



Sooting limits of nonpremixed *n*-heptane, *n*-butanol, and methyl butanoate flames: Experimental determination and mechanistic analysis



Sili Deng*, Jeremy A. Koch, Michael E. Mueller, Chung K. Law

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

HIGHLIGHTS

- Measured sooting limits of nonpremixed flames in a stagnation-flow configuration.
- Comparison with simulations using detailed chemistry and soot models.
- Examined soot response to strain, chemical pathways for PAH, and rate-limiting steps.
- Methyl butanoate found significantly less sooting compared to *n*-heptane and *n*-butanol.
- Fuel breakdown processes to soot precursors account for sooting tendency differences.

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ABSTRACT

The sooting limits of nonpremixed *n*-heptane, *n*-butanol, and methyl butanoate flames were determined experimentally in a liquid pool stagnation-flow configuration. In addition, complementary simulations with detailed polycyclic aromatic hydrocarbon (PAH) chemistry and a detailed soot model, based on the Hybrid Method of Moments (HMOM), were performed and compared with the experimental critical strain rates for the sooting flames. Argon dilution was used to keep the thermal environment for the three fuel cases nearly the same to elucidate the chemical effects. Both experiment and simulation showed that *n*-heptane and *n*-butanol had similar sooting characteristics, while methyl butanoate had the least sooting propensity. Further sensitivity and reaction path analysis demonstrates that the three fuels share similar PAH chemical pathways, and C₅ and C₆ ring formation from the intermediate chain species is found to be the rate-limiting step. The differences in sooting propensity lie in the fuel breakdown processes. Specifically, the oxygen bounded in *n*-butanol does not reduce soot precursor concentrations but is primarily involved in intramolecular water elimination reactions. On the contrary, the fuel bound oxygen in methyl butanoate shortens the carbon chain of the soot precursors and promotes their oxidation, which reduces the total carbon available for soot formation.

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1. Introduction

The utilization of biofuels, which are potential partial replacements for liquid fuels derived from fossil fuels, is garnering wide attention not only because these fuels are renewable, locally producible, and carbon neutral [1] but also due to their potential positive impacts on particulate matter (PM) emission control. Biofuels, including bioalcohols and biodiesels, mainly consist of oxygenated hydrocarbons, such as ethers, alcohols, and esters. When used as additives in conventional diesel fuels, PM emissions have been found to decrease as oxygenated additive concentrations increase [2].

However, the precise role of oxygenated additives on soot emission reduction has not yet come to a scientific consensus. For example, Frijters and Baert [3] attributed the PM reduction to the fuel oxygen content, which reduced the local equivalence ratio and, by implication, the flame temperature. However, even with the same oxygen content, the oxygenates had different efficiencies in soot precursor reduction, as Westbrook et al. [4] found through simulations of premixed *n*-heptane and oxygenates flames. Furthermore, Pepiot et al. [5] proposed a structural group contribution approach to interpret diesel engine experimental data and quantify the soot reduction tendency of oxygenated fuels. As noted by the authors, the aromatics contained in the conventional diesel fuels have very strong sooting tendencies, which are moderated through substitution by the clean-burning oxygenated additives; this

* Corresponding author.

E-mail address: silideng@princeton.edu (S. Deng).

replacement effect should be identified and quantified to reveal the role of the oxygen moieties.

Conversely, a number of studies show that oxygenated fuels do not necessarily have lower sooting tendencies than regular hydrocarbons. McEnally and Pfefferle [6,7] found that butanol isomer doped methane co-flow diffusion flames produce more soot than the undoped ones. As only 1000 ppm of each test compound was added to the methane stream, the study was able to identify the direct chemical effects of the additives. It was subsequently found that the effect of carbon chain length on soot formation is often larger than the direct chemical effects of oxygen and branches in the carbon chain promote soot formation. Similar conclusions were reached by Camacho et al. [8] by probing the evolution of the detailed particle size distribution function in a set of laminar premixed flames of *n*- and *i*-butane/butanol with fixed C/O ratio and maximum temperature.

To further explore the sooting characteristics of oxygenated fuels and understand the chemical pathways for soot formation processes, additional well-controlled fundamental experiments and detailed chemical kinetic analyses need to be performed. In particular, it is recognized that, besides the thermal and replacement effects of oxygenated additives, the residence times of soot precursors are also expected to influence the sooting propensities [9] since soot formation is a kinetically controlled process [10]. Therefore, the present experimental and computational study focuses on the sooting limits (a residence time effect) of three neat liquid diesel/biofuel components, specifically, *n*-heptane, *n*-butanol, and methyl butanoate, in a nonpremixed stagnation-flow. A combined chemical kinetic model with detailed polycyclic aromatic hydrocarbon (PAH) chemistry is constructed to investigate the important pathways of soot formation with these three fuels.

This choice of the target fuels is motivated by both practical and scientific concerns. First, butanol has more diverse non-food sources of supply than ethanol, which has been derived primarily from corn. Second, methyl butanoate is chosen not only because it is a typical biodiesel surrogate but also due to the availability of detailed chemical kinetic models. Third and most important, the boiling points of *n*-butanol and methyl butanoate are 391 K and 375 K, respectively, which are very close to that of *n*-heptane (372 K). This similarity in the vaporization characteristics enables similar fuel vapor concentrations above the stagnation liquid pool and assures similar rates of supply of the vaporized fuel to the flame region.

2. Experimental methodology

The sooting limits of nonpremixed model diesel/biofuel components, in terms of the critical strain rate (CSR) at which soot inception starts to happen when the residence time, which is the inverse of the strain rate, is further increased, were measured at atmospheric pressure in a liquid pool stagnation-flow configuration. An unheated oxidizer stream impinged against the liquid fuel pool, and flames were established by spark ignition. Coflowing nitrogen was utilized as the shielding gas to minimize the disturbance from the surroundings. With the 20 mm nozzle and pool diameter, the separation distance between the oxidizer nozzle and liquid pool was maintained at 13 mm to assure a well-characterized stagnation flow and also to enable better measurement of the velocity field by Laser Doppler Velocimetry (LDV). The schematic of the liquid pool stagnation-flow apparatus is shown in Fig. 1, and details about the auxiliary system can be found elsewhere [11].

Due to the oxygen content in *n*-butanol and methyl butanoate, their flame temperatures are lower than *n*-heptane. Since soot formation is highly sensitive to temperature [12], this thermal effect

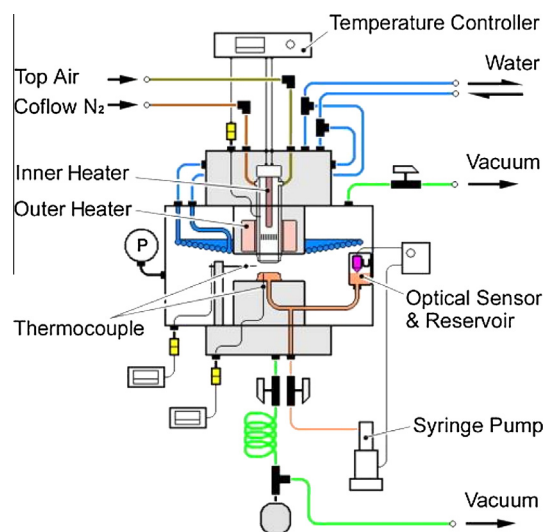


Fig. 1. Schematic of the liquid pool stagnation-flow apparatus [11]. The heating system was not activated in the current study.

has to be eliminated to elucidate the chemical effects. In the present study, *n*-butanol and methyl butanoate flame temperatures were increased to be the same as *n*-heptane by replacing a portion of the nitrogen in the oxidizer stream with argon, which is the same approach taken by Axelbaum, Law, and co-workers [13–15]. The amount of nitrogen replacement was calculated with CHEMKIN's equilibrium solver EQUIL [16] for stoichiometric fuel/oxidizer mixtures, and the diluent concentrations are summarized in Table 1. Although the replacement was calculated based on premixed stoichiometric mixtures, the thermal environment of all three fuels cases under the same strain rate and oxygen mole fraction in the stagnation-flow configuration is nearly the same, according to the simulations, which will be discussed in detail in Section 4. Liquid *n*-heptane, *n*-butanol, and methyl butanoate were fed to the liquid pool by a syringe pump at room temperature.

Soot detection was based on luminosity observations with a Nikon D700 camera, for Du et al. [13] found that such measurements agreed well with light scattering detection and were a convenient indicator of the presence of soot particles. The experimental procedure to identify the sooting limit is briefly summarized here. First, the oxidizer component flow rates were set, and a non-sooting blue flame was established. Then, the bypass valve placed upstream of the oxidizer nozzle was slowly adjusted to divert oxidizer out of the system, effectively reducing the velocity of the stream and, consequently, the strain rate. The residence time was further increased until yellow luminosity began to appear on the fuel rich side of the flame. A standard single-component LDV measurement was performed along the axial centerline under this threshold flow condition, and the local strain rate was determined as the axial velocity gradient upstream of the flame [13]. Following this procedure, the sooting limits for the three fuels with different oxygen concentrations in the oxidizer streams were identified. Although this luminosity measurement was not quantified, the CSR measurements were found to be repeatable.

3. Computational methodology

The liquid pool stagnation-flow flames were simulated with the FlameMaster code [17], including detailed PAH chemistry and a detailed soot model. The boundary conditions on the fuel side were specified following Bui-Pham and Seshadri [18]. In brief, the Antoine equation [19] was used to close the boundary value prob-

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