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Sooting tendency and particle size distributions of n-heptane/toluene mixtures burned in a wick-fed diffusion flame

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HIGHLIGHTS

- Particle size distributions of heptane/toluene mixtures and gasoline in a diffusion flame were measured.
- The addition of toluene shifts the primary and aggregate size distribution to larger diameters.
- A gasoline with a smoke point similar of 50% toluene–50% heptane forms soot with smaller sizes.

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ABSTRACT

The sooting characteristics of binary mixtures of n-heptane and toluene and a commercial gasoline were studied. The experiment involves the non-premixed combustion of the fuel in wick-fed burner. The particle size distributions (PSDs) of soot were measured at the tip of flames of different heights, using a differential mobility spectrometer (DMS). Transmission electron microscopy (TEM) was used to investigate the morphology of the particles formed. Pure n-heptane and toluene were studied along with blends of 10%, 30%, and 50% by volume of toluene in n-heptane. The addition of toluene to heptane shifts the PSD to larger diameters. As toluene is added to n-heptane the dependence of soot particle size on flame height changes from resembling a paraffinic to resembling an aromatic fuel in a non-linear fashion. A tolerance to toluene addition at the lowest flow rates was found, where particles were not detected. A commercial gasoline with approximately 44% by mass of aromatics was also analysed. The smoke point and PSDs are similar to the mixture 50% toluene 50% n-heptane, but the mean aggregate mobility size, number of particles and primary particle size formed by the gasoline are smaller.

1. Introduction

Commercial transportation fuels such as gasoline are mixtures of hundreds of hydrocarbons. The primary chemical classes of hydrocarbons in fuels are paraffins, olefins and aromatics. Although the composition of these fuels are variable, there are some common trends [1,2]. The high complexity of fuels encouraged the search for mixtures of limited components to ease the development of new combustion technologies through computational tools, and to generate insight and understanding of underlying fundamental processes.

A surrogate fuel is defined as a mixture of a small number of hydrocarbons which aims to emulate chemical and physical properties of a real fuel. The study of surrogate fuels and its formulation has been used basically for the development of kinetic mechanisms that describe the real kinetic behaviour of non-sooting phenomena [3,4]. The knowledge regarding the soot formation process from single as well as mixtures of hydrocarbons remains in a poor stage [5].

In the last century strong efforts were made to understand the mechanisms of soot formation. There is an agreement that the pathway begins with the formation of molecular precursors such as polyacetylenes and polycyclic aromatic hydrocarbons (PAHs) [6]. The rate limiting reaction is the formation of the first aromatic ring, for which various mechanisms have been proposed [7]. Collision and sticking of PAHs contributes to particle inception [8,9]. Once primary particles are formed, these nascent soot particles undergo surface growth [10] and competing oxidation, and the small particles will agglomerate into larger fractal structures [8,11,12]. However, there are still many unresolved questions in this process, such as the transition from gas to solid phase and

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the influence of the fuel composition. In the last decade efforts have been focused on experimentally understand such processes [13,14] as well as to model and predict them [8,12,15].

Significant contribution analysing the smoking process of some hydrocarbons and their mixtures have been made recently [3,5,16–19], showing that the soot formation have a strong correlation with hydrocarbons' structure. One of the targets used to assess a fuel surrogate mixture in terms of its sooting propensity is the threshold sooting index (TSI) [20,21] that is based on the smoke point (SP) [22]. This property enables the analysis of hydrocarbon mixtures because of its linear relationship to fuel composition [23,24], facilitating its estimation over a large amount of possible surrogate mixtures. However, no information on the characteristics of the soot particles is available through this targeted property.

The aromatic content has been considered to be responsible for the formation of soot particles [25–27]. In an optically accessible combustion chamber study, it was found that the aromatic content dominates over effects of partial premixing and results in higher total soot mass [25,27]. An opposite trend was found by Wang et al. [28] on experiments and simulation of a diesel engine. A higher toluene content in n-heptane/toluene mixtures actually produced the lowest soot emissions, due to the slightly longer ignition delay, indicating that the mixing process also plays an important role. Binary mixtures of n-heptane/iso-octane, n-heptane/toluene and iso-octane/toluene have been investigated in counterflow diffusion flames [17]. Their results showed a tolerance in the mixing of toluene below which its effect on soot formation was minimal, this was observed as well in shock tube experiments [29].

The simplest and most studied surrogate in diesel engines is the mixture of n-heptane and toluene [19,30,31]. Higher concentrations of toluene in the mixture results in a longer ignition delay [30,31]. In an optical combustion chamber, experiments showed that the higher the toluene content the more premixed combustion occurs. As a small quantity of toluene (5%) was added to n-heptane, the soot mass concentration increased while generally keeping the same diameter [31]. However, when the toluene content was increased to 10% both mass concentration and particle size increased, resembling that produce from diesel fuel. A similar observation was also made in a co-flow diffusion flame [19], where the aromatic addition seemed to contribute to the soot volume fraction by increasing soot aggregate concentrations but having insignificant effect on the soot morphology.

Even though important steps have been taken towards the understanding of soot formation in commercial fuels through the experimentation with surrogate fuels, scarcity of detail information remains, particularly on the soot particle size distributions. This paper follows a series of studies of the sooting tendency of pure hydrocarbons [32,33]. The purpose is to study soot particles formed from fuel mixtures to learn more about the nature of soot as well as providing additional information that can aid modelling. The mixtures of heptane/toluene were selected because it is a simple binary mixture that allows the determination of the effect of each component. Additionally, it has been widely studied and characterised in the literature in terms of its combustion properties, as described above. A commercial petrol-station gasoline was studied as well in order to compare its sooting behaviour with the surrogate mixtures. Currently there is a strong trend moving away from traditional premixed operations towards gasoline direct injection (GDI) where soot formation is an issue.

The soot PSDs and morphology in the non-premixed combustion of n-heptane and toluene mixtures was investigated. In order to capture the influence of aromatic addition, we characterise the soot particles formed in a wick-fed laminar diffusion flame of pure n-heptane, toluene and its mixtures at different flame heights, using differential mobility spectroscopy (DMS). In-flame soot samples were analysed by transmission electron microscopy (TEM).

2. Experimental methodology

2.1. Soot particle size measurements

The fuels tested are: n-heptane, toluene, and their mixtures with volumetric additions toluene of 10% (H90T10), 30% (H70T30) and 50% (H50T50). A commercial unleaded gasoline (RON 95) was also tested, GC–MS was used to obtain the fuel composition.

The experimental set-up and procedure used in this study is the same as described previously [32,33]. A standard smoke point lamp where the fuel is supplied via a wick was used to generate a laminar diffusion flame [22]. The flame height was adjusted by increasing the wick exposure (*i.e.* increasing the fuel flow rate). At each flame height the fuel flow rate was calculated from the weight loss of the burner as described by [34].

Fig. 1 depicts the flame sampling system, detailed information can be found in [33]. The soot particles were sampled using a stainless steel probe with 8 mm inner diameter, enclosed by two water cooling jackets either side of a 0.3 mm sampling hole. The sample is drawn into a constant nitrogen dilution flow of approximately 8 l/min at 0.25 bar (zero-referenced to complete vacuum). A secondary diluter within the particle analyser reduces the load to the particle classifier. The dilution in this experiments is calculated to be in the range 10,000–15,000. This accounts for variations in the sample and/or diluent flow rates. The variation in dilution ratio in a determined sampling period is minimal, and the variation between different sampling runs ranged between 11,500 and 13,700 (worst case scenario). The residence time of the gas sample passing through the orifice is less than 8 μs before it was diluted with cold nitrogen. At these experimental conditions independence of the PSD with dilution ratio was achieved.

The particle analyser used in the present work is a Differential Mobility Spectrometer 500 (DMS) developed and manufactured by Cambustion Ltd. The particles are sized based on their mobility diameter, which is the diameter of a sphere with the same migration velocity as the particle of interest in a constant electric field.

The soot particles are always sampled at the tip of the flame, and therefore at the centerline, for a series of different flame heights. The flame height was adjusted and sampled again at the tip, this is repeated until the tip of the flame is no longer defined for sampling. Each flame height is sampled for 30 s, which corresponds to at least 6 averaged PSDs measured by the DMS. This procedure is repeated at least three times for each fuel.

2.2. Temperature measurements

Centerline temperature measurements were performed with an uncoated 75 μm type R thermocouple (Pt/Pt-13%R), using a rapid insertion procedure to minimise soot deposition [35]. The constant-tension thermocouple design [36] was used as a reference for the set-up. Detailed information on the measurements and correction due to thermocouple radiation losses can be found elsewhere [33]. Radiation correction was in the range of 15–50 K.

2.3. Thermophoretic sampling and HRTEM

The technique used is a common in-flame sampling method for microscopy imaging is based on the phenomenon of thermophoresis occurring in the vicinity of a cold probe introduced inside the flame. Soot particles are driven thermophoretically to the probe [37]. A fast insertion technique is used to protect the grid from thermal damage. A pneumatic solenoid was use to drive the sample in and out the flame in a very short period [38]. The system was