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*

**Abstract**

The role of oxygenated additives on soot emission reductions has not yet come to a scientific consensus. Although valuable contributions have been made, well-controlled fundamental experiments and detailed chemical kinetic analyses are still needed to understand the chemical pathways for soot formation with oxygenated fuels. Moreover, since soot formation is a kinetically controlled process, the residence times of soot precursors are also expected to influence the sooting propensities, and these effects have not yet been explored in detail for oxygenated fuels. 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 system.

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, this thermal effect has to be eliminated to elucidate the chemical effects. In the present study, *n*-butanol and methyl butanoate flame temperatures were kept at the same as *n*-heptane by replacing a portion of the nitrogen in the oxidizer stream with argon. Sooting limits were determined by increasing the oxidizer flow rates until yellow luminosity appears in the flames. The local strain rate at which this yellow luminosity first appears, was determined as the axial velocity gradient upstream the flame, utilizing the standard single-component Laser Doppler Velocimetry. Correspondingly, computations were conducted for the same configuration using detailed polycyclic aromatic hydrocarbon (PAH) chemistry and a detailed soot model based on the Hybrid Method of Moments.

Both experimental and computational results showed the critical strain rates of the three fuels, based on the absolute soot volume fraction, increase with increasing oxygen mole fraction in the oxidizer, due to the thermal effect. Moreover, although *n*-heptane and *n*-butanol show similar sooting propensities, methyl butanoate produces significantly less soot. Sensitivity and reaction path analysis was performed for naphthalene, the first PAH species from which soot forms. This analysis revealed that, despite different sooting tendencies, the three fuels shared similar PAH chemical pathways. C5, C­6, C7, C9 rings, and naphthalene are formed sequentially through the combination of C3 and smaller chain radicals resulting from fuel cracking processes. Due to the fuel bound oxygen in methyl butanoate, less and shorter chain radicals are available for soot formation, compared with the other fuels, such that methyl butanoate forms the least soot and has the lowest critical strain rates. The strain rate effects on soot formation were also examined. Despite different sooting propensities, for all three fuels, C5 and C6 ring formation reactions are the rate limiting steps. Their concentrations drop as the residence time is reduced, such that the downstream PAH chemistry is consequently inhibited, resulting in the sooting limits.

*Keywords:* Soot, Nonpremixed stagnation-flow flame, Hybrid Method of Moments, *n*-Butanol, Methyl butanoate