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Ignition delay times measurement and kinetic modeling studies of 1-heptene, 2-heptene and n-heptane at low to intermediate temperatures by using a rapid compression machine

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ABSTRACT

In this work, we have firstly investigated the auto-ignition behaviors of 1-heptene, 2-heptene and *n*-heptane in the low to intermediate temperature range (650–950 K) over various equivalence ratios at 15 and 23 bar using a rapid compression machine. Results show that n-heptane exhibits the expected negative temperature coefficient (NTC) behavior and shows the shortest IDTs among the three fuels, while the NTC behavior for 1-heptene and 2-heptene is moderated and quasi-Arrhenius temperature dependence of the 1st stage IDTs is observed at all test conditions. As the temperature increased over 900 K, the IDTs of the three fuels begin to be consistent indicating a moderated effect of the unsaturated bond. In the NTC temperature region, 1-heptene shows higher reactivity than 2-heptene, while opposite relative reactivity is observed in the temperature beyond the NTC region. The IDT data of 1-heptene, 2-heptene and n-heptane were then used to validate several kinetic models. Results show that the performance of the *n*-heptane models is generally good, while all the models underestimate the low temperature reactivity of 1-heptene. Finally, a model refinement has been made and the prediction shows better agreement with the present measured IDT as well as the experimental pressure evolution trace in literature.

1. Introduction

Advanced engine techniques, such as the low temperature combustion (LTC) [1], homogeneous charge compression ignition (HCCI) [2], high boost and dual fuel combustion [3], have been strongly motivated in increasing the fuel efficiency as well as reducing the emissions. The development of these techniques relies more and more on combustion simulation in the confined chamber over wide range of thermal and mixture condition. Though coupling of computational fluid mechanics and combustion chemistry for engine combustion simulation challenges the cost of computation, there is a growing interest in pursuit of more accurate combustion chemistry for either fossil or bio-fuels due to the rapid increase of computer power. However, because of the complexity of the practical engine fuel composition, a complete description of combustion chemistry for practical engine fuels is still beyond the present computational capability and the current understanding on combustion chemistry. As a consequence, the surrogates with representative functional groups for fossil fuels or biofuels are typically selected for approximation.

Over the years, alkanes, aromatics and esters have been respectively selected as the major component in surrogate formulation such as primary reference fuel (PRF) [4–11], toluene reference fuel (TRF) [12–14] and biodiesel [15,16]. Their combustion parameters and oxidation kinetics over wide range of pressure and temperature conditions have been the objectives of extensive literatures, as reviewed in [17–19]. Recently, there has been a growing interest to understand the oxidation of alkenes (with double bond in molecular structures) through both experimental and kinetic modeling studies. The reason is that firstly, alkenes are important component in gasoline (up to 20%) and the presence of double bonds in their chemical structure significantly increases the octane number and also sooting tendency, compared to the alkanes with the same carbon number. As such alkenes have been included in recently reported gasoline surrogate formulation [4,5,20]. In addition, biodiesel, the composition of which is characterized by the long chain unsaturated fatty acid methyl esters (FAME) have been emerging because of their potential for carbon mitigation. For reliable combustion behavior prediction of biodiesel, it is crucial to understand the oxidation kinetics of long carbon alkenes because they are representative of alkenyl side chains of the FAMEs [15,21].

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Further, alkenes are important intermediate species in the oxidation of alkanes [7,22], cycloalkanes [23] and biodiesel [24]. Thus the oxidation kinetics of alkenes are important for combustion behaviors prediction, and a complete oxidation scheme of alkenes not only favor our understanding on the double bond kinetics, but also shed light on the combustion chemistry of various fuels.

Extensive works on the low temperature oxidation of C5 and C6 alkenes have been recently studied [4,25–31]. Specifically, Minetti [27] compared the low temperature (600-900 K) oxidation of n-pentane and 1-pentene by using a rapid compression machine (RCM). They showed that both n-pentane and 1-pentene exhibit a two stage ignition behavior with a similar lower core gas cool flame temperature (~700 K) at which ignition takes place. However, the 1-pentene shows a significantly weaker first stage ignition with 5 times longer first stage ignition delay time, compared to n-pentane and they ascribed this weaker first stage ignition of 1-pentene to the competition between the restricted peroxidation channels with the radical addition to the double bond. Vanhove et al. [25] investigated the influence of the double bond position by comparing the low temperature (630–850 K) ignition delay times of stoichiometric 1-hexene, 2-hexene, and 3-hexene/ air mixture in a rapid compression machine. They showed that 1-hexene shows a similar two stage ignition behavior with n-pentane while this similarity is absent for 3-hexene because the double bond position influences the result of the competition between the alkyl chain chemistry and the double bond chemistry. Touchard et al. [26] adopted EXGAS system and automatically generated an oxidation kinetic mechanism of 1-pentene and 1-hexene. Their model predicted ignition delay times of 1-hexene agree well with experimental data of Vanhove et al. [25]. However, it yields a discrepancy up to a factor of 4 when compared with the low temperature (600–900 K) ignition delay time data of 1-pentene [27]. They suspected that this disagreement was caused by the experimental uncertainty due to temperature inhomogeneity in the RCM in [27]. A detailed kinetic model for the 1-hexene isomers was generated, also using system EXGAS by Bounaceur and co-workers [30]. The model reproduces the reduced low temperature reactivity when going from 1- to 3-hexene that was experimentally demonstrated through the RCM ignition data by Vanhove et al. [25]. Mehl et al. [29] also developed an oxidation kinetic model for n-hexene isomers and it shows a generally good agreement with limited experimental data in the shock tube, rapid compression machine and jet stirred reactor and they outlined the significant value of the experimental data for gaining a better comprehension of the fundamental mechanism underlying oxidation processes of n-alkenes. They subsequently updated their model by refining the rate constants of abstraction, radical decomposition and internal isomerization, and initiation reactions [4]. The position of the double bond proved to be the determining factor for the reactivity of the different isomers not just in the low temperature region, but also at high temperature. Frédérique Battin-Leclerc et al. [32] studied the three isomers of hexene in a jet-stirred reactor in temperature ranging from 500 to 1000 K, which covers the negative temperature coefficient zone. The relative reactivity among the three fuels varies in different temperature range and this behavior was attributed to the double bond influence on the reaction kinetics. More recently, Meng and co-workers [28] re-visited 1-hexene low-temperature oxidation. By updating rate coefficients of relevant elementary reactions, the new model yields satisfactory level of agreement with most of the newly collected experimental data.

For even larger alkenes, heptene for instance (C7 alkene), however, very limited investigations have been conducted for the low temperature chemistry. Tanaka et al. [33] measured the ignition delay times of 1-heptene, 2-heptene and 3-heptene in a rapid compression machine at 41.6 bar, 827 K and equivalence ratio of 0.4 in air. The pressure trace of 1-heptene and 2-heptene showed obvious two-stage ignition behavior while 3-heptene did not. However, no oxidation model was attempted. Bounaceur et al. [30] attempted to model the oxidation of the linear heptene isomers by using the EXGAS system and the data of Tanaka et al [33] was then used for validation. Meng et al. [34] conducted the experimental study of the oxidation of 1-octene in jet-stirred reactor for temperatures from 500 to 1000 K and developed a new detailed model for 1-octene oxidation following the same rules as in a modeling work of 1-hexene [28].

The objectives of this work are the following, concerning that the low temperature ignition delay time measured by Tanaka et al. [33] at a single physical condition (41.6 bar and 827 K) for a single mixture condition (ϕ= 0.4 dilution in air) is the only literature reported data for C7 alkenes, we will firstly provide ignition delay data for 1-heptene over the temperature range from 650 to 950 K for two pressures and different mixture conditions by using a well validated rapid compression machine. In addition, because several works have investigated the double bond position influence on the overall reactivity at low temperature for C6 alkenes, we will then collect and compare the ignition data for 2-heptene (trans-2-heptene) and n-heptane with 1-heptene to access if the reported double bond influence for lower alkene is still valid for C7 alkenes. Finally, because Bounaceur's model [30] has been validated only against the single point ignition delay time data of Tanaka et al. [33], they have concluded the complexity of the modeling of the oxidation of alkenes and the need of further investigations concerning the rate coefficients of the involved elementary reactions, especially for larger alkenes. Our third objective is then to validate their model against our newly measured low temperature ignition delay times data and make possible refinements on the low temperature oxidation channels.

2. Methodology

The ignition delay times (IDTs) of 1-heptene (ACROS, 98%), 2-heptene (TCI, 98%) and n-heptane (Energy Chemical, 99%) were collected using the Tsinghua University rapid compression machine (TU-RCM). Details of the experiments can be found in Refs. [35,36]. Briefly, the RCM contains five sections: the high pressure air tank, the drive section, the hydraulic section, the driven section, and the reaction section. A creviced piston is employed to ensure the temperature homogeneity in the reaction section. The length of the reaction section is adjustable to realize different compression ratios. The gas mixture is prepared in a stainless steel tank according to the partial pressure of each component for the desired mixture. The partial pressure of each component is kept below 1/3 of its saturated vapor pressure to avoid fuel condensation effect. The effective pressure and temperature after end of compression as adopted in our previous work [35,36] is used as the physical condition for ignition delay time determination. The effective pressure is defined as the integral average of the end-of-compression pressure and the lowest pressure due to heat loss before ignition $\mathrm{P_{eff}}=\frac{1}{(\mathrm{t_{P_{min}}}-\mathrm{t_{P_{max}}})}\int_{\mathrm{t_{P_{max}}}}^{\mathrm{t_{P_{min}}}}\mathrm{P\,dt}$, and the effective temperature is calculated accordingly using isentropic compression integral $\int_{\mathrm{T_0}}^{\mathrm{T_{eff}}}\frac{\gamma}{\gamma-1}\mathrm{d\ lnT}=\ln(\frac{\mathrm{P_{eff}}}{\mathrm{P_0}})$, where T_0 is the initial temperature, P_0 is the initial pressure, γ is the temperature-dependent specific heat ratio of the gas mixture. The thermodynamic data used to calculate γ is adopted from the n-heptane model of Zhang et al. [7] which has been updated based on the group additivity method proposed by Benson [37]. Figure 1 shows the typical pressure evolution histories for the three fuels studied in this work. The end of compression is selected as time zero. An obvious two stage ignition behavior was observed for n-heptane, as represented by twice rises of pressure after the end of compression. The ignition delay times are determined from the pressure histories and the first stage (1st)