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Gasoline surrogate modeling of gasoline ignition in a rapid compression machine and comparison to experiments

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Abstract

The use of gasoline in homogeneous charge compression ignition engines (HCCI) and in duel fuel diesel – gasoline engines, has increased the need to understand its compression ignition processes under engine-like conditions. These processes need to be studied under well-controlled conditions in order to quantify low temperature heat release and to provide fundamental validation data for chemical kinetic models. With this in mind, an experimental campaign has been undertaken in a rapid compression machine (RCM) to measure the ignition of gasoline mixtures over a wide range of compression temperatures and for different compression pressures. By measuring the pressure history during ignition, information on the first stage ignition (when observed) and second stage ignition are captured along with information on the phasing of the heat release. Heat release processes during ignition are important because gasoline is known to exhibit low temperature heat release, intermediate temperature heat release and high temperature heat release. In an HCCI engine, the occurrence of low-temperature and intermediate-temperature heat release can be exploited to obtain higher load operation and has become a topic of much interest for engine researchers. Consequently, it is important to understand these processes under well-controlled conditions.

A four-component gasoline surrogate model (including *n*-heptane, *iso*-octane, toluene, and 2-pentene) has been developed to simulate real gasolines. An appropriate surrogate mixture of the four components has been developed to simulate the specific gasoline used in the RCM experiments. This chemical kinetic surrogate model was then used to simulate the RCM experimental results for real gasoline. The experimental and modeling results covered ultra-lean to stoichiometric mixtures, compressed temperatures of 640–950 K, and compression pressures of 20 and 40 bar. The agreement between the experiments and model is encouraging in terms of first-stage (when observed) and second-stage ignition delay times and of heat release rate. The experimental and computational results are used to gain insight into low and intermediate temperature processes during gasoline ignition.

1. Introduction

With increasingly stringent requirements on pollutant emissions and limited availability of fossil fuel reserves, the scientific community has been searching for clean and efficient energy conversion technologies. Among them, Homogeneous Charge Compression Ignition (HCCI) technology, with low NOx emissions and 10–15% higher fuel efficiency than conventional engines, is an attractive alternative. HCCI is controlled primarily by autoignition chemistry. Understanding the chemical kinetics which governs autoignition is a pre-requisite for implementing this technology.

The kinetics of gasoline combustion are complex due to the near continuous spectrum of constituents. The use of a surrogate mixture comprising of selected neat hydrocarbon constituents is a widely adopted research method for replicating the combustion response of real gasoline fuel. The choice of surrogate constituents is greatly influenced by the desired end application. A binary *n*-heptane and *iso*-octane blend may suffice to predict some aspects of combustion in spark ignition engines. However, the operation under the HCCI mode requires an alternative approach to surrogate formulation, with specific emphasis on factors such as low temperature heat release.

Various research groups have proposed different surrogate mixtures to emulate gasoline autoignition. Gauthier et al. [1] proposed two ternary surrogates containing n-heptane, isooctane, and toluene. Naik et al. [2] suggested a five-component surrogate mixture including n-heptane, isooctane, toluene, 1-pentene, and methylcyclohexane. Vanhove et al. [3] used a ternary mixture of 47% isooctane/35% toluene/18% 1-hexene in their studies. Lenhert et al. [4] conducted studies in a pressurized flow reactor using a four-component surrogate consisting of n-heptane, isooctane, toluene, and 1-pentene. In addition, there have been efforts towards the development and validation of detailed kinetic models for gasoline combustion, notably the studies of [5-11]. In particular, the mechanism of Mehl et al. [10, 11] has been validated against the experimental data of [1, 3, 12], showing a good agreement.

While the study of Gauthier et al. [1] on autoignition of full-blend gasoline in a shock tube (ST) has been extensively used for validating various surrogate models reported in literature, it is noted that their experiments were conducted in the temperature range of 850–1280 K and pressures of 15–60 atm. For combustion in a HCCI engine, the temperature range needs to be extended down to about 700 K. Hence, there is a significant lack of ignition delay data available in the regime relevant to HCCI combustion of gasoline. Recognizing the need of kinetic information at high pressures and low-to-intermediate temperatures, this work aims to fill this void by conducting an experimental study of gasoline ignition in a rapid compression machine (RCM). The experimental database obtained using a well-characterized research-grade gasoline will assist in a comparison and subsequent validation of the ignition delay response for various gasoline surrogates. Furthermore, the RCM data are simulated using a four-component surrogate model developed by Mehl et al. [11]. Such a surrogate modelling study is also expected to provide insight into the fundamental basis for choice of neat constituents and their relative proportions.

2. Experimental Specifications and Results

A heated rapid compression machine is used for the current study. The machine is a single piston type, driven pneumatically, and stopped hydraulically at the end of compression. It has a compression time of about 30 milliseconds. Further details about the geometry and the design

can be found elsewhere [13]. Dynamic pressure is measured using Kistler 6125B transducer with 5010B charge amplifier, and pressure trace is used as indicator for the onset of ignition.

Research grade gasoline labelled as RD387 and supplied by Chevron-Phillips is used for the current experiments. Key properties of RD387 include 9.5% (liq. Vol.) of *n*-paraffin, 42.3% *iso*-paraffin, 4.7% olefins, 16% napthenes, 26.4% aromatics, H/C ratio of 1.869, RON of 91, and MON of 82.7. The desired fuel/oxidizer mixture is made in a magnetically stirred stainless steel vessel equipped with heaters. It is ensured that the partial pressure of each major fuel component is less than its saturation pressure corresponding to the set initial temperature. In addition, synthetic air is prepared using ultra high purity oxygen and nitrogen in the molar proportion of 1:3.76. The pre-mixture is heated and stirred for 3 hours to ensure homogeneity.

Test conditions include fuel/air equivalence ratios of ϕ=0.4, 0.5, and 1.0 and compressed pressures (i.e. the pressures at the end of compression) of P_C=20 and 40 bar. The desired compressed conditions can be obtained by changing initial pressure, compression ratio, and initial temperature. The compressed temperature (the temperature at the end of compression), T_C, is calculated using the adiabatic core hypothesis [13] and the thermodynamic properties of the surrogate constituents reported in Mehl et al. [11] (57% isooctane, 16% n-heptane, 23% toluene, and 4% 2-Pentene by liquid volume).

The homogeneous fuel/air mixture is compressed rapidly to the desired pressure and temperature. Subsequent to the compression and after an initial induction period, a rapid rise in pressure is observed on account of autoignition. Ignition delay time is defined as the time interval between the end of compression and the maximum rate of pressure rise. First- and second-stage ignition delays are defined similarly. This definition of ignition delay is illustrated in Fig. 1. A minimum of 5 concordant experimental runs are carried out for each data point reported. A representative pressure trace experimental close to the mean is chosen for reporting the ignition delay. The typical scatter is ~10% of the reported value. Figure 2 demonstrates the typical reproducibility. For each reactive experiment, the corresponding inert run is taken by replacing oxygen with nitrogen while maintaining the same fuel concentration, in order to infer the heat loss characteristics during the compression stroke and the post-compression period [13].

Figure 3 shows the Arrhenius plots of overall and first-stage ignition delay measurements for the conditions investigated, along with the previously reported results of Gauthier et al. [1] scaled as $P^{-1.05}$ to the current operating pressures as a comparison. It is seen from Fig. 3 that the negative temperature coefficient (NTC) response is observed to be flatter at higher pressures.

3. Modeling Results and Discussion

RCM simulations were conducted using the surrogate model of Mehl et al. [11]. The surrogate proposed by Mehl et al. [11] was based on information relative to a RD387 gasoline fuel reported by Dec and Yang in [14]. Table 1 provides the main characteristics of the gasoline used in the experiments, the target gasoline and of the surrogate.

The batch of RD387 gasoline used in this work differs slightly from the batch used in the Sandia engine experiments by Dec and Yang's [14]. As seen in Table 1, the amount of aromatics and olefins is slightly higher and the total amount of alkanes (n-alkanes, iso-alkanes and naphthenes) is slightly lower (67.8 % instead of 71.1%). The composition of the surrogate was targeted to match the relative content of alkanes, alkenes and aromatics present in the RD387 batch used by Dec and Yang [14] as well as its RON and MON values. The correlations proposed in [11] were used to establish its composition. Since the amount of n-alkanes, iso-

alkanes and naphthenes in the gasoline was not reported in [14], the author's used the amount of *n*-alkanes and *iso*-alkanes as a tuning parameter to match the behaviour of the real gasoline. Also, they decided not increase the complexity of the surrogate by including naphthenes. The authors compensated for the actual presence of naphthenes in the gasoline by increasing the amount of *iso*-alkanes in the surrogate beyond that actually present in the target gasoline. The four component gasoline surrogate representing n-alkanes, iso-alkanes, alkenes, and aromatics (but not naphthenes) successfully reproduced the engine experiments by Dec and Yang [11, 15]. The ignition behaviour of the RD387 gasoline in [14] and the RD387 used in this work is very similar based on their reported RON and MON values (Table 1). Since the surrogate proposed by Mehl et al. [11] predicted HCCI ignition characteristics that are very similar to those measured in [14] with the prior batch of RD387, we assume that it will predict autoignition behaviour similar to the present batch of RD387 gasoline as well.

Two sets of calculations – (1) a constant volume, adiabatic simulation using P_C and T_C as initial conditions and (2) a variable volume simulation accounting for the full compression stroke and the heat loss effect, are compared. As mentioned earlier, the heat loss parameters are deduced from the corresponding inert run. Figure 4 shows the comparison of overall ignition delays obtained from experiments and simulations. The simulations labelled as variable volume are compared to the RCM experiments presented in this work, while the constant volume simulations should be compared with the shock tube data by Gauthier et al. [1].

The surrogate model proposed by Mehl et al. [11] reproduces correctly the autoignition behaviour of the RD387 gasoline measured by Gauthier et al. [1] in the high temperature region for all the conditions considered here. More important for engine applications is the agreement in the low temperature region, where the model provides a remarkable good agreement with the RCM data. The model correctly reproduces the NTC behaviour exhibited by the gasoline for all the conditions here considered. The only relevant discrepancies are present in the temperature region around 850 K at 20 bar and lean conditions, where the model tends to be more reactive than the real fuel.

The model also captures the first stage ignition, as can be observed in the simulated pressure traces shown in Fig. 5.

The model shows good agreement with the experimental pressure traces both in terms of overall ignition timing and low temperature ignition confirming the validity of the model. Minor discrepancies can be observed in regard to the pressure rise associated with the first stage, which appears to be slightly higher for the modelled trace at ϕ=1. These differences might be connected to the compositional differences between the real fuel and the surrogate. To clarify this point future work will focus on the effect of variation in the surrogate composition, introducing a cycloalkane component in the surrogate fuel formulation.

4. Conclusions

The autoignition of the RD387, a full blend non-oxygenated gasoline, was studied experimentally and numerically. The first experimental dataset of low temperature ignition delay data for this type of fuel has been measured in a rapid compression machine at pressures and equivalence ratios relevant to spark ignition and HCCI engines. The experimental measurements here presented showed to be consistent with previous data collected at Stanford by Gauthier et al. [1] covering the high temperature region. A gasoline surrogate model developed by Mehl et al. [11] has been used to simulate the data. The surrogate formulation was based on the overall

composition of a similar batch of RD387 and on the octane rating of the fuel. The model successfully reproduced the ignition delay times over the entire range of pressure, temperature and stoichimetries analyzed in this work. Further investigations will focus on the experimental validation of the surrogate composition proposed as well as different formulations obtained using the correlations proposed by Mehl et al. [11].

Acknowledgments

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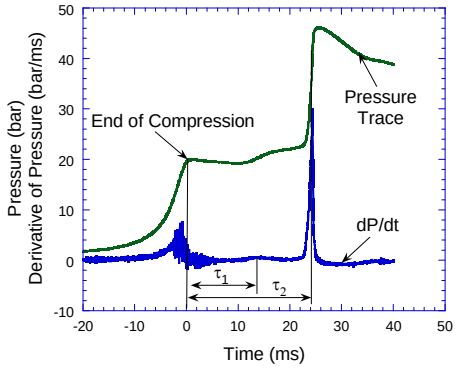

Fig. 1. Plot illustrating the definitions of ignition delays in the RCM.

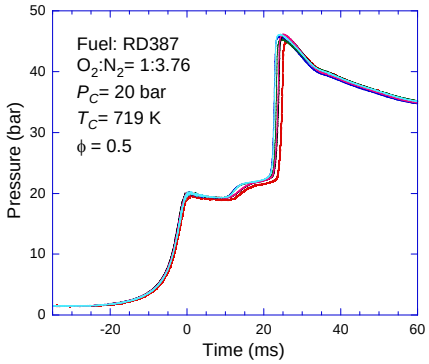

Fig. 2. Reproducibility of six experimental runs in the RCM.

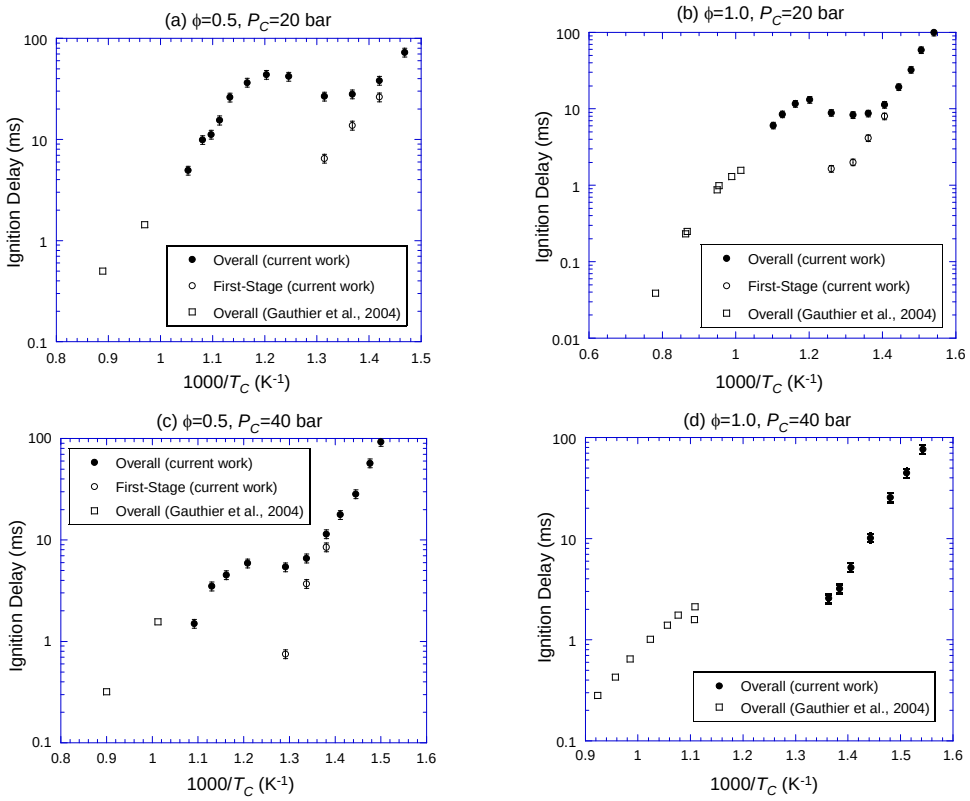

Fig. 3. Arrhenius plots of overall and first-stage (when observed) ignition delay times in the RCM after the end of compression with temperature. Shock tube ignition delay times for gasoline [1] are included for comparison.

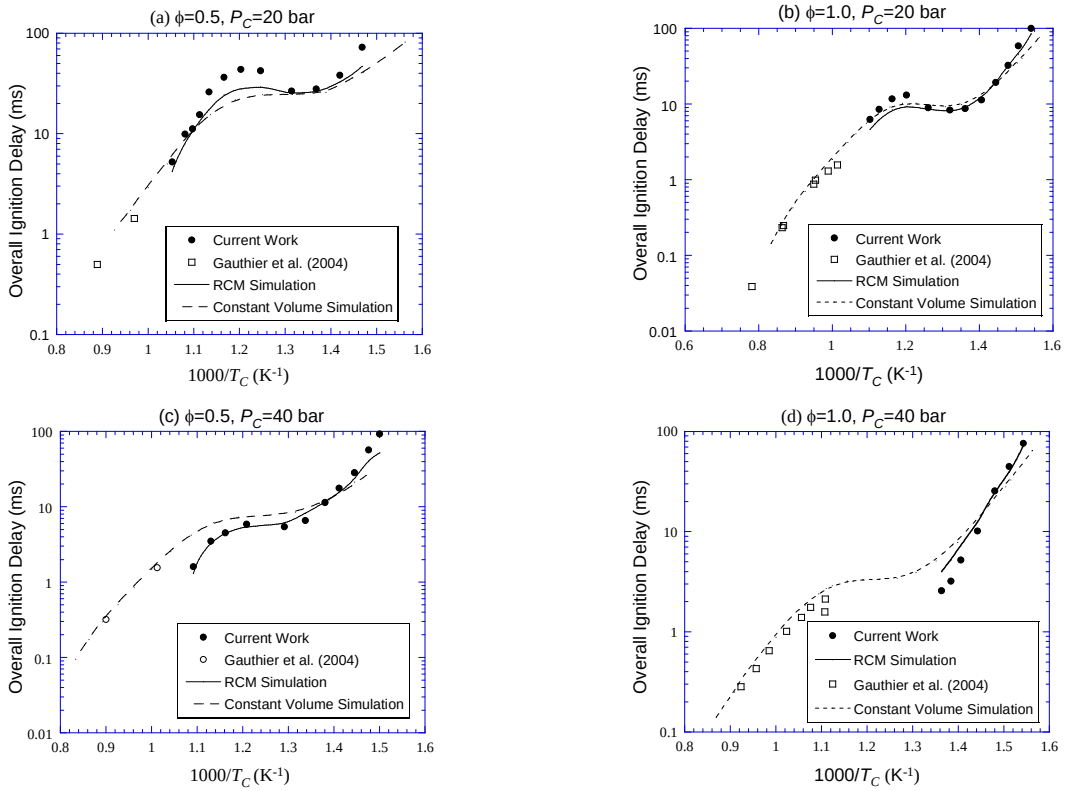

Fig. 4. Comparison of experimental and simulated overall ignition delays in the shock tube [1] and RCM after the end of compression.

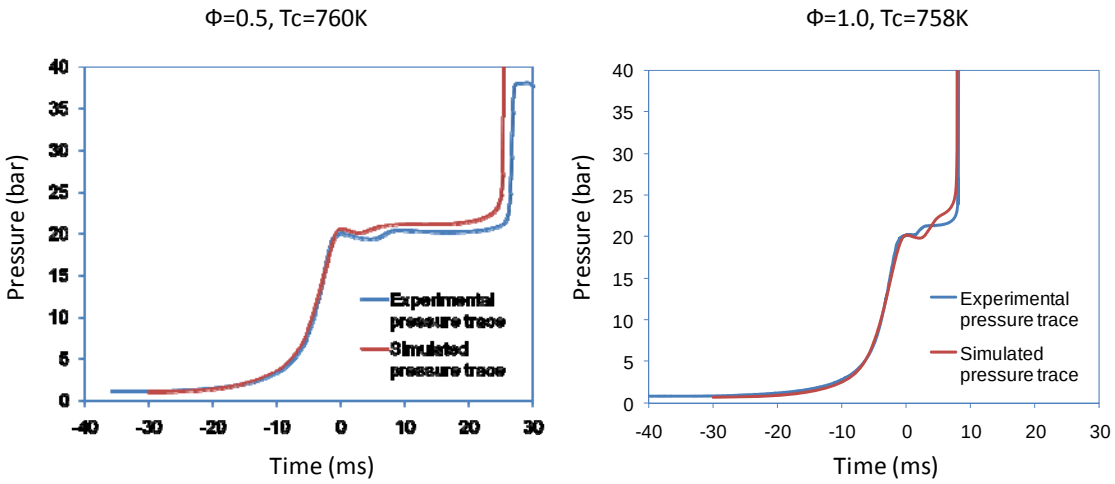

Fig. 5. Comparison of experimental and simulated pressure traces in the RCM at P_C=20 bar.

	Gasoline [this work]	Gasoline [14]	Surrogate
iso-Alkanes	42.3%	73.1 % (Total)	57%
n-Alkanes	9.5%		16%
naphthenes	16%		--
Aromatics	26.4%	22.7 %	23%
Olefins	4.7	4.2 %	4%
H/C	1.869	1.946	1.925
MON	82.7	83.2	83 (Estimated)
RON	91	90.8	91 (Estimated)

Table 1. Composition (in liquid volume percentage) and octane ratings of the real gasolines and of the surrogate.