

## Comparative Analysis of Methanol, Natural Gas And Hydrogen as Alternative Engine Fuels

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### Abstract

The continuous consumption of fossil fuels and environmental pollution are the main causes of the increasing global warming trend and energy crisis. About 23% of CO<sub>2</sub> emissions come from the transportation sector, and there is an urgent need in many countries to develop and apply alternative fuels to reduce CO<sub>2</sub> emissions. The challenge for alternative fuels for automotive engines is to meet human needs by improving the overall performance of engines while reducing emissions of combustion pollutants. This paper mainly discusses three mainstream alternative fuels for engines, including methanol, natural gas and hydrogen, and analyzes the physical and chemical characteristics, combustion characteristics and pollutant emission characteristics of the fuels, and compiles the current applications and latest research progress of the three alternative fuels to provide a theoretical basis for further exploration of more comprehensive and efficient alternative fuels.

**Keywords:** alternative fuels; environmental pollution; energy; carbon emissions

### 1. Introduction

With the increase of industrialization and energy demand in the world, the demand for fossil fuels is increasing day by day. In order to achieve sustainable and stable development of resources, researchers have conducted a lot of research on oxygenated fuels, mainly alcohols, ethers and esters, and gaseous fuels, mainly compressed natural gas (CNG), liquefied natural gas (LNG) and hydrogen, expecting to improve engine performance and reduce the emission of harmful pollutants from internal combustion engines by increasing combustion efficiency.

Methanol, natural gas and hydrogen have significant advantages as alternative fuels for internal combustion engines due to their excellent physical and chemical properties and renewable nature. In this paper, methanol, natural gas and hydrogen are the main objects of study (Physical and chemical properties are shown in Table 1). Detailed comparisons and analyses were made in terms of intake mixture formation, combustion and emissions, respectively.

### 2. Internal combustion engines fueled by simple methanol and hydrogen-methanol mixtures

#### 2.1 Pure methanol engine

Methanol is considered as one of the most promising alternative fuels to conventional fossil fuels due to its abundant raw material, low cost and the absence of harmful substances produced by combustion [1,2]. First, methanol has a higher octane number and better rarefied combustion properties [3], which allows engines to run at higher compression ratios without detonation [4],

which is more beneficial to improve engine fuel economy and extend the rarefied combustion limit [5,6]. Secondly, due to the higher oxygen content and higher hydrogen to carbon ratio and laminar flame speed in methanol [7], methanol as an internal combustion engine fuel provides more timely and complete combustion and lower carbon emissions than pure gasoline fuel spark ignition engines [8].

**Table 1. Physical and chemical properties of different fuels**

properties	Methanol	Natural gas	hydrogen	gasoline	diesel
Chemical formula	CH <sub>3</sub> OH	CH <sub>4</sub>	H <sub>2</sub>	C <sub>n</sub> H <sub>1.87n</sub> (l)	C <sub>n</sub> H <sub>1.8n</sub> (l)
Density (kg/m <sup>3</sup> )	791.8	0.7174	0.089	725	810~855
Low calorific value (kJ/kg)	19.6	50	119.98	44	43
Latent heat of evaporation (kJ/kg)	1168	509	447	305	270
boiling point (°C)	64.7	-162	-253	27~225	180~330
Octane Number	109	125	130	92-98	20~30
Flame speed (m/s)	0.52	0.38	3.1	0.37~0.43	-

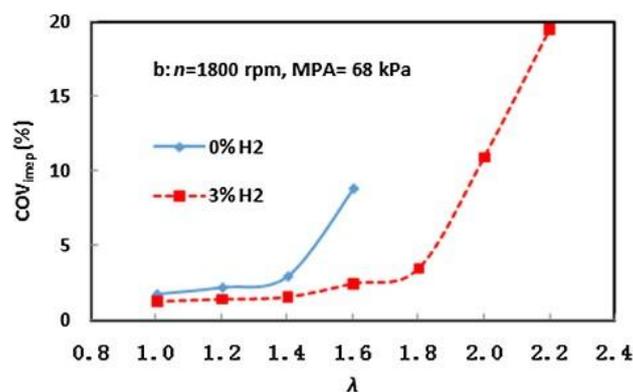
In addition, methanol has a high latent heat of vaporization, which is conducive to cooling the intake charge and lowering the greatly combustion temperature, so methanol fuel can be injected through the intake tract can improve the engine filling efficiency and power output, greatly reduce NO<sub>x</sub> emissions, and can avoid abnormal combustion in internal combustion engines [9,10]. In addition, as a liquid fuel, methanol is similar to gasoline and diesel in terms of storage and transportation, making it easier to be utilized [11]. However, the use of methanol fuel as an alternative fuel for internal combustion engines is not without advantages and disadvantages. The high latent heat of vaporization of methanol makes it difficult to evaporate in the cylinder, resulting in difficulty in forming a homogeneous methanol-air mixture under cold starting and part-load engine conditions, especially at low ambient temperatures, and a methanol-fueled spark-ignition engine may have difficulty starting or even fail to run properly without auxiliary preheating measures [12].

Methanol has a higher octane rating, so methanol-fueled engines have better detonation resistance and can run in spark ignition mode at high compression ratios without detonating the engine. Xiaoyan Li et al [13] studied the combustion of a spark ignition methanol engine with a compression ratio of 17.5 at different EGR rates. The results showed that EGR can reduce the intensity of detonation and delay the onset of detonation, while without EGR, the intake side of the engine combustion chamber is prone to detonation, and as the EGR rate increases, the odds of detonation on the exhaust side of the combustion chamber become greater.

Rare combustion is an effective way to improve thermal efficiency and reduce spark ignition engine emissions, and methanol fuel has better rarefaction capability. Changming Gong et al [14] concluded that dual spark plug synchronous ignition is an effective means to improve combustion stability and extend the lean combustion limit of spark ignition engines. They investigated the mixture concentration distribution, combustion and emission characteristics in detail in order to evaluate the lean combustion performance of a dual spark plug synchronous ignition methanol direct injection engine and to solve the problem of stable combustion at medium compression ratio. The results show that the injection and ignition moments and the flow rate distribution at ignition determine the distribution of the mixture concentration in the cylinder, which in turn affects the flame surface temperature and emissions. Delaying the ignition timing resulted in a significant increase in unburned methanol emissions and a rapid decrease in NO<sub>x</sub> emissions. Optimal engine performance is obtained at the optimal injection timing of 110° CA BTDC and the optimal ignition timing of 21° CA BTDC. Thus, simultaneous ignition with dual spark plugs ensures stable combustion and produces good performance at medium compression ratios under lean combustion conditions.

## 2.2 Hydrogen-doped methanol engine

Hydrogen doping is an effective way to increase the flame propagation speed and extend the lean ignition limit of spark ignition engines. Changming Gong et al[15] investigated the combustion and emission characteristics of a dual-fuel spark ignition engine equipped with an inlet tract hydrogen injection and a methanol direct injection system with different excess air coefficients under a methanol post-injection strategy, in which the hydrogen doping ratio was set at 0% and 3%. The experimental results show that hydrogen doping can shorten the flame propagation period and fast combustion period, and bring the combustion center closer to the upper to the point, so that the lean combustion limit of methanol engine can be extended from the excess air factor of 1.6 to 2.2. At 1800 r/min engine speed, the COV<sub>imep</sub> increased significantly with the increase of the excess air coefficient from over 1.4 in the non-hydrogen-doped methanol engine to over 1.8 in the hydrogen-doped engine (as shown in Figure 1). Moreover, at 1200 rpm and 1800 rpm, CO and HC emissions decreased, NO<sub>x</sub> emissions increased slightly, and maximum soot emissions were 59% and 30% lower, respectively, than without hydrogen blending after 3% hydrogen blending.



**Fig.1 Hydrogen-doped and non-hydrogen-doped methanol engine COV<sub>imep</sub> with excess air coefficient(n=1800r/min)**

The high latent heat and vaporization temperature of methanol make it difficult to evaporate completely at low temperatures, especially under low load cold starting conditions. Therefore, it is more difficult to start methanol engines at low ambient temperatures.

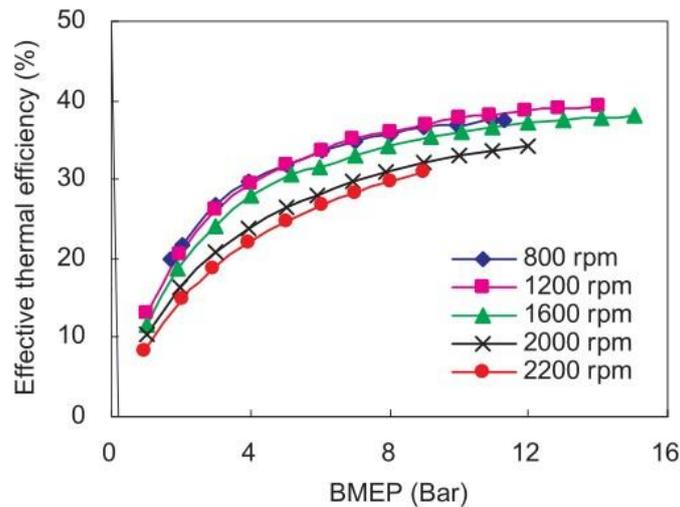
In a spark ignition engine, a laminar flame propagates in the initial stage, and then, the laminar flame rapidly develops into a turbulent flame. For laminar flame propagation, the combustible mixture is ignited by the electric spark and the flame front surface propagates to the unburned region, followed by high temperature combustion reactions. The chemical reaction is concentrated at the flame front, as a result, a large temperature and concentration gradient is created at the flame front, leading to a strong exchange of heat and material, which in turn causes a chemical reaction in the adjacent unburned mixture. For turbulent flame speeds depend on the physical and chemical properties of the different fuels, that is the laminar combustion characteristics. Therefore, the study of laminar flame is the basis of turbulent flame and the laminar combustion velocity (LBV) is an essential parameter to verify the chemical reaction kinetic mechanism and to study the engine performance [16].

### **3. Internal combustion engines fueled by pure natural gas and hydrogen-doped natural gas**

#### **3.1 Pure natural gas engine**

Natural gas is abundant, low cost and produces less greenhouse gases from combustion. It is considered a potential future energy source to replace conventional fuels such as gasoline and diesel, and has many advantages in terms of reducing emissions and lowering fuel consumption. Compared to conventional fuels, including gasoline and diesel, natural gas has a higher octane number, which allows the engine to operate at a higher compression ratio without detonation, thus allowing an increase in the effective thermal efficiency and effective fuel consumption rate of the engine [17]. In addition, natural gas, whose main component is methane, has a high hydrogen-to-carbon ratio and has the advantage of reducing CO<sub>2</sub> emissions when used as a fuel in vehicle engines, in line with the current direction of emission regulations [18]. However, methane has a higher minimum ignition energy (MIE), lower laminar combustion rate, longer minimum quenching distance and lower mass diffusion coefficient in air compared to gasoline and diesel [19], making natural gas-fueled spark ignition engines prone to misfires, high cycle variability and high HC and NO<sub>x</sub> emissions when operated under lean conditions. It is due to these drawbacks that researchers are still required to conduct a lot of experimental explorations on them in order to be able to match natural gas fuels better to automotive engines. In order to improve the energy saving potential of natural gas engines, many studies have focused on their thermal efficiency and thermodynamic properties. Feng Zhou et al [20] conducted a heat balance test of a liquefied natural gas (LNG) engine to decompose the various energy losses. On this basis, the influencing factors of various energy flows of the LNG engine were explored and analyzed in the context of combustion and thermodynamic processes. The results show that the high-pressure cycle indicated work, exhaust energy fraction and heat transfer losses are mainly affected by the engine speed. The high-pressure cycle efficiency increases with increasing engine speed, reaching a maximum of 49.6% due to the higher compression ratio. The exhaust energy fraction is similar, but the heat transfer losses decrease with increasing engine speed. Although the maximum high-pressure cycle efficiency occurs at high speed conditions, the maximum effective thermal efficiency still occurs at low speeds due to friction and pumping losses (as shown in Figure 2). Therefore, the effective thermal efficiency of LNG can be further improved by optimizing the thermodynamic process (or combustion parameters) for low speed conditions, and friction and pump gas losses should be minimized for high speed conditions. Kamran Poorghasemi et al [21] investigated a natural gas/diesel reactivity controlled compression ignition (RCCI) Amin Yousefiet al [22] studied the effect of swirl ratio on the combustion performance and emissions of a natural gas/diesel dual fuel engine and concluded that swirl motion provides better mixture formation conditions and higher thermodynamic efficiency, but leads to higher

heat losses at very high swirl ratios .



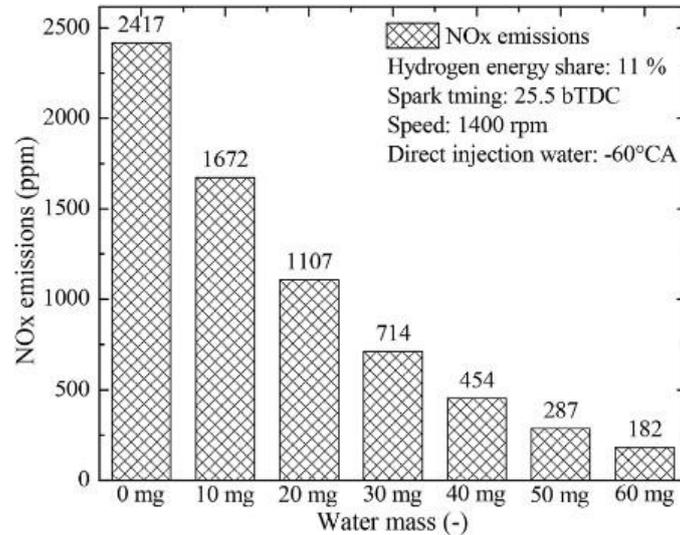
**Fig.2 Variation of effective thermal efficiency of LMG engine with load (average effective pressure) at different speeds**

### 3.2 Hydrogen-doped natural gas engine

The wider flammability limits and dilution limits of hydrogen, greater diffusivity in air, and lower ignition energy make it possible for hydrogen doping in natural gas engines to break through the limitations of pure natural gas engines in terms of lean combustion and further improve engine performance. J. Pradeep Bhasker et al [23] studied the compression ratio and hydrogen doping of a natural gas spark ignition engine under lean combustion conditions at full throttle opening and 1500 r/min. The results of the study pointed out that the effective thermal efficiency and effective power of the engine increased with the increase of the compression ratio, reaching the peak effective thermal efficiency at a compression ratio of 12.5, above which the increase of emissions was excessive. In addition, blending with 10% hydrogen extends the dilute ignition limit from 0.5 to 0.42 equivalent ratios with pure CNG as fuel, and its resistance to detonation is also greatly improved. In terms of emissions, CO and HC emissions are significantly reduced after hydrogen blending, and NO<sub>x</sub> emissions are not significantly increased due to delayed ignition timing to avoid detonation.

Dilute combustion and stoichiometric combustion are two types of combustion that occur in natural gas engines [24]. To comply with stricter emission regulations, some natural gas engines have shifted from lean combustion to stoichiometric combustion to reduce emissions and costs [25]. However, under stoichiometric combustion conditions, natural gas engines are prone to suffer from higher thermal loads, higher tendency to burst and higher turbine inlet temperatures, among other critical issues. Water injection is a cutting-edge method to reduce heat load and NO<sub>x</sub> emissions and inhibit internal combustion engine detonation is a cutting-edge method. Jinfei Wang et al [26] investigated the effects of water injection volume and water injection timing on the thermodynamic, combustion and emission characteristics of a hydrogen-doped natural gas engine. The results showed that the peak combustion pressure and peak heat release rate decreased with the increase of water injection volume, in addition, the 50% combustion position and peak combustion pressure position were delayed with the increase of water injection volume. With the increase of water injection volume and the delay of water injection timing, NO<sub>x</sub> emission decreased (as shown in Fig.3,4). Zhanming Chen et al [27] experimentally investigated the effects of different water injection amounts and ignition timing on the combustion

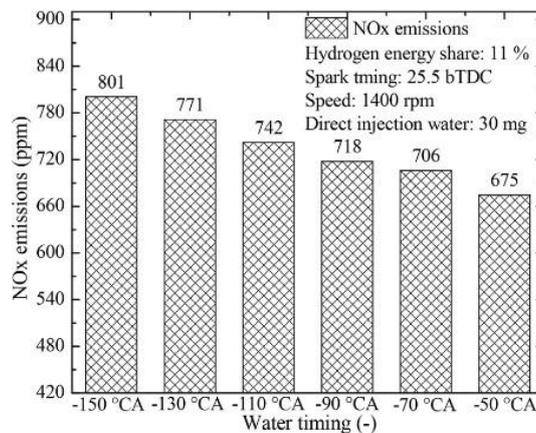
performance characteristics of heavy-duty natural gas engines. The results showed that water injection reduced the combustion rate of natural gas, resulting in lower peak in-cylinder pressure, peak heat release rate and combustion temperature. The flame development period and flame propagation period increased as the amount of water injected into the natural gas increased. They also found that the effective thermal efficiency at optimal ignition timing increased from 27.8% to 28.2% at a water injection rate of 0.35 compared to pure natural gas. Due to the lower combustion temperature resulting in lower heat load, the tendency of deflagration was reduced and NO<sub>x</sub> emissions continued to decrease with increasing water injection rate, while HC and CO emissions increased slightly.



**Fig. 3 Variation of NO<sub>x</sub> emission with the amount of water spray**

#### 4.1 Hydrogen Fuel Engine Abnormal Combustion Issue

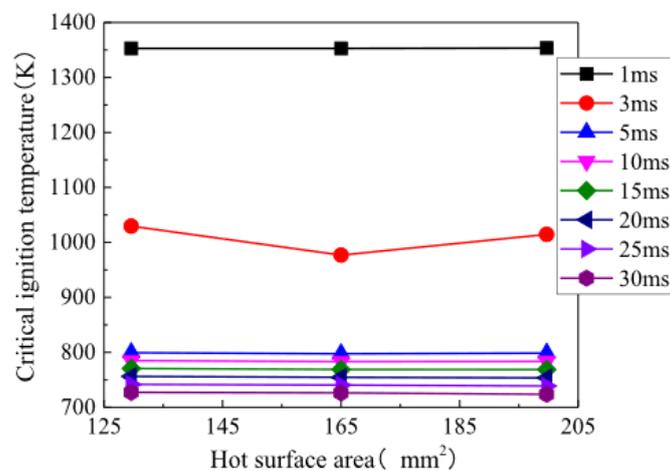
The use of hydrogen as an engine fuel is expected to significantly improve the performance of spark ignition engines. Hydrogen has a higher octane number, and hydrogen internal combustion engines can achieve greater ignition advance angle at small loads, which facilitates engine operation at higher compression ratios and improves thermal efficiency [28,29]. Hydrogen has a higher ignition temperature and is about three times higher than conventional gasoline fuels and five to six times higher than ethanol fuels in terms of mass energy consumption, thus, hydrogen fuels can improve the effective efficiency of engines and reduce fuel consumption [30].



**Fig.4 Variation of NO<sub>x</sub> emission with water injection timing**

#### 4. Hydrogen-Fueled Internal Combustion Engines

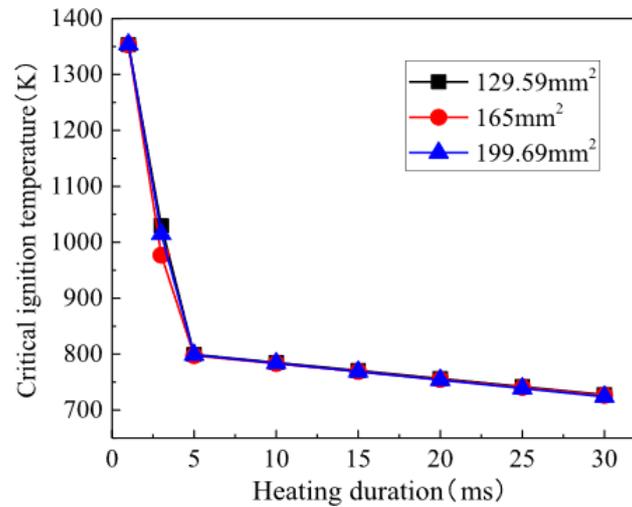
A combustible mixture of hydrogen and air can be burned in a conventional spark-ignition engine at an equivalent ratio below the lean combustion limit of the gasoline-air mixture, producing lower flame temperatures and leading directly to lower wall heat transfer and lower NOx emissions [31,32]. The high combustion rate of the hydrogen/air mixture and the high diffusivity of hydrogen in air can significantly improve the homogeneity of the mixture, allowing the engine to obtain higher combustion efficiency and can reduce the cycle variation of the internal combustion engine [33]. In addition, the combustion of hydrogen in oxygen produces only water, while in air, it produces mainly some NOx [34]. These properties make hydrogen potentially an excellent fuel to meet increasingly stringent emission regulations and reduce greenhouse gas emissions. However, the conflict between increasing engine output and reducing NOx emissions often becomes a technical threshold when hydrogen is used as an engine fuel in practice [35], and it can cause abnormal combustion phenomena such as premature combustion and backfire [36].



**Fig.5 Variation of critical ignition temperature with hot surface area for different heating durations**

Zhenzhong Yang et al [36] analyzed the mechanism of premature combustion and tempering of hydrogen internal combustion engines in order to solve the contradiction between abnormal combustion and increased power output of hydrogen internal combustion engines. They developed a multivariate, multi-objective, and multi-constrained optimal control model and performed simulations using genetic algorithms. The results show that the excess air coefficient and ignition advance angle can be adjusted by the weighting factor to optimize the power output and suppress abnormal combustion. To further reveal the early ignition characteristics of hydrogen internal combustion engines, Zhenzhong Yang and others [37] investigated the effects of different combustion-to-air equivalent ratios, initial temperature of hydrogen-air mixture, initial pressure of hydrogen-air mixture, hot surface temperature and hot surface area on the heating duration of the hot surface of hydrogen-air mixture. The results showed that the effects of each factor on the hot surface ignition were in the following order: hot surface temperature > initial pressure of hydrogen-air mixture > combustion-to-air equivalent ratio > initial temperature of hydrogen-air mixture > hot surface area. On this basis, they also established the relationship between critical ignition temperature, heating duration and hot surface area, and found that heating duration was the only major factor affecting critical ignition temperature (as shown in Figs.5,6). In addition, they pointed out that eliminating the incandescent point in the cylinder

before ignition and controlling the pre-ignition cylinder temperature below 800 K can effectively avoid the occurrence of premature ignition.



**Fig.6 Critical ignition temperature versus heating duration**

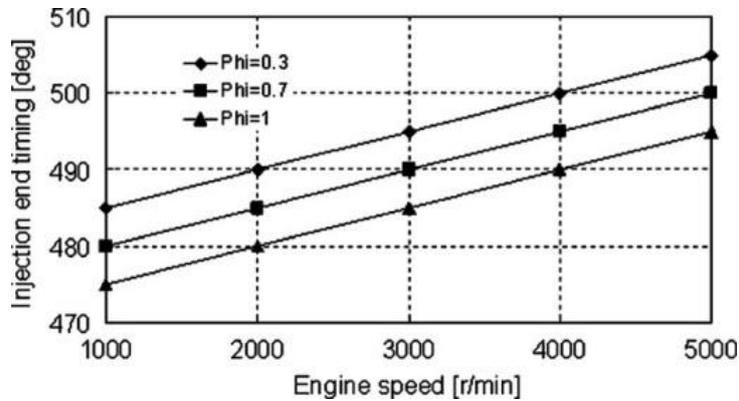
One of the main reasons for the occurrence of backfire is the presence of high-temperature heat sources, including hot spots, in the engine combustion chamber during the intake process. Vipin Dhyani et al. [35], by changing the temperature and position of the hot spots in the combustion chamber of the engine, analyzed their influence on the basic characteristics of the hydrogen engine intake manifold tempering origin and tempering propagation. The results show that the minimum temperature of the incandescent point at which tempering occurs is 950 K. The probability of tempering occurs increases with the increase of the incandescent point temperature. They also found that the location of the incandescent point does not affect the characteristics of the tempering, but affects the moment of tempering onset. Therefore, they suggested that the spark plug and exhaust valve of a hydrogen internal combustion engine be tailored so that the temperature of the spark plug tip and exhaust valve during the intake process does not exceed 900 K, thus eliminating the occurrence of backfire. In addition, Fushui Liu et al [38], in order to prevent the inlet manifold backfire of hydrogen internal combustion engine, considered that there should be a limit value for the end moment of hydrogen injection, and they used CFD numerical simulation to investigate the limit value of the end moment of hydrogen injection without backfire of hydrogen internal combustion engine at different speed and equivalent ratio. They found that the lower the engine speed and the more concentrated the hydrogen-air mixture is, the earlier the end of hydrogen injection should be (as shown in Fig. 7).

#### 4.2 Emission mechanism of hydrogen-fueled engines

The high temperature in the combustion process of hydrogen internal combustion engine causes the oxidation of  $N_2$  in the air and generates a large amount of NOx emissions, and the formation of NOx emissions is mainly affected by high temperature, oxygen concentration and high temperature duration, based on these three factors, researchers have conducted many types of studies from different aspects to achieve the reduction of NOx emissions.

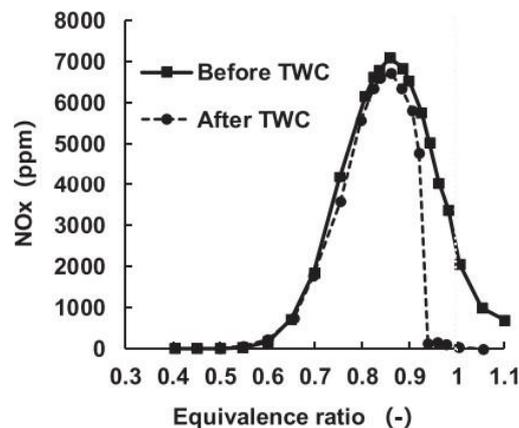
Jeongwoo Lee et al [39] investigated the effects of excess air coefficient and ignition advance angle on the combustion and NOx emissions of a hydrogen internal combustion engine under partial load conditions. The results showed that high effective thermal efficiency (34.17%) and sufficiently low NOx emissions (0.07g/kW.h) could be achieved by performing spark ignition

engine combustion with pure hydrogen at a lean mixture ( $\phi=2.2$ ) and an early ignition advance angle ( $25^\circ$  CA BTDC).



**Fig.7 End moment of hydrogen injection for different engine speed and equivalent ratio**

Junfa Duan et al [40] developed a CFD simulation model of a hydrogen internal combustion engine containing a detailed chemical reaction mechanism to study the NO<sub>x</sub> generation mechanism, and they found that at high loads, thermal NO plays a key role in NO<sub>x</sub> emissions, accounting for more than 75% of the total NO<sub>x</sub> emissions. In contrast, unburned hydrogen can be used to reduce NO emissions in a conventional triple-acting catalytic converter (TWC) when the equivalence ratio of the hydrogen internal combustion engine is slightly higher than the stoichiometric ratio.



**Fig.8 Variation of NO<sub>x</sub> concentration with equivalence ratio before and after TWC**

Therefore, an experimental study on the reduction of NO by unburned hydrogen in a TWC was conducted by Sun, Lingzhi Bao et al [41]. The results showed that the unburned H<sub>2</sub>/NO mixing ratio in TWC was greater than 1.5, which ensured 100% NO conversion efficiency, and the suitable reaction temperature for TWC was 400°C-500°C. The NO<sub>x</sub> concentration was reduced from 2056 ppm to 41 ppm at the stoichiometric ratio after TWC treatment, and the NO<sub>x</sub> concentration was reduced to 41 ppm at the equivalence ratio of The NO<sub>x</sub> concentration reached 0 ppm at an equivalence ratio of 1.05 (as shown in Figure 8). The experiment proved that the hydrogen engine can achieve 100% NO conversion efficiency and zero emission by unburned H<sub>2</sub> in conventional TWC when the temperature and mixing ratio meet the requirements.

#### 4. Conclusion

Diversification of fuel forms for automobiles is the two major challenges to solve the energy crisis and environmental pollution. This paper systematically summarizes the advantages and shortcomings of methanol, natural gas and hydrogen as automotive alternative fuels when applied to automobile engines relative to traditional gasoline engines, and obtains the following conclusions:(1) Methanol fuel, as an oxygenated fuel, will play a role in the reduction of conventional emissions, but there are also some defects that lead to the current inability to promote a large area. First, alcohol fuel combustion intermediate products have aldehydes and other harmful gases to human body. Second, although the current engine can be improved by using alcohols instead of combustion, but there is a certain negative impact on the dynamics.(2)As a gaseous fuel, hydrogen has more advantages than natural gas, and due to its excellent physical and chemical characteristics, it has become the first choice for the study of alternative fuels for vehicles in the world, and has great potential for development.

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