Soot formation characteristics of *n*-heptane/toluene mixtures in laminar premixed burner-stabilized stagnation flames

Quanxi Tang [a,b], Boqing Ge [a,c], Qi Ni [b], Baisheng Nie [c], Xiaoqing You [a,b,*]

[a] *Center for Combustion Energy, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China*
[b] *Key Laboratory of Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China*
[c] *School of Resource and Safety Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China*

ARTICLE INFO

ABSTRACT

The soot formation characteristics in laminar premixed flames of pure *n*-heptane and binary mixtures of toluene and *n*-heptane with liquid volume ratios ranging from 0.2 to 1 were studied with the C/O ratio and unburned gas-mixture velocity being kept the same for all tested flames. The particle size distribution functions (PSDFs) at several selected burner-to-stagnation surface separation distances (H_p) were measured by using the burner-stabilized stagnation probe/scanning mobility particle sizer (SMPS) technique. In addition, the morphology of soot particles sampled from the probe was examined using transmission electron microscopy (TEM). From the PSDFs at different H_p and TEM images, it was observed that with the addition of toluene, soot inception occurred at lower flame heights and the primary particle size of soot aggregates was significantly reduced. A combustion kinetics model for toluene and *n*-heptane was used to explore the precursor chemistry. The modeling results were found to be consistent with the observations of the measured PSDFs.

© 2017 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Increasingly stringent regulations in many countries on soot emission for on-road vehicles are driving the need for higher accurate computational soot models for internal combustion engine design. The commercial transportation fuels we use such as gasoline, diesel, and jet fuel are mixtures of hundreds of hydrocarbons. The high complexity of fuels has encouraged the search for limited fuel formulation (surrogate fuels) to emulate the physical and chemical properties of a real fuel. Among various surrogate fuel formulations [1,2], *n*-alkanes and aromatics are essential, in that *n*-heptane and toluene are often used to optimize both the fuel formulation and engine design [3,4].

The studies on surrogate fuels have been widely conducted with a focus on auto-ignition, flame propagation, and extinction characteristics [5–12]; they are indispensable for the understanding of combustion properties of various fuel formulations. By contrast, the soot formation characteristics of surrogate fuels remain less understood, especially the synergistic effects of multi-component mixtures. It has been reported that in a spherical droplet flame in an optically accessible sealed chamber, adding toluene significantly enhanced sooting propensities of *n*-heptane [13]. Mathieu et al. [14] studied the soot tendency of a diesel fuel surrogate composed of *n*-propylcyclohexane, *n*-butylbenzene, and 2,2,4,4,6,8,8-heptamethylnonane in a heated shock tube and found that the soot induction delay time and soot yield depend strongly on the structure of the hydrocarbon and the concentration of oxygen, and the soot inception process was initiated by the fuel molecule that produces soot fastest. A similar observation was also made in a premixed *n*-heptane flame study [15], where the *n*-propylbenzene addition gave rise to a faster soot inception at lower heights above burner, yet the ultimate soot loading was similar to those flames without aromatics addition due to slightly lower temperature and lower acetylene formation. Choi et al. [16] investigated the binary fuels of toluene/*n*-heptane and toluene/*iso*-octane in the counterflow diffusion flames, a synergistic effect was observed to have caused an initial increase and then decline in PAH concentration with toluene addition. The soot amount, however, was marginally changed with the addition of small amount of toluene. Another study of *n*-heptane/toluene mixtures in a wick-fed diffusion flame [17] showed that the dependence of soot particle size distributions on height changed to resembling an aromatic fuel from resembling a paraffinic with an increased ratio of toluene in the binary mixtures with *n*-heptane.

---

* Corresponding author at: Center for Combustion Energy, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China.

E-mail addresses: xiaoqing.you@tsinghua.edu.cn, youxiaoqing@gmail.com (X. You).

Table 1
Summary of flame conditions.[a]

Flame	Volume ratio of $C_6H_5CH_3$ to C_7H_{16}	Mole fraction		Equivalence ratio	T_{max}(K)[b]
		$C_6H_5CH_3$	C_7H_{16}		
H10	0	0.0000	0.0512	1.89	1764 ± 84
H10T2	0.2	0.0111	0.0401	1.81	1780 ± 88
H10T4	0.4	0.0183	0.0329	1.76	1822 ± 94
H10T10	1	0.0298	0.0214	1.69	1913 ± 108

[a] Unburned gas composition: 0.0512 fuel-0.2988 O_2- 0.65Ar; cold gas velocity:4 cm/s (298 K, 1 atm); C/O: 0.6.

[b] T_{max} is the measured maximum flame temperature with radiation correction at H_p = 1.2 cm.

All these studies show that fuel structures indeed play a very important role in soot formation process, and a few reaction pathways have been proposed to explain the experimental observations. For aliphatic fuels, such as *n*-alkanes, the formation of the first ring is regarded as the rate-limiting step in the reaction sequence to large aromatics and is generally described by the reactions involving radicals such as CH_3, i-C_4H_5, i-C_4H_3, C_3H_3, C_5H_5 [18–21]. As for aromatic hydrocarbons such as toluene, research results show that the second aromatic ring instead of the first controls the rate of soot formation through the pathway of $C_6H_5CH_2 + C_3H_3 = A_{2\,(C_{10}H_8)} + 2H$ [22,23]. Once small aromatic rings are formed, the subsequent growths are similar through the hydrogen-abstraction-C_2H_2-addition (HACA) and the PAH condensation pathways [19,20,24].

Despite the significant gains in understanding of combustion characteristics and soot formation of surrogate fuels, more quantitative experimental data from well-defined configurations are still needed for model validation and for a better understanding of the mechanism of soot formation, such as the measured soot particle size distribution functions at different heights above burner using burner-stabilized stagnation flame (BSSF). BSSF does not only have the advantages of well-defined boundary conditions but also well-understood probe effects [25,26]. On top of that, the detailed characteristics of soot formation, including nucleation and mass growth can be captured from the evolution of soot particle size distribution functions. In the present study, we investigate the evolution of soot particle size distribution functions and particle morphology in BSSF of pure *n*-heptane and binary mixture fuels of *n*-heptane/toluene. Since *n*-heptane/toluene mixtures are regarded as representative components in gasoline fuel and their combustion characteristics have been widely studied in the literature [3,15,16,27–29], we expect our study on their sooting behaviors would deepen our understanding of the particulate emission characteristics.

2. Experimental setup

The laminar premixed fuel-rich flames on a stainless steel McKenna burner at atmospheric pressure were studied with four different compositions (Table 1): pure *n*-heptane (H10), and binary mixtures of toluene and *n*-heptane with liquid volume ratios of 0.2 (H10T2), 0.4 (H10T4), and 1 (H10T10), respectively. The C/O ratio (0.6) and unburned gas-mixture velocity (4 cm/s, 298 K & 1 atm) were kept the same for all conditions. The flames were stable and isolated from the air by a shroud of nitrogen flowing at 30 cm/s through a concentric porous ring.

Details of the BSSF setup (Fig. 1) and the experimental procedure were introduced in our previous works [25,30,31]. Briefly, the sample probe was made of a stainless steel tube with a 160 μm orifice in the middle and embedded in a flat aluminum plate. Soot particles were sampled in the axial centerline at several selected burner-to-stagnation surface separation distances (H_p) with a positional accuracy of ± 0.04 cm, and were diluted immediately by a
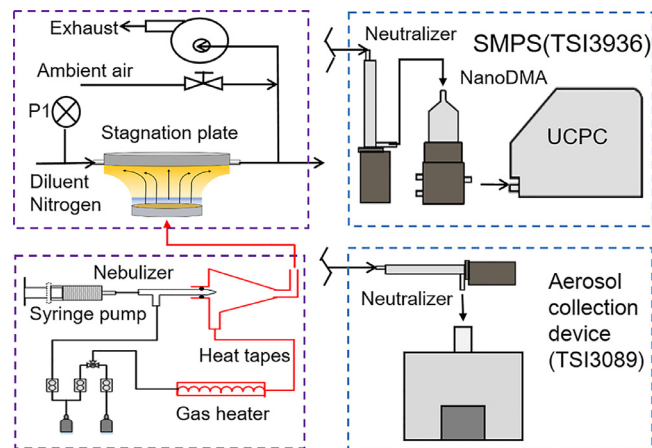

Fig. 1. The schematic diagram of experiment.

30 L/min nitrogen flow to quench chemical reactions, prevent particles from coagulation, and reduce wall diffusion loss in the sampling line. The flow rate of the unburned gas was controlled by sonic nozzle calibrated by a soap-film flow-meter. The orifice temperature was about 450 ± 30 K, which was measured by a type-K thermocouple embedded inside the stagnation aluminum plate. The procedure introduced in [25] for determining the optimal dilution ratio was used. Since soot PSDFs are insensitive to the dilution ratios ranging from 1500 to 5000 for the present experimental setup, we took a dilution ratio of ~3000 when taking samples. The detailed procedure for data inversion of the absolute number density (N) in the flame related to the number density (N_s) measured by SMPS can be found in [25,31].

The fuel vaporization system is similar to the one used in [32]. Liquid fuels were injected into a conical vaporization chamber by a syringe pump (Longer, LSP01-1A). To ensure complete liquid fuel vaporization, a nebulizer was used to atomize liquid fuels with a stable constant argon flow of 0.5 L/min (STP) at the upstream to shear liquid fuels into small droplets. Then the atomized fuel droplets were vapored immediately by a hot mixture gas flow of oxygen and argon (403 ± 2 K). The conical vaporization chamber and the transfer line to the burner were maintained at a constant temperature (403 K) by strip heaters. Different from Ref. [32], the burner was cooled with hot water at 348 ± 2 K to prevent both fuel condensation in the porous plug and overheat of the burner. Note the boiling temperatures of *n*-heptane and toluene are 371.5 ± 0.3 and 383.8 ± 0.3 K, respectively [33]. According to the Antoine equation [34], the boiling temperature of the binary mixtures of *n*-heptane and toluene will be slightly lower than 383.8 K. Hence, the temperature of 403 K is adequate to vaporize the fuel mixture.

The flame temperature was measured by an S-type thermocouple coated with a Y/Be/O mixture (12% yttrium oxide and 88% beryllium oxide [35]) to prevent surface catalytic reactions. The