Brief Communications

Measuring the soot onset temperature in high-pressure *n*-dodecane spray pyrolysis

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A B S T R A C T

Soot formation in pyrolyzing sprays of *n*-dodecane is visualized and quantified in a high-pressure, high-temperature, constant-volume spray chamber at 38 bar, 76 bar, and 114 bar. Sprays of *n*-dodecane are injected at 500 bar from a single-hole, 186-μm orifice diameter fuel injector. We quantify the temporal evolution of the soot optical thickness and the total soot mass formed in the pyrolyzing sprays using a high-speed extinction imaging diagnostic. The vessel ambient temperature and pressure are varied independently to identify the soot onset temperature for *n*-dodecane pyrolysis. Linear extrapolation of the maximum soot formation rates as a function of ambient temperature reveals a soot onset temperature near 1450 K. The onset temperature determined here for *n*-dodecane is within 50 K of those previously measured along the centerline of atmospheric pressure coflow diffusion flames for smaller alkane fuels.

1. Introduction

Laminar flame studies conducted at atmospheric pressure by Gomez et al. [1] and Saito et al. [2] revealed a relatively consistent soot onset temperature between 1310 K and 1400 K for a variety of hydrocarbon fuels. To determine the onset temperature, the authors used a fine-wire thermocouple and measured the temperature along the flame centerline until soot deposits were observed. The radiation corrected temperature at the highest centerline axial location prior to soot deposition defined the onset temperature. For clarity, we mention that the onset temperature as it is defined and used in the present work differs from the soot "inception" temperature near 1600 K (or higher) reported in [3–8]. Whereas, the onset temperature measured in [1,2] was determined in a region where oxidation is not expected to inhibit soot formation, studies referencing the inception temperature have generally been conducted under conditions where competition between soot formation and oxidation occurs.

Of the 12 flames studied in Gomez et al. [1], all were established at the smoke height condition with the exception of one of the butene flames. Saito et al. [2] selected small diffusion flames for their study since such flames remain in the early stage of soot formation. For all cases in Gomez et al. [1], the soot onset location was observed at a height in the flame between 25% and 40% of the luminous flame height, while Saito et al. [2] reported that the first

soot deposits onto their probe occurred between 2 mm and 4 mm below the first visible appearance of yellow emission. Recognizing that the centerline in the near-burner region of a non-lifted coflow diffusion flame is oxygen deficient [9], these early soot processes are more representative of a pyrolysis pathway. As such, the soot onset temperatures measured by Gomez et al. [1] and Saito et al. [2] provide a suitable reference for the study of soot onset limits under pyrolytic conditions or conditions expected to have very small quantities of oxidizing species.

In addition to diffusion flame studies, shock tubes have been widely used to investigate pyrolytic soot formation processes and establish temperature dependencies for a wide range of fuels. Graham and co-workers [10] were pioneers in this area followed by the large body of work from Frenklach [11–17]. Soot yields are generally negligible in shock tube pyrolysis experiments at temperatures below 1500 K; however, with the addition of a small amount of oxygen soot has been observed during acetylene/oxygen/argon mixtures in the shock tube below 1400 K [14]. To understand the effect of oxygen on soot formation, Gülder [18] added oxygen to the fuel stream in laminar coflow flames of methane, propane, and *n*-butane. They observed that oxygen suppressed soot formation in methane flames while enhancing soot formation in propane and *n*-butane flames. Suppression of soot in methane flames was attributed to a reduction in acetylene as a pyrolysis product while the enhancement observed for propane and *n*-butane flames was related to oxygen stimulating fuel pyrolysis and the production of H atoms and other hydrocarbon radicals. Hwang et al. [19] investigated the influence of adding a small amount of oxygen to the fuel in counterflow ethylene diffusion flames and concluded that

reactions between O atoms and acetylene enhance the formation of key soot precursor species. Oxygen's enhancement of fuel decomposition and soot precursor formation leading to increased soot in these flame studies is consistent with the reduced soot onset temperature in shock tube studies when a small amount of oxygen was included in the mixture.

This brief communication presents measurements of the soot onset temperature in pyrolyzing sprays of *n*-dodecane in a constant volume, high-pressure, high-temperature, pre-burn chamber. We use the term "pyrolyzing" loosely here as the pre-burn products, which consist mainly of nitrogen, also include small amounts of carbon dioxide and water. Over the range of temperatures and pressures considered (1400 K – 1750 K, 38 bar – 114 bar) ppm quantities of the hydroxyl radical (OH), hydrogen, and oxygen would be present at equilibrium. Such small quantities of OH and oxygen may promote earlier and/or more rapid fuel decomposition than a purely inert environment, but would not be sufficient to open oxidation pathways in competition with soot formation. A high-speed, diffused back-illumination extinction imaging (DBIEI) diagnostic enabled time-resolved, quantitative measurements of the total soot mass. The maximum formation rate of soot as a function of ambient temperature was derived from the time-resolved imaging extinction measurements and a linear extrapolation was performed to determine the soot onset temperature. We observed a soot onset temperature near 1450 K for the pyrolyzing *n*-dodecane sprays, which is within 50 K of the onset temperatures measured for smaller alkanes in atmospheric pressure, coflow diffusion flames [2].

2. Experimental

2.1. Combustion vessel and injection system

Sprays of *n*-dodecane were injected into the optically accessible, high-pressure, constant-volume combustion vessel depicted in Fig. 1. The combustion chamber is nearly cubical with a characteristic dimension of 108 mm. Six round ports of 105-mm diameter constitute the four sides and top and bottom of the chamber with eight 19-mm diameter ports located at the corners. The water-cooled fuel injector (Bosch 3-22) is mounted horizontally in one of the side ports with two spark plugs mounted in the top port and three fine-wire type-R thermocouples mounted in the bottom port. Sapphire windows occupy the remaining three side ports for optical access. Pneumatic intake and exhaust valves reside in two of the corner ports on the injector side of the vessel along with a pressure transducer (Kistler K-6001). The fourth corner port on the injector side is unused. A second pressure transducer, a sheathed
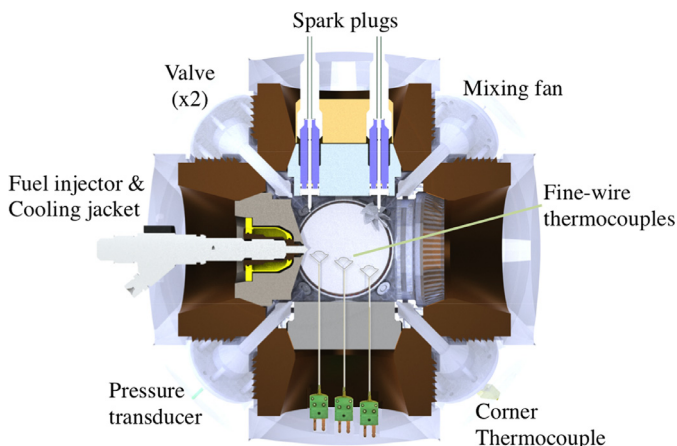

Fig. 1. Schematic cross-section of constant volume pre-burn vessel.
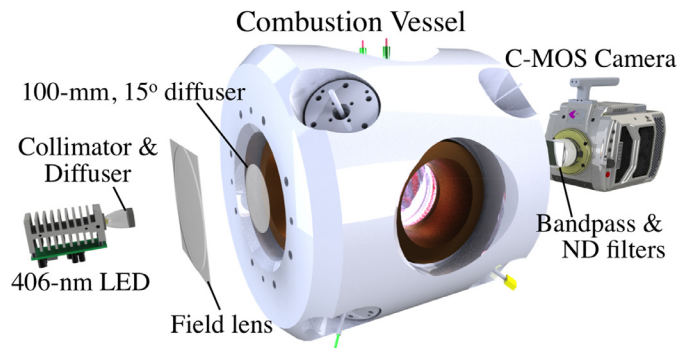

Fig. 2. Diagram of the high-pressure combustion vessel and diffused back-illumination extinction imaging (DBIEI) optical arrangement.

type-J thermocouple, and the mixing fan occupy three of the four corner ports on the opposite side of the injector port with the fourth corner port on this side also unused.

The temperatures and pressures desired for this study were achieved via the combustion of a spark-ignited premixed charge. The premixed charge gases include acetylene, hydrogen, nitrogen, and oxygen and batches of the desired mixture are prepared manometrically and stored external to the laboratory prior to the experiments. Following the aforementioned "pre-burn" event, a cooldown period ensues resulting in a time-dependent range of thermodynamic conditions into which the fuel spray can be injected. The present work employed a stoichiometric pre-burn charge resulting in an ambient environment containing 89.71% nitrogen, 6.52% carbon dioxide, and 3.77% water by volume. The conditions therefore do not represent pyrolysis in the purest sense since ppm levels of OH and O_2 are expected based on equilibrium calculations at temperatures exceeding 1400 K.

Target ambient conditions ranged from 1400 K to 1700 K (50 K steps) at pressures of 38 bar, 76 bar, and 114 bar. Temperature measurements at three axial locations within a few millimeters of the penetrating fuel vapor/soot boundary were acquired using the thermocouples mounted in the bottom vessel port. Radiation corrections were performed and uncertainty in the temperature measurements is estimated to be ± 25 K

A syringe pump (Teledyne 30D) pressurizes the fuel to 500 bar prior to injection and the injector has a single axial orifice with a 186-μm nominal diameter. We targeted short injection durations (120 μs) and a relatively low common-rail injection pressure to limit vapor penetration and the mass of fuel injected. By limiting vapor penetration, the conversion of fuel vapor to soot can be imaged over a longer period of time while the entire spray remains within the field of view of the imaging system described in the next section.

2.2. Diffused back-illumination extinction imaging (DBIEI)

We quantified soot formation following pyrolytic decomposition of *n*-dodecane using the high-speed imaging extinction diagnostic illustrated in Fig. 2. The main components of this diagnostic include a high-output, ultra-fast, deep blue (406-nm, 17-nm FWHM) light emitting diode (LED) equipped with a collimator, two engineered diffusers, a field lens, and a high-speed camera. The first engineered diffuser (25-mm diameter, circular 50-degree distribution) was mounted at the exit of the LED collimator. The light passing through this first diffuser was collected by the 150-mm diameter, 150-mm focal length field lens. The field lens directed the nearly collimated light to the second diffuser, which has a 100-mm diameter and a circular 15-degree distribution. The high speed camera was operated at 50,000 frames per second and was