Autoignition and Chemical-Kinetic Mechanisms of Homogeneous Charge Compression Ignition Combustion for the Fuels with Various Autoignition Reactivity

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Additional information is available at the end of the chapter

Abstract

This work demonstrates the autoignition and chemical-kinetic mechanisms of homogeneous charge compression ignition (HCCI) combustion for the fuels with various autoignition reactivity. This is done for four fuels: methane, dimethyl ether (DME), iso-octane and n-heptane. Methane and iso-octane are selected as the single-stage ignition fuel, and DME and n-heptane are selected as the two-stage ignition fuel. As a tool for understanding the characteristics of autoignition and combustion process in HCCI engine, a zero-dimensional single-zone engine model of 'CHEMKIN' in Chemkin-Pro was used. The complete compression and expansion strokes were modeled using an engine with a connecting-rod length to crank-radius ratio of 3.5 and a compression ratio of 13. A detailed chemical-kinetic mechanism for methane and DME is Mech_56.54 (113 species and 710 reactions). For iso-octane and n-heptane, a detailed chemical-kinetic mechanism from Lawrence Livermore National Laboratory (1034 species and 4236 reactions) is used. The results show that methane and iso-octane exhibit only the main heat release, 'high-temperature heat release (HTHR)' by high-temperature reactions (HTR). In contrast, both DME and n-heptane exhibit the first heat release 'low-temperature heat release (LTHR)' associated with low-temperature reactions (LTR) before HTHR.

Keywords: homogeneous charge compression ignition, autoignition, chemical-kinetic mechanisms, fuel autoignition reactivity, low-temperature reaction, intermediate-temperature reaction, high-temperature reaction

1. Introduction

1.1. Background

Since their introduction around a century ago, internal combustion engines have played a key role in shaping of the modern world [1]. Because of their simplicity, ruggedness and high power/weight ratio, internal combustion engine has found wide application in transportation [2]. Though there are technologies that could theoretically provide more environmentally sound alternatives, internal combustion engines, such as fuel cells and electric vehicles, practically, cost, efficiency and power density issues, will prevent them displacing internal combustion engines in the near future. However, in recent decades, serious concerns have been raised with regard to the environmental impact of emissions arising from operation of internal combustion engines. Eventually, concerns about climate change lead to ever-stricter fuel-economy legislations [2-4]. In addition, concerns about the world's finite oil reserves result in heavy taxation of road transport, mainly via on duty on fuel [5]. These two factors have led to massive pressure on vehicle manufacturers to research, develop and produce ever cleaner and more fuel-efficient vehicles. Ultimately, all legislations for emissions from vehicles are targeted to improve technologies to the point where an affordable, practical zero emissions vehicle (ZEV) with outstanding performance becomes a reality [6]. Even though there are many types of real ZEVs, operated by fuel cells that consume hydrogen generated from water by electricity produced from renewable sources, it is very unlikely that the resulting vehicles could even come close to meeting any of the other criteria listed above in the short and medium terms [1, 2]. For this reason, the bulk of vehicle research and development resources are still being applied to the internal combustion engines to increase their efficiency.

1.2. Homogeneous charge compression ignition (HCCI) engine

The purpose of internal combustion engines is the production of mechanical power from the chemical energy contained in the fuel. This chemical energy is released by burning or oxidizing the fuel inside the engine. The fuel-air mixture before combustion and burned products after combustion are the actual working fluids. The work transfers, which provide the desired power output, occur directly between these working fluids and the mechanical components of the engine.

As **Figure 1** shows, there are three main types of internal combustion engines:

- Spark ignition (SI) engine

- Compression ignition (CI) engine

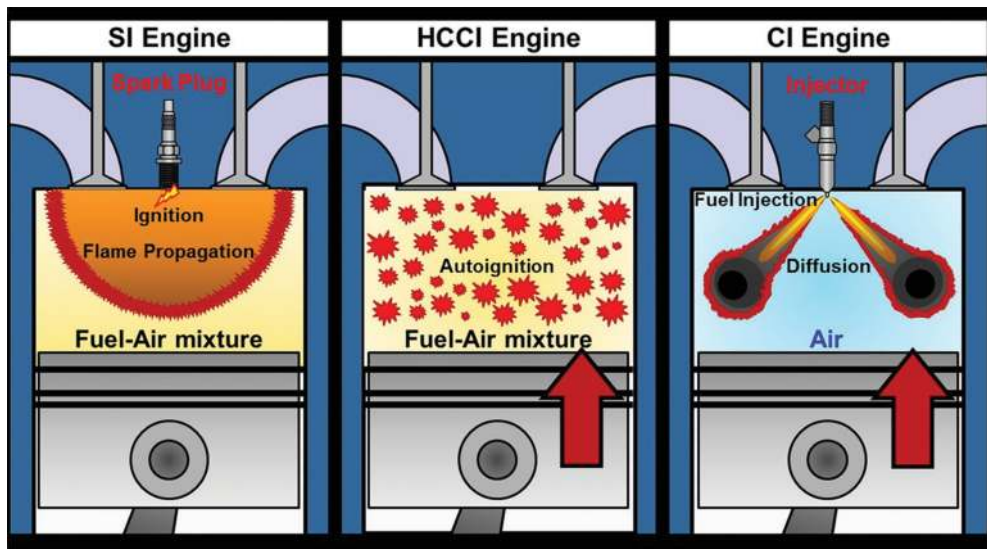- Homogeneous charge compression ignition (HCCI) engine

Figure 1. Illustration of the combustion characteristics for spark ignition (SI) engine (left), compression ignition (CI) engine (right) and homogeneous charge compression ignition (HCCI) engine (middle).

In a SI engine, the fuel and air are mixed together in the intake system, inducted through the intake valve into the cylinder. Then, the fuel-air mixture is compressed towards the end of the compression stroke, and the combustion is initiated by a spark discharge at the spark plug. By spark discharge, an inflammation is occurred, and then a turbulent combustion developed fully through the premixed fuel-air mixture until it reaches the combustion chamber walls, and then extinguishes [7]. For CI engine, fuel is injected by the fuel-injection system in the engine cylinder towards the end of the compression stroke, just before the desired start of combustion. The liquid fuel is usually injected at high velocity through small nozzles in the injector tip, and atomized into small drops while penetrating into the engine in-cylinder. Then, with the high-temperature high-pressure in-cylinder air, the fuel is vaporized and mixed. When the in-cylinder air temperature and pressure are increased above the fuel's ignition point, the ignition of portions of the already-mixed fuel and air occurs spontaneously after a delay period of a few milliseconds. The consequent compression of the unburned portion of the charge shortens the delay before ignition for the fuel and air which has mixed within combustible limits, which then burns rapidly [8]. Fundamentally, the HCCI combustion is a controlled autoignition of the homogeneous mixture through compression by piston [9]. To a degree, the HCCI engine is able to combine the best feature of SI engine and CI engine [10]. Similar to the SI engine, the fuel and air are mixed together and inducted to obtain a homogenous mixture, which can eliminate fuel-rich diffusion combustion, and can thus dramatically reduce the particulate matter (PM) that is the main problem of CI combustion. With the ignition process, similar to that of CI combustion, HCCI combustion is achieved

through the autoignition of the fuel-air homogeneous mixture around the top dead centre (TDC) as it is compressed via the piston, which can lead to very low nitrogen oxides (NO_x) by reducing a high-temperature flames when compared to that of SI combustion. Furthermore, the unthrottled operation of HCCI engines with relatively high compression ratio is possible at a very low fuel/air equivalence ratio (φ) and a high rate of external exhaust gas recirculation (EGR) without misfire, thus yielding a high thermal efficiency with a very low cycle-to-cycle variations of combustion. Therefore, the HCCI combustion is an attractive technology that can ostensibly provide engine efficiencies comparable to that of diesel engine, and engine-out emissions comparable to or less than that of SI engine with a three-way catalyst. These advantages have led to considerable interest in HCCI in recent years and to substantial research efforts aimed at overcoming the technical challenges to its widespread implementation [11]. The technical challenges are briefly summarized as follows:

• Combustion-phasing control

• Excessive heat-release rate (HRR) at high loads

• Narrow operating range

The successful operation of an HCCI engine depends on using mechanical means to control both the autoignition and the combustion processes. The heat-release rate (HRR) from HCCI combustion depends not only on the unique reaction chemistry of the fuel but also on the thermal conditions that the in-cylinder charge mixture goes through during compression by piston. To enable to control the start of combustion as well as the overall combustion rate for HCCI combustion, it is critically important to have a resolute understanding of the interaction between the chemical-kinetic mechanisms of the fuel-air mixture and the history of in-cylinder temperature and pressure during the compression and expansion strokes.

2. Chemical-kinetics modelling setup for numerical calculation

2.1. Zero-dimensional single-zone engine model

A zero-dimensional single-zone engine model (referred to here as 'single-zone model') of CHEMKIN [12] in Chemkin-Pro [13] was used for this work. Using an engine with a connecting-rod length to crank-radius ratio of 3.5 and a compression ratio of 13, the complete compression and expansion strokes (i.e. from compression bottom dead centre (BDC) to expansion BDC) were modeled according to the standard slider-crank relationship [14]. The crevices and boundary layers were not included. The numerical calculations were conducted under following assumptions:

• The in-cylinder charge is treated as a single lumped mass with uniform mixture composition and thermodynamic properties (homogenous in-cylinder charge).

• The in-cylinder charge is compressed and expanded adiabatically (adiabatic change).

• All species present in the in-cylinder charge are considered as the ideal gas (following the ideal gas law).

- The total energy of the in-cylinder charge remains constant (following the first law of thermodynamics).

- For the in-cylinder charge, the total mass of products equal to the total mass of reactants (following the law of conservation of mass).

These are great oversimplification of a real engine in which the fuel-air mixture will never be completely mixed and there will always be residuals from the previous cycle (mixture inhomogeneity). In addition, there are at least four causes for temperature inhomogeneity: (1) heat transfer from the in-cylinder charge to the cylinder wall, (2) presence of hot residuals from the previous cycle as a result of incomplete mixing, (3) dynamic flow effects during the intake stroke and (4) vaporization of the fuel, especially if injected directly into the cylinder. Because both mixture and temperature inhomogeneities for the in-cylinder charge will significantly affect the heat-release rate, the burn duration, the peak in-cylinder charge pressure, the peak combustion temperature and the amount of emissions, the single-zone model cannot accurately predict these values. Nonetheless, the single-zone model can provide useful results in at least two ways. First, the single-zone model has an advantage for predicting the autoignition timing with a reasonable accuracy because the autoignition timing is dominated by the autoignition reactions of the hottest zone in the core of in-cylinder charge. It can be thought as representing the close-to-adiabatic core in the experiment because the single-zone model is adiabatic. This indicates that the changes in the autoignition timing with EGR addition and boosting, and the amount of initial in-cylinder charge temperature at BDC required to compensate for these changes in the autoignition timing are realistic values. Second, the single-zone model is a useful tool for investigating certain fundamental aspects of HCCI combustion, since eliminating the complexities of mixture-temperature inhomogeneities, heat transfer, blow-by, and crevices and boundary layers simplifies the analysis and allows cause-and-effect relationships to be more easily identified. This means that it allows the effects of the bulk-gas (gases not in crevices or boundary layers) chemical-kinetics and thermodynamics to be isolated in order to understand how they alone influence the autoignition and the combustion process.

2.2. Fuel selection

Since HCCI engine has the capability of operating with a variety of fuels, HCCI operation has been demonstrated for various fuels that have autoignition reactivity spanning a wide range. Although each fuel exhibits different autoignition reactivity even for the same experiment conditions, the autoignition characteristics of fuels can be broadly divided into two types: those with single-stage ignition fuel and those with two-stage ignition fuel which exhibits the first heat-release 'low-temperature heat release (LTHR)' associated with cool-flame chemistry before the main heat-release 'HTHR'. Many factors ultimately affect the choice of fuel, but each fuel-type has advantages for HCCI engines, respectively. A brief summary for the advantages of each fuel-type follows:

- Advantages of single-stage ignition fuel for HCCI engine
  - The use of high compressions ratio is allowed, which leads to high thermal efficiency.

- The ignition timing is much less sensitive to changes in speed and load than that of two-stage ignition fuel, which indicates that significantly less compensation will be required to maintain optimal ignition timing over the required load and speed range.

- Advantages of two-stage ignition fuel for HCCI engine

  - Because the amount of LTHR produced by a two-stage ignition fuel increases with the local fuel/air equivalence ratio (φ), fuel stratification can be used for controlling combustion phasing.

  - This local φ-dependence of the LTHR also provides a means for reducing the peak HRR.

For this work, methane and iso-octane are selected as the single-stage ignition fuel, and DME and n-heptane are selected as the two-stage ignition fuel. Methane and DME are classified as a gaseous fuel. On the other hand, iso-octane and n-heptane are classified as a liquid fuel. **Figure 2** presents the chemical formula and the illustration of chemical structure, and **Table 1** lists the properties for these four test fuels [15, 16].

2.3. Chemical-kinetic mechanism for test fuels

An overall reaction includes very complex and sophisticated reactions that cannot be analyzed without a proposed chemical-kinetic mechanism, a series of steps that a reaction takes before reaching the final products. The chemical-kinetic mechanism is step-by-step descriptions of what happens on a molecular level in chemical reactions. Each step of the reaction mechanism for the overall reaction is known an elementary reaction. The term elementary reaction is used to describe a moment in the reaction when one or more molecules change geometry or perturbed by the addition or omission of another interacting molecule. For methane and DME, a detailed chemical-kinetic mechanism (Mech_56.54; 113 species and 710 reactions) by Burke et al. [17] was used, which has been developed to be capable of predicting the combustion of both methane and DME in common combustion environments such as compression ignition engines and gas turbines. For iso-octane and n-heptane, a detailed
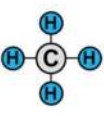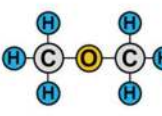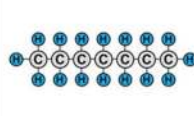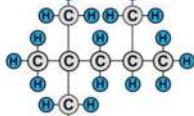
	Methane	DME	n-Heptane	iso-Octane
Chemical formula	CH_4	CH_3OCH_3	C_7H_{16}	C_8H_{18}
H: Hydrogen C: Carbon O: Oxygen				
Mechanism	Mech_56.54 [37]		PRF: iso-Octane/n-Heptane Mixtures [38]	
Species	113		1034	
Reaction	710		4236	

Figure 2. Chemical formula and illustration of chemical structure with reaction mechanism for methane, DME, n-heptane and iso-octane.

Property (unit)	Methane	DME	n-Heptane	iso-Octane
Boiling point (°C)	−161.5	−25.1	98.4	99.2
Liquid density (g/cm³@20°C)	—	0.67	0.68	0.6878
Relative gas density (air = 1)	0.55	1.6	3.46	3.9
Vapor pressure (MPa)	—	0.61@25°C	0.0046@20°C	0.0051@20°C
Ignition temperature (°C)	650	235	285	417
Lower heat value (MJ/kg)	49.0	28.8	44.57	44.31

Table 1. Properties of DME [15], methane [15], n-heptane [16] and iso-octane [16].

chemical-kinetic mechanism from Lawrence Livermore National Laboratory (LLNL; 1034 species and 4236 reactions) [18] was used, which has been developed for the oxidation of primary reference fuels (PRFs), iso-octane and n-heptane, for gasoline. This mechanism was developed by combining the iso-octane [19] and n-heptane [20] mechanisms.

2.4. Comparison of autoignition delay times

Autoignition, the spontaneous ignition of a fuel and oxidizer mixture in the absence of any external ignition source, occurs when slow thermal reactions initially have a large chain branching component sufficiently to maintain and accelerate oxidation. The increasing radical concentration leads to the increase in reaction rate build on themselves, and eventually result in an ignition through a rapid explosive rise in radical concentration, oxidation rate and temperature. Most of these reactions typically release heat, and eventually increasing the temperature and pressure of the system, and at the same time, their rate is also strongly dependent on pressure, temperature and charge composition. These characteristics cause a complicated interaction of negative and positive feedback loops that determine when the ignition will happen. In fact, autoignition is very sensitive to details of chain branching and chain terminating in the initial reactions, and hence depends sensitively on the chemical structure of the fuel.

The autoignition reactivity of the fuel is a very important parameter, impacting the design and the potential high-load performance of HCCI engines. The accurate prediction of autoignition times and their dependence on pressure, temperature and composition is essential for advanced engine technologies, such as HCCI, where the ignition event is timed by chemical kinetics. An autoignition delay time (τ) of fuels is one of the crucial indicators to present the extent of fuel autoignition reactivity for the combustion optimization of internal combustion engines, especially for HCCI engines. The autoignition delay time is defined as the time interval required for the fuel-air mixture to spontaneously ignite at some prescribed conditions. The rapid compression machine (RCM) and shock tube are two of the most widely used facilities for the studies of ignition delay time. RCM gives a direct way of measuring the ignition delay time by simulating the process of adiabatic compression and ignition. While the shock tube is applied to study autoignition characteristics of gas mixtures at a higher temperature and pressure than those of RCM, RCM is used to study the autoignition characteristics of test fuels in the temperature range of low to intermediate, compared with shock tubes. To

understand the reaction activity for the test fuels, the autoignition delay times are exam-
ined by conducting the numerical calculation using 'Closed Homogeneous Batch Reactor' in
CHMEKIN-Pro with the chemical-kinetic mechanisms explained in the section describing the
chemical-kinetic mechanism for test fuels. The initial pressure was set as 3.0 MPa to represent
the maximum in-cylinder pressure for motored operation of engine modeled for this work.
In addition, the initial fuel/air equivalence ratio (ϕ_o) was set as 0.5 since HCCI engines are
generally operated with lean in-cylinder charge mixture. **Figure 3** compares the results of
autoignition delay times between test fuels. As can be observed, methane does not exhibit any
of the low-temperature reaction (LTR) or negative temperature coefficient (NTC) behavior
typical of larger paraffinic fuels such as n-heptane. (The term 'negative temperature coeffi-
cient' is used to denote the temperature regime where the rate of fuel consumption decreases
with increasing temperature, rather than increases as in all other regimes.) This indicates that
methane is very resistant to autoignition and correspondingly has a very high octane number
(=120). In contrast, for DME, the highest fuel autoignition reactivity (i.e. the shortest autoigni-
tion time) is observed until the initial temperature of 1170 K. In addition, DME displays NTC
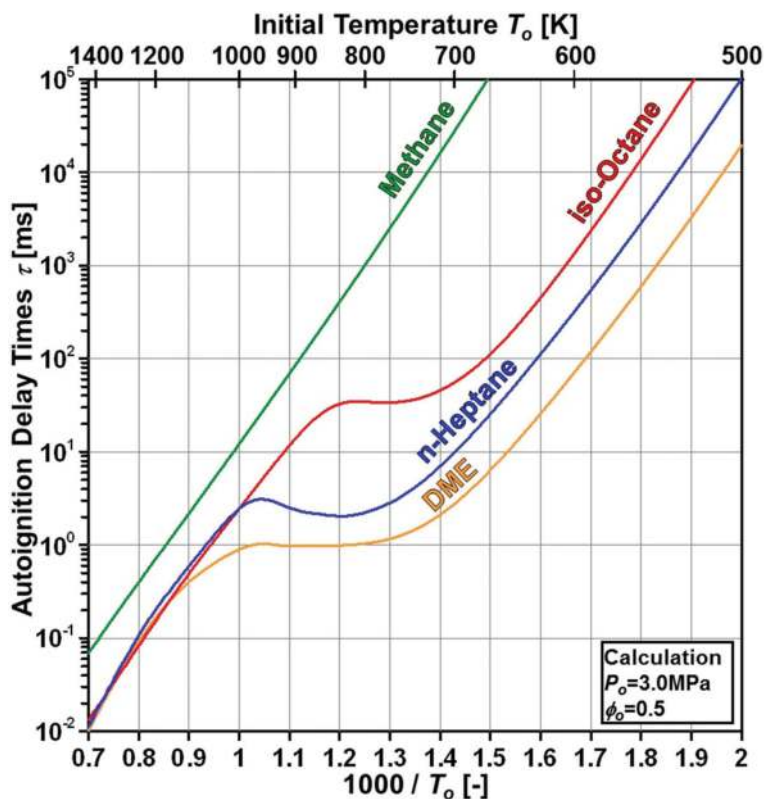

Figure 3. Comparison of autoignition delay times for methane, DME, n-heptane and iso-octane.
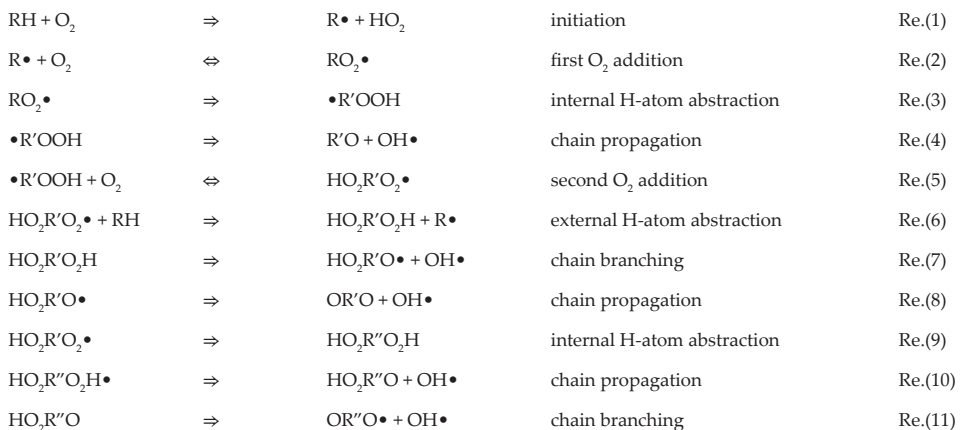
behavior where the autoignition delay times increase with increasing initial temperature. Similar to that of DME, the autoignition delay time for n-heptane also shows NTC behavior with relatively high-fuel autoignition reactivity due to very low octane number (=0). For iso-octane, surprisingly, NTC behavior is observed despite of high octane number (=100) even for relatively longer than autoignition time delay of DME and n-heptane. As shown in Ref. [21], which systematically investigates autoignition properties of iso-octane at conditions relevant to practical combustion devices using RCM, iso-octane can exhibit NTC region under conditions of elevated initial pressure.

3. Chemistry of HCCI combustion

As discussed above, reactants in HCCI combustion begin at room temperature and are steadily heated during the compression stroke by piston. As the reactant temperature increases, the specific elementary reactions that contribute to fuel consumption in general and chain branching and autoignition in particular also change. The reactants pass through three distinct temperature ranges, each with its own unique chain branching reaction pathways that contribute to the eventual autoignition. With reference to **Figure 4** as an example of HCCI combustion, this section explains the chemical reactions that play a role in the process, which are classified as low-temperature reactions (LTR), intermediate-temperature reactions (ITR) and high-temperature reactions (HTR).

3.1. Low-temperature reactions

Virtually, no significant reaction takes place until the reactant temperature reach about 550 K. As the reactant heats up during the compression stroke, chemistry becomes increasingly active at temperatures above 600 K. At these conditions, fuel dissociation is described by the following low-temperature mechanism [22].

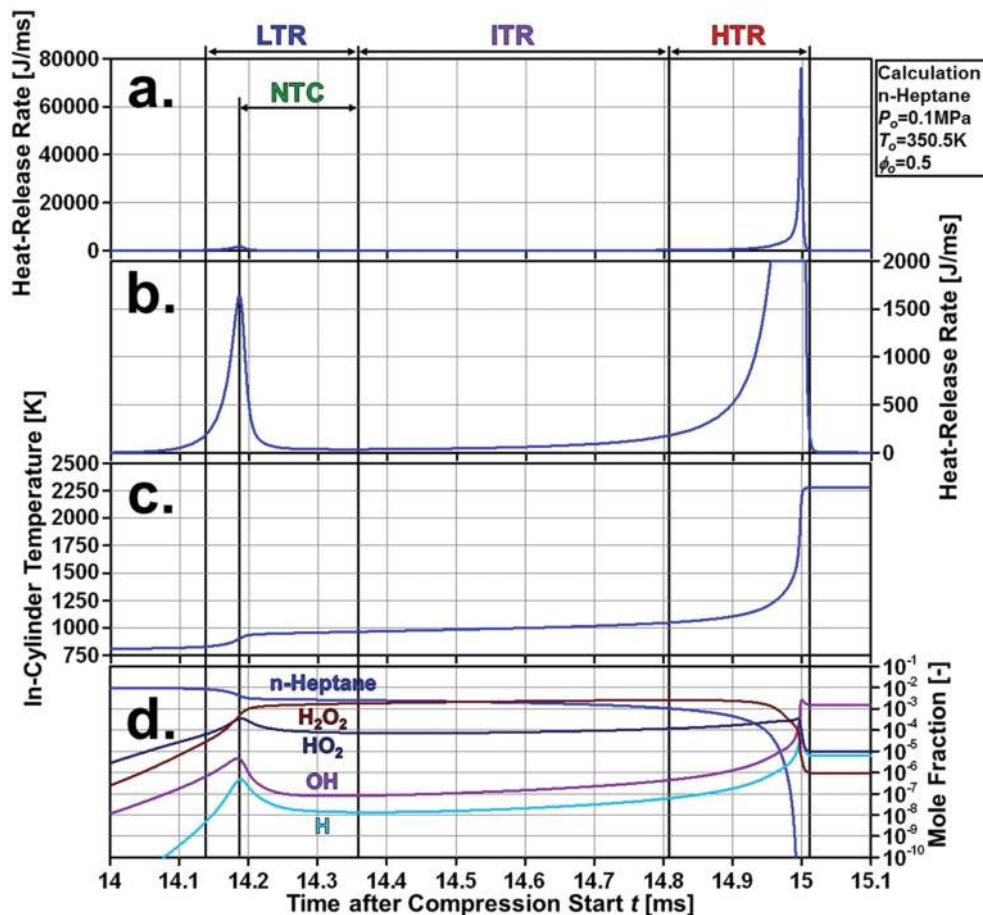|				
$RH + O_2$	$\Rightarrow$	$R\bullet + HO_2$	initiation	Re.(1)
$R\bullet + O_2$	$\Leftrightarrow$	$RO_2\bullet$	first O_2 addition	Re.(2)
$RO_2\bullet$	$\Rightarrow$	$\bullet R'OOH$	internal H-atom abstraction	Re.(3)
$\bullet R'OOH$	$\Rightarrow$	$R'O + OH\bullet$	chain propagation	Re.(4)
$\bullet R'OOH + O_2$	$\Leftrightarrow$	$HO_2R'O_2\bullet$	second O_2 addition	Re.(5)
$HO_2R'O_2\bullet + RH$	$\Rightarrow$	$HO_2R'O_2H + R\bullet$	external H-atom abstraction	Re.(6)
$HO_2R'O_2H$	$\Rightarrow$	$HO_2R'O\bullet + OH\bullet$	chain branching	Re.(7)
$HO_2R'O\bullet$	$\Rightarrow$	$OR'O + OH\bullet$	chain propagation	Re.(8)
$HO_2R'O_2\bullet$	$\Rightarrow$	$HO_2R''O_2H$	internal H-atom abstraction	Re.(9)
$HO_2R''O_2H\bullet$	$\Rightarrow$	$HO_2R''O + OH\bullet$	chain propagation	Re.(10)
$HO_2R''O$	$\Rightarrow$	$OR''O\bullet + OH\bullet$	chain branching	Re.(11)

Figure 4. An example of HCCI combustion for (a) overall heat-release rate, (b) magnified view of heat-release rate, (c) in-cylinder temperature and (d) mole fraction.

In the initiation step, a hydrocarbon (RH) reacts with oxygen (O_2) to make a hydrocarbon radical (R•), which reacts with oxygen to make a peroxy radical (RO_2•). (Radical species are denoted by the '•' symbol next to the character.) Next, an internal hydrogen-atom abstraction takes place (i.e. the abstraction of a hydrogen atom from the molecule itself). Following the internal abstraction, the radical •R'OOH reacts internally to eliminate (eject) OH and forms a compound without free valences (unpaired electrons) such as an aldehyde or ketone (Reaction (4)). The mechanism continues with a second O_2 addition to the peroxy radical initially formed (Reaction (5); [23]). After a few steps, keto-hydroperoxide ($HO_2R''O$) is formed (Reaction (10)). Keto-hydroperoxide decomposes at around 800 K, producing further hydroxyl (OH•) that consumes the fuel (Reaction (11)). In the hydrogen abstraction reaction (Reaction (3)), the molecule isomerizes by 'reaching around' and abstracting a hydrogen

atom from somewhere on the hydrocarbon chain. Straight chain molecules such as n-heptane are long enough for flexible internal abstraction of hydrogen (Reaction (1)). In addition to this, H atoms in n-heptane are bound to 'secondary sites' (the -CH_2- backbone), which makes them easier to abstract H atoms in primary sites, where the hydrogen is attached to the end of a chain (the -CH_3 group). Iso-octane is actually a short pentane chain with three methyl groups attached to the chain. The short chain has difficulty 'reaching around' to abstract a hydrogen atom and furthermore, most of the H atoms in iso-octane are primary, thus harder to abstract. This flexibility and abstraction theory explains the higher reactivity and lower octane number of n-heptane (octane number = 0) with respect to iso-octane (octane number = 100). The theory further explains the high octane number of methane (octane number = 120) where no internal abstraction is possible. The mechanism from Reaction (1) to Reaction (11) listed above also explains the observation of so-called 'two-stage ignition', also called 'negative temperature coefficient (NTC)' zone. At low temperature, the oxygen addition (Reactions (2) and (5)) leads to a product '**P**' that then undergoes reactions that lead to chain branching (Reactions (7) and (11)). These chain branching reactions lead to a rapid increase in the temperature of the mixture. As the temperature increases, the NTC zone is reached where the newly formed product '**P**' can now either continue towards chain branching or decompose beak to the reactants (i.e. reverse reaction, see the bi-directional arrow on Reactions (2) and (5)). The increase in the reverse rate results in a lower concentration of products '**P**' which in turn leads to a reduction of chain branching, causing a reduction in the rate of temperature increase; the ignition delay is prolonged. As a consequence, one observes what is called 'two-stage ignition'. At low temperatures, the reactions are proceeding at a slow, but observable rate. Starting at temperature below the NTC zone, the energy release by these reactions slowly increases the temperature. With this increased temperature, the reaction rates increase, the temperature is increasing faster and faster. This is the 'first stage' of ignition. The temperature increase until the NTC zone is reached. At this temperature, the concentration of '**P**' decreases, and thus the rate of increase in temperature slows down, but is never zero. With time, the slowly increasing temperature reaches a point where low concentration of product '**P**' is more than compensated by the increased chain branching reaction rate and then, the system explodes: this is the 'second stage' of ignition. Surprisingly, if one starts the system in the NTC zone, the concentration of '**P**' is extremely low and the ignition delay can be longer than if one stared the system at a temperature below the NTC zone. This is why it is called 'negative temperature coefficient (NTC)' zone.

3.2. Intermediate-temperature reactions

As the temperature increases above about 850 K, where the equilibria of Reactions (2) and (5) have effectively extinguished the low-temperature chain branching pathways, the next reaction sequences involve consumption of fuel (RH), primarily by hydrogen (H) atom abstraction by OH and hydroperoxyl (HO_2), and the temperature increases gradually, accompanied by a steady increase in the level of hydrogen peroxide (H_2O_2), as shown in **Figure 4d**. This new set of chemical reactions contributing to the increase in the level of H_2O_2 with the increase of temperature is called 'intermediate-temperature reactions (ITR)' and is described by the following main intermediate-temperature mechanism [24].

$H_2O_2 + M + 216kJ$	$\Rightarrow$	$OH + OH + M$	Re.(12)
$OH + CH_2O$	$\Rightarrow$	$HCO + H_2O + 122kJ$	Re.(13)
$HCO + O_2$	$\Rightarrow$	$CO + HO_2 + 138kJ$	Re.(14)
$HO_2 + HO_2$	$\Rightarrow$	$H_2O_2 + O_2 + 168kJ$	Re.(15)

These four reactions, which are also called 'H_2O_2 loop reactions', show similar activation energies and reaction rates. The rate constants of Reactions from (13) to (15) are significantly larger than that of Reaction (12), and their activation energies are very small. These suggest that Reactions from (12) to (15) compose a reaction loop in which the rate-determining process is Reaction (12), as schematically shown in **Figure 5**. On the assumption that 100% of OH, HCO and HO_2 generated by 'H_2O_2 loop reactions' are consumed by the succeeding reactions, the overall reaction is to be Reaction (16).

$2CH_2O + O_2$	$\Rightarrow$	$2H_2O + 2CO + 472kJ$	Re.(16)

This is a reaction to release a considerable amount of heat from CH_2O without consuming H_2O_2. In addition, following reactions support 'H_2O_2 loop reactions' by supplying the key species of formaldehyde, formyl (HCO) and OH.

$C_2H_3 + O_2$	$\Rightarrow$	$CH_2O + HCO + 359kJ$	Re.(17)
$CH_2CHO + O_2$	$\Rightarrow$	$CH_2O + CO + OH + 212kJ$	Re.(18)
$CH_3 + O$	$\Rightarrow$	$CH_2O + H + 293kJ$	Re.(19)

The sub intermediate-temperature mechanism, Reactions from (17) to (20), also participates in the process.

$H + O_2 + M$	$\Rightarrow$	$HO_2 + M + 202kJ$	Re.(20)
$H_2O_2 + OH$	$\Rightarrow$	$H_2O + HO_2 + 130kJ$	Re.(21)
$HO_2 + OH$	$\Rightarrow$	$H_2O + O_2 + 297kJ$	Re.(22)
$HO_2 + CH_2O$	$\Rightarrow$	$H_2O_2 + HCO - 7kJ$	Re.(23)

Reaction (20) enhances 'H_2O_2 loop reactions' by supplying HO_2 using H generated mainly by Reaction (19). In the real process, Reaction (23) and Reactions from (17) to (19) contribute to additional H_2O_2.

3.3. High-temperature reactions

The heat-release rate by intermediate-temperature reactions grows steadily, until at about 1000 K, four important events occur. The H_2O_2, which has been relatively stable due to the strength of its O–O bond and the correspondingly large value of the activation energy of its decomposition reaction, begins to decompose at ever-increasing rates by following reaction.
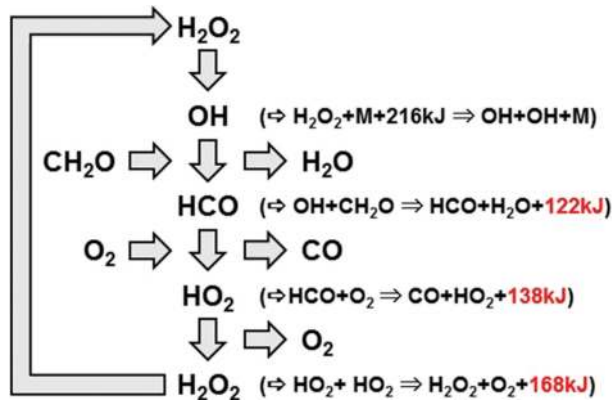
$H_2O_2 + M$	$\Rightarrow$	$OH\bullet + OH\bullet + M$	chain branching	Re.(24)

Figure 5. Schematic of H_2O_2 reaction loop [24].

This decomposition causes the concentration of OH• to grow very quickly. The importance of Reaction (24) is clearly seen in **Figure 4d** for mole fraction, where the concentration of H_2O_2 decreases rapidly during HCCI combustion as OH radicals are being formed, increasing the temperature of the reacting mixture and setting in motion as effective chain branching sequence. As a result, the fuel is very rapidly consumed by reacting with this sudden source of OH•, and the temperature increases very rapidly, due to the production of significant amounts of water by reaction of 'RH + OH ⇒ R• + H_2O', further accelerating the rate of H_2O_2 decomposition. All of these events occurring together create an autoignition event. The Reaction (24) sequence proceeds until the temperature has increased sufficiently that the high-temperature chain branching sequence take over, controlled by H• + O_2 ⇒ O• + OH• which dominates the remainder of the overall HCCI combustion process. The decomposition of H_2O_2 (Reaction (24)) 'triggers' ignition in HCCI combustion. This reaction has a critical temperature for ignition that is also a function of the pressure of the reactive system. H_2O_2 decomposition can be written, ignoring for the moment all other reactions of H_2O_2, by the simple differential equation

$$\frac{d[H_2O_2]}{dt} = -k_5[H_2O_2][M] \tag{1}$$

where M is the molar concentration and k_5 is the rate of Reaction (24). This equation can be rearranged to define a characteristic decomposition time (α).

$$\alpha = [H_2O_2]/(d[H_2O_2]/dt) = 1/(k_5[M]) \tag{2}$$

The rate expression for this reaction is

$$k_5 = 1.2 \times 10^{17} \times \exp(-45500/RT) \tag{3}$$

so the characteristic decomposition time α becomes

$$\alpha \;=\; 8.3 \times 10^{-18} \times \exp\left(+22750/T\right) \times [M]^{-1} \tag{4}$$

As the temperature increases, τ becomes smaller and also decreases with increasing total concentration $[M]$ or, equivalently, with increasing pressure at constant temperature. This also means that, as pressure increases, the critical temperature for ignition decreases gradually. Usually, the autoignition occurs at temperature between 1050 and 1100 K. The consistency of this temperature is a recognized feature of HCCI combustion. Not surprisingly, this temperature is comparable to the ignition temperature that is observed during engine knock in SI engines [25].

4. Comparison of combustion characteristic between test fuels in HCCI engine

This section will compare the combustion characteristics of the test fuels in HCCI engine. As discussed in conjunction with **Figure 3**, each respective test fuel shows different autoignition delay times even for the same initial condition due to its fuel autoignition reactivity. Because of this, we should expect quiet different combustion phasing for each fuel depending on the resistance to autoignition under the constant initial condition. The combustion phasing is a critical parameter impacting the thermal efficiency of HCCI engine. If the combustion is too advanced, knocking combustion occurs easily, thus quickly increasing to the risk for engine damage and NO_x emissions. On the other hand, excessive combustion-phasing retard leads to unacceptable coefficient of variation (COV) of HCCI combustion with partial-burn and/or misfire cycles. To facilitate comparison of the combustion characteristics in HCCI engine, the initial temperature is adjusted in the numerical simulation to set the 50% burn point (CA50) at 0degATDC (i.e. TDC). Effectively, the reported combustion phasing refers to CA50 for the main combustion event, starting at the crank angle of minimum heat-release rate between LTHR and HTHR. Presenting the data referring to the main combustion event alone is considered more relevant from the standpoint of quantifying the onset of the main combustion event.

With the effects of fuel autoignition reactivity isolated, **Figure 6** compares (a) in-cylinder temperature, (b) heat-release rate, (c) magnified view of heat-release rate and (d) accumulated heat release for the test fuels. The required initial temperature (T_o) to maintain CA50 = 0degATDC is 559.5, 301.5, 464.d and 350.5 K for methane, DME, iso-octane and n-heptane, respectively. If the fuel has high resistance to autoignition (i.e. methane and iso-octane), high in-cylinder charge temperature is required during the compression stroke in order to ensure autoignition. As can be seen, methane and iso-octane both require relatively high T_o, which typically has a negative influence on the peak load that can be obtained. This happens because these two fuels exhibit single-stage ignition at this calculation condition. For a given initial pressure (P_o), higher T_o causes high peak combustion temperature, as shown in **Figure 6a**, so excessive NO_x can become the load-limiting factor. Furthermore, as **Figure 6b** shows, the increase of peak combustion temperature contributes to the increase
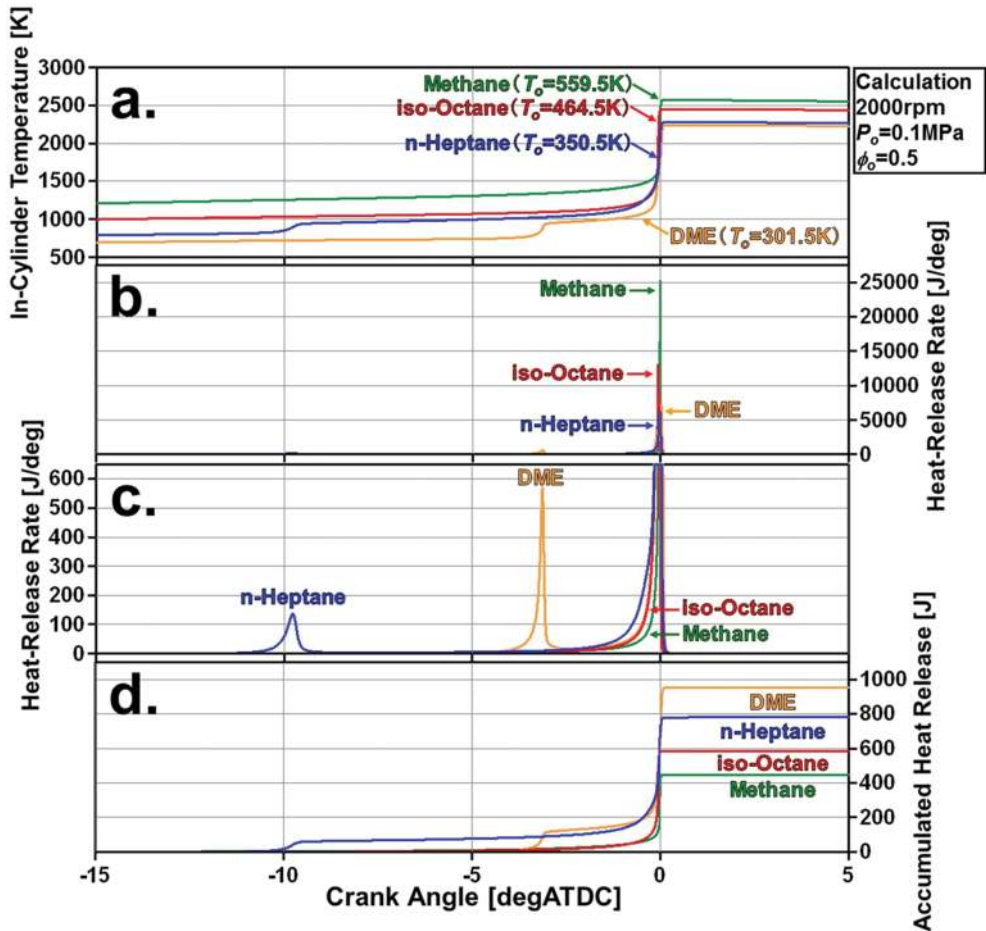
Figure 6. Comparison of (a) in-cylinder temperature, (b) heat-release rate, (c) magnified view of heat-release rate and (d) accumulated heat release for methane, DME, iso-octane and n-heptane.

of maximum heat-release rate. In addition, the higher T_o leads to lower in-cylinder charge density and thus the smaller amount of fuel when φ_o is constant. This can be explained by the data in **Figure 6d** for the accumulated heat release, which shows the lower accumulated heat release for the higher T_o. DME shows the highest accumulated heat release and methane the lowest. This is an important aspect that potentially can help to increase the higher power output. On the other hand, DME and n-heptane exhibit two-stage ignition with LTHR for this calculation condition, as shown in **Figure 6c**. The more advanced onset of LTHR than that of DME results from the higher T_o. As **Figure 6a** shows, the LTHR accelerates the temperature rise towards the end of the compression stoke. Therefore, T_o has to be reduced to achieve the same CA50.

5. Summary

HCCI is an alternative engine combustion process with potential for efficiencies as high as compression ignition (CI) engines while producing ultra-low particulate matter (PM) and nitrogen oxides (NO_x) emissions. HCCI engines operate on the principle of having a dilute premixed charge as like SI engines, which reacts and combusts throughout the in-cylinder as it is compressed by the piston. As stated above, HCCI incorporates the best features of both SI and CI engines. As like in SI engines, the charge is well mixed, which minimizes particulate emissions, and as like in CI engines, the in-cylinder charge is compression ignited by piston without the throttling losses, which leads to high thermal efficiency. Experiments and analysis to date suggest that chemical kinetics dominates thermal autoignition in HCCI. Detailed chemical-kinetics approaches have the advantage of directly simulating all the chemical processes leading to autoignition in HCCI engine. Detailed chemical-kinetic mechanisms have been developed for a wide variety of fuels, including methane, dimethyl ether (DME), iso-octane, n-heptane and many others. These mechanisms capture reaction rate information for elementary reaction steps. In other words, they capture the collisions that convert on molecule to another. The advantage of detailed chemical kinetics is that the processes leading to ignition are directly modeled and processes such as low-temperature reactions (LTR), intermediate-temperature reactions (ITR) and high-temperature reactions (HTR) can be solved. Numerical calculations for HCCI are often conducted with lumped (single-zone model) chemical-kinetics models, which assume spatially uniform temperature, pressure and composition in a fixed-mass, variable volume reactor. For this chapter, a zero-dimensional single-zone engine model of 'CHEMKIN' in Chemkin-Pro is applied to investigating the autoignition and chemical-kinetic mechanisms of HCCI combustion for the fuels with various autoignition reactivity. This is done for four fuels: methane, dimethyl ether (DME), iso-octane and n-heptane. Methane and iso-octane are selected as the single-stage ignition fuel, and DME and n-heptane are selected as the two-stage ignition fuel. A detailed chemical-kinetic mechanism for methane and DME is Mech_56.54 (113 species and 710 reactions). For iso-octane and n-heptane, a detailed chemical-kinetic mechanism from Lawrence Livermore National Laboratory (1034 species and 4236 reactions) is used. The results show that methane and iso-octane only exhibit the main heat release, 'high-temperature heat release (HTHR)' by HTR. In contrast, both DME and n-heptane exhibit the first heat-release 'low-temperature heat release (LTHR)' associated with LTR before HTHR. Because the LTHR accelerates the temperature rise towards the end of the compression stroke, the initial temperature has to be reduced to achieve the same combustion phasing. For a given initial pressure, a lower initial temperature leads to higher charge density and thus the higher amount of fuel when φ_o is constant. Eventually, the higher amount of fuel is advantageous for increasing the power output of HCCI engines.

Abbreviations and nomenclature

BDC   Bottom dead centre

CAI   Controlled auto ignition

CI   Compression ignition

CO	Carbon monoxide
COV	Coefficient of variation
DME	Di-methyl ether
EGR	Exhaust gas recirculation
HC	Hydrocarbon
HCCI	Homogeneous charge compression ignition
HRR	Heat-release rate
HTHR	High-temperature heat release
HTR	High-temperature reaction
ITR	Intermediate-temperature reaction
LTHR	Low-temperature heat release
LTR	Low-temperature reaction
NO$_x$	Nitrogen oxides
NTC	Negative temperature coefficient
PM	Particulate matter
RCM	Rapid compression machine
PRF	Primary reference fuel
SI	Spark ignition
TDC	Top dead centre
ZEV	Zero emissions vehicle
CA50	50% Burn point
To	Initial temperature
Po	Initial pressure
φ	Fuel/air equivalence ratio
φo	Initial fuel/air equivalence ratio
α	Characterisitic decomposition time
τ	Ignition delay time

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