Measurement of the sooting propensity of aviation fuel mixtures

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Abstract

The influence of molecular structure and concentration of aromatic compounds on soot formation was investigated experimentally using a premixed laminar planar flame. For the experiments, a synthetic paraffinic kerosene (SPK) surrogate was prepared as a base for the addition of the aromatics to be investigated. The aromatics that were either added individually or in mixtures were toluene, n-propylbenzene, indane, 1-methylnaphthalene and biphenyl. Furthermore, four synthetic fuels, a fossil Jet A-1 and four neat fuel components – n-dodecane, n-octane, iso-octane and cyclohexane – were studied. In addition to the experiments, a numerical study was performed where besides the dependency on the aromatic's molecular structure and content also the influence of temperature, pressure, fuel stoichiometry, and residence time on soot volume fraction was investigated. Both the experimental as well as the numerical investigations point out that the individual aromatic compound's molecular structure exerts a larger influence on soot formation than the content of the aromatic compound.

Introduction

The combustion of a fuel in an aircraft in cruising altitude leads to the direct emission of different pollutants in the upper troposphere and lower stratosphere. Here, nearly all exhaust gas components, especially carbon dioxide (CO_2), nitrogen oxides (NO_x) and soot particles but also sulfur oxides (SO_x), unburned hydrocarbons and water vapor, contribute to climate change by interacting with atmospheric processes affecting the elements of radiative forcing [1, 2]. The percentage of anthropogenic radiative forcing caused by aviation is between 3.5% and 5.0% with contrail cirrus as major factor. The formation of cirrus clouds due to contrails is catalyzed by soot emission since soot particles act as nuclei for the condensation of water vapor [1, 3].

It is well-known that aromatics, representing an important constituent of crude-oil based fuel, promote the formation of soot particles [2-4]. For this reason the percentage of aromatics is limited to max. 25 vol-% in conventional crude-oil based jet fuels [5] as well as in synthetic (alternative) jet fuels [6]. Whereas the existence of aromatics in conventional fuels results naturally from their occurrence in crude oil, the majority of synthetic fuels lack aromatics. Due to safety reasons – it is known that aromatics contribute to the swelling of certain elastomers (seals) [4, 7] – a minimum aromatic content of 8 vol-% is required for each jet fuel containing synthetic components [6]. Since alternative aviation fuels provide potential to reduce emissions a more profound knowledge of the influence of aromatics on soot formation is necessary. For this reason the project *SynTreAmR* (Synthetische Treibstoffe – Einfluss des Aromatengehaltes auf die Rußbildung) was initiated to study the correlation between the aromatic's molecular structure and soot formation in synthetic fuels. In detail the sooting propensity of jet fuel surrogates with different aromatic compounds characteristic for those occurring in conventional and synthetic fuels as well as of different alternative jet fuels and a conventional jet fuel was determined experimentally.

In contrast to the commonly used threshold sooting index (TSI) [8-10] the sooting propensity was estimated by the definition of a soot threshold as a fuel-air-equivalence ratio (φ). Here the particle concentrations were measured continuously in the exhaust gas of a premixed flame during varying the φ-value. With the significant increase of the particle concentration the sooting threshold was determined.

In addition to the experimental work, a numerical study was carried out where the soot volume fractions were calculated to investigate not only the dependency of soot formation on the aromatic's molecular structure and concentration but also on temperature, pressure, fuel stoichiometry, and residence time.

Experimental approach

The experimental set-up consists of four parts: (I) the fuel-air-mixture preparation unit, (II) the burner, (III) the sampling probe, and (IV) the particle detection unit. A scheme of the set-up is presented in Fig. 1. For the preparation of the fuel-air-mixture the vaporized fuel is first mixed with preheated nitrogen (N_2), secondly conditioned to the set temperature of 473 K and finally oxygen (O_2) is added according to the natural N_2/O_2-ratio in air. The liquid fuel is carried using a HPLC-pump (LC-20AD, Shimadzu); the gas flows are controlled with mass flow controllers (mini Cori-Flow, Bronkhorst). During the whole measurement the gas velocity of the unburned fuel-air-mixture is kept constant at 35 cm/s.

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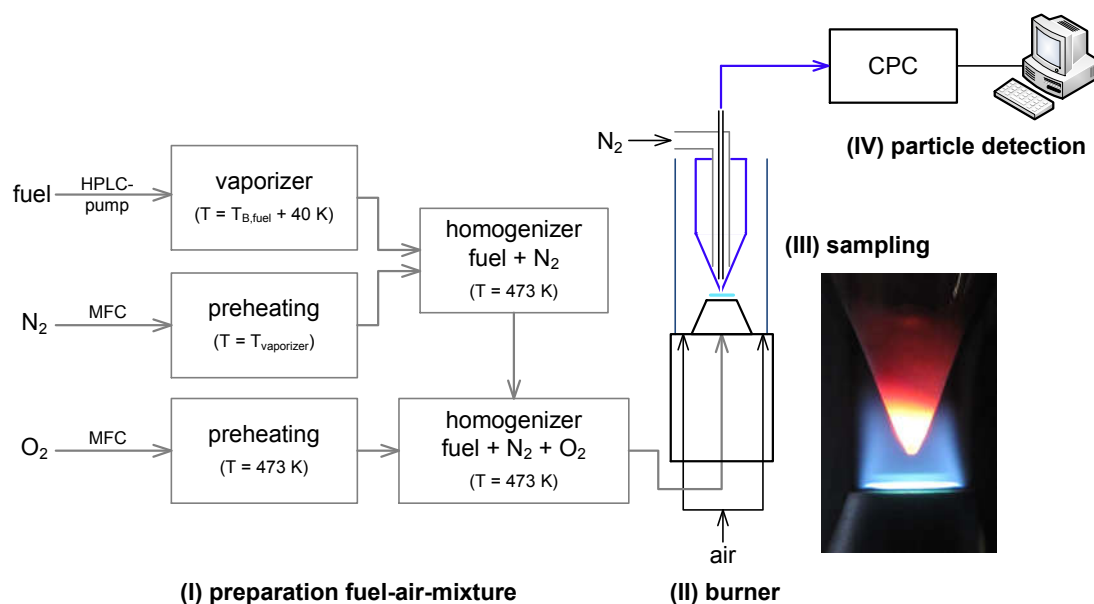
Fig. 1 Scheme of the experimental set-up for the measurement of the particle concentration in the exhaust gas of a plane laminar flame; CPC – condensation particle counter, HPLC – high performance liquid chromatography, MFC – mass flow controller, T_B – boiling temperature / final boiling point

The nozzle of the burner has an outlet diameter of 12 mm and contains a fine pored sinter plate to stabilize the planar laminar flame. To avoid disturbance of the flame the nozzle is surrounded by a laminar purified air coflow and a cylinder made from quartz glass. The sampling unit, consisting of three concentric pipes, is fixed above the burner and reaches into the exhaust gas. The outer pipe is also made from quartz glass and has a cone with a fine orifice at the tip where the exhaust gas from the flame is expanded into the inner pipe. In the middle pipe (made from Pyrex glass) N_2 is added with a volume flow of about 1300 ml/min to delay particle coagulation in the exhaust gas by dilution. The sample is transferred into the particle counter (CPC 3022A, TSI) with a total volume flow of 1500 ml/min leading to a low pressure of about 880 mbar in the sampling unit compared to an ambient pressure of about 965 mbar.

Starting with $\varphi = 1.40$ the fuel fraction is increased during the measurement. As soon as the particle concentration starts to raise, the φ-value is kept constant for 15 minutes. For averaging of the measured particle concentration (every 10 seconds a measured value is recorded) the first 3 minutes are not considered in order to respect the slight time delay between the increase of fuel volume flow and the adjustment of the φ-value.
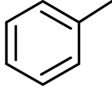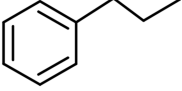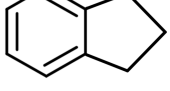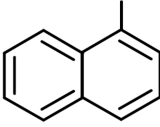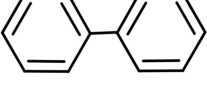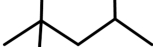
Results of the measurements

The sooting propensity was measured for the neat synthetic paraffinic kerosene (SPK) surrogate as well as after addition of different aromatic compounds, to work out the dependency on molecular structure and concentration of the aromatics. The SPK surrogate consists of 11.72 mol-% n-dodecane + 30.02 mol-% isooctane + 58.26 mol-% n-propylcyclohexane. This composition was chosen based on the alkane content in the synt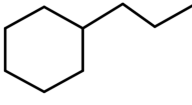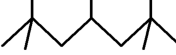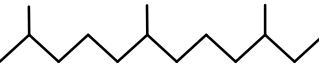hetic fuels ReadiJet and AtJ-SKA [7] determined by GCxGC-MS analyses. Both fuels were also studied within the *SynTreAmR* project. The aromatics considered as representative for synthetic as well as fossil fuels were toluene (although not present in aviation turbine fuels), n-propylbenzene, indane, 1-methyl-naphthalene, biphenyl and a mixture containing all of them (24.69 mol-% toluene + 47.78 mol-% n-propylbenzene + 19.55 mol-% indane + 7.24 mol-% 1-methyl-naphthalene + 0.73 mol-% biphenyl). The concentration of the aromatic content was varied in each surrogate mixture: from 8.0 vol-% to 16.5 vol-% and 25.0 vol-%. An exception had to be made for biphenyl being only soluble in alkanes up to about 17 mol-% (15.6 vol-%) [11, 12]. For comparison the sooting propensity of a conventional Jet A-1 was determined ("123" kerosene from [7]). Beyond that the sooting behavior of two further paraffinic alternative fuels (AtJ-SPK and farnesane [7, 13]), and four neat fuel components (all belonging to the groups of n-, iso-, or cycloalkanes) was investigated, too. In Tab. 1 an overview on the added aromatics and measured fuels is given.

As a measure for the sooting propensity, the φ-value is defined as soot threshold obtained from the maximum gradient of the normalized particle concentration by extrapolation to the baseline. All particle concentrations were normalized to 10000 particles/cm³; the corresponding φ-value was determined by interpolation. As an example the comparison of the normalized particle concentrations for the neat SPK surrogate and the respective surrogates with added n-propylbenzene are shown in Fig. 2.

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Tab. 1 Overview of the used aromatics, measured alkanes and tested fossil and synthetic fuels; *note*: sooting tendencies of neat n-propylcyclohexane as well as the aromatics were not determined; AtJ – Alcohol to Jet, SKA – Synthetic Kerosene with Aromatics, SPK – Synthetic Paraffinic Kerosene

Aromatics	Toluene	n-Propylbenzene	Indane	1-Methylnaphthalene	Biphenyl

Alkanes	n-Dodecane	n-Octane	Isooctane	Cyclohexane	n-Propylcyclohexane

Real Fuels	Jet A-1	ReadiJet	AtJ-SKA	AtJ-SPK	Farnesane
	o 15.1 vol-% aromatics	o 25.1 mass-% n+iso-alkanes o 51.0 mass-% cycloalkanes o 20.9 vol-% aromatics	o predominant iso-alkanes o 9.5 mass-% (8.7 vol-%) aromatics	83 mol-% 17 mol-%	
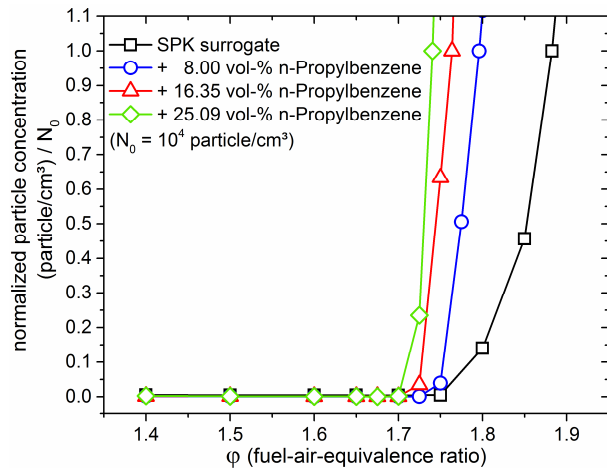
Fig. 2 Normalized particle number density as a function of the fuel-air-equivalence ratio on for the SPK surrogate and the surrogates with n-propylbenzene

The gradient at $N_0 = 10000$ particles/cm³ results from the first derivation and the soot threshold (φ_{ST}) can be calculated from the equation

$$\varphi_{ST} = \varphi_{10000} - \frac{N_{norm}}{N'_{norm}} = \varphi_{10000} - \frac{1}{N'_{norm}}$$

with the φ-value at a particle number density of 10000 particles/cm³ (φ_{10000}), the normalized particle number density (N_{norm}) being equal to 1, and its first derivative (N'_{norm}). The uncertainty of the calculated soot thresholds is ± 0.01 determined from repeated measurements of the neat fuel components. The results

for the soot threshold of all studied fuels and fuel components are summarized in Fig. 3. Regarding the different concentrations of aromatics in the surrogates, it is noticeable that the addition of 8.0 vol-% aromatic to the SPK surrogate has a considerably greater impact on the sooting propensity than the increase of the aromatic concentration from 8.0 vol-% to 16.5 vol-% or 25.0 vol-%. This conclusion regarding the sooting behavior of aromatic mixtures was also drawn by Crossley et al. [14]. Comparing the influence of the different aromatics it is obvious that the aromatic's molecular structure is more important for soot formation than concentration.

Due to their similar molecular structure (see Tab. 1) toluene and n-propylbenzene have a nearly identical sooting propensity whereas soot formation due to the presence of the bi-aromatics 1-methylnaphthalene and biphenyl starts at distinctly lower φ-values. The sooting propensity of indane, a mono-aromatic with nine carbon-atoms (same as n-propylbenzene), is found between that of the mono- and bi-aromatics since the cycloalkyl-moiety of indane leads to a smaller H:C-ratio of 1.11 compared to 1.33 for n-propylbenzene. Moreover, it is specific for cycloalkane structures that they have a higher sooting propensity than their corresponding n- or iso-alkanes [14, 15]. This characteristic is also reflected in the comparison of cyclohexane with n-dodecane and n-octane. Here, cyclohexane shows a lower soot threshold than both n-alkanes. The difference between n-dodecane and n-octane (see Fig. 3) can be attributed to their different size meaning that the soot threshold for n-hexane should be higher than for n-octane, which would be a clear difference to cyclohexane.
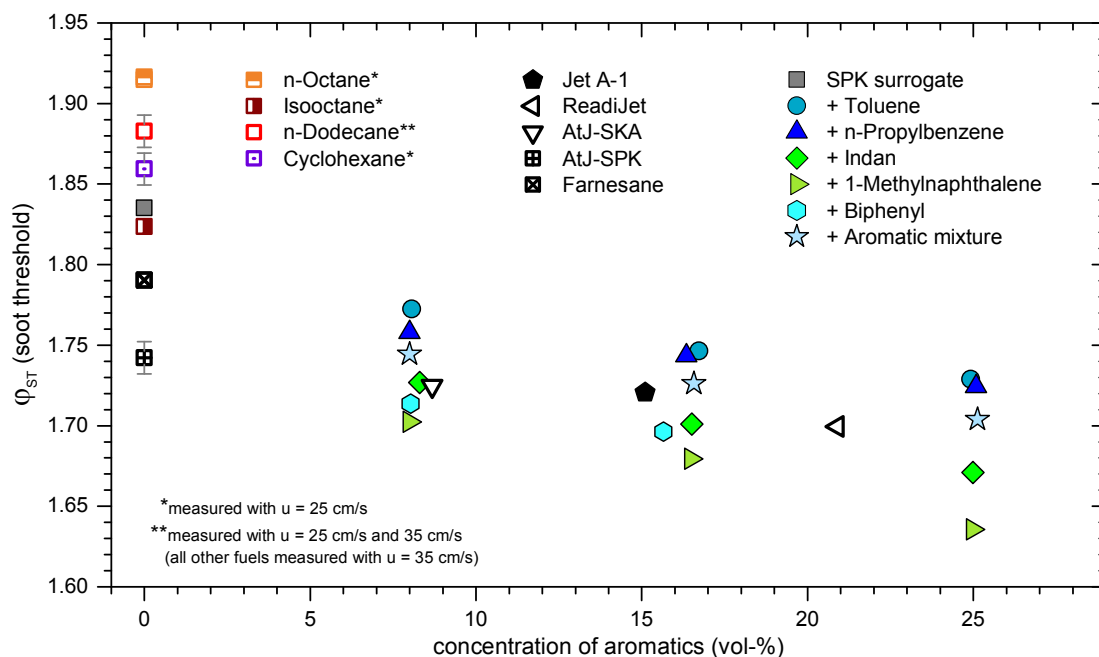
Fig. 3 Results of the calculated soot thresholds as measure for the sooting propensity; composition of the initial SPK surrogate (in mol-%): 11.72% n-dodecane + 30.02% isooctane + 58.26% n-propyl-cyclohexane, composition of the aromatic mixture (in mol-%): 24.69% toluene + 47.78% n-propyl-benzene + 19.55% indane + 7.24% 1-methylnaphthalene + 0.73% biphenyl; SPK – synthetic paraffinic kerosene, u – gas velocity of the unburned fuel-air-mixture

Since the main components of the aromatic mixture, consisting of 24.69 mol-% toluene + 47.78 mol-% n-propylbenzene + 19.55 mol-% indane + 7.24 mol-% 1-methylnaphthalene + 0.73 mol-% biphenyl, are mono-aromatics the sooting propensity is closer to n-propylbenzene and toluene than to indane or the bi-aromatics. The height of the soot threshold for the surrogate with 16.5 vol-% aromatic mixture is similar to the studied Jet A-1 having an aromatic content of 15.1 vol-%.

Due to the higher amount of aromatics the alternative fuel ReadiJet shows a slightly higher sooting propensity than Jet A-1. In contrast AtJ-SKA has less aromatics but the value of the soot threshold is nearly identical to that of Jet A-1. To explain this behavior the whole composition of the fuel has to be considered. As listed in Tab. 1, AtJ-SKA consists predominantly of iso-alkanes whereas a conventional jet fuel contains typically a significant amount of n-alkanes. Since the sooting propensity rises with the degree of branching in alkanes [14, 15] the similar soot threshold of AtJ-SKA compared to Jet A-1 is attributed to the iso-alkanes. The influence of branching is even more obvious by comparing n-octane and isooctane or farnesane and AtJ-SPK. Although farnesane has a higher molecular weight than the average in AtJ-SPK its sooting propensity is distinctively lower due to the highly branched structure with quaternary C-atoms in molecules contained in AtJ-SPK. Moreover, these branched molecules lead to a sooting threshold for AtJ-SPK as high as determined for the surrogates with 8.0 vol-% aromatic mixture or 16.5 vol-% mono-aromatics.

Modeling of the sooting propensity

In addition to the experimental determination of sooting propensity, the dependence of soot formation on molecular structure and the amount of the specific aromatic compounds present in a fuel was investigated in a numerical study. Here, the numerical investigation on the SPK surrogate was carried out in a zero dimensional reactor. The soot volume fractions (f_v) were calculated for the pre-vaporized homogeneous fuel mixtures under varying conditions of temperature, pressure, and residence time using Cantera [16] and soot post processing with the program from Wang and Frenklach [17] based on the soot model described in [18]. Similar to the experiments, the types of aromatic compounds and their contents were varied for the synthetic kerosenes.

To the aromatic free SPK surrogate, aromatics were added to compare their influence on soot emissions. The amounts of the added aromatic compound was increased from 8.4 mol-%, to 17.0 mol-%, and 22.0 mol-% to account for the lower to upper limits in jet fuel specifications [5, 6]. The aromatics added to the mixtures were n-propylbenzene, indane, biphenyl, and 1-methylnaphthalene. Toluene was not considered in the numerical study since it acts very similar to the n-propylbenzene as shown in the section before.

The soot formation can depend on the different conditions arising in a combustor. To assess the influence of different boundary conditions on the soot formation, a parameter field was selected for numerical investigation. The parameter field of the calculation matrix is briefly shown in Tab. 2. The specified parameter field supplies information on the soot formation as a function

of temperature, pressure, residence time, and fuel stoichiometry. The soot formation was calculated in terms of soot volume fraction (f_v – cm^3 soot per cm^3 volume).

Tab. 2 Parameter field for numerical investigation

	Parameter
Pressure (p)	1 bar, 10 bar
Stoichiometry (φ)	1.5, 2.0
Temperature (T)	1200 K, 1400 K, 1700 K, 2000 K
Residence time (τ)	1 ms, 5 ms
Aromatic concentration	8.4 mol-%, 17.0 mol-%, 22.0 mol-%
Aromatics	– n-Propylbenzene – Indane – Biphenyl – 1-Methylnaphtahlene
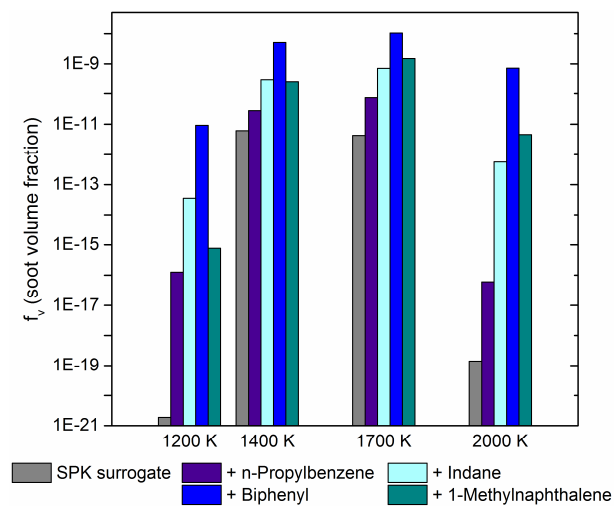
Fig. 4 Influence of temperature on soot volume fraction, data are presented for the SPK surrogate and mixtures with 17 mol-% aromatics at p = 1 bar, φ = 2.0, and τ = 1 ms
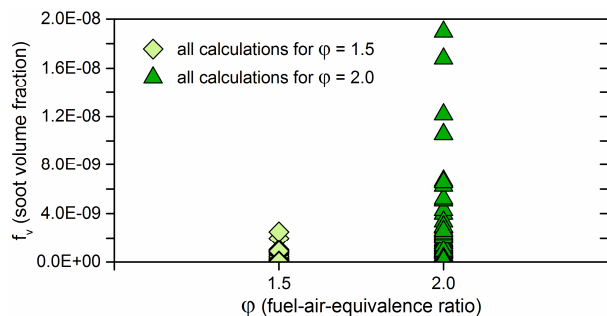
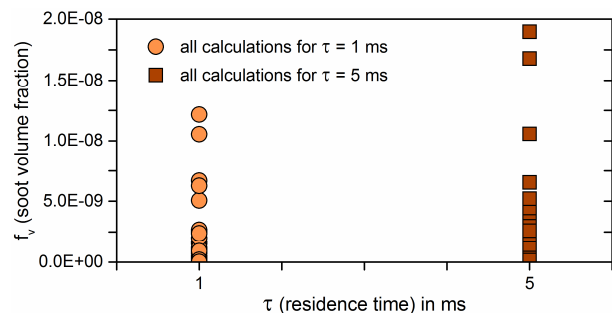The effect of temperature on soot volume fractions are plotted in Fig. 4 for the SPK surrogate and mixtures with 17.0 mol-% aromatics at p = 1 bar, φ = 2.0, and τ = 1 ms. It shows that the maximum soot formation occurs at temperatures of 1700 K. At 1400 K and 1700 K soot is formed several orders of magnitude higher compared to the other two temperatures. The data are plotted only for limited conditions but this trend remains the same for all conditions studied.

Regarding the pressure dependence it is known through the range of studies that the soot formation increases with pressure. Within this study the soot volume fractions for 10 bar are about one order of magnitude higher than at 1 bar for most sooting components. Furthermore the pressure dependence is independent of aromatic concentration.

The results from the study on the influence of fuel stoichiometry and residence time are shown in Fig. 5 and Fig. 6, where all the modelled data points are plotted. The increase in amount of fuel compared to oxidizer leads to more fuel and fuel fragments available to react with fuel and therefore to more soot. This is well known and can be seen in Fig. 5. The soot volume fraction obtained at φ = 2.0 is almost one order of magnitude higher than at φ = 1.5. Also expected was the increase in soot volume fraction with an increasing residence time (Fig. 6) since a larger residence time allows time for coagulation and soot surface growth. The variation of the soot volume fraction amounts to 50%. However this increase is negligible compared to the other factors studied.

In Fig. 7 the influence of aromatic compound additions on soot volume fraction is presented. Here, all the data points of varying parameters of aromatic concentration, fuel stoichiometry, pressure, dilution, and residence time are included. In this figure (log scale) one can see the minimum and maximum range of soot formed. The figure shows that the addition of bi-aromatics leads to more soot compared to the mono-aromatics. Also seen in Fig. 7, the maximum soot obtained from mixtures containing mono-aromatics is two orders lower than bi-aromatics. This difference arises due to the different size of aromatics formed from these added molecules. Also seen from the data is that the fuel containing biphenyl forms more soot at all conditions, apparent from the narrow spectrum of f_v formed.

Fig. 5 Influence of fuel stoichiometry on soot volume fraction (all data points from the modelling are plotted)

Fig. 6 Influence of residence time on soot volume fraction (all data points from the modelling are plotted)
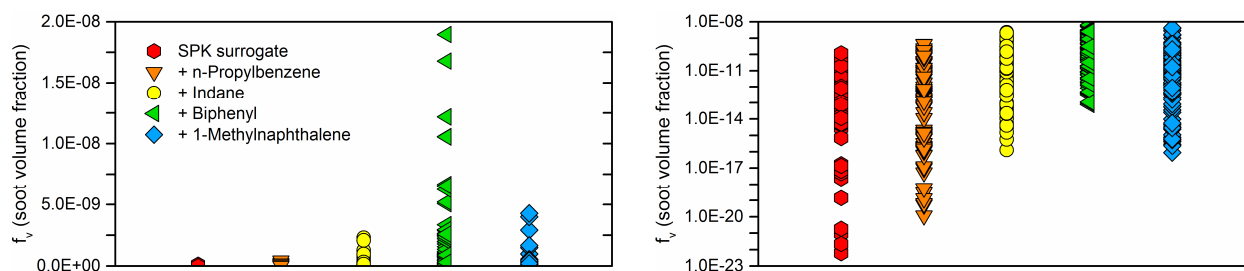
Fig. 7 Influence of aromatic's molecular structure on soot volume fraction (left: linear scale, right: log scale; all data points from the modelling are plotted)

Conclusions

Both, the experimental work as well as the numerical study show that the individual aromatic's molecular structure plays a larger role for the sooting propensity than the aromatic's content. In detail the increase of the sooting propensity follows the order mono-aromatics < cyclo-aromatics < bi-aromatics. A difference between experiment and modelling turns out for the two bi-aromatics studied. Considering the simulations the addition of biphenyl to the SPK surrogate leads to the largest amount of soot in a fuel mixture whereas in the experiments this has been found for 1-methylnaphthalene. This requires further investigation. The numerical study indicates further that at conditions of the present study, the chemical nature of the aromatic compound in the fuel has a larger influence on soot formation than the combustion conditions in terms of temperature, pressure, residence time and fuel stoichiometry.

Acknowledgement

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