A numerical study of the effects of primary reference fuel chemical kinetics on ignition and heat release under homogeneous reciprocating engine conditions

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ABSTRACT

In the current work, numerical simulations are used to evaluate the effects of detailed reaction chemistry of different primary reference fuel (PRF) blends of *iso*-octane and *n*-heptane on heat release in one-dimensional engine simulations. A simplified slider-crank model was used to represent the engine cycle. The contributions of specific reaction classes to ignition and heat release were quantified. Maps of ignition phasing and heat release were created as a function of pressure and temperature to indicate the change in reactivity (defined by the first and second stages of ignition) as a function of state conditions as well as the fraction of heat release associated with the two stages of ignition. For the conditions studied, the reactivity of the second stage of ignition always increased with increasing temperature, i.e. the phasing of autoignition advanced with increasing temperature, whereas the reactivity of the first stage of ignition exhibited negative temperature dependence where increasing temperature delayed the first stage of ignition and decreased the heat release at the first stage of ignition for some conditions. The results show low-temperature chemistry radicals like $C_7 RO_2$ species are not uniquely indicative of low-temperature heat release, but they are formed at earlier times, higher rates and higher concentrations with PRF blends with higher fractions of *n*-heptane. A modified approach to the Livengood–Wu integral is presented to capture the integrated effects of the compression stroke on the potential for using the first stage of ignition to distribute heat release. The results of the modified ignition integral analysis are presented as a function of engine speed and fuel/air preheat temperature and demonstrate the utility of the approach to design and interpret fueling strategies of fuel blends.

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1. Introduction

Modern internal combustion engines operate at low temperatures and with high levels of dilution, conditions where heat release is often affected by low-temperature fuel chemistry. In particular, homogeneous charge compression ignition (HCCI) is a low temperature combustion strategy that has successfully yielded high thermal efficiencies and low emissions [1 and references therein]. Relying on fuel chemical kinetics rather than a spark for ignition, HCCI remains difficult to control [1–4] and therefore difficult to develop for commercial powertrains. But the HCCI operating mode provides an opportunity to consider fuel chemistry effects on engine performance at conditions particularly sensitive to combustion chemistry and where chemistry dominates the rate of heat release, as compared with strategies in which heat release rate is controlled by fuel/air mixing and flame propagation convolved with reaction chemistry. The results of autoignition studies also provide understanding of pre-ignition and end-gas knock phenomena.

Many studies have considered the effects of primary reference fuel (PRF) blends of *n*-heptane and *iso*-octane on HCCI engine performance [1 and references therein] and on the relationship between PRF blends, octane number, and engine knock [5]. Some outcomes of these studies demonstrate sensitivity to PRF blends that are attributed to differences in the reaction pathways important for *n*-heptane (PRF0) and *iso*-octane (PRF100). For example, blends with low PRF number (i.e. large fractions of *n*-heptane in the fuel blend, where the PRF number indicates the volume fraction of *iso*-octane in the binary fuel blend), which exhibit more low-temperature heat release (LTHR), have been found to be more sensitive to partial fuel stratification, and are thus more effective at decreasing the rate of pressure rise during the HCCI [6,7].

Simultaneous to the development of the understanding of PRF engine performance at HCCI operating conditions, the elementary chemical kinetics of *n*-heptane and *iso*-octane have been explored at

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length using many experimental and computational methods [e.g., [8–20], and references therein]. These studies have carefully and systematically elucidated the reactions controlling low- and high-temperature heat release, as well as the reactions responsible for negative temperature coefficient (NTC) behavior. While several studies present chemical kinetics simulations performed using detailed reaction mechanisms, what remains elusive are the connections between elementary reaction chemistry and engine performance metrics. Some key contributions to the literature on this topic include the work by Silke et al. [2] and Mehl et al. [16–19]. In one of the earlier studies by Mehl and co-workers [16], the authors used detailed reaction chemistry and a simplified engine model for several pentane and pentene fuel blends to study the effects of a range of research and motoring octane numbers on fuel reactivity. Importantly, Mehl et al. [16] superimposed pressure–temperature trajectories for different engine conditions on reactivity maps (defined by ignition delay times), providing insight into when state conditions in the engine overlap with NTC regions of the fuels. In Silke et al. [2], detailed reaction chemistry was used to quantify low temperature heat release as a function of boosted intake air pressure and compared with HCCI engine data for a PRF80 fuel blend. Reaction path and sensitivity analyses were used to identify the classes of reactions important for forming OH and for phasing of the low-temperature heat release. In Mehl et al. [17], measured intermediate species were well predicted using detailed chemistry for PRF20 blends. In another study, Mehl et al. [18] compared predicted and measured phasing to low temperature heat release using detailed chemistry for a range of PRF blends and for different generations of PRF reaction mechanisms.

Because reciprocating engines create wide-ranging trajectories of temperature and pressure conditions during their cyclical operation, it is challenging to extrapolate the results of the many high-quality isothermal and/or isobaric studies of PRF reaction chemistry to engine behavior. Building on the methods used in the simplified HCCI engine modeling studies like those by Silke et al. [2] and Mehl et al. [16], the objective of this work was to identify links between elementary reaction chemistry for PRF blends and engine performance metrics using a simplified engine modeling approach and focusing on the cumulative effects of the temperature/pressure trajectories on heat release at chemically limited operating conditions. A simplified slider/crank model was used with a detailed chemical kinetic model for PRF blends to simulate a reciprocating engine compression process. The results were analyzed to determine the relative effects of individual as well as groups of chemical reactions on engine performance metrics such as ignition phasing. Additionally the behavior of the combustion intermediates was evaluated to determine if sentinel species could be identified as proxies for low-temperature heat release.

2. Technical approach

As noted above, significant efforts have been made for developing detailed chemical kinetic mechanisms for the primary reference fuels *n*-heptane and *iso*-octane, and several mechanisms focus on high-temperature chemistry (see, for example, [20]). Many mechanisms incorporate low-temperature kinetic schemes making them applicable over wider temperature ranges. Comprehensive explanations of the development and validation of these reaction mechanisms can be found elsewhere (see, for example, [8–10,14,15,18,19] among others). Researchers at Lawrence Livermore National Laboratories (LLNL) have recently incorporated the detailed kinetics of large linear alkenes into their PRF mechanism [19], and have also added cross-reactions between large fuel molecules and fuel fragments (for example, *n*-heptyl + *iso*-octane). Research by Vanhove et al. [21] and others has shown these cross reactions between fuel fragments and fuel molecules are important determinants of whether detailed mechanisms can adequately represent global reactivity of

fuel/oxidizer mixtures. Consequently, the LLNL reaction mechanism was selected for the present study.

The LLNL mechanism consists of a C_1–C_4 detailed mechanism core with three additional blocks of reactions, including reaction pathways for saturated and unsaturated linear hydrocarbons through C_7, as well as similar reactions for branched hydrocarbons from C_5 to C_8, along with aromatic hydrocarbon reactions. Reactions of small radicals with alkyl (R) and alkylperoxy radicals (RO_2) from different fuels are also included. These reactions determine the low-temperature reactivity of PRFs (see, for example, [8–10,14,15 among numerous other references].

The LLNL mechanism has been built gradually and improved upon consistently with the availability of new computational chemistry studies and new experimental data for validation and verification. (For details on this continuous improvement, please see [22].) The mechanism has been validated over a range of conditions and for diverse data sets. The goal of this work was not to further validate the detailed chemical kinetic model, but rather to use our understanding of detailed reaction schemes represented in the model to understand the sensitivity of the engine simulations to various PRF blends and engine operating conditions.

The CHEMKIN suite of software (version 10131, x64 [23]) was used for the two categories of simulations performed and presented in this paper. First, adiabatic constant volume simulations were used to quantify the ignition characteristics of the fuel blends, and second, adiabatic variable volume simulation using the dynamic state conditions for the crank-slider approach of engine simulations were used to study the effects of fuel blends on engine performance. The results of these simulations are presented below.

3. Results and discussion

3.1. Constant volume autoignition characteristics of PRF blends

Calculations of constant volume, adiabatic ignition delay times provide a baseline understanding of the ignition characteristics of the fuels as a function of temperature, pressure and mixture conditions. While many such results can be found in the literature, the trends are briefly reviewed here to provide a basis of comparison with the results of the variable volume simulations. The ignition delay time characteristics of four PRF blends—PRF0, PRF60, PRF88 and PRF100—over the temperature range of 625–1200 K, at pressures of 10 and 25 bar with an equivalence ratio (ϕ) of 0.33 and inert/O_2 ratio of 3.76 are presented in Fig. 1. The lean equivalence ratio was selected due to the relevance to HCCI engine operation [1]. CO_2 and H_2O comprised a total of 5% of the diluent gas composition for all simulations to incorporate the effect of internal exhaust gas recirculation (EGR) of an engine. The balance of the diluent gas composition was N_2. The EGR values were selected based on estimates for internal residual for a single-cylinder cooperative fuel research (CFR) engine [24]. The pressures of the calculations span the range expected during the compression stroke of wide-open-throttle operation of an engine with a compression ratio of 12:1.

As expected and as seen in Fig. 1, the ignition of PRF100 is significantly slower than that of PRF0 at the same pressure for temperatures below ~1000 K. The results in Fig. 1 also demonstrate the predicted magnitude of non-Arrhenius behavior of the blends at different state conditions. For some fuel blends and conditions, the non-Arrhenius behavior is significant and negative temperature coefficient trends are predicted, i.e. where increasing temperature results in lower fuel reactivity. The NTC regime occurs at lower temperatures for *iso*-octane compared with *n*-heptane, and the NTC region shifts to higher temperatures with increasing pressure. Two stages of heat release are observed in the low temperature portion of the non-Arrhenius regions. For these cases, the first stage of ignition is defined by the first local maximum in the rate of pressure rise in the