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Autoignition of gasoline surrogates at low temperature combustion conditions

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ABSTRACT

Understanding the autoignition characteristics of gasoline is essential for the development and design of advanced combustion engines based on low temperature combustion (LTC) technology. Formulation of an appropriate gasoline surrogate and advances in its comprehensive chemical kinetic model are required to model autoignition of gasoline under LTC conditions. Ignition delays of two surrogates proposed in literature for a research grade gasoline (RD387), including a three-component mixture of *iso*-octane, *n*-heptane, and toluene and a four-component mixture with the addition of an olefin (2-pentene), were measured in this study using a rapid compression machine (RCM). The present RCM experiments focused on two fuel lean conditions in air corresponding to equivalence ratios of $\phi = 0.3$ and 0.5, at two compressed pressures of $P_C = 20$ bar and 40 bar in the compressed temperature range of $T_C = 665$–950 K. Comparison of the measured ignition delays of two gasoline surrogates with those of RD387 reported in our previous study shows that the four-component surrogate performs better in emulating the autoignition characteristics of RD387. In addition, numerical simulations were carried out to assess the comprehensiveness of the corresponding gasoline surrogate model from Lawrence Livermore National Laboratory. The performance of the chemical kinetic model was noted to be pressure dependent, and the agreement between the experimental and simulated results was found to depend on the operating conditions. A good agreement was observed at a compressed pressure of 20 bar, while a reduced reactivity was predicted by the chemical kinetic model at 40 bar. Brute force sensitivity analysis was also conducted at varying pressures, temperatures, and equivalence ratios to identify the reactions that influence simulated ignition delay times. Finally, further studies for improving the surrogate kinetic model were discussed and suggested.

1. Introduction

Internal combustion engines (ICEs) are expected to power light-duty transportation vehicles over the coming decades [1] despite the emergence of other energy conversion technologies. Therefore, advanced ICEs capable of operating at both high efficiencies and low emission levels need to be developed to overcome the prevailing challenges of depletion of fossil fuel reserves and detrimental effects of combustion generated emissions. Low temperature combustion (LTC) technology is one novel approach that operates with extremely lean fuel/air or highly diluted mixtures and under high compression ratios resulting in high efficiency and low emissions [1]. Homogeneous charge compression ignition (HCCI), reactivity controlled compression ignition (RCCI), and premixed charge compression ignition (PCCI) engines are some variants of LTC. Since LTC relies heavily on autoignition kinetics of the fuels, it is imperative to develop high fidelity chemical kinetic models to simulate the autoignition process over a wide range of operating conditions. As gasoline is the major transportation fuel for light-duty vehicles, this study focuses on gasoline autoignition kinetics.

The modeling of gasoline chemical kinetics is complicated by the compositional complexity of the real fuel which typically consists of hundreds of hydrocarbons. Developing a chemical kinetic model describing autoignition of all the gasoline components is currently not feasible; therefore simpler surrogates with a limited number of hydrocarbons are commonly used to replicate the autoignition kinetics of real gasoline. A comprehensive chemical kinetic model for a real fuel requires the identification of an appropriate surrogate and the development of a chemical kinetic model

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to describe the combustion kinetics of the surrogate. Pitz et al. [2] reviewed and identified the targets for the formulation of gasoline surrogates, and recommended the hydrocarbon candidates for surrogate formulation. Considering the relevance of flame propagation, knocking, and ignition phasing to advanced ICEs, a surrogate should be formulated to match H/C ratio, octane rating, and crank angle degrees corresponding to 10% and 50% of the total heat release (denoted as CA 10 and CA 50, respectively) of the target gasoline [2]. Regarding the octane rating, it is also essential to match Research Octane Number (RON), Motor Octane Number (MON), and Sensitivity (S) of the surrogate to those of the target gasoline. In addition, Pitz et al. [2] pointed out the needs for fundamental experimental data from flow reactors, shock tubes, rapid compression machines, laminar flames, and jet stirred reactors, at varying pressures, temperatures, and equivalence ratios.

In terms of gasoline surrogate components, *n*-heptane, *iso*-octane, toluene, cyclohexane, methyl-cyclohexane (MCH), 1-pentene, 2-pentene, di-isobutylene, ethanol, etc. have been identified as candidates for surrogate constituents. Several surrogate mixtures have been formulated to emulate the combustion characteristics of gasoline fuels. Although the Primary Reference Fuels (PRF's), mixtures of *iso*-octane and *n*-heptane, have been widely used to understand ignition of gasoline in spark ignition engines, they are not able to meet some targets, specifically the H/C ratio and Sensitivity, highlighting the need for a more complex surrogate formulation. This led to the use of ternary surrogate mixtures, such as Toluene Reference Fuels (TRF's), which are mixtures of *iso*-octane, *n*-heptane, and toluene [3,4], and blends of *iso*-octane, toluene, and 1-hexene [5]. Additionally, a four-component mixture consisting of TRF and 2-pentene was proposed by Mehl et al. [6] as a gasoline surrogate, while Naik et al. [7] suggested a five-component surrogate consisting of *n*-heptane, *iso*-octane, toluene, MCH, and 1-pentene. Furthermore, investigations have been conducted to understand the kinetic interactions between the constituents of these surrogates [e.g., 5,8,9].

While fundamental investigations on fully-blended gasoline fuels are essential for validation and formulation of their surrogates, there were only a limited number of studies reported in the literature. Using a shock tube, Gauthier et al. [4] measured ignition delays of a full blend non-oxygenated, research grade gasoline (RD387) at varying equivalence ratios of ϕ = 0.5, 1.0, and 2.0 covering two pressures ranges of 15–25 atm and 45–60 atm in the high temperature range of 850–1280 K. A recent study on RD387 by Kukkadapu et al. [10] conducted autoignition delay measurements in a rapid compression machine (RCM) at varying equivalence ratios (ϕ = 0.3, 0.5, and 1.0) and compressed pressures (P_C = 20 and 40 bar), in the low-to-intermediate temperature range of 640–955 K. Sjöberg et al. [11] and Dec et al. [12] have used RD387 for their engine experiments, showing different heat release characteristics at different operating conditions and temperature ranges. In addition, laminar flame speeds of gasoline fuels were reported by Jerzembeck and Peters [13] and Tian et al. [14]. Recently, Sarathy et al. [15] studied ignition characteristics of two gasoline blends and a PRF mixture which exhibited identical ASTM octane ratings. These experimental studies on gasoline fuels [4,10–15] have provided validation datasets for the formulation of gasoline surrogates and the development of surrogate models over different combustion modes.

The shock tube study of Gauthier et al. [4] also found that the ignition delays of a TRF mixture comprising 63% *iso*-octane/17% *n*-heptane/20% toluene (all by liquid volume) compared well with those of RD387 at high-temperature conditions investigated therein. This TRF surrogate proposed by Gauthier et al. [4] is hereafter referred to as Stanford A surrogate. As mentioned earlier, Mehl et al. [6], led by Lawrence Livermore National Laboratory (LLNL), formulated a quaternary gasoline surrogate, consisting of 57% *iso*-octane/16% *n*-heptane/23% toluene/4% 2-pentene (by liquid volume), using a surrogate formulation methodology based on a chemical kinetic model. This four-component surrogate is denoted as LLNL surrogate in the following. In addition, the surrogate model of Mehl et al. [6] was shown to emulate the shock tube ignition delays, laminar flame speeds, and engine data of gasoline fuels available in the literature with a good level of agreement. In view of the importance of the low-to-intermediate temperature chemistry in advanced engines operating at LTC conditions, Kukkadapu et al. [16] measured the ignition delays of two gasoline surrogates, namely Stanford A and LLNL, in an RCM for stoichiometric fuel/air mixtures at compressed pressures of P_C = 20 and 40 bar.

Table 1 shows that both the Stanford A and the LLNL surrogates match closely with the key properties of the target RD387 gasoline. A detailed discussion on the selection of these two gasoline surrogates can be found in [16]. By comparing the ignition delays of the two surrogates with those of RD387 from [10], it was demonstrated in [16] that the four-component LLNL surrogate better matches the RCM ignition characteristics of gasoline than the three-component Stanford A surrogate. It was further observed in [16] that though the simulated ignition delays using the chemical kinetic model of the LLNL surrogate [6,17] compared well with the experimental data of gasoline, the comparison of the measured and simulated ignition delays of two surrogates did not exhibit similar level of agreement. Furthermore, based on the comparison of surrogate experiments and modeling results, a significant difference in reactivity was observed especially at conditions of low temperature and high pressure [16].

The objective of the current study is to extend the work of Kukkadapu et al. [16] by investigating the autoignition characteristics of the Stanford A and the LLNL surrogates under LTC-relevant conditions, i.e. elevated pressures (10–75 bar), low-to-intermediate temperatures (600–1100 K), and fuel lean equivalence ratios, in an RCM. Understanding the performance of gasoline surrogates and their model at these off-stoichiometric conditions with respect to gasoline autoignition is vital for the development of next-generation advanced-combustion engines. In addition, direct comparisons of the experimental ignition delays using surrogates with those predicted by the corresponding chemical kinetic model will help assess the fidelity of the surrogate model [6,17], as well as provide insights into the model refinement. Therefore, the current study aim to close the gap under fuel lean and high pressure

Table 1
Property comparison of gasoline and surrogates investigated in this study.

Blend	Composition[a]	AKI[b]	Sensitivity[d]	H/C ratio
RD387 gasoline [10]	42.3/9.5/26.4/4.7/16	86.8	8.3	1.87
Mehl et al. [6]	57/16/23/4/0	87[c]	8[c]	1.94
Gauthier et al. [4]	63/17/20/0/0	86.5[c]	5[c]	1.97

[a] Composition order: *iso*-alkanes/*n*-alkanes/aromatics/olefins/napthenes (volume fraction in liquid phase at 25 °C).
[b] Anti-Knock Index (AKI) = (RON + MON)/2.
[c] The values are estimated using the correlations proposed in Mehl et al. [6].
[d] Sensitivity = RON–MON.

Table 2
Pre-heat conditions of the present and previous [10,16] RCM experiments.

ϕ	P_C (bar)	T_0 (°C)	RD387 gasoline	Surrogates
0.3	40	60	[10]	This study
0.5	20	90, 125	[10]	This study
0.5	40	60	[10]	This study
1	20	60, 90	[10]	[16]
1	40	60	[10]	[16]