A comparative study on the sooting tendencies of various 1-alkene fuels in counterflow diffusion flames

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ABSTRACT

Alkenes are important components in transportation fuels, and are known to have increased sooting tendencies compared to analogous saturated hydrocarbons with the same carbon number. This work aims to understand the sooting tendencies of various 1-alkenes through experiments and numerical simulations for counterflow diffusion flames. Soot and PAH formation tendencies of 1-alkene fuels, including ethylene (C_2H_4), propene (C_3H_6), 1-butene ($1\text{-}C_4H_8$), 1-pentene ($1\text{-}C_5H_{10}$), 1-hexene ($1\text{-}C_6H_{12}$) and 1-octene ($1\text{-}C_8H_{16}$), were experimentally studied using laser induced-incandescence (LII) and laser-induced fluorescence (LIF) techniques, respectively. From the LII results, $1\text{-}C_4H_8$ was found to be the most sooting fuel, followed by $C_3H_6 > 1\text{-}C_5H_{10} > 1\text{-}C_6H_{12} > 1\text{-}C_8H_{16} > C_2H_4$. The LIF data with a detection wavelength of 500 nm indicated the PAH formation tendencies followed the order of $1\text{-}C_4H_8 > 1\text{-}C_5H_{10} \sim 1\text{-}C_6H_{12} > C_3H_6 > 1\text{-}C_8H_{16} > C_2H_4$, which were different from the order of sooting tendencies. Numerical simulations with a comprehensive chemical kinetic model including PAH growth chemistry for the tested 1-alkene fuels were conducted to elucidate the aromatic formation pathways and rationalize the experimentally observed trends. The numerical results highlighted the importance of intermediate species with odd carbon numbers in aromatic species formation, such as propargyl, allyl, cyclopentadienyl and indenyl radicals. Their concentration differences, which could be traced back to the parent fuel molecules through rate of production analysis, rationalize the experimentally observed differences in soot and PAH formation tendencies.

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1. Introduction

Soot emission from the combustion of hydrocarbon fuels adversely affects human health and the environment [1–3]. In particular, soot particles with diameters on the order of nanometers are extremely hazardous, as they are able to penetrate human lung tissue and enter the blood circulation system [4,5]. Soot is also known to contribute significantly to climate change by altering surface albedo in polar regions [6]. A recent study has linked soot emission from the combustion of fossil fuels to the severe particulate matter ($PM_{2.5}$) pollution [7], raising wide social concerns. In such context, it becomes paramount for combustion scientists and engineers to develop new technologies of controlling soot emission in practical combustion devices. To accomplish this, soot formation pathways from various hydrocarbons needs to be well understood, thus motivating fundamental combustion research on soot.

Decades of research have identified fuel type to be a major factor controlling soot formation [8–12], making investigations on the correlation between fuel molecular structure and sooting tendency especially important. From the viewpoint of scientific understanding, systematic comparisons of sooting characteristics among various fuels help to identify important reaction pathways leading to soot precursors general to a class of fuels [13,14]. On the other hand, practical knowledge of sooting tendencies of individual fuel components can also find applications in assessing and designing fuels with increased molecular complexities [15].

Fundamental studies on sooting tendencies have been performed in laboratory-scale flames targeting both single component fuels [12,16–23] and fuel mixtures [24–28], with a recent shift of focus toward oxygenates [12,29–33]. Various sooting indexes have been proposed to quantify the sooting tendencies of fuels. These include threshold soot index (TSI) [8], yield soot index (YSI) [17], normalized smoke point (NSP) [34] and oxygen extended sooting index (OESI) [12]. A further look into this body of work reveals that most are based on either smoke point or co-flow diffusion flames, which are both two-dimensional in nature. As a result, numerical modelling using detailed reaction mechanisms for these flames is

challenging, especially considering the complexities in PAH growth mechanisms for high molecular weight fuels. This may partially explain the scarcity of accompanied simulations in those works. However, detailed kinetic modelling and subsequent reaction pathway analysis are essential for a fundamental understanding of the differences in sooting tendencies among the fuels. In this regard, we proposed to measure sooting tendencies in counterflow diffusion flame (CDF) and introduced sooting temperature index as a quantitative sooting metric [35]. The quasi-one-dimensional nature of counterflow diffusion flame makes detailed kinetic simulation more tractable, such that chemical kinetic and transport information regarding soot formation pathways can be more efficiently extracted. It should be noted that several sooting tendency studies with numerical modelling do exist, such as those by Deng *et al.* in liquid pool stagnation-flow [31], Markatou et al. in premixed flat flames [36], Chernov et al. [37] and Xuan and Blanquart [38] in co-flow diffusion flames.

The relative ranking of sooting tendencies among different fuels is dependent on flame structure. For example, alkenes have a higher propensity to soot than alkanes in smoke point diffusion flames, while the trend is reversed in premixed flames [8]. As a canonical configuration, counterflow diffusion flames can be classified into soot formation (SF) flames and soot formation oxidation (SFO) flames depending on the location of the flame relative to the stagnation plane [39]. In a SF flame, the flame is on the oxidizer side of the stagnation plane, so the soot produced is convected away from the flame and towards the stagnation plane without much oxidation. In a SFO flame the soot is transported toward the high temperature flame zone for further oxidation. Previous studies have demonstrated that sooting characteristics are drastically different between SF flames and co-flow or SFO flames [39]. As such, sooting tendency studies in soot formation counterflow diffusion flames could complement those performed in co-flow flames. This is particularly important considering that in SF flames, we can investigate the tendency of the fuel to *form* soot while minimizing interference from soot oxidation, as opposed to smoke point flames where the smoke point is essentially a critical condition when soot formation and oxidation are balanced. Additional features of counterflow diffusion flames as compared to smoke point or co-flow flames include the ability to vary strain rate to be more representative for practical combustion systems, and their relation to and application in flamelet models for turbulent combustion modelling.

Alkenes are an important class of fuels whose combustion and pollutant formation characteristics deserve systematic investigations. Alkenes are essential components of practical fuels: liquid petroleum gas contains significant amount of propene; the well characterized FACE (Fuels for advanced combustion engines) F and G gasolines contain 10% and 7.9% of alkenes by mole, respectively [40]; a recent surrogate formulation of practical gasoline also include 1-hexene as a key component [41]. Alkenes are also key intermediates during alkane oxidation and pyrolysis, so an improved understanding of alkene combustion is prerequisite for refinement of alkane reaction kinetics. However, despite its importance, systematic studies on the sooting tendency of alkenes are scarce, especially on the effects of carbon number. Even oxidation and ignition studies for alkenes with different carbon chain length are lacking in the literature [42–52], which motivated a recent study on C_2–C_5 1-alkenes [53].

This work presents an experimental and kinetic modelling study on the PAH and soot formation characteristics of C_2–C_8 1-alkene fuels in counterflow diffusion flames. The results were discussed together with reaction pathway analyses to gain a fundamental understanding of the underlying reaction mechanisms. It is worthwhile to point out that most previous studies of sooting tendencies (in smoke point or coflow flames) were focused on the effects of structural groups of the fuels, while this study focused more on the effect of number of carbon atoms within the same class of fuels, namely, 1-alkenes. It is also relevant here to mention a recent study on the sooting behaviors of C_1–C_4 n-alkanes in a micro flow reactor [54], which targeted similarly on the effects of carbon number.

2. Experiment

The PAH and soot formation tendencies of the various 1-alkene fuels were experimentally measured in laboratory-scale, laminar counterflow diffusion flames at atmospheric pressure. A schematic is shown in Fig. 1 for the experimental apparatus, which consisted of a counterflow burner, a gaseous and liquid flow control system and laser-based measurement setups. The counterflow burner had two identical nozzles (10 mm i.d.) opposing each other with a separation distance of 8 mm. The fuel and oxidizer streams were introduced from the lower and upper nozzles, respectively. Annular slots surrounding both nozzles provided nitrogen shields to avoid disturbances from ambient flow. The shields were also necessary to eliminate secondary diffusion flames due to the reaction of fuel and ambient air.

The flow rates of the gases (i.e., N_2, O_2, C_2H_4, C_3H_6, 1-C_4H_8) were controlled by thermally-based mass flow controllers, which were calibrated using piston-driven positive displacement flow meters. The liquid fuel flow rates were adjusted by a high-precision syringe pump. A commercially available evaporation system was used to vaporize the liquid fuels with N_2 as the carrier gas. To avoid liquid fuel re-condensation, the vaporizer, transfer lines and the bottom burner were heated with resistive heating tapes. Note this was also done for gaseous fuels for consistent comparisons. The temperatures at fuel stream outlet were measured by type K thermocouples, and it was around 140 °C with variation of less than 3 degrees, while the oxidizer streams were maintained at room temperature. The nozzle exit velocities were 20 cm/s in all cases.

The soot volume fractions of the flames were quantified using the planar laser-induced incandescence (LII) technique, which utilized the blackbody radiation of the laser heated soot particles as an indication of their concentrations. The fundamental emission (1064 nm) of a 10-Hz pulsed Nd-YAG laser, through a series of cylindrical and spherical lenses, formed a laser sheet of 8 mm high at the center of the burner. The beam energy was continuously adjusted by a combination of half-wave plate and polarization beam splitter, and was set to be within the saturation regime such that the LII signals became independent of incident laser fluence [55]. The LII signals, after passing a narrow-band interference filter with center wavelength of 400 nm and bandwidth of 40 nm, were then detected by an intensified CCD (ICCD) camera, which was synchronized with the laser Q-switch signal through a digital delay generator. The camera gate was set to open immediately after the incident laser reached the flame (i.e., zero gate delay) and the gate width was 80 ns. Note, by recording soot radiation at flame temperature without the firing of the laser, we could eliminate the contribution of flame emission to the LII signal through background subtraction. The LII signals at all experimental conditions were averaged for 600 laser shots to increase the signal to noise ratio. The measurement uncertainty, as estimated from the standard deviation, was around 4.7%. Note in LII experiments, the soot particles are heated by a high energy infrared beam to a temperature up to 4000 K and under such condition all the volatile components condensed on the soot particles are expected to vaporize [56]. Therefore, only the thermal radiation of soot particles contributes to the LII signal.

LII measurements alone cannot provide absolute values of soot volume fractions without proper calibration, although it has been shown that the signal intensity is linearly proportional to soot