combustion is water and pollution-free, the high heat released during the combustion process promotes the chemical reaction of nitrogen and oxygen in the air.

$$\frac{1}{2}N_2+\frac{x}{2}O_2\rightarrow NO_x$$

NO_x is an air pollutant. The water produced by the combustion of hydrogen and air can be converted back into hydrogen by electrolysis. The chemical reaction formula of water electrolysis is

$$H_2O\rightarrow H_2+\frac{1}{2}O_2$$

Therefore, hydrogen energy has the characteristics of circularity and sustainability in the process of use. Because hydrogen is prone to spontaneous combustion, if the volume of hydrogen mixed in the air reaches 4.0~74.2 % of the total volume, an explosion will occur when it is ignited. Therefore, the purity of hydrogen must be tested during the use of hydrogen [6].

Study on the Application of Hydrogen in Internal Combustion Engines

Ideality of Hydrogen as an Alternative Fuel for Internal Combustion Engines

Hydrogen is an ideal alternative fuel for internal combustion engines due to its efficient and clean combustion characteristics. Hydrogen is a carbon-free fuel, which produces H_2O after combustion. It does not emit CO_2, CO, HC and sulfides. Hydrogen production resources are abundant and can be obtained through electrolysis using water as raw material. Water resources are much more abundant on Earth than the major fuel oil and coal. The mass fuel calorific value of hydrogen is the highest among all kinds of fuels. It is measured to be 140 MJ/kg, which is about 3 times that of gasoline, but the theoretical air-fuel ratio is 2.5 times that of gasoline [6]. The minimum ignition energy of hydrogen is 1/3 of that of gasoline, and the flame propagation characteristics are very good. The flame propagation speed of hydrogen is 2.91 m/s, which is 7.7 times that of gasoline. The ignition limit is wide (4.1~75%), the combustion adjustment is flexible, and it is easy to achieve lean combustion. It has the advantages of good economy, more complete combustion, and low combustion temperature. Hydrogen fuel is easy to ignite and has good starting performance. The spontaneous combustion temperature under atmospheric pressure is lower than that of diesel (625K) and gasoline (770K), and the density is small, which is conducive to improving the compression ratio and the thermal efficiency of hydrogen internal combustion engines [7]. The diffusion coefficient of hydrogen in the atmosphere is 8 times that of gasoline, which can quickly form a combustible mixture. It has low requirements on the inlet structure and combustion chamber shape of the internal combustion engine, and the combustion speed and the combustion temperature are high. Hydrogen has a high flame propagation speed at the theoretical air-fuel ratio, which is close to constant volume combustion. The hydrogen internal combustion engine cycle is closer to the ideal cycle, the pumping loss is small, and the thermal efficiency is higher than that of the gasoline engine.

Hydrogen has a shorter quenching distance of 0.64 mm during combustion, which is 1/3 of gasoline. A smaller quenching distance allows the flame to propagate to the cylinder wall and even reach the piston clearance, making the combustion more complete. Hydrogen has a higher spontaneous combustion temperature, a shorter ignition delay, a faster flame propagation speed, a higher octane number, and is less likely to produce knock. Hydrogen can be used in many forms, such as gas, liquid, or solid hydride. Solid hydride is the ideal form of hydrogen, because of its safety and convenience [8, 9]. There are generally two ways to use hydrogen as an internal combustion engine fuel: One is the electrochemical method, which converts the chemical energy of hydrogen into electrical energy and thermal energy in a fuel cell. The other is the thermochemical method, that is, combustion, which converts the chemical energy of hydrogen into heat or kinetic energy. There are two main forms of hydrogen as an internal combustion engine fuel, namely pure hydrogen and mixed hydrogen.

Pure Hydrogen

There are two ways to use hydrogen as a fuel, namely fuel cells and hydrogen internal combustion engines. The product of fuel cells is water, with zero emissions, they are not limited by the Carnot cycle efficiency, and have high energy conversion efficiency. Because there are no moving parts in the battery, the noise is low. Hydrogen fuel cells have strong overload capacity and convenient design. However, the high cost of batteries and the lack of infrastructure and maintenance have limited its development. Compared with fuel cells, hydrogen internal combustion engines are easier to implement. The combustion products of hydrogen internal combustion engine are only H_2O and NO_x, and the emission of NO_x is very small at low load. Only at full load or near full load, there is a little more NO_x emission than gasoline engine. But measures can be taken to reduce it. The hydrogen internal combustion engine does not have HC, CO, CO_2 and soot emissions. It can achieve full combustion in lean combustion, high system efficiency, and long engine life [10, 11].

Mixed Hydrogen

Blending hydrogen with other fuels (such as natural gas, gasoline, diesel, etc.), that is, hydrogen blending, can compensate for the power loss caused by other fuels due to low energy density or lean combustion, and improve the fuel economy. The amount of hydrogen required for a hydrogen-blended fuel engine is not large. It is mainly used as a fuel additive to improve the thermal efficiency of the engine and reduce fossil fuel consumption and emissions. Currently, hybrid hydrogen fuel engines are easier to implement in cars than pure hydrogen fuel engines.

Hydrogen-Natural Gas

As a vehicle fuel, natural gas can reduce the emissions of pollutants such as CO, SO, Pb and particulate PM2.5. However, since methane, the main component of natural gas, has a high calorific value of 36,000 kJ/m3, and its combustion temperature can reach 2,300°C under high temperature and high pressure, it is easy to generate NO_x. Therefore, in actual use, compared with gasoline engines and diesel engines, natural gas internal combustion engines do not reduce NO_x emissions. Blending hydrogen into natural gas can effectively reduce the combustion temperature, thereby reducing NO_x emissions. Hydrogen is easy to diffuse and can be easily mixed with natural gas in any proportion, and both can be stored in the same container. Adding a certain amount of hydrogen to natural gas can extend the lean combustion limit of the mixture, shorten the ignition delay period and combustion duration, improve thermal efficiency, and reduce HC, CO, CO_2 emissions. NOx emissions are also lower than pure hydrogen engines. Experiments have shown that the mixed combustion of 5~7 % mass or 15~20 % volume of hydrogen and natural gas has the lowest NO_x emission [13]. Liu *et al.* [12] studied natural gas mixed with hydrogen. When the ignition timing can be changed in time with the hydrogenation rate, a higher compression ratio can improve the thermal efficiency under high and low loads. In particular, when 20% volume hydrogen is added, the performance of the internal combustion engine is significantly improved. The research results of Subramanian *et al*. [13] on the combustion of natural gas mixed with hydrogen show that the emissions of NO_x, HC and CO produced by the combustion of natural gas mixed with hydrogen are lower than those of natural gas. Xu, *et al*. [14] used hydrogen-natural gas mixed fuel on large buses. The results show that the performance of the internal combustion engine is almost the same as that of the pure natural gas internal combustion engine.

Hydrogen-Gasoline

Since hydrogen plays a promoting role in combustion, the main purpose of gasoline-hydrogen mixed combustion is to improve thermal efficiency and reduce fuel consumption. The ignition energy of hydrogen is low, the diffusion coefficient is large, and the ignition delay period of the mixture is shortened. The ignition delay period of gasoline mixed with hydrogen will be shortened and the flame propagation speed will be accelerated. The actual cycle is closer to the constant volume cycle than that of the gasoline engine, which can achieve lean and fast combustion and improve the economy of the engine. The chain combustion reaction of hydrogen produces a large number of activation centers, which is conducive to the full reaction of HC and CO components in the cylinder, greatly reducing their emissions. CO emissions are reduced to less than 1/4 of the original gasoline engine, and HC emissions are reduced to less than 3/4 of the original gasoline engine. Active ions such as OH, H, and O produced during the combustion of gasoline-mixed hydrogen play a role in accelerating combustion, suppressing deflagration, and improving the compression ratio and thermal efficiency of the internal combustion engine. There is an optimum value for the hydrogen content in gasoline. If the amount of hydrogen is too little, the advantages of hydrogen in optimizing combustion cannot be fully utilized. If the amount of hydrogen is too much, flashback is likely to occur. The specific optimal amount of hydrogen is determined by the speed and load of the internal combustion engine.

Hydrogen-Diesel

Diesel engines are widely used as power sources for agricultural machinery due to their high thermal efficiency, strong reliability, long service life, good power performance and fuel economy. However, one of the biggest defects of diesel engines is that NO_x and particulate emissions are high, and it is difficult to effectively reduce both emissions at the same time due to the limitation of the compromise curve. Therefore, how to effectively reduce the emission of pollutants under the premise of ensuring the power and economy of diesel engines is an urgent problem to be solved. It has been found that almost all NO_x emitted by diesel engines is generated within 20 °CA after the start of combustion, and delaying fuel injection is a simple and effective way to reduce its emissions. However, delaying fuel injection will lead to an increase in fuel consumption and exhaust smoke. At present, diesel engines mainly use exhaust gas recirculation (EGR) technology to reduce NO_x emissions. But high EGR rates mean less fresh air and worse combustion in the cylinder, which reduces the economy of diesel engines and increases soot emissions.

The conditions of soot formation are high temperature and hypoxia. The high compression ratio of diesel engine structure and the inhomogeneity of combustion make two conditions of high temperature and hypoxia always exist in the combustion process. In order to reduce soot and NO_x emissions at the same time. Many researchers [15] took advantage of the combustion characteristics of hydrogen and mixed an appropriate amount of hydrogen into the diesel combustion process to optimize combustion. When a diesel engine uses hydrogen diesel fuel, it can not only maintain the high compression ratio and high thermal efficiency of the diesel engine, but also ensure stable ignition (diesel ignition). It does not require high ignition timing and can easily achieve lean combustion, thereby reducing NO_x and particulate matter emissions.

According to measurements, the amount of hydrogen added has an optimal value or optimal range. If too little hydrogen is added, it will not optimize combustion, but too much will worsen combustion. Studies have shown that when the hydrogen content is 5%, soot emissions reach a minimum, and 5% hydrogen content has little effect on the excess air coefficient. Dinesh & Kumar [16] added hydrogen into the intake air of a ZS195 diesel engine and then used EGR technology to reduce the emissions. Through research, it was found that under high load conditions, when the EGR rate is constant, as the hydrogen blending rate increases, the peak pressure and pressure rise rate in the cylinder of the ZS195 diesel engine will increase. This is due to the high combustion rate and diffusion rate of hydrogen. Under hydrogen-rich conditions, HC, CO and soot emissions are reduced. The reason is that hydrogen optimizes combustion, and technology breaks through the limitations of the NO_x-soot trade-off curve and can reduce emissions of both. The thermal efficiency and NO_x emission of the ZS195 diesel engine are increased by fixing EGR rate and increasing hydrogen mixing amount. The peak pressure and temperature in cylinder are increased, which is beneficial to NO_x generation. NO_x emission can be reduced by lean combustion and delaying fuel injection. Qian *et al.*

[17] found that when the EGR rate of the ZS195 diesel engine is low, the combustion of hydrogen is optimized and the thermal efficiency of diesel engine is improved. At high EGR rates, the effect of hydrogen optimizing combustion is not enough to offset the impact of deteriorated in-cylinder combustion caused by high EGR rates, and the thermal efficiency of the diesel engine is basically not improved. Therefore, there is an optimal value or optimal range of EGR rate [15]. The hydrogen-rich gas produced by diesel reforming technology is mixed with air and enters the cylinder for combustion, which can effectively improve the performance of the diesel engine and reduce various emissions of the diesel engine to varying degrees.

Problems to be Solved in the Development of Hydrogen Internal Combustion Engine

Hydrogen exists in gaseous form at room temperature, with low ignition energy, fast diffusion speed and easy leakage. Its safe storage, transportation, packaging and on-board installation are all difficult. As a result, diesel engines need to be able to produce hydrogen (such as diesel reforming to produce hydrogen) to implement HEGR technology. At the same time, the cost of hydrogen production is high and the technology is relatively complex. Therefore, it will take a long time to achieve large-scale application and commercialization of hydrogen fuel in internal combustion engines. In the hydrogen-air mixture, the concentration of oxygen atoms is high, and the cycle temperature is relatively high during hydrogen combustion, and the NO_x emission concentration is high. Therefore, the hydrogen internal combustion engine needs to solve the problem of reducing NO_x emissions and restoring power. For the former, water injection, EGR, N_2 and CO_2 can be used to reduce it. For the latter, the conventional power improvement method is limited by the combustion characteristics of hydrogen, so the power recovery is more difficult. For example, increasing the compression ratio will cause premature combustion or backfire, increasing the equivalent fuel-air ratio will cause the increase of NO_x emissions and incomplete combustion, and the use of pressurized intercooling will increase the probability of premature combustion and NO_x emissions.

Although hydrogen can make the internal combustion engine easy to cold start, it can lead to abnormal combustion problems such as pre-ignition, flashback, deflagration and knock. Premature combustion leads to low efficiency and rough work of internal combustion engine, increases the mechanical load and thermal load of internal combustion engine, increases the exhaust temperature, and even stops the hydrogen internal combustion engine. Tempering causes the hydrogen internal combustion engine to produce strong noise, which is easy to damage the internal combustion engine. Cylinder knocking will cause the hydrogen internal combustion engine to work unstably, generate vibration and noise, and even cause misfire, damage the intake pipe and hydrogen supply system. Deflagration is a sharp combustion phenomenon of the end mixture. Mild deflagration is conducive to combustion in the cylinder. Moderate or above deflagration may lead to a sharp increase in gas pressure, rough combustion, knocking on the cylinder, early termination of combustion, decrease of output power and thermal efficiency of the internal combustion engine, increase of fuel consumption, overheating of the cylinder, increase of stress of parts, accelerated wear of parts, and deterioration of emission performance of the internal combustion engine. The abnormal combustion problem of hydrogen internal combustion engine is the bottleneck problem in its development and application.

When using hydrogen-gasoline fuel, it is necessary to install a hydrogen supply system on gasoline vehicles. Although this is technically feasible, it is not economical. At the same time, gasoline hydrogen blending combustion needs to solve the problem of coordination between factors such as output power, combustion thermal efficiency, fuel economy, emission quality and abnormal combustion based on different working conditions of the engine.

Direct injection hydrogen internal combustion engine can improve the excess air coefficient and compression ratio, effectively avoid premature combustion, eliminate backfire, increase output power and improve thermal efficiency. However, the structure of its hydrogen injection system is complex, the reliability of components needs to be solved, the uniformity of mixture formation needs to be improved, the difficulty of ignition organization needs to be reduced, the time and quantity of hydrogen injection and the ignition time need to be accurately controlled, and the cyclic variation at the initial stage of combustion needs to be controlled.

The structure of the hydrogen injection system of the intake pipe injection hydrogen internal combustion engine is not complex, and the mixture formation and combustion are easy to organize. The structure is not changed much when the traditional internal combustion engine is modified. However, the hydrogen internal combustion engine is prone to abnormal combustion phenomena such as pre-ignition, knocking and tempering. At present, it can be avoided by accurately controlling the ignition timing.

In general, hydrogen internal combustion engine can mainly use technologies (such as compound intake, lean combustion, electronically controlled high pressure direct injection, supercharging, intercooling, increasing compression ratio, EGR, reducing intake temperature, and catalytic post-processing) to solve the problems of pre-ignition, tempering, low output power density, high NO_x emissions. But the best solution is to numerically simulate the working process of the internal combustion engine, establish various calculation models, and realize the comprehensive optimization control of hydrogen injection timing, ignition timing, combustion process, starting, idle speed, variable speed and other working conditions, so as to realize the optimal combination of combustion and emission of hydrogen internal combustion engine. This is an issue that needs further study [18, 19].

CONCLUSIONS

Hydrogen has been considered as one of the best alternative fuels for internal combustion engines due to its high efficiency and clean combustion. Effectively solving the problems existing in the development of hydrogen internal combustion engines can promote their development and application, ultimately leading to industrialization, solving the environmental pollution problem in the current automobile era, and promoting sustainable social and economic development. However, in order to welcome the arrival of a true "hydrogen economy", hydrogen internal combustion engines still need to carry out a large amount of continuous basic research, such as how to improve combustion thermal efficiency and output power density and achieve optimal control of composite modes, how to optimize the structural design of internal combustion engines and improve material performance and optimize solutions.

CONFLICTS OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this paper.

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