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Compositional effects on PAH and soot formation in counterflow diffusion flames of gasoline surrogate fuels

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ABSTRACT

Gasoline surrogate fuels are widely used to understand the fundamental combustion properties of complex refinery gasoline fuels. In this study, the compositional effects on polycyclic aromatic hydrocarbons (PAHs) and soot formation were investigated experimentally for gasoline surrogate mixtures comprising n-heptane, iso-octane, and toluene in counterflow diffusion flames. A comprehensive kinetic model for the gasoline surrogate mixtures was developed to accurately predict the fuel oxidation along with the formation of PAHs and soot in flames. This combined model was first tested against ignition delay times and laminar burning velocities data. The proposed model for the formation and growth of PAHs up to coronene ($C_{24}H_{12}$) was based on previous studies and was tested against existing and present new experimental data. Additionally, in the accompanied soot model, PAHs with sizes larger than (including) pyrene were used for the inception of soot particles, followed by particle coagulations and PAH condensation/chemical reactions on soot surfaces. The major pathways for the formation of PAHs were also identified for the surrogate mixtures. The model accurately captures the synergistic PAH formation characteristics observed experimentally for n-heptane/toluene and iso-octane/toluene binary mixtures. Furthermore, the present experimental and modeling results also elucidated different trends in the formation of larger PAHs and soot between binary n-heptane/iso-octane and ternary n-heptane/iso-octane/toluene mixtures. Propargyl radicals (C_3H_3) were shown to be important in the formation and growth of PAHs for n-heptane/iso-octane mixtures when the iso-octane concentration increased; however, reactions involving benzyl radicals ($C_6H_5CH_2$) played a significant role in the formation of PAHs for n-heptane/iso-octane/toluene mixtures. These results indicated that the formation of PAHs and subsequently soot was strongly affected by the composition of gasoline surrogate mixtures.

1. Introduction

Particulate matter emissions are presently a concern in gasoline fueled direct-injection spark-ignition (DISI) engines. To better understand the combustion behavior of refinery gasoline fuels [1–7] and their emission characteristics, surrogate fuels are typically adopted for the development of predictive tools. Gasoline contains straight and branched-chain aliphatics, aromatics, alkenes, and cycloalkanes [1]. It has been shown that toluene primary reference fuels (TPRFs), the ternary mixtures of n-heptane, iso-octane, and toluene can match the ignition quality of gasoline fuels [8,9]. The presence of aromatics in gasoline fuels and their surrogates enhances the formation of polycyclic aromatic hydrocarbons (PAHs) and soot, which may cause adverse health and environmental problems [10]; however, fundamental studies on the formation of PAHs and soot from real fuel combustion are rather limited. In particular, direct fuel injection strategies aimed at enhancing fuel efficiency in gasoline engines often result in increased emission of smaller sized particulate matters, which are being regulated under new stringent emission laws. An accurate prediction of PAH concentrations, which are molecular precursors for soot formation and growth, is required to understand the effects of gasoline fuel composition on sooting characteristics, such as soot volume fraction, number density, and particle size distribution.

Several studies have been performed on the formation and growth of PAHs during the combustion of gasoline relevant fuels. Inal and Senkan [11] quantified the concentration profiles of PAH species in several fuel-rich laminar premixed flames of n-heptane at atmospheric pressure using a gas chromatography/mass spectrometry technique. Choi et al. [12] investigated PAH and soot

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formation characteristics for gasoline surrogate fuels in counterflow diffusion flames using laser-induced fluorescence (LIF) and laser-induced incandescence (LII) techniques. Detailed analysis of their experimental results indicated an interesting synergistic effect on PAHs in the n-heptane/toluene and iso-octane/toluene mixture flames, meaning the enhanced PAH formation for certain fuel mixtures as compared to corresponding single fuel components, similar to the synergistic effects observed for gaseous fuel mixtures [13–15]. The experimental [16,18] and numerical [17] studies of the effects of fuel composition on soot formation of binary PRF/TRF fuels in coflow diffusion flames have been conducted using methane flames doped with different blends of gasoline surrogate components. Li et al. [19] studied toluene decomposition and PAH formation in premixed flames at low pressure using synchrotron-based vacuum ultraviolet photoionization mass spectrometry. D'Anna et al. [20] investigated the process of soot growth in an n-heptane premixed flame and found the formation of larger particles in the aromatic-doped n-heptane flame. Mosbach et al. [21] presented a detailed model for soot formation in internal combustion engines coupling a gas-phase kinetic mechanism for primary reference fuel (PRF, mixtures of n-heptane and iso-octane). Blanquart et al. [1] and Marchal et al. [22] investigated PAH growth processes and proposed kinetic models for the formation of soot precursors in the combustion of engine relevant fuels. Wang and coworkers proposed reduced mechanisms for TPRF mixtures [23] and n-heptane/n-butanol mixtures [24], and tested their applications in engine simulations. Based on previous skeletal models [22], Raj et al. [25] presented a mechanism for gasoline surrogate fuels (KAUST PAH Mech 1; KM1) by adding relevant reactions using the density functional theory and transition state theory to account for the growth of PAHs up to coronene (A7, $C_{24}H_{12}$); these updates offered improvements in predicting PAH concentrations for n-heptane premixed flames [11] and diffusion flames of binary mixtures of toluene/n-heptane and toluene/iso-octane.

A closer look at existing literature reveals that among the previous studies for gasoline surrogate fuels, systematic investigations on the effects of fuel compositions on PAH/soot formation are rather limited, especially for ternary TPRF mixtures in non-premixed systems. Considering that TPRF mixtures were shown to better represent fundamental combustion properties of real gasoline fuels [26], detailed investigation of sooting characteristics of TPRF in diffusion flames are of great interests. As such, the purpose of the present study is set to expand the experimental data available for gasoline surrogate fuels in diffusion flames to better understand the effects of fuel blending on PAH formation, with a special focus on TPRF mixtures. Furthermore, an updated detailed chemical kinetic model for TPRF gasoline surrogate mixtures was also developed, with an emphasis on the formation of PAHs, to simulate and elucidate the experimental observations.

2. Experiment

In order to obtain a systematic understanding of the chemical cross-linking effects among TPRF mixture components in non-premixed flames, a new set of experiments were conducted using a counterflow diffusion flame configuration. A schematic including the counterflow burner and the laser diagnostic systems (LII system) is shown in Fig. 1.

The counterflow burner system has been described previously [12] and a brief summary is given here. The burner consists of two opposing nozzles with an inner diameter of 10 mm and a separation distance of 8 mm. Concentric slits (2 mm wide) surrounding the nozzles provide shield nitrogen to prevent the flames from being affected by ambient air and to avoid the formation of secondary diffusion flames in globally fuel-rich conditions. The average flow velocities at the nozzle exits for both the fuel and oxidizer streams were kept at 20 cm/s for all experiments. Gas and liquid flow rates were controlled by thermally-based mass flow controllers and precision syringe pumps, respectively. The oxidizer stream was composed of O_2 and N_2 with various O_2 mole fractions and the fuel stream was 65% N_2 diluted on a molar basis. To vaporize the liquid fuels, a commercially-available evaporation system was used with N_2 as the carrier gas. The fuel supply line and the fuel nozzle were both electrically heated to temperatures of 180 and 150°C, respectively, to prevent re-condensation of the

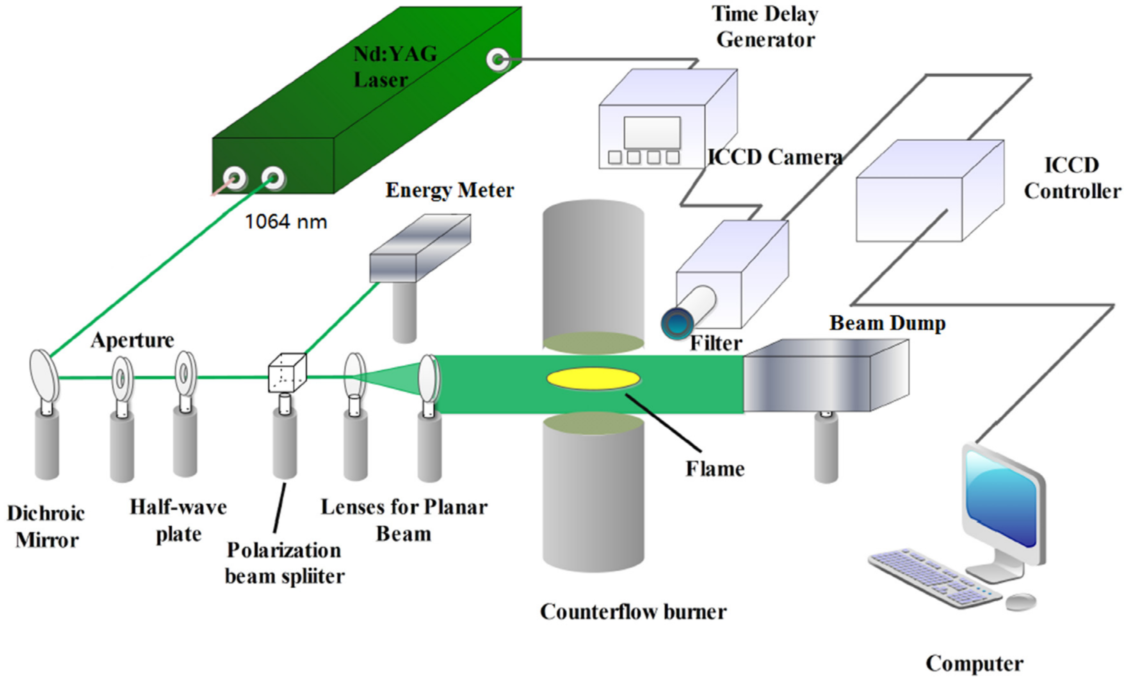

Fig. 1. Schematic of the experimental setup including the burner and the laser diagnostic (LII) system.