Sooting tendency of paraffin components of diesel and gasoline in diffusion flames

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HIGHLIGHTS

- Particle size distribution of several liquid hydrocarbons in a diffusion flame were measured.
- A decrease in soot particle size with increase in number of carbons was observed.
- Cyclo-alkanes produce larger soot particles than iso-alkanes and n-alkanes the smallest.

ARTICLE INFO

ABSTRACT

The influence of the chemical structure on the sooting characteristics of some paraffin class hydrocarbons which are found in gasoline and diesel fuel is studied experimentally. The experiment involves the combustion of the paraffin in a wick-fed burner. Differential mobility spectrometry is used to measure the particle size distribution (PSD) at different flame heights. The wick-fed laminar diffusion flame is sampled at the tip; the flame height is modified systematically from small heights to large heights. Normal, iso and cyclo paraffins PSDs evolve in a similar way with flame height. At very low flame heights the PSD is unimodal, but rapidly evolves into a multi-modal one. The total number of particles peaks at small heights, and then decreases as flame height increase until it approaches constant values for all considered fuels. The mean soot particle diameter increases with flame height until a height where a maximum is achieved and sustained. Among each type of fuel, a systematic decrease in the maximum mean soot particle diameter was observed as the number of carbon atoms in the molecule increased. At all flame heights, comparing fuels with the same carbon number, cyclic paraffins presented the largest mean soot particles sizes, followed by iso-paraffins and the smallest particles for normal paraffins.

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1. Introduction

One of the major causes for atmospheric pollution is soot, produced from incomplete combustion, and widely emitted from engines, combustion furnaces and other applications. As a consequence, environmental government agencies are implementing strict regulations on the emission of particle matter from different sources. Soot mass and the introduction of particle number regulations in Europe [1] for on road vehicles, lead to the necessity to study the sooting characteristics of different fuels in terms of their particle sizes.

Liquid fuels such as diesel and gasoline are mixtures of hundreds of hydrocarbons produced from distillation of crude oil. Paraffins, being one of the major components of such fuels [2–4], constitute an important group of hydrocarbons to study, and just a few recent investigations were devoted to assess their effect on soot characteristics. They are present in commercial fuels with structures in the carbon range of C_{10}–C_{24} for diesel mixtures and C_5–C_7 for gasoline mixtures. Cyclo-paraffins in diesel may comprise one-third or more by weight, the most common are single-ring cyclohexane with alkyl side chains, and larger species with two or more rings usually represent less than 5% of the fuel [2]. In gasoline mainly normal and iso-paraffins are present, with a smaller concentration of naphthenes [4].

The sooting tendency of different hydrocarbons in diffusion flames has been subject of study for many years [5–10], with a

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general agreement that the rate at which hydrocarbons produced soot increases as follows:

$$paraffins < isoparaffins < mono\text{-}olefins < naphthenes < alkynes$$
$$< aromatics$$

Alkanes exhibit a very low tendency to soot, as the number of carbons increases the smoke points of alkanes decreases [11], but tends to achieve a common value. Alkanes with more than 7 carbon atoms exhibit very large smoke points and, taking into account the large error involved in this measurement, the values are similar [12]. The more compact the structure, the greater the tendency to soot. Therefore isomeric or cyclic structures of alkanes and alkenes present lower smoke points, indicating an increase in the sooting tendency [6]. The variations in smoking tendency among different fuel types has been explained as the result, mainly, of a dehydrogenation process [6]. The chances of dehydrogenation increase with the stability of the carbon structure (bond strengths increases: C—C > C—H > C=C > C≡C), facilitating the removal of hydrogen atoms in comparison with the breaking of carbon bonds. The more readily the hydrogen atoms are removed as compared to the breaking of carbon bonds, the greater is the probability of smoke formation [13].

Significant efforts to understand sooting phenomena have led to a general agreement on the processes involved [8,14–21]: (a) formation of radical precursors from the oxidation of the hydrocarbon fuel (b) a complex process that comprises the formation of the first aromatic ring and its growth to polycyclic aromatic hydrocarbons (PAHs) through radical reactions of small molecules and/or fragments; (c) particle inception, defined as the formation of solid primary particles; (d) molecular growth; (e) coagulation; and (f) oxidation. Although a lot of research has been devoted to study each one of the mentioned processes, only a few investigations employ liquid fuels probably due to difficulties with vaporisation of the fuels and in their chemical complexity, especially for multi-component fuels.

Although paraffins are major components of commercial fuels, just a few recent studies devoted to assess their effect on soot characteristics. They have being studied either by using a purely aliphatic single component fuel or multi-component fuel with a high content of aliphatic species in its composition. For example, hexane was studied in terms of its sooting characteristics in a diffusion flame and compared with benzene; they were found to have very different flame structures [22]. Compared to benzene, n-hexane flame was found to have lower PAH and soot emission levels. In another investigation, *Velásquez et al.* [23] studied the chemical and morphological characteristics of soot formed in an inverse diffusion flame of n-hexane and a surrogate fuel containing several paraffins (cyclohexane, n-hexane, iso-octane) and aromatics (benzene and toluene). They observed that the surrogate fuel produced five times more soot than the aliphatic one, and concluded that the decomposition of the fuel depends not only on the temperature but also on the chemical nature of the fuel. They also found that at higher flame height positions the primary particle size shifted to small ranges, mainly due to thermal and oxidation processes being more drastic for the aliphatic n-hexane flame than for the surrogate, probably because of a higher temperature.

The formation of PAHs and soot from paraffin fuels in a diffusion flame was recently studied [24] using two gaseous fuels (methane and propane) and a liquid fuel (hexane). As the carbon number of fuel increased, the position of PAHs formation and its transition to soot particles occurred at an early stage in the flame, this was also found for the peak concentration of benzene and toluene. *Witkowski et al.* [25], also studied the sooting properties of n-heptane and several surrogate fuels using a methane diffusion flame seeded with the desired fuel. When seeding the methane flame with n-heptane, no significant impact on the primary particle diameter size and surface growth rates was found. Instead, an increase in inception rate was found, resulting in higher rates of agglomeration and larger soot aggregates.

Information on the particle size distribution (PSD) is nowadays of mayor importance and remains scarce for paraffins. The main objectives of the present work are to capture the influence of chemical structure on the sooting properties of paraffin fuels, and to compare the soot formation behaviour among different fuel structures. Soot formed in a nonpremixed, laminar, atmospheric pressure flame is studied at at different flow rates, i.e. flame heights. The soot PSDs are experimentally determined using differential mobility spectrometry with a DMS500. This is a fast particle analyser that enables measuring PSD in real-time, used in many studies of particulate matter emissions from diesel [26–30] and gasoline engines [31,32]. The following hydrocarbons were studied: n-heptane, n-decane, n-dodecane, n-hexadecane, iso-octane, iso-cetane, decalin (decahydronaphthalene; mixture of cis and trans) and methylcyclohexane (MCH).

2. Experimental methodology

2.1. Burner and sampling system

In this study, a wick-fed burner that has being previously described [33] was used to generate a laminar diffusion flame of liquid fuel. The smoke point test burner [34] was used as simple, known and standardised way to test different liquid fuels in terms of their combustion at atmospheric conditions. The burner consists of a cylindric reservoir, with an inner concentric hole where the wick is placed, and a 7 mm i.d noozle. A light weight Delrin™ fitting was adapted to the outside of the burner tube, and connected to the wick sheath via four brass struts. Thus, the flame height could be adjusted by rotating the threaded fitting and 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 from the burner, and measured with and analytic balance [33]. Fig. 1 depicts the adapted burner and flame sampling system.

The soot particles were sampled using a probe system with high dilution, similar to previously reported systems [35–38]. A stainless steel probe of 80 mm length and 8 mm i.d, enclosed by two water cooling jackets either side of a 0.3 mm sampling hole was used to sample soot particles. The probe was machined such that the sampling hole was at the centre of a flat rectangle of 20×7 mm, acting as a sampling plate. Previous work on premixed flames using a sampling orifice of ∼0.3 mm to draw a small sample into a stream of N_2 proved that at sufficiently high dilution the size distributions become independent of dilution ratio and probe geometry [37].

Probe sampling is known to be a highly intrusive technique, and at higher soot levels, as those present in the considered diffusion flames, rapid clogging of the orifice by thermophoretic deposition would be expected if the probe is inserted in the flame [39,40]. To overcome this problem, it has been proposed to enlarge the sampling orifice, this will reduce the immediate dilution and trigger coagulation mainly of small particles [39,40], leading to an artificial fall-off of the concentration of particles of sizes below ∼10 nm [41].

Due to the mentioned problems associated with inserting the probe inside the flame, in the present work the sampling point is always the tip of the flame (touching the flame at its visible tip). Even then, cooling effects are expected with a reduction of the flame height. For this reason the flame height reported in this paper is measured with the sampling probe placed at the tip of the