Combustion and Flame 160 (2013) 1129–1141

Contents lists available at SciVerse ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Evaluation of the sooting properties of real fuels and their commonly used surrogates in a laminar co-flow diffusion flame

Dustin Witkowski *, Katsufumi Kondo, Gokul Vishwanathan [1], David Rothamer

Department of Mechanical Engineering, University of Wisconsin–Madison, United States

ARTICLE INFO

Article history:
Received 15 August 2012
Received in revised form 24 December 2012
Accepted 25 January 2013
Available online 7 March 2013

Keywords:
Soot
Laminar diffusion flame
Fuel surrogates
Laser Induced Incandescence (LII)
Transmission electron microscope (TEM)

ABSTRACT

In an effort to help determine the fidelity of simple surrogate fuels to represent real fuel chemistry in computational fluid dynamic simulations of engines, quantitative two-dimensional soot volume fraction measurements were made in a laminar coflow methane–air diffusion flame seeded with approximately 2200 ppm of real and surrogate fuels. A combined laser extinction and laser-induced incandescence (LII) method was used to measure soot volume fraction. Additionally, soot particles were thermophoretically sampled from the flame and soot morphology data were collected with a transmission electron microscope (TEM). Vaporized liquid fuels were seeded at low concentrations to maintain constant thermodynamic conditions for each experiment. In all, 14 different fuels were investigated, including: three real fuels (gasoline, diesel, and jet fuel), two alkanes, and a variety of simple surrogate fuels. A toluene reference fuel (TRF) (30% aromatics) and gasoline (28% aromatics) were found to have similar soot volume fractions and soot morphology. The addition of toluene to the long-straight chain of *n*-tetradecane in similar concentrations (30 vol.%) as the aromatic concentration of diesel (31.1 vol.%) resulted in soot volume fractions that were very similar, although the primary particle size and mass-weighted radius of gyration were both smaller for the surrogate than for the conventional diesel fuel. Finally, the jet-fuel surrogate tested was found to have a lower sooting tendency than the jet-A fuel despite the jet-A fuel having a lower concentration of aromatics than the surrogate. Soot morphology between jet-A and the jet-fuel surrogate were the same within experimental uncertainty. The current work provides an experimental dataset for validation of fuel-surrogate chemistry and soot models.

1. Introduction

The evaluation of sooting tendencies of real fuels (diesel, gasoline, and jet fuel) in simple environments, such as laminar flames, is fundamentally important for understanding soot formation processes and developing robust soot models. This understanding is needed to improve the models used to predict soot formation in engineering CFD calculations used to design internal-combustion (IC) engines and gas turbine combustors. Increasingly stringent regulations on soot mass and the introduction of particle number regulations in Europe [1] for on road vehicles are driving the need for higher fidelity computational models of soot formation in IC engines.

Currently, CFD modeling of fuel chemistry for IC engine simulations is generally performed using simple surrogate fuels to represent real fuel chemistry. Fuel surrogates are often limited to single components or to simple mixtures of a few components in order to minimize computational time. Typical diesel fuel chemistry surrogates used in engineering CFD modeling of IC engines include: *n*-heptane, *n*-tetradecane, and gasoline primary reference fuels (GPRFs) (mixtures of *n*-heptane and iso-octane). Gasoline surrogates for IC engine CFD modeling include: iso-octane, GPRFs, and toluene reference fuels (TRF) (mixtures of *n*-heptane, iso-octane, and toluene) [2–7].

Most IC engine modeling of compression ignition engines regards ignition delay and the in-cylinder pressure trace as the governing validation parameters between the real and surrogate fuels. However, it is also vital to obtain similar emission formation characteristics. Particularly, soot emission predictions are challenging due to the complexities associated with modeling fuel chemistry, fuel composition, and particle physics. For example, fuel aromatics in diesel and gasoline may contribute significantly to soot formation, but are seldom taken into account even in detailed IC engine soot modeling approaches [8].

The current work combines line-of-sight soot extinction with laser-induced incandescence (LII) measurements to obtain two-

* Corresponding author. Address: Department of Mechanical Engineering, University of Wisconsin–Madison, 1500 Engineering Drive, Room B106, Madison, WI 53706, United States.
E-mail address: dwitkowski@wisc.edu (D. Witkowski).
[1] Address: Cummins Technical Center, Columbus, IN, United States.

0010-2180/$ - see front matter © 2013 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.combustflame.2013.01.027

dimensional quantitative soot volume fraction data for real fuels and commonly used simple surrogates in an atmospheric-pressure laminar co-flow diffusion flame. To gain insight into the fuel chemistry impact on soot morphology, thermophoretic sampling and transmission electron microscope (TEM) analysis were carried out. All measurements were taken in thermodynamically-similar steady-state combustion environments. This was ensured by seeding low concentrations (2200–2300 ppm) of vaporized liquid fuels into an atmospheric pressure methane-air laminar diffusion flame. Due to the low sooting tendencies of some of the fuels, a nominal seeding rate of 2200 ppm mole fraction was necessary to discern the impact on soot volume fraction. As will be discussed, this concentration is sufficiently low to limit the impact of the seeded fuels on the thermodynamic environment of the flame. Thus, the net sooting tendencies of the resulting flames are predominantly due to fuel-chemistry effects and the influence of surrogate fuel chemistry verses real fuel chemistry can be assessed.

The goal of the current work is to compare the sooting tendency of simple fuel surrogates that are commonly used in CFD simulations of IC engines to the real fuels being modeled. The hope is to provide initial evidence as to whether simple surrogates can replicate realistic soot formation behavior. The results acquired in a simple flame environment will hopefully supply guidance to the engine computational community regarding the level of surrogate complexity required to capture real-fuel sooting tendencies, and provide an experimental dataset for testing and validating fuel-surrogate chemistry and soot models applicable for CFD modeling in IC engines. The paper is organized as follows: first the background pertaining to soot formation pathways and the diagnostics used for the measurements are presented, next the experimental setup and experimental procedures used in the study are outlined, finally the results are presented and discussed and conclusions from the work are drawn.

2. Background

2.1. Soot formation pathways in non-aromatic and mono-aromatic hydrocarbons

Understanding some of the basic concepts and underlying mechanisms regarding soot formation in both non-aromatic and aromatic hydrocarbons is important when trying to understand the relative sooting propensity of different fuel surrogates. For this research in particular, previous work related to soot formation pathways for the mono-aromatic hydrocarbon toluene are of interest since it was used in the surrogates that were tested to mimic the behavior of the aromatics found in gasoline, diesel, and jet fuels. Alkyl-benzenes make up the majority of aromatics found in all three fuel types (diesel, gasoline, and jet fuel) [9–11]. In particular, toluene often makes up a significant fraction of the aromatics in gasoline, but is less common in diesel fuel [9] and jet fuel [11] where larger alkyl-benzene aromatics with higher sooting tendencies [12] are more common. Toluene is used in all surrogates as the aromatic for this study due to its low cost and its comparatively well-known chemistry.

There has already been extensive research in the area of soot formation for non-aromatic and aromatic hydrocarbons. In particular, it has been shown previously [13–16] that the rate limiting step for soot formation in non-aromatic hydrocarbons is the formation of the benzene ring. Once the first ring is formed, the hydrogen-abstraction-C_2H_2-addition (HACA) mechanism controls the formation of naphthalene, as well as, further PAH growth [13,14]. Wang and Frenklach [15] showed in shock-tube studies of ethylene and acetylene that the first aromatic ring is formed primarily through the following reactions:

$$C_3H_3 + C_3H_3 = A_1(C_6H_6) \quad (R1)$$

$$n\text{-}C_4H_3 + C_2H_2 = A_{1-}(C_6H_5) \quad (R2)$$

$$n\text{-}C_4H_5 + C_2H_2 = A_1 + H \quad (R3)$$

Aromatic ring nomenclature follows that of Frenklach [14], where A_1 is a single aromatic ring, A_2 is a two ring aromatic, and A_i is a PAH containing i rings. Other investigators have also previously suggested that there may be additional important aromatic ring pathways involving the cyclopentadienyl radical (C_5H_5) [17].

$$C_5H_5 + CH_3 = A_1 + 2H \quad (R4)$$

$$C_5H_5 + C_5H_5 = A_2 + 2H \quad (R5)$$

Once the first ring is formed, further growth of aromatics for the un-doped methane flame, as well as, when the flame is seeded with non-aromatic hydrocarbons, will be controlled by the HACA mechanism (R6), (R7), (R8), (R9).

$$A_i + H = A_{i-} + H_2 \quad (R6)$$

$$A_{i-} + C_2H_2 = A_iC_2H + H \quad (R7)$$

$$A_iC_2H + H = A_{i-}C_2H + H_2 \quad (R8)$$

$$A_{i-}C_2H + C_2H_2 = A_{i+1-} \quad (R9)$$

For mono-aromatic hydrocarbons such as toluene, there is evidence that the rate of formation of soot is no longer controlled by the formation of the first aromatic ring, but rather the formation of the second aromatic ring. McEnally and Pfefferle [18] conducted measurements of mono-aromatic hydrocarbons, including toluene, doped in a methane diffusion flame similar to the one reported in this study. They found that the HACA mechanism alone was not able to predict the formation of the second ring (naphthalene) sufficiently. They also demonstrated that for non-aromatic hydrocarbons soot formation was limited by the formation of the first aromatic ring, whereas the limiting step for mono-aromatic hydrocarbons, like toluene, was the formation of naphthalene.

Toluene decomposition primarily follows two paths [19–21]:

$$C_6H_5CH_3 + M = C_6H_5CH_2 + H + M \quad (R10)$$

$$C_6H_5CH_3 + M = C_6H_5 + CH_3 + M \quad (R11)$$

(R10) is apparently dominant over (R11) at temperatures below 1800 K [21]. The phenyl radical created from reaction (R11) could potentially undergo growth through HACA to form naphthalene. Since this is the minor pathway, it would seem insufficient to explain the large amounts of naphthalene that has been found previously in toluene flames [18,20]. In modeling performed by Colket et al. [20], they found that the fastest step for naphthalene formation during toluene pyrolysis occurs from the reaction of benzyl with propargyl.

$$C_6H_5CH_2 + C_3H_3 = A_2(C_{10}H_8) + 2H \quad (R12)$$

This effect was previously suggested as responsible for the naphthalene concentrations in the flame reported by McEnally and Pfefferle [18]. Modeling performed by Agafonov et al. [22] and validated with shock tube pyrolysis studies also suggested that the dominant path for naphthalene formation in toluene was reaction (R12).