A comparative study of the oxidation characteristics of two gasoline fuels and an n-heptane/iso-octane surrogate mixture

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HIGHLIGHTS

- Experimental study of two gasolines and a primary reference fuel surrogate blend.
- Ignition delay and species time-histories measured.
- Gasolines with different compositions showed similar reactivity and species profiles.
- PRF surrogate captured the kinetic trends of the gasolines reasonably well.
- The experimental data can be used for improving prediction of kinetic mechanisms.

ARTICLE INFO

ABSTRACT

Ignition delay times and CO, H_2O, OH and CO_2 time-histories were measured behind reflected shock waves for two FACE (Fuels for Advanced Combustion Engines) gasolines and one PRF (Primary Reference Fuel) blend. The FACE gasolines chosen for this work are primarily paraffinic and have the same octane rating ($\sim$RON = 84) as the PRF blend, but contain varying amounts of iso- and n-paraffins. Species time-histories and ignition delay times were measured using laser absorption methods over a temperature range of 1350–1550 K and pressures near 2 atm. Measured species time-histories and ignition delay times of the PRF blend and the two FACE fuels agreed reasonably well. However, when compared to recent gasoline surrogate mechanisms, the simulations did not capture some of the kinetic trends found in the species profiles. To our knowledge, this work provides some of the first shock tube species time-history data for gasoline fuels and PRF surrogates and should enable further improvements in detailed kinetic mechanisms of gasoline fuels.

1. Introduction

Gasoline is the most widely used transportation fuel for light duty vehicles. Gasoline is primarily comprised of hydrocarbons in C_4–C_{10} range [1], however, the actual composition varies significantly depending primarily on the geographic origin of the fuel [2]. As such the commercial transportation-grade gasoline is a complex mixture of hundreds of hydrocarbons including linear and branched paraffins, naphthenes, olefins and aromatics. It becomes extremely inefficient to accommodate all of these species in any real world computational/experimental scenario. These difficulties can be overcome by considering a surrogate mixture of a few well-known components in a well-defined composition to emulate the target properties of the real fuel. Generally, these target properties include desired combustion characteristics (ignition delay, flame speed, etc.) and/or physical properties (molecular weight, H/C ratio, distillation curve, etc.). However, it should be noted that a given surrogate may not be able to match all physical and kinetics targets simultaneously. A conventional scale for rating the ignition properties of gasoline fuels is the research octane number (RON) and/or the motor octane number (MON) based on blends of gasoline primary reference fuels (PRF), n-heptane and iso-octane. Blends of primary reference fuels have previously been used as gasoline surrogates. The chemical kinetics of PRFs has been studied quite comprehensively over the last decade or so. Work by Curran et al. [3,4] on n-heptane/iso-octane and by Mehl et al. [5] on gasoline surrogates provide good account of the experimental and chemical kinetic modeling studies of primary reference fuels. Ignition delay times of PRF blends have been measured previously by a few groups [6–8]. More complex multi-component gasoline surrogates have been proposed in ignition delay studies under HCCI-like conditions [9–11].

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The US Department of Energy and the Coordinating Research Council comprising of research institutes, automotive and oil companies have recently formulated a set of fuels, known as Fuels for Advanced Combustion Engines (FACE). One of the basic aims of formulating these FACE fuels is to provide a consistent set of fuels with well-characterized properties and compositions, making it easy to compare research results at various institutions and facilities. In the current study, we have investigated the oxidation characteristics of FACE gasoline A and C. Table 1 shows some of the key features of these two fuels; more detailed compositional analysis of FACE gasoline and diesel fuels can be found in [12,13]. Both gasolines have very similar octane rating but they differ in their compositions; FACE C has more than double the amount of n-paraffins than FACE A. Also, small amount (∼4%) of aromatics is present in FACE C but are almost negligible in FACE A. The two gasoline fuels are compared here against a PRF blend of 84% iso-octane/16% n-heptane (by volume), referred to as PRF 84 in this work.
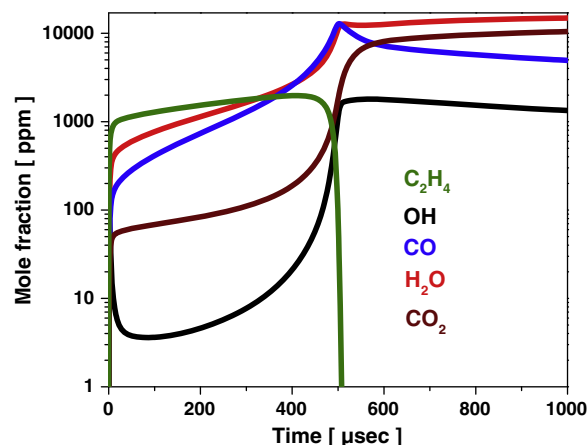
Chemical kinetics models are often validated against global kinetics targets such as ignition delay and flame speed data obtained from shock tubes, rapid compression machines, and simple canonical flames. Such data provide an overall view of the kinetic mechanism behavior and its ability to predict fuel reactivity but these data cannot be used to validate complex reaction pathways which are important, for example, in predicting emissions. The detailed chemical kinetics also play important role in controlling the fuel reactivity under HCCI- or PCCI-like conditions. Comprehensive validation of detailed chemical kinetic mechanism would benefit greatly by experimentally measured species time-history profiles. Shock tube / laser absorption experiments are particularly well-suited for acquiring species time-history data [14–18] because of the step change in test conditions behind shock waves, the highly uniform temperatures and pressures, and the fast time response of laser absorption diagnostics.

Fig. 1 shows the predictions for the evolution of five major species formed during the oxidation of PRF 84. Simulations are carried out using gasoline surrogate mechanism of Mehl et al. [5] with constant internal energy and volume (constant UV) gasdynamic model in Chemkin-Pro [19]. The fuel decomposes immediately within the first 10–50 μs producing fuel fragments, C_1–C_4 intermediate species and an active radical pool. The concentrations of the reaction progress markers (CO, H_2O and CO_2) increase slowly at early times, over the 50–450 μs window in this example, until there is an exponentially fast growth of OH radicals and significant energy release from the $CO + OH \leftrightarrow CO_2 + H$ reaction. Post-ignition CO_2 and H_2O concentrations will eventually approach their equilibrium values governed primarily by their thermochemical properties. Details of the species time-histories in the pre-ignition region are very important, and can provide very stringent constraints on mechanism prediction and validation.

Fig. 1. Simulated profiles of major species formed during the oxidation of PRF 84. Mixture: 0.2% PRF84/O_2/Ar (Φ = 1), T = 1500 K, P = 2 atm. Constant internal energy and volume (constant UV) simulations performed in Chemkin-Pro [19] using Mehl et al. mechanism [5].

In this study, we present species time-history and ignition delay time measurements for FACE gasolines A and C as well as a PRF 84 surrogate. Measurements are performed over a temperature range of 1350–1550 K and at pressures near 2 atm. In all experiments, the fuel concentration was kept at 0.2% with an equivalence ratio of 1 and argon is the diluent gas. Time-histories of OH, CO, CO_2 and H_2O were measured using laser-based UV and IR absorption spectroscopy. The reactivity and speciation of the three fuels were compared based on the fuel composition and also compared with predictions from recent gasoline surrogate mechanisms.

2. Methodology

2.1. Chemical kinetics shock tube facility

All experiments were performed in the chemical kinetics shock tube facility at King Abdullah University of Science and Technology (KAUST). This shock tube facility has been reported previously in literature [20–22] and only a brief account will be given here. The stainless steel shock tube has an inner diameter of 14.2 cm, driven section is 9 m long and a modular driver section with maximum length of 9 m. The driven section can be pumped down to 1×10^{-6} mbar using a turbomolecular pump. As the gasoline and PRF surrogate are multi-component fuels, the mixtures were prepared by direct injection of the fuel into a heated (75 °C) mixing vessel, equipped with a magnetically driven stirrer. These liquid fuels can readily adsorb on the mixing vessel walls and shock tube inner surface. The mixture composition was measured by Fourier Transform Infrared (FTIR) absorption spectroscopy by taking samples from the mixing vessel and the shock tube. The sampled mixtures were found to be within 5% of the manometrically determined values. Additionally, partial pressure of the fuel was kept well below the saturation vapor pressure relatively to avoid fuel condensation. The PRF 84 blend was prepared volumetrically using high purity (>99.5%) n-heptane and iso-octane (Sigma–Aldrich). FACE gasoline A and C were obtained from Conoco Philips Specialty Chemicals and research-grade argon and oxygen were supplied by AHG Gases.

Incident shock velocity was calculated by measuring the time interval between five PCB 113B26 piezoelectric pressure transducers (PZTs) that were located axially along the last 1.3 m of the driven section. The incident shock speed at the end-wall was determined by linear extrapolation of the velocity profile. One-dimensional shock-jump equations were used to calculate

Table 1
Properties of FACE gasoline fuels and PRF surrogate. The hydrocarbon types for FACE A and C were determined by Detailed Hydrocarbon Analysis (DHA) technique.

Fuel properties	FACE gasoline A	FACE gasoline C	PRF 84
RON	83.5	84.7	84
MON	83.6	83.6	84
Sensitivity	−0.1	1.1	0
Avg. mol. wt.	97.8	97.2	112
Hydrocarbon type, liquid mol%			
n-Paraffins	13.2	28.6	17.6
iso-Paraffins	83.7	65.1	82.4
Aromatics	0.3	4.4	0
Alkenes	0.4	0.4	0
Cycloalkanes	2.4	1.5	0
H/C ratio	2.29	2.27	2.26