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The Effect of Hydrogen Addition on Combustion and Emission Characteristics of an n-Heptane Fuelled HCCI Engine

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Abstract

The mechanisms of the influence of hydrogen enrichment on the combustion and emission characteristics of an n-heptane fuelled homogeneous charge compression ignition (HCCI) engine was numerically investigated using a multi-zone model. The model calculation successfully captured most available experimental data. The results show that hydrogen addition retards combustion phasing of an n-heptane fuelled HCCI engine due to the dilution and chemical effects, with the dilution effect being more significant. It is because of the chemical effect that combustion duration is reduced at a constant compression ratio if an appropriate amount of hydrogen is added. As a result of retarded combustion phasing and reduced combustion duration, hydrogen addition increases indicated thermal efficiency at a constant combustion phasing. Hydrogen addition reduces indicated specific unburned hydrocarbon emissions, but slightly increases normalized unburned hydrocarbon emissions that are defined as the emissions per unit burned n-heptane mass. The increase in normalized unburned hydrocarbon emissions is caused by the presence of more remaining hydrocarbons that compete with hydrogen for some key radicals during high temperature combustion stage. At a given hydrogen addition level, N₂O emissions increases with overly retarding combustion phasing, but hydrogen addition moderates this increase in N₂O emissions.

Keywords: HCCI combustion, hydrogen enrichment, diesel combustion, multi-zone model

1. Introduction

Hydrogen is a clean fuel whose combustion does not generate carbon dioxide, particulate matter (PM) and unburned hydrocarbons (HC). It has been shown that hydrogen provides satisfactory performance in internal combustion (IC) engine applications, although there are various challenging issues [1-4].

Unfortunately hydrogen is an energy carrier and has to be obtained from hydrocarbon fuels or water. The use of pure hydrogen as a primary fuel for internal combustion engines is still too expensive today. Alternatively, hydrogen enrichment, i.e. use of a small amount of hydrogen as additive to conventional fossil fuels, may be a more practical way to apply hydrogen. Previous studies have shown that hydrogen enrichment helps to extend lean flammability limits and to increase flame speeds of hydrocarbon fuels [5,6]. As a result, the addition of hydrogen to a spark-ignition (SI) engine extends the lean operational limits and thus allows the engine to operate at leaner conditions with reduced NO_x emissions [7,8].

Homogeneous charge compression ignition (HCCI) combustion has been attracting more and more attention from scientists and engineers due to its potential to virtually eliminate NO_x and PM emissions from engine combustion. The effect of hydrogen enrichment on the performance of HCCI combustion has also been investigated by many researchers. Shudo et al. [9-11] investigated the effect of hydrogen enrichment on HCCI combustion of dimethyl ether and found that the addition of hydrogen retarded the combustion phasing. On the other hand, the addition of hydrogen to a natural gas fuelled HCCI engine has been shown to advance combustion phasing and to extend the lean operational limits [12-15]. Checkel et al. [14-18] investigated the effect of reformer gas (hydrogen rich gas) enrichment on isooctane and n-heptane fuelled HCCI combustion and found that the effect depended on the octane number of the base fuel.

Diesel engines are widely used in transportation and off-road vehicles. The advantages of HCCI combustion make it a potential alternative combustion mode to conventional diesel engines [19]. Diesel

fuels usually have two-stage combustion, a low temperature heat release (LTHR) stage that initiates the ignition process and a primary high temperature heat release (HTHR) stage. One issue with diesel HCCI combustion is the earlier ignition that limits the maximum compression ratio and thus the fuel conversion efficiency [20]. Appropriate combustion phasing (ignition timing) and reasonable combustion duration are crucial for a diesel HCCI engine to obtain higher fuel conversion efficiency and lower pollutant emissions [20,21]. Hydrogen is a fuel with higher auto-ignition temperature which may help to control the combustion phasing of a diesel HCCI engine. Meanwhile, hydrogen has a higher flame speed and leaner extinction limit, suggesting that the addition of hydrogen may enhance the primary high temperature combustion process and thus reduce the combustion duration of a diesel HCCI engine. Our experimental measurements [22] show that hydrogen enrichment does help to retard the combustion phasing, reduce the combustion and improve the fuel conversion efficiency of a diesel fuelled HCCI engine. However, not enough attention has been paid for the fundamental mechanisms behind the phenomena of hydrogen enriched HCCI combustion in [22] and other previous publications.

This paper further investigates the effect of hydrogen enrichment on the combustion and emission performances of an HCCI engine fuelled by n-heptane, a primary reference fuel of diesel, numerically by a multi-zone model with relatively detailed chemistry. Being different from [22], this paper focuses on the fundamental mechanisms associated with hydrogen enrichment of HCCI combustion. The paper starts with the brief description of the numerical model and the studied engine, followed by the presentation and analysis of results. Finally, concluding remarks are drawn.

2. Numerical Model

The studied engine is a Cooperative Fuel Research (CFR) engine used in the experimental study in [22]. It is a single-cylinder, four-stroke, variable compression ratio engine. The basic engine specifications are listed in table 1. A port fuel injector that is the same as that employed in [23] was used

to atomize and inject n-heptane just upstream of the intake port. Hydrogen was introduced to the intake port after the injection of n-heptane. More details about the engine can be found from [22].

A multi-zone model was employed to do the simulation. It assumes the working fluid to be an ideal gas and simulates a full four-stroke cycle of engine operation, starting from top dead center (TDC) during the exhaust stroke and finishing at the same point after the intake, compression, combustion and exhaust strokes, i.e. from -360 degrees to 360 degrees after top dead center (ATDC).

Eight zones were used in the model, including one crevice zone, one boundary zone and six core zones. The model assumes that the temperature of the crevice zone is always lower than or equal to the cylinder wall temperature due to the large ratio of surface area to volume. The volume of the crevice zone was assumed to be constant as 2% of the clearance volume of the investigated engine. The mass distribution in the boundary zone and core zones was assumed to be a normal distribution.

Heat transfer between working fluid and cylinder wall is assumed to happen through the boundary zone due to convection in the model. Each zone exchanges heat with its neighboring zones due to conduction and with cylinder wall due to radiation. There is mass exchange between crevice zone and other zones if pressure and temperature changes. To simplify the calculation, the mass exchange has been neglected during each time step. However, a mass adjustment is conducted after each time step. Then the adjusted masses are used during the next time step. The mass adjustment is conducted based on the total mass inside cylinder and the mass in the crevice zone. Before and after each time step, the mass of crevice zone can be calculated by the ideal gas state equation according to the crevice zone temperature, volume, composition and cylinder pressure. Then the adjusted crevice zone mass Δm_{ere} can be obtained. During the pressure increase process, fluid flows from boundary zone and core zones to crevice zone, i.e. Δm_{ere} is positive. Oppositely, Δm_{ere} is negative during the pressure decrease (expansion) process. More details of the multi-zone model can be found elsewhere [24] and from the supplementary material that provides all details, governing equations and related references for the model.

A reduced kinetics mechanisms developed by Golovichev [25] was used. The NO_x formation chemistry in GRI Mech 3.0 [26] was added to the base chemistry to calculate NO_x emissions.

The study in this paper focuses on the operating condition of engine speed = 900 rpm, EGR = 0% and λ = 3.5, with EGR and λ being the exhaust gas recirculation rate and the relative mass air/fuel ratio (defined as the ratio of real mass air/fuel ratio to the stoichiometric mass air/fuel ratio), respectively. Both n-heptane and hydrogen have been considered in the calculation of air/fuel ratio. A detailed analysis is provided for the case with compression ratio of 9.0 when hydrogen is gradually added. Then the results at different compression ratios are provided for various hydrogen fractions. For the sake of comparison, the variation of indicated thermal efficiency for the operating condition of engine speed = 900 rpm, EGR = 60% and λ = 1.2 is also presented.

The fraction of hydrogen is defined as

$$\alpha_{H2} = m_{H2} / (m_{H2} + m_{n-heptane}) \tag{1}$$

where m_{H2} and $m_{n-heptane}$ are the input mass of hydrogen and n-heptane, respectively, per engine cycle. For all the studied cases, the engine parameters of intake pressure, exhaust pressure and intake mixture temperature have been kept constant at 150 kPa, 170 kPa and 75 °C, respectively.

The calculated results are compared with the experimentally measured data in [22].

3. Results and Discussion

Figure 1 shows the effect of hydrogen addition on cylinder pressure profiles at a constant compression ratio (CR) of 9.0. The results at other compression ratios are qualitatively similar. It is observed that the multi-zone model successfully reproduced the pressure profiles. The crank angle position of the peak cylinder pressure is retarded with increasing mass fraction of hydrogen. The value of the peak pressure does not significantly change when a small amount of hydrogen is added, but decreases with further increasing mass fraction of hydrogen. The decrease of the peak pressure at a

larger hydrogen fraction is due to the late ignition that results in incomplete combustion and near misfire.

Combustion phasing is an important parameter that directly affects fuel conversion efficiency of an HCCI engine. The highest cycle efficiency of a diesel engine is usually obtained when heat release happens near top dead center [27]. In this paper, combustion phasing is represented by CA50, the crank angle at which 50% of total heat release is reached. Figure 2 shows the calculated and measured [22] variation of combustion phasing as a function of hydrogen fraction at a constant compression ratio of 9.0. The model calculation captured the correct trend of the combustion phasing with hydrogen addition, although slight quantitative differences exist. Both calculation and measurement show that hydrogen addition retards the combustion phasing of an n-heptane fuelled HCCI engine. This is qualitatively consistent with the results obtained by Konsereeparp and Checkel [14,18] and Hosseini and Checkel [15-17] for the effect of reformer gas (hydrogen rich gas) enrichment on HCCI combustion of low octane number fuels. It is also consistent with the result of Shudo et al. [9] for the effect of hydrogen addition on dimethyl ether HCCI combustion. However, this result is opposite to that of Yap et al. [12] who showed that hydrogen addition advanced the combustion phasing of natural gas HCCI combustion. Since both n-heptane and dimethyl ether are low octane number fuels, while natural gas is high octane number fuel, the result of this paper and those in [9,12,14-18] suggest that the effect of hydrogen addition on combustion phasing of a HCCI engine depends on the octane number of the primary fuel. Hydrogen addition retards the combustion phasing of HCCI combustion for low octane number fuels, but advances the combustion phasing for high octane number fuels.

The addition of an additive to the primary fuel may cause the combustion phasing change due to dilution, thermal and chemical effects. The thermal effect is due to the variation in thermal properties of the mixture inside cylinder due to the addition of hydrogen. The specific heat of hydrogen is smaller than that of n-heptane. Therefore, the addition of hydrogen should not have retarded the combustion

phasing of an n-heptane fuelled HCCI engine due to thermal effect. The dilution effect is usually caused by the variation in the concentrations of reactants, while the chemical effect is due to the participation of an additive in reactions. To identify the relative contributions of the dilution and chemical effects of hydrogen addition on the retardation of combustion phasing observed in Fig. 2, an additional calculation was conducted. In the additional calculation, an artificial inert component (AH₂) that has the same thermal and transport properties as hydrogen was added instead of hydrogen. Since the sole difference between the two simulations is that the additive in the additional simulation does not participate in reactions while it does in the normal simulation, the differences between the results from the two simulations are due to the chemical effect. On the other hand, the difference between the case without any additive and the case with artificial inert component addition is caused by the dilution effect. The results from the additional calculation are also shown in Fig. 2. It is observed that the addition of hydrogen retards the combustion phasing of an n-heptane fuelled HCCI engine due to both dilution and chemical effects, with the dilution effect being more significant. To our knowledge, this observation has not been reported in any previous publication.

n-Heptane is a fuel with two stage-combustion. The ignition of n-heptane is controlled by the reactions during the low temperature stage (LTS) [28]. The calculation results suggest that the low temperature stage reactions are initiated by the reactions $n-C_7H_{16} + O_2 = C_7H_{15} + HO_2$, $n-C_7H_{16} + OH = C_7H_{15} + H_2O$ and some others, with the reaction $n-C_7H_{16} + OH = C_7H_{15} + H_2O$ dominating. The reaction pathways during the low temperature stage for cases with and without hydrogen addition at the compression ratio of 9.0 are displayed in Fig. 3, where the arrow line thickness represents the calculated magnitude of the mean reaction rate inside cylinder. It is observed that the addition of hydrogen significantly reduces the reactivity during low temperature stage. The rates of reactions after the initial hydrogen abstraction from n-heptane do not significantly change during the whole low temperature stage for both cases with and without hydrogen addition, suggesting that the initial hydrogen abstraction reaction is the key to the low temperature kinetics.

When hydrogen is added, the concentration of n-heptane is decreased. Meanwhile, since hydrogen combustion requires less oxygen, the concentration of oxygen is also decreased at the same air/fuel ratio. Therefore, hydrogen addition reduces the rate of initial hydrogen abstraction reaction, such as $n-C_7H_{16} + O_2 = C_7H_{15} + HO_2$ and $n-C_7H_{16} + OH = C_7H_{15} + H_2O$, and thus decreases the low temperature stage reactivity and the heat release during the low temperature stage, as shown in Fig. 4 where cumulative heat release profiles for cases with and without hydrogen addition are plotted as a function of crank angle. As a result, the combustion phasing is retarded when hydrogen is added. This is how hydrogen addition retards combustion phasing due to dilution effect. This dilution effect has not been discussed in any previous publication, although some researchers, such as Shudo et al. [9], noted the chemical effect that will be discussed below.

Since hydrogen is not an inert component, it also participates in some reactions during the low temperature stage, especially the reaction $H_2 + OH = H_2O + H$. The consumption of OH by this reaction slows down the oxidation reactions of n-heptane, which also contributes to the decrease of the overall heat release shown in Fig. 4 during the low temperature stage. This is because OH is involved in the reaction $n-C_7H_{16} + OH = C_7H_{15} + H_2O$, a key reaction during low temperature stage, as mentioned above and shown in Fig. 3. Accordingly, hydrogen addition also retards the combustion phasing of an n-heptane fuelled HCCI engine owing to the chemical effect. This is similar to the analysis by Shudo et al. [9]. Because of the relatively large activation energy, the reaction $H_2 + OH = H_2O + H$ only consumes a very small amount of OH during low temperature stage. Therefore, the chemical effect is much smaller than the dilution effect during low temperature stage when hydrogen is added.

Combustion duration is another parameter that affects the fuel conversion efficiency of an HCCI engine. Figure 5 shows the effect of hydrogen addition on combustion duration at a constant compression ratio of 9.0. Combustion duration is defined as CA_{10-90} , the difference between the two crank angles at which 10% and 90% of total heat release happened, respectively. It is noted that the

model calculation quantitatively underpredicted the measured combustion duration but captured the qualitative variation trend. Both experiment and calculation show that combustion duration decreases slightly when a small amount of hydrogen is added at a constant compression ratio, but then increases when mass fraction of hydrogen is higher.

The results from the above mentioned additional calculation using AH_2 are also shown in Fig. 5. It is noted that combustion duration would have monotonically increased if the added hydrogen is replaced by AH₂ that has the same thermal and transport properties but does not participate in chemical reactions, suggesting that the dilution effect of hydrogen addition monotonically increases combustion duration. Therefore, the slight decrease in combustion duration at a constant compression ratio when a small amount of hydrogen is added is due to the chemical effect of hydrogen addition. This is because the addition of hydrogen intensifies the reactivity of the high temperature combustion stage, which is usually controlled by the chain branching reaction $H + O_2 = O + OH$. As a result, the heat release rate at the high temperature stage is enhanced and combustion duration is reduced when hydrogen is added. However, furthering increasing mass fraction of hydrogen starts to increase the combustion duration. This is due to the fact that the combustion phasing is overly retarded and thus incomplete combustion happens when a large amount of hydrogen is added. It should be pointed out that the chemical effect of hydrogen addition always significantly reduces combustion duration, as shown by the difference from the normal calculation and the additional calculation using AH₂. This suggests that although the retardation of combustion phasing is primarily due to the dilution effect, combustion duration is significantly reduced by the chemical effect when hydrogen is added. This is the difference between the addition of hydrogen and an inert component. The reduced combustion duration due to hydrogen addition may lead to increased heat release around top dead center and thus improve cycle efficiency if reasonable combustion phasing is obtained.

Figure 6 shows the variation of indicated thermal efficiency (η_t) as a function of mass fraction of hydrogen addition at a constant compression ratio of 9.0. The indicated thermal efficiency is defined as

$$\eta_t = \frac{\int p dV}{m_{n-hep \tan e} H_{n-hep \tan e} + m_{H2} H_{H2}} \times 100$$
⁽²⁾

where p is pressure, V is cylinder volume, and H represents the low heating value, with subscripts nheptane and H2 representing n-heptane and hydrogen, respectively. The integration calculation was conducted over the compression and expansion strokes only. It is observed that although the model calculation quantitatively overpredicted the measured indicated thermal efficiency, it qualitatively captured the variation trend. At a constant compression ratio, indicated thermal efficiency first increases and then decreases as mass fraction of hydrogen gradually increases. The indicated thermal efficiency of pure n-heptane HCCI combustion is low due to the overly advanced combustion phasing relative to top dead center, as shown in Fig. 2. When a small amount of hydrogen is added, combustion phasing is retarded to closer to top dead center and combustion duration is reduced, which results in the improved thermal efficiency. However, with further increasing mass fraction of hydrogen, combustion phasing is overly retarded relative to top dead center, which results in a decrease in the indicated thermal efficiency due to incomplete combustion or misfire. Therefore, there is an optimal mass fraction of hydrogen addition at a constant compression ratio and engine operating condition. The quantitative difference between the numerical and experimental results may be caused by the simplifications in the multi-zone model, especially the blowby that was not taken into account in the model.

Figure 7 further displays the effect of hydrogen addition on the indicated thermal efficiency as a function of combustion phasing. The variation of combustion phasing at each hydrogen fraction was obtained by changing compression ratio. It is noted that with increasing hydrogen fraction, the indicated thermal efficiency increases at a fixed combustion phasing, except when combustion phasing is overly advanced. This is because hydrogen addition retards combustion phasing (Fig. 2) and thus a higher compression ratio is used to obtain the same combustion phasing when hydrogen is added. When the combustion phasing is overly advanced relative to top dead center, hydrogen addition slightly decreases the indicated thermal efficiency due to the shortened combustion duration, as shown in Fig. 5, which

results in more heat being released before top dead center and thus lowers the cycle efficiency. Therefore, shortened combustion duration has to be combined with reasonable combustion phasing to help improve engine efficiency.

Figure 7 also shows that at a constant hydrogen fraction, a maximum indicated thermal efficiency is obtained when the combustion phasing is gradually retarded to an optimal value by reducing the compression ratio. When hydrogen fraction is increased, this maximum indicated thermal efficiency also increases and the combustion phasing at which the maximum indicated thermal efficiency happens becomes more retarded. This suggests that an n-heptane fuelled HCCI engine does benefit from hydrogen enrichment in terms of power output and fuel conversion efficiency. Figure 8 illustrates the enhancement of the indicated thermal efficiency, which is defined as the ratio of the maximum indicated thermal efficiency of a hydrogen enriched case to that of the case without hydrogen enrichment. For comparison, the corresponding enhancement of the indicated thermal efficiency for the intake mixture EGR- λ combination of 60%-1.2 is also shown in Fig. 8. Both calculation and experiment show that hydrogen enrichment is more effective for EGR = 0% and λ = 3.5 than for EGR = 60% and λ = 1.2, in terms of the improvement in indicated thermal efficiency. This is due to the fact that the case with intake mixture of EGR = 0% and λ = 3.5 has a more advanced CA50 than the case with intake mixture of EGR = 60% and λ = 1.2 at the same compression ratio. For the former, hydrogen enrichment significantly retards combustion phasing and thus the engine can operate at a much higher compression ratio to reach the optimal combustion phasing, which results in a significant improvement in indicated thermal efficiency. On the other hand, the combustion phasing was closer to top dead center for the intake mixture of EGR = 60% and λ = 1.2 even when hydrogen was not added. Therefore, the addition of hydrogen only slightly retards the combustion phasing and causes less improvement in indicated thermal efficiency for the intake mixture of EGR = 60% and λ = 1.2.

One of the drawbacks of HCCI combustion is higher unburned hydrocarbon emissions. Therefore, it is of great interest to examine the effect of hydrogen enrichment on HC emissions. Figure 9 displays the variation of indicated specific HC emissions (isHC), which are defined as the ratio of emitted HC mass to power output, as a function of mass fraction of hydrogen addition at a constant compression ratio of 9.0. Both model calculation and experiment show that with increasing mass fraction of hydrogen, indicated specific HC emissions first slightly decrease and then increase. When a small amount of hydrogen is added, the decrease in indicated specific HC emissions is desirable but it is not surprising, since the percentage of hydrocarbon fuel (n-heptane) decreases with an increase in hydrogen fraction. With further increasing the fraction of hydrogen addition, indicated specific HC emissions start to increase maybe due to the overly retarded combustion phasing that results in incomplete combustion or misfire, as discussed before.

It is more interesting to examine if hydrogen enrichment affects the normalized HC emissions, defined as the ratio of emitted HC mass to the input n-heptane mass. Figure 9 also displays the variation of the normalized HC emissions as a function of mass fraction of hydrogen addition. We observe that the normalized HC emissions monotonically increase with increasing mass fraction of hydrogen, which is different from what was observed for indicated specific HC emissions. This suggests that hydrogen addition actually increases HC emissions per unit burned n-heptane mass. This result occurs because hydrogen addition slows down the low temperature kinetics of n-heptane and therefore relatively more hydrocarbons are present during high temperature stage, as shown in Fig. 10 where the calculated concentrations of normalized unburned hydrocarbons during high temperature stage is affected by hydrogen due to the competition for some key radicals (OH, H, etc.), which results in the slight increase in unburned hydrocarbon emissions when hydrogen is added.

Figure 11 displays the variations of indicated specific (top) and normalized HC (bottom) emissions as a function of combustion phasing at different mass fractions of hydrogen addition. Both model

calculation and experiment show that indicated specific HC emissions decreases at a constant combustion phasing, although Fig.8 indicates that a large amount hydrogen addition leads to an increase in indicated specific HC emissions at a constant compression ratio. This is because a higher compression ratio is used at a constant combustion phasing when hydrogen is added. However, hydrogen addition slightly increases normalized HC emissions at a constant combustion phasing, although a higher compression ratio is used for the same combustion phasing. Therefore, hydrogen enrichment may not help to reduce the HC emissions per unit burned n-heptane mass.

Figure 12 shows the effect of hydrogen addition on NO_x (NO+NO₂) and N₂O emissions as a function of combustion phasing. Note that only the results for two hydrogen fractions are shown to simplify the graph. N_2O data were not collected in the experiment [22] and therefore only the calculated result is shown. It is noted that by gradually retarding combustion phasing from an advanced crank angle position, both experiment and model calculation show that NO_x emissions decrease at a given hydrogen fraction and hydrogen addition increases NO_x emissions at a constant combustion phasing except when combustion phasing is overly retarded. This is because retarding the combustion phasing reduces the temperature inside cylinder at a given hydrogen fraction and hydrogen addition increases temperature at a constant combustion phasing, as discussed before. However, when the combustion phasing is further overly retarded at a given fraction of hydrogen, the experiment shows a slight increase but the model calculation suggests a monotonic decrease in NO_x emissions. Besides, at this later stage, the experiment shows that hydrogen addition decreases NO_x emissions at a constant combustion phasing while the model calculation shows the opposite trend. Therefore, the model calculation failed to predict the variation trend of NO_x emissions when combustion phasing is overly retarded. It is not clear what caused the slight increase in NO_x emissions at a given fraction of hydrogen when the combustion phasing is overly retarded due to the decrease in compression ratio in the experiment [22], since temperature kept decreasing. Further investigation for this issue is needed in the future.

Being different from the monotonic decrease in the calculated NO_x emissions, Fig. 12 also shows that with gradually retarding combustion phasing, the model calculated summation of NO_x and N₂O emissions first decreases and then slightly increases at a given hydrogen fraction. Since the calculated NO_x emissions monotonically decrease with retarding combustion phasing, this suggests that N₂O emissions slightly increase when combustion phasing is overly retarded at a given fraction of hydrogen. Although the experiment in [22] did not collect N₂O emissions data, an earlier experiment study [29] did show that N₂O emissions increased with overly retarded combustion phasing for an n-heptane fuelled HCCI engine. A further analysis of the details of the calculated data indicates that the slight increase in N₂O emissions with overly retarded combustion phasing at a given fraction of hydrogen is due to the reaction N₂O (+M) <=> N₂ + O (+M), a primary reaction for N₂O formation. When combustion phasing is overly retarded by decreasing compression ratio at a given fraction of hydrogen, the combined effect of lower pressure and temperature inside the cylinder causes this reaction to move backward toward the direction in favour of N₂O formation.

Further, when combustion phasing is overly retarded, the model calculation shows that hydrogen addition reduces the summation of NO_x and N₂O emissions at a constant combustion phasing, suggesting that hydrogen addition reduces N₂O emissions for the cases with overly retarded CA50. This is because hydrogen addition slightly increases cylinder temperature and thus moderates the above mentioned shift of the reaction N₂O (+M) $\leq N_2 + O$ (+M) at a constant combustion phasing. Therefore, hydrogen enrichment may moderate N₂O emissions in an HCCI engine.

4. Conclusions

The effect of hydrogen enrichment on the combustion and emission characteristics of an n-heptane fuelled HCCI engine has been numerically studied at various operating conditions by a multi-zone model using a detailed chemical reaction scheme. The numerical results were compared with previously experimentally measured data. The results show that the calculation reasonably captured most experimentally observed phenomena. The details of numerical results revealed some fundamental mechanisms behind the observed phenomena in hydrogen enriched HCCI combustion.

- (1) Both experiment and calculation show that hydrogen addition retards combustion phasing of an n-heptane fuelled HCCI engine. The analysis of the detailed numerical results indicates that the combustion phasing retardation by hydrogen addition is due to both dilution and chemical effects, with dilution effect being more significant. The dilution effect is caused by reduced n-heptane and oxygen concentrations when hydrogen is added, and the chemical effect is due to the reaction $H_2 + OH = H_2O + H$ that consumes OH and therefore decreases hydrogen abstraction rate from n-heptane during low temperature stage;
- (2) At a constant compression ratio, combustion duration is also reduced if an appropriate amount of hydrogen is added. The numerical result suggests that this reduction of combustion duration is due to the chemical effect that intensifies the reactivity of the high temperature combustion stage;
- (3) When an appropriate amount of hydrogen is added, indicated thermal efficiency increases at a constant compression ratio due to the optimization of combustion phasing. However, unless the combustion phasing is overly advanced, hydrogen addition always improves indicated thermal efficiency at a constant combustion phasing owing to the optimized combustion phasing and the higher compression ratio used;
- (4) Hydrogen addition reduces indicated specific unburned hydrocarbon emissions, but slightly increases unburned hydrocarbon emissions per unit burned n-heptane mass. The numerical simulation suggests that this increase in unburned hydrocarbon emissions per unit burned n-heptane mass is because hydrogen addition slows down the low temperature kinetics of n-heptane and therefore relatively more hydrocarbons are present during high temperature stage. The oxidation of the remaining hydrocarbons during high temperature stage is affected by hydrogen due to the competition for some key radicals and thus relatively more unburned hydrocarbons are emitted;

(5) The numerical simulation result also shows that N₂O emissions may increase with overly retarding combustion phasing at a constant fraction of hydrogen, but hydrogen addition can moderate this increase in N₂O emissions.

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Table Captions:

Table 1 Engine Specifications.

Figure Captions:

Fig. 1 Effect of hydrogen addition on pressure profiles at a constant compression ratio.

Fig. 2 Effect of hydrogen addition on combustion phasing at a constant compression ratio.

Fig. 3 Reaction pathways with and without hydrogen addition during low temperature stage. CR = 9,

EGR = 0%, $\lambda = 3.5$.

Fig. 4 Cumulative heat release for cases with and without hydrogen addition.

Fig. 5 Effect of hydrogen addition on combustion duration at a constant compression ratio.

Fig. 6 Effect of hydrogen addition on indicated thermal efficiency at a constant compression ratio.

Fig. 7 Variation of indicated thermal efficiency as a function of combustion phasing at various hydrogen addition levels.

Fig. 8 Enhancement of indicated thermal efficiency due to hydrogen enrichment.

Fig. 9 Variation of unburned hydrocarbon emissions at a constant compression ratio.

Fig. 10 Variations of normalized total hydrocarbons and mole fraction of hydrogen as a function of crank angle.

Fig. 11 Variations of indicated specific (top) and normalized (bottom) HC emissions as a function of combustion phasing.

Fig. 12 Variation of indicated specific NO_x emissions as a function of combustion phasing.

Supplementary material:

A multi-Zone Model for the Simulation of Homogeneous Charge Compression Ignition Combustion

Cylinder Bore	8.255 cm
Stroke	11.43 cm
Displacement Volume	611.7 cm^3
Connection Road Length	25.4 cm
Compression Ratio	6 ~ 16
Combustion chamber	Pancake shape, flat top piston
Intake valve open	10 °CA ATDC [*]
Intake valve close	34 °CA ABDC
Exhaust valve open	40 °CA BBDC
Exhaust valve close	5 °CA ATDC
Fuel System	Air-assisted port fuel injection

Table 1 Engine Specifications.

*ATDC: after top dead center.



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