DNSs of the Ignition of a Lean \( n \)-Heptane/Air Mixture under SCCI Conditions: Chemical Aspects

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1 Introduction

In the first part-parametric study of the present study, the effects of different mean temperature, \( T_0 \), within and outside the negative temperature (NTC) regime together with both thermal and equivalence ratio stratification on the ignition of \( n \)-heptane/air mixture under homogeneous-charge compression ignition (HCCI) conditions were investigated [1]. For the details of twenty-three DNS cases, readers are referred to the part I of the present study [1].

In this second part of the present study, the chemical aspects of thermally- and/or compositionally-stratified \( n \)-heptane/air mixture are examined by analyzing the available data to obtain the insight of the ignition process in HCCI combustion. Based on the temporal evolution of important species and the overall reaction pathways of \( n \)-heptane oxidation mechanism, the effects of \( T_0 \), \( T' \) and \( \phi' \) on the ignition characteristics of HCI combustion are further elucidated. Chemical explosive mode analysis (CEMA) is adopted to understand the spatial ignition characteristics of the lean \( n \)-heptane/air mixture by identifying controlling species and elementary reactions at different locations and times. CEMA has been applied to various DNS problems such as turbulent lifted jet flames in heated coflows, turbulent reacting jet flames in cross flows, and ignition of hydrocarbon fuel/air mixtures under HCCI conditions [2-8]. From these studies, CEMA has been proved as a reliable computational flame diagnostics tool to systematically detect important species and reactions for premixed flames and limited phenomena including ignition and extinction.

2 Results and Discussions

2.1 Characteristics of temporal species evolution

The overall reaction pathways of \( n \)-heptane oxidation relevant to HCCI combustion are discussed. As shown in Fig. 1, the low-temperature chemistry (LTC) of \( n \)-heptane oxidation is first initiated by the H-atom abstraction from a fuel molecule, RH, reacting with molecular oxygen (RH + O\(_2\) \( \rightarrow \) R + HO\(_2\)). As such, HO\(_2\) increases significantly as a result of rapid \( n \)-heptane decomposition during the first-stage ignition. Alkyl radical, R, then reacts with O\(_2\) to produce alkylperoxy radical, RO\(_2\), via R + O\(_2\) + M \( \rightarrow \) RO\(_2\) + M. The rate of addition of O\(_2\) to alkyl radical and its equilibrium depend strongly on pressure, temperature, and equivalence ratio and hence, the temperature threshold for separating the low- and high-temp-

![Fig. 1 Schematic of reaction pathways of n-heptane oxidation at different temperatures](image-url)
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At low temperature, reaction path varies depending on specific conditions. Next, RO2 radical isomerization occurs to form hydroperoxyalkyl, QOOH, (RO2 → QOOH) followed by another O2 addition (QOOH + O2 → O2QOOH). The overall rate of the LTC is primarily controlled by the rate of chain branching reactions through the production and decomposition of keto-hydroperoxide, KOOH; i.e., O2QOOH → KOOH + OH and KOOH → OH + KO.

The low-temperature reaction cycle is suppressed when temperature exceeds a critical value at which the competing reaction (R + O2 → olefin + HO2) terminates the first-stage ignition. Between the first- and second-stage ignitions, the intermediate-temperature chemistry (ITC), which is actually the combination of the low- and high-temperature chemistries, dominates the ignition of n-heptane/air mixture; alkyl radical and hydroperoxyalkyl species convert into the other fuel species (e.g., cyclic ether species, olefins, and ketens) plus OH and HO2. In this period, the rate of temperature increase is significantly reduced due to a lower reactivity of the system. Over a certain temperature threshold, the chain branching reaction of hydrogen peroxide (H2O2 + M → OH + OH + M) becomes highly reactive, resulting in large enough temperature increase to initiate the chain branching reactions at high temperatures, controlled by H + O2 → O + OH. At this point, the high-temperature chemistry becomes predominant over the LTC and the second-stage ignition starts to occur. The high-temperature chemistry (HTC) of n-heptane oxidation can be simply understood as a process of sequential decomposition of large fuel species to small radicals, down to CH2O, CHO, H2O2, HO2, and CO. At the final stage of the ignition, therefore, reaction pathways involve the core of H2/CO oxidation mechanism.

Based on the above discussion, the temporal evolution of the mean mass fraction of important species (e.g., n-C7H16, HO2, H2O2, OH, CO, and CO2) and the mean HRR is shown in Figs. 2-4. Three distinct behaviors of the species are readily observed from the figures depending on T0.

![Figure 2. Temporal evolutions of the mean mass fractions of important species and mean HRR at T0 = 805 K](image-url)
Figure 3. Temporal evolutions of the mean mass fractions of important species and mean HRR at $T_0 = 933$ K

First, for Cases 4 and 11, almost all $n$-heptane is rapidly consumed by the LTC (RH + O$_2$ → R + HO$_2$) and as such, HO$_2$ mass fraction increases significantly and has its first peak during the first-stage ignition, which is similar to their corresponding 0-D case with $T_0 = 805$ K. Since $T'$ for Cases 4 and 11 are relatively small compared to those of other cases (Cases 2, 14, and 21), the overall combustion proceeds similarly to their corresponding 0-D ignition during the first-stage of ignition; however, for Cases 2, 14,
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and 21 with relatively large $T'$, the wide span of the first-stage ignition delay in the initial mixture results in the gradual reduction of \textit{n}-heptane and increment of HO$_2$, which is manifested in the relatively-small and temporally-distributed HRR during the early stage of the ignition (see Figs. 4a and 6a). In either case, however, the temporal spread of HRR (Cases 2, 4, and 21) during the second-stage ignition is manifested in a gradual increase of OH and decrease of H$_2$O$_2$ as HTC dominates the overall combustion, implying that the overall combustion occurs not only by the spontaneous auto-ignition mode but also by the deflagration mode of combustion.

Second, for cases with $T_0 = 933$ K, only a small fraction of \textit{n}-heptane is rapidly consumed during the first-stage ignition and then, it decreases linearly until the end of combustion. Since the HRR from the first-stage ignition at $T_0 = 933$ K is much smaller than at $T_0 = 805$ K, the consumption of \textit{n}-heptane for cases with $T_0 = 933$ K during the first-stage ignition becomes smaller compared to cases with $T_0 = 833$ K. For all cases with $T_0 = 933$ K, HO$_2$ has two peaks at the first- and second-stage ignition; the first peak occurs through RH + O$_2$ $\rightarrow$ R + HO$_2$ and the second is attributed to the accumulation of HO$_2$ via R + O$_2$ $\rightarrow$ olefin + HO$_2$ of ITC. Similar to cases with $T_0 = 833$ K, the temporal distribution of the mean HRR during the second-stage ignition is manifested in the progressive increment of OH and reduction of H$_2$O$_2$.

Third, for cases with $T_0 = 1025$ K, \textit{n}-heptane is first gradually consumed and then, the consumption rate keeps increasing till the end of the overall combustion. At high $T_0$ of 1025 K, there is no first-stage ignition and the intermediate-to-high temperature chemistries govern the ignition such that the consumption of \textit{n}-heptane and accumulation of HO$_2$ occurs gradually through the ITC as shown in Fig. 12.

2.2 Chemical explosive mode analysis

The key features of CEMA are (1) CEM is an intrinsic chemical feature of ignitable mixtures, Re($\lambda_e$) > 0 indicates the propensity of the local mixture auto-ignited; (2) mixture with $Da_c$ greater than, equivalent to, and much less than unity respectively indicates reaction dominates over diffusion, reaction balancing mixing, and strongly burning flames; (3) the explosive index (EI) and participation index (PI) can use to identify critical species and reactions, respectively during the ignition. Details of CEMA formation can be found in [2-3]. Figure 5 shows the isocontours of HRR, temperature, $Y_{n-c7Hl6}$, the log-scale of Re($\lambda_e$), and the EI values of important species which exhibit relatively-large EI values for Case 16 at $t/\tau^{+} = 0.67$. Two points are to be noted from the figure.

First, it is readily observed from Figs. 16a-d that mixture with Re($\lambda_e$) < 0 is already burned while the ignition of mixture with Re($\lambda_e$) > 0 is still underway. In between the two distinct regions, there exist thin deflagrations with large HRR and $Da_c \sim O(1)$. Second, temperature, \textit{n}-heptane, and H$_2$O$_2$ are the main species that render the mixture to be explosive in the unburnt region. More specifically, temperature and \textit{n}-heptane are the main source of the CEM at relatively-low temperature region ($T \sim 1000$ K) while H$_2$O$_2$ becomes important for the ignition of unburnt mixture at relatively-high temperature region ($T \sim 1100$ K). This is because fuel decomposition still occurs at the relatively-low temperature region with large fuel concentration. At $T \sim 1100$ K, however, the chain-branching reaction of H$_2$O$_2$ becomes highly reactive, which subsequently results in initiating high temperature chemistry. CO and OH are also found to be the most important species in the burnt region, in which the HTC remains controlling the combustion process. From 1-D profiles of key species and their EI values (not shown here), from upstream to downstream through deflagrations, EI(CO) increases nearly up to unity while EI(T) and EI(H$_2$O$_2$) vanish rapidly, which is consistent with the characteristics of \textit{n}-heptane oxidation observed in freely-propagating premixed flames and auto-ignition.
Figure 5. Isocontours of (a) HRR, (b) temperature, (c) Y_{C7H16}, (d) sign(Re(\lambda e))\times\log(1 + |Re(\lambda e)|), and EIs for Case 16 at t/\tau = 0.67. The white solid line represents \( Da_\alpha = 1.0 \).

Figure 6. Isocontours of PIs of controlling reactions for Case 16.

To further identify critical reactions involving the important EI species, the isocontours of PI values of important reactions with large PI values are shown in Fig. 6. Note that Fig. 6f shows the cumulative PI value of R293–R300 through which fuel converts into various isomers of alkyl radical: \( RH + (OH, HO_2) \rightarrow R + (H_2O, H_2O_2) \). It is generally believed that \( CO + OH \rightarrow CO_2 + H (R7) \) and \( H + O_2 \rightarrow O + OH (R8) \) are the two most important reactions in a hydrocarbon/air combustion process regardless of specific fuel type. In the present study, both reactions are also found to be important to the CEM especially across the deflagrations. This is primarily because R7 is the main conversion path of CO to CO2 and R8 is the most important chain-branching reaction at high temperature. In addition, \( HO_2 \) formation reaction, \( H + O_2 + M \rightarrow HO_2 + M (R24) \), is also found to be important at the deflagrations because it is one of the most exothermic reactions in hydrogen/air premixed flames.

In the unburnt region upstream of the deflagrations (Figs. 6e–f), however, it is readily observed that the chain branching of \( H_2O_2 \) (R48) and the generation of alkyl radical and \( H_2O_2 \) (R292–R300) are the most important reactions to the CEM. Consistent with the EI analysis above, the conversion of fuel to alkyl
radical and $\text{H}_2\text{O}_2$ is important for unburnt mixtures with $T$$\sim$1000 K and relatively-high fuel concentration; however, the chain branching reaction of $\text{H}_2\text{O}_2$ becomes more important at $T$$\sim$1100 K. The result implies that $\text{H}_2\text{O}_2$ generated from fuel decomposition reactions becomes reactive at relatively-high temperature region, subsequently inducing the thermal ignition of the unburnt mixtures as explained earlier.

The same EI and PI analyses are applied to Case 16 at the maximum HRR (not shown here). Even thin deflagrations with high HRR are readily observed—these characteristics are similar to early nascent deflagrations in terms of EI and PI values. Unlike the ignition characteristics at the early time, however, significant heat is released upstream of the deflagrations by the thermal ignition of unburnt mixtures, which is manifested in large EI values of temperature together with relatively-small EI values of $\text{H}_2\text{O}_2$ and non-zero EI values of $\text{OH}$. The occurrence of thermal ignition in the unburnt region is also manifested in relatively-large PI values of high-temperature chain branching reaction (R8) and $\text{HO}_2$ formation/consumption reactions (R24 and R47). Because of high temperature of the unburnt mixtures, 1200–1600 K, the HTC starts overwhelming the ITC; the high-temperature chain-branching reaction (R8) becomes more important to CEM than $\text{H}_2\text{O}_2$ decomposition reaction (R49). Since $n$-heptane is already decomposed into smaller radicals, it exhibits low concentration and has no effect on the CEM.

3 Conclusions

The chemical aspects of the ignition of thermally- and/or compositionally-stratified lean $n$-heptane/air mixture under HCCI conditions were investigated. CEMA together with the characteristics of temporal evolution of species identifies important species and reactions for the ignition of $n$-heptane/air mixture at different locations and times. In regions where the spontaneous auto-ignition mode of combustion is predominant, temperature, $\text{H}_2\text{O}_2$, and $n$-heptane are identified as the key species for the CEM prior to thermal ignition while the chain branching reaction of $\text{H}_2\text{O}_2$ and the conversion reaction of $n$-heptane to alkyl radical and $\text{H}_2\text{O}_2$ are the main reactions of the ITC. During thermal ignition, however, temperature is found to be the predominant species and high-temperature reactions represented by $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ are responsible for the thermal ignition. At deflagrations, temperature, $\text{CO}$, and $\text{OH}$ are found to be the most important species while the conversion reaction of $\text{CO}$ to $\text{CO}_2$ and high-temperature chain branching reaction of $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ are identified to be important to the CEM.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2015R1A2A2A01007378). This research used the resources of the Supercomputing Laboratory at King Abdullah University of Science and Technology (KAUST).

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