# Sooting tendency of surrogates for the paraffinic fractions of diesel and gasoline in diffusion flames

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#### Abstract

The influence of the chemical structure in the sooting characteristics of surrogates for the paraffinic fraction of gasoline and diesel fuel is studied experimentally. The experiment involves the combustion of the paraffin in a smoke point lamp (ASTM D1322). 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 (in some cases beyond the smoke point). 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 to a multi-modal one. The total number of particles decreases with flame height and approaches constant values for all considered fuels. As flame height increases so does the mean soot particle diameter until a height where a maximum is achieved and sustained. As the number of carbon atoms increases in the molecule the final mean soot particle diameter decreases. Cyclic and iso-paraffins produce soot particles with larger mean sizes compared to normal paraffins of the same carbon number.

## **1** Introduction

Conventional fuels such as diesel, gasoline, kerosine are complex mixtures of large numbers of hydrocarbons. Surrogate fuels are mixtures of a very small number of components of defined composition. They are meant to sufficiently emulate the chemical and physical complexity of conventional fuels. The amount of each species in the surrogate mixture is selected to mimic properties of a real fuel, such as physical properties: composition, C/H ratio, density, evaporation characteristics; and/or chemical characteristics relevant for engine modelling: ignition behaviour, combustion efficiency, emissions [10].

A variety of suitable surrogate species have been proposed, and some of their combustion characteristics are well-understood, but it is still unclear whether they are suitable to mimic the sooting behaviour of a commercially available fuel. For example, *Westbrook et al* [41] and *Dooley et al* [7] only tested ignition delays and species concentrations. The sooting behaviour of conventional and surrogates fuels is still not well-understood. This is mainly because the characterisation 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 [8]. There is a clear need to develop kinetic mechanisms for surrogates that can simulate the formation of soot in the combustion of practical fuels. This demands the knowledge of the role that each species is playing during the combustion and formation of soot particles.

Significant efforts to understand sooting phenomena have lead to a general agreement on the processes involved [17, 27, 32]. On this basis, models aiming to represent these phenomena were formulated [1, 3, 39, 40, 46], comprising the synthesis of the first aromatic ring structure and its growth to large polycyclic aromatic hydrocarbons (PAH) to form soot. So far, these models have been validated mainly for  $C_2$  molecules [1, 3, 9, 39, 40, 46], but recently steps have been made towards the development of mechanisms for larger hydrocarbons. For example, the formation of aromatics from gasoline surrogates have been studied [31, 45] and chemical mechanisms were proposed. These new models are build upon the ones proposed for small hydrocarbons, combined with mechanisms created for the oxidation of large hydrocarbons [23, 34]. *Saffaripour et al.* [34] were able to numerically represent the formation of soot from a jet-fuel surrogate diffusion flame, at the centerline of several flame heights. They used a combination of kinetic mechanisms of the gas-phase surrogate combustion, plus PAH and soot formation from aforementioned studies [1, 9].

Experimentally, one of the targets used to asses a fuel surrogate mixture in terms of its sooting propensity is the threshold sooting index (TSI) [5, 29] that is based on the smoke point (greatest flame height without smoke emission under laminar diffusion combustion) [2]. This property enables the analysis of hydrocarbon mixtures because of its linear relationship to fuel composition [15, 28], facilitating its estimation over a large amount of possible surrogate mixtures. However, they only give information on the tendency to soot of hydrocarbons. Information on the characteristics of the soot formed that can aid soot modelling is not available through this property; experimental data on this matter remains scarce.

The sooting tendency of different hydrocarbons has been subject of study for many years.

In 1950's the first studies trying to relate the molecular structure of hydrocarbons with smoke point were published [20, 36]. The results indicated that the rate at which hydrocarbons produced soot increased as follows:

#### *paraffins* < *isoparaffins* < *mono-olefins* < *naphthenes* < *alkynes* < *aromatics*

While this statement is qualitatively true, the inequality signs are not of equal weight [5]. Alkanes exhibit a very low tendency to soot, as the number of carbons increases the smoke points of alkanes decreases [29], 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 [22]. The more compact the structure, the greater the tendency to soot. Therefore isomeric or cyclic structures of alkanes and alkenes present lower smoke points, although the effect is small compared with the increase in sooting tendency derived from the increase of aromatic character. Branching would also increase the soot tendency in paraffins [36].

*Gomez et al.*[17–19] conducted several studies on the sooting behaviour in diffusion flames. They found that pyrolysis of fuel plays a controlling role in the sooting tendency, that leads to the formation and growth of soot precursors and the heterogeneous oxidation of soot particles. The variations in smoking tendency among different fuel types has been explained as the result, mainly, of a dehydrogenation process [36]. The chances of dehydrogenation increase with the stability of the carbon structure (bond strengths increases:  $C-C > C-H > C=C > C\equiv C$ ), 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 [37]. In diffusion flames, the fuel is heated to high temperatures before being in contact with oxygen, promoting thermal dehydrogenation. In addition, the presence of other active atoms would probably initiate the formation of smoke [37].

Recently experimental studies on soot precursors and particle matter of different hydrocarbons in diffusion flames were reported [14, 21]. Light paraffins below  $C_6$  were analysed using laser techniques [14], and their sooting behaviour was studied. Two different stages consisting of PAHs formation and soot formation were encountered, passing trough a transition region from PAHs to soot. They found that as the carbon number of fuel increases, the transition region PAHs to soot was shifted to lower flame heights, indicating that PAHs and soot were formed at an early stage in the flame.

The purpose of the paper is to study the influence of the paraffin structure on the formation of soot in diffusion flames. In order to capture the influence of chemical structure on sooting tendencies, we characterised the soot particles formed in the non-premixed combustion of several hydrocarbons targeted as surrogates for the paraffinic fraction of diesel and gasoline fuels. Soot is characterised using the simple smoke point lamp burner in conjunction of differential mobility spectroscopy (DMS), obtaining information about the particle size distribution at different flame heights. The fuels were selected to comprise the most abundant paraffin classes in real fuels (n-alkanes, iso-alkanes, cyclo-alkanes). The fuels were selected based on previous extensive reviews on surrogate fuels [6, 10, 30].

## 2 Experimental methodology

The ASTM D1322 smoke point test [2] uses a standardized apparatus involving a wickfed laminar diffusion flame. The smoke point test burner was used as simple, known and standardized 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. A light weight Delrin<sup>TM</sup> 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. **Figure 1** depicts the adapted burner and flame sampling system.

A stainless steel probe of 80 mm, enclosed by two water cooling jackets either side of a 0.3 mm sampling hole was used to sample soot particles from the flame tip. The distance between the flame and the sample hole is adjusted using a scissor lift. The gas sample is driven to the particle analyzer as shown in **Figure 2**. The particle mobility spectrometer used in the present work is a Differential Mobility Spectrometer 500 (DMS) developed and manufactured by Cambustion Ltd. This is a fast particle analyser that enables to measure PSD in real-time. Particles are sized based on their mobility diameter, from now onwards referred to as particle diameter. The DMS can detect particles from 5 to 1000 nm.



Figure 1: Sampling system for particle size analysis.

The DMS uses a classifier column operating at 0.25 bar with an external vacuum pump. The sample gas passes through a corona discharge charger, and then flows within a uniform particle-free sheath flow, that is just a cylindrical column of air designed to carry the particles in a predictable way. The particles are then deflected by the repulsion from a high voltage rod placed in the centre of the cylinder, towards the rings of a grounded electrometer. The landing ring would depend on the particle electrical mobility, which is related to the particle diameter if assumed to be spherical; this enables to classify them.

The particles transfer their charge to the electrometers amplifier and the resulting currents are translated in to particle number and size.

In order to mitigate the effects of coagulation and oxidation of soot particles during transport along the probe, it is usually necessary to dilute the sample flow by a factor of as small as 10 [11], or as large as 10000 [47], depending on the nature of the particles and their concentration. In each of these papers, it is heavily stressed that similar work should always include rigourous analysis of the effects of dilution on the observed PSD. Dilution greater than 1000 times the sample rate was suggested by Siegmann et al. [38] and over 3300 [24] for highly sooting fuels such as gasoline.



Figure 2: Primary and secondary dilutions for DMS.

The DMS passes a constant nitrogen flow of approximately 8 litres/min into the sampling probe in order to dilute the sample. The high flowrate within the sampling system caused by the high nitrogen flow and low pressure from the DMS leads to simultaneous dilution by a factor of 20 (first dilution); as well as expansion of the sampled gas avoiding particles agglomeration or coalescence post sampling. A secondary diluter within the DMS500 reduces the particle load on the instrument, using an integral mechanical rotating disc diluter, and allowing another dilution between 20 - 500 times. In order to meet the DMS optimum operation, reducing cleaning cycles, the maximum secondary dilution of 500 was set in all the experiments. The total dilution factor is the product of the first and secondary dilutions and is calculated by the DMS, ranging from 10000 – 15000. Independence of the PSD with dilution ratio was achieved at the experimental conditions mentioned.

The fuels tested are: n-heptane, n-decane, n-dodecane, n-hexadecane, iso-octane, isocetane, methylcyclohexane (MCH) and decalin (decahydronaphthalene; mixture of cis+trans); their chemical structure is presented in **Figure 3**. The burner is fuelled and the fuel is lighted; starting from a very small flame height, the tip of the flame is sampled at the centerline. The threaded fitting is turned to increase the flame height and the flame is 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 seconds, which corresponds to at least 6 averaged PSDs measured by the DMS. This procedure is repeated at least three times for each fuel.

An issue regarding this experimental set-up was the instability of the flame due to its natural flicker. This is a consequence of the absence of significant oxidiser co-flow. The flick-



Figure 3: Chemical structure of fuel's tested.

ering flame causes some difficulties to sample exactly the same position every time, but following the proposed methodology we found a good reproducibility and errors within the normal values of the studied literature.

## **3** Results

Starting at very short, bluish flame heights and increasing the height systematically, a maximum flame height is attained, which for some fuels exceeded the smoke point. This maximum flame height sampled is different for each fuel. In most of the cases, the maximum flame heights were those after which the tip of the flame was no longer defined, but blurry (opened tip with soot trail formation). For fuels with very high smoke points (such as n-alkanes), the largest flame height sampled was below the smoke point, due to flame instabilities and apparatus limitation. **Figure 4** shows images of sampled flames at different heights for n-heptane and n-hexadecane.

From the PSD important parameters are calculated, such as the total number density N and the mean diameter weighted by the number density  $\langle dp \rangle$ .

#### Alkanes

The evolution of the particle size distribution with flame height for different alkanes is presented in **Figure 5**. The maximum flame heights sampled were 70, 70, 56 and 50 mm for n-heptane, n-decane, n-dodecane and n-hexadecane respectively.

At a very low height of 5 mm where the flame is still bluish (see **Figure 4**), the PSD consists of a single mode with particles smaller than 10 nm, mainly primary particles in the inception process. At flame heights of 10 mm and beyond, coagulation occurs at increasingly fast rates together with surface growth, shifting the PSD to the right, to larger diameters. Once the flame height increases above 10 mm, the yellow luminosity that characterise the presence of soot is clearly observed (see **Figure 4**), and a second mode starts to raise indicating the presence of both primary and coagulated particles. After 15 mm a clear multi-modal behaviour is observed, with a greater accumulation mode at higher particle diameters due large agglomerates.

**Figure 6** shows the evolution of *N* and  $\langle dp \rangle$  with flame height for each fuel. For all the fuels, *N* is large or increases fast at very low flame heights indicating the formation of primary particles. The large number densities and high reactivity of young soot particles causes intense coagulation and agglomeration, resulting in a sharp decrease of *N*. For



**Figure 4:** *Images of n-heptane (top row) and n-hexadecane (bottom row) flames at different flame heights.* 

larger flame heights N remains fairly constant.

 $\langle dp \rangle$  also increases fast changing from a primary particle size to larger nano-particles, and achieves a point where it remains fairly constant. Until flame heights around 15 mm, all fuels present a similar increase in  $\langle dp \rangle$ , suggesting that the surface growth and coalescence of primary particles follow the same paths among them. After this height, each fuel achieves a maximum and sustained soot  $\langle dp \rangle$ . This approximate constant  $\langle dp \rangle$  is different for each fuel, being larger for n-heptane, followed by n-decane, n-dodecane and the smallest for n-hexadecane. Results show a systematic decrease in the mean diameter at moderate to high flame heights with the increase in the paraffin carbon chain.

#### Iso-alkanes

**Figure 7** shows the evolution of the particle size distribution at different flame heights for two iso-alkanes. The maximum flame heights sampled were 50 mm and 30 mm for iso-octane and isocetane respectively.

Iso-alkanes present a behaviour very similar to that shown by n-alkanes. At low heights a single-mode PSD reveals the presence of small primary particles, that quickly evolves into multi-modal PSD with larger particle diameters. At 10 mm flame height the PSD has already a bi-modal shape, consisting of a larger accumulation mode of  $\langle dp \rangle$  around 40 nm. From this flame height onwards the PSD evolution consist on the enlargement of this accumulation mode.



Figure 5: PSDs for n-alkanes at different flame heights.



**Figure 6:** Number concentration N (empty symbols) and  $\langle dp \rangle$  (full symbols) evolution with flame height for alkanes.

The evolution of N and  $\langle dp \rangle$  with flame height for each fuel is presented in **Figure 8**. At very small flame heights N is large and decreases fast to achieve a steady value around



Figure 7: PSDs for iso-alkanes at different flame heights.

 $2 \times 10^9$ .  $\langle dp \rangle$  increases fast and reach a fairly constant value for the moderate to large flame heights. Iso-octane achieves higher  $\langle dp \rangle$  compared to isocetane. The latter has a larger carbon chain and is more branched.



**Figure 8:** Number concentration N (empty symbols) and  $\langle dp \rangle$  (full symbols) evolution with flame height for iso-alkanes.

#### Cycloalkanes

The last paraffin group structure studied were cyclic alkanes. MCH and decalin were analysed and maximum flame heights of 45 mm and 23 mm respectively were achieved.

The evolution of the particle size distribution with flame height for the studied cycloalkanes is presented in **Figure 9**. The behaviour observed is similar to other alkane structures. At low flame heights a single mode appears. A 2 mm larger flame height exposed the growth of a lower mode of larger particles, that will evolve into the dominant accumulation mode at moderate to large flame heights.



Figure 9: PSDs for cyclo-alkanes at different flame heights.

**Figure 10** presents the PSD calculated parameters evolution with flame height. The same tendencies of normal and iso-alkanes are observed. The achieved maximum  $\langle dp \rangle$  is larger for MCH than decalin.



**Figure 10:** *Number concentration N (empty symbols) and*  $\langle dp \rangle$  *(full symbols) evolution with flame height for cyclo-alkanes.* 

### 4 Discussion

A common trend in the evolution of the PSD at different heights was found for all tested paraffins. The shift from a single mode to a multi-mode PSD observed in the flames is in agreement with recent studies of soot formation in gasoline flames [25]. Two stages in the evolution of  $\langle dp \rangle$  and N were detected: an initial stage at flame heights smaller than 15 mm approximately, and a posterior stage of flames beyond that height. A recent study of light paraffins [14] reported a transition region in the PAHs to soot formation in methane, propane and hexane flames, all occurring around a 20 mm height above the burner. This discussion will be addressed according to the two stages observed in this work:

#### Small flame heights ( $\leq 15 \text{ mm}$ )

- At very small heights particles with diameters below 10 nm are detected in high concentrations, *N* increases fast and is very large consisting of newly nucleated primary particles. These primaries quickly coalesce increasing their diameter and sharply decreasing in number, as seen in other investigations [18].
- Among each class of fuel  $\langle dp \rangle$  is similar (see for example **Figure 10**), this suggests that inception and growth processes at this stage follow a common path. **Figure 11** shows the variation of the particle mean diameter with the number of carbon atoms in the fuel at small flames (~ 5 mm) and large flames. At small heights mainly inception and growth are taking place, the particle diameter appears to be constant with carbon number for each group of fuels. This observation implies that among groups of fuels particle growth is independent of fuel chain length, which is in agreement with widely recognized speculations [13].
- Between different fuel structures, cycloalkanes present higher  $\langle dp \rangle$  when compared to iso-alkanes of the same carbon number. N-alkane flames produce the smallest  $\langle dp \rangle$  as shown in **Figure 11**. It has been thought that fuel structure influences soot process only at its early stages [13], and the rate limiting process to the formation of large PAHs and soot is the formation of the first aromatic [12, 42].

There is evidence that large-branched chain hydrocarbons soot more than the straight ones [18]. Less-branched alkanes tend to produce more ethylene, while morebranched alkanes tend to produce larger alkenes [26]. The alkene products subsequently decompose or grow to produce benzene precursors. Normal paraffins, that produce primarily ethylene precursors, must follow a much more complex and slower path to produce benzene [43]. In diffusion flames cyclic paraffins form cycloalkyl radicals through H-abstraction. At high temperatures, these radicals decompose predominantly through the  $\beta$ -scission at a C-H bond to produce cycloalkenes [4]. This pathway preserves the ring and eases the formation of benzene, which strongly impacts aromatics formation. At lower temperatures, when the cyclic structure is destroyed, the mechanisms of formation of benzene are similar to those of normal paraffins; however, cycloalkanes tend to produce more benzene than noncyclic alkanes [44]. Presumably because noncyclic alkane decomposition produces more ethylene and other small alkenes, but cycloalkanes produce alkenes with the same carbon number.



Figure 11: Weighted mean diameter variation with the number of carbon atoms in the fuel structure at small (5 mm; red symbols) and high (< 20 mm; black symbols) flame heights.

#### *Large flame heights* ( $\geq 20 \text{ mm}$ )

As the flame height increases, i.e the fuel flow rate increases, the final  $\langle dp \rangle$  achieves a nearly constant value. This value appears to be related to the size of the fuel. **Figure 11** presents the final constant  $\langle dp \rangle$  attained by each fuel versus the number of carbon atoms. As the size of the molecule increases the final  $\langle dp \rangle$  decreases. Possible reasons for these tendencies are given:

After a certain flame height, around 20 mm, (dp) and N stop increasing and become independent of fuel flow rate increments, for all tested fuels. The cease in particle growth is thought to be a consequence of particle oxidation. As the fuel flow rate increases the luminosity of the flame gets larger due to augmented soot radiation. Several studies have exposed that as the fuel flow is further increased, the luminosity extends beyond the boundary of the stoichiometric diffusion flame [18, 33]. As the flame height increases, the ratio between the observable luminous flame and the stoichiometric diffusion flame also increases. Consequently the oxidation region will increase. Also, in larger flames the particles that have being formed have a longer residence time, and more time to grow. This entails that at our sampling point (tip of the luminous flame) particle size is influenced by both growth and oxidation, and as the flame height is increased both processes are expected to be

strengthened. What experimental observations suggest is that after a certain flame height the growth of particles and their subsequent oxidation balance such that  $\langle dp \rangle$  and N remain fairly constant a the tip of the visible flame. Former studies have also showed that in the region where particle oxidation is observed, the growth of the particles ceases [35].

• Figure 11 presents the final constant  $\langle dp \rangle$  attained by each fuel versus the number of carbon atoms. As carbon number increases, the  $\langle dp \rangle$  appears to attain a smaller final steady value, this could be the consequence of more intense oxidation. In the previous stage (small flame heights), where mainly inception and growth is expected, the evolution of  $\langle dp \rangle$  appear to be similar for all fuels of the same structure class. This hints that there is a stronger effect of oxidation in higher flames. Flame temperature strongly affects soot oxidation [19]. At our sampling point particles have pierced the stoichiometric flame front and oxidise in that process, as well as in the remaining luminous flame. Even though large energy losses are expected through radiation, the adiabatic flame temperature can be an illustrative reference at the stoichiometric diffusion flame. As carbon number increases and hydrogen to carbon ratio decreases, it is expected that the adiabatic flame temperature raises [16]. This would suggest that soot particles that pass through the flames of larger hydrocarbons are exposed to higher temperatures, and are more intensely oxidised resulting in a smaller final  $\langle dp \rangle$ .

## **5** Conclusions

PSDs of soot formed in a series of paraffin diffusion flames were examined by probe sampling/differential mobility spectroscopy. The influence of fuel structure in the soot weighed mean diameter  $\langle dp \rangle$  at different flame heights was studied. The way particles were sampled (always at the tip of the visual flame), enabled to detect two different stages.

At low flame heights soot particles are being formed and large amount of incepted particles are observed, followed by fast coagulation. Among each paraffin group, at each flame height the values of  $\langle dp \rangle$  were almost the same. Cyclic and isomeric structures produce larger  $\langle dp \rangle$  compared to straight alkanes. At large flame heights, the luminosity of the flame gets larger due to augmented soot radiation, oxidation is also taking place at the sampling point. For all fuels tested,  $\langle dp \rangle$  and N achieve constant values. A consistent increase in attempted  $\langle dp \rangle$  was observed with larger molecule size.

We speculate that the effect of fuel chemical structure size on the final soot  $\langle dp \rangle$  is a consequence of differences in temperatures at the sampling point. Further studies of temperature and morphology in these flames would be both useful and of interest. Similarly, the analysis of aromatics is of major interest, as they are significant components of commercial fuels and play an important role on their sooting characteristics.

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