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Investigation of the sooting propensity of aviation fuel mixtures

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Abstract

Aromatic compounds occurring naturally in jet fuels are precursors for the formation of soot in the exhaust gas of jet engines. Directly emitted in cruising altitude, soot particles lead to the formation of contrails and clouds influencing the radiation balance of the atmosphere. Hence, a detailed knowledge on the effect of aromatics on the sooting behavior is of great importance, especially for the development of alternative synthetic jet fuels. Investigations on the sooting propensity influenced by the molecular structure and concentration of diverse aromatic compounds contained in synthetic and fossil aviation fuels as well as blends of synthetic paraffinic kerosene (SPK) with aromatic compounds (SKA) were carried out experimentally. Using a predefined SPK fuel, five different blends—each containing a single aromatic compound—were prepared in addition to one blend with a typical composition consisting of all these aromatic compounds. In subsequent measurements, the concentration of the aromatics was increased from initially 8.0 vol%, to about 16.5, and 25.0 vol%. The aromatics added were toluene, *n*-propylbenzene, indane, 1-methylnaphthalene, and biphenyl. The studied jet fuels include fossil-based Jet A-1 as well as different synthetic jet fuels (with and without aromatics). Furthermore, the experimental results of the sooting propensity are compared with the results of the hydrogen deficiency model being a measure for the amount of cyclic and unsaturated molecular structures occurring in a hydrocarbon fuel. This study shows the hydrogen deficiency as a useful tool to make predictions about the sooting behavior of different fuels compared to a reference fuel at a specified condition. Additionally, it is observed from the measured sooting propensities as well as from the model predictions of hydrogen deficiency that the structure of aromatic compounds presents greater influence on the soot formation than the aromatic concentration.

Keywords Aviation fuel · Alternative fuels · Sooting behavior · Hydrogen deficiency · Aromatics · Emissions

1 Introduction

The combustion of a fuel in a jet engine of an aircraft in cruising altitude is connected with the direct emissions of different pollutants such as carbon dioxide (CO₂), nitrogen oxide (NO_x), sulfur dioxide (SO₂), and soot particles in the upper troposphere and lower stratosphere. Here, the soot particles act as nuclei for the condensation of water vapor leading to contrails and cloud formation, which eventually influences the radiation balance of the earth's atmosphere

and contributes to an increase in the radiative forcing. According to [1–3], the percentage of anthropogenic radiative forcing caused by aviation is estimated between 3.5 and 5.0% with contrail cirrus as major factor. It is already well-known that aromatic components in fuels promote the soot formation, but due to safety reasons—aromatics contribute to the swelling of certain elastomers (seals) [4, 5]—a minimum content of 8.0 vol% aromatics is required for jet fuels containing synthetic components according to ASTM standard D7566-19 [6]. Due to this specification aromatics cannot be simply left out from jet fuels to reduce the soot emissions when synthetic fuels are developed. Hence, a better understanding of the influence not only of aromatics themselves but also of structural effects on soot formation is to be gained and necessary for the development of alternative synthetic jet fuels.

Therefore, investigations on the sooting propensity depending on the molecular structure and concentration of different aromatic compounds contained in synthetic and

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fossil aviation fuels as well as blends of synthetic paraffinic kerosene (SPK) with aromatic compounds (SKA) were determined experimentally. In contrast to the commonly used threshold sooting index (TSI) [7–9], the sooting propensity was estimated by the definition of a soot threshold as a function of the fuel–air equivalence ratio (φ). Here, the soot emissions in terms of particle number concentration were measured continuously in the exhaust gas of a premixed flat flame varying the φ -value, i.e., increasing the fuel fraction in the fuel–air mixture.

A useful correlation to compare the sooting propensity of different known jet fuels arises from the definition of the ‘Hydrogen Deficiency’ (HD). Indeed, the hydrogen deficiency does not provide data to quantify the soot emission, but is beforehand a measure for the amount of cyclic and unsaturated molecular structures occurring in a fuel. Though cyclic and especially aromatic (cyclic and unsaturated) components in a jet fuel account for most of the soot formation in contrast to bulk *n*-, and iso-alkanes, the hydrogen deficiency nevertheless correlates with the sooting propensity of jet fuels. The HD-number poses an easy way to assess the sooting behavior of a jet fuel knowing its molecular composition [10]. Therefore, the experimental results of the sooting propensity will be compared with the predictions according to the hydrogen deficiency correlation.

2 Experimental investigation of the sooting propensity

2.1 Measured fuels and fuel mixtures

The sooting propensity was determined for different mixtures as well as for a crude oil-based aviation fuel

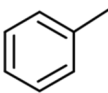
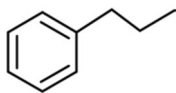
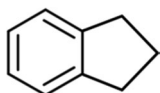
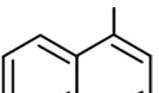
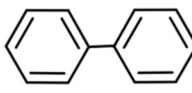

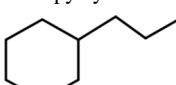
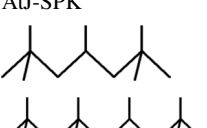
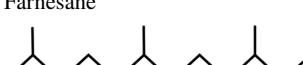
(Jet A-1) and four alternative fuels [11]. These fuels comprise two aromatic containing alternative fuels named ReadJet and AtJ-SKA (Alcohol to Jet Synthetic Kerosene with Aromatics) as well as two paraffinic fuels named AtJ-SPK (Alcohol to Jet Synthetic Paraffinic Kerosene) and farnesane.

The initial, aromatic free synthetic paraffinic kerosene (SPK) consists of 11.72 mol% *n*-dodecane + 30.02 mol% iso-octane + 58.26 mol% *n*-propylcyclohexane. This composition is derived from the GC × GC–MS analysis of synthetic jet fuels [12]. With the restriction of lacking an affordable and adequate iso-paraffinic species in the C₁₂-range, the mixture is supposed to represent aromatic free fuels in general, thus called ‘SPK surrogate’.

Using this SPK surrogate, five different blends—each containing a single aromatic compound (toluene, *n*-propylbenzene, indane, 1-methylnaphthalene, or biphenyl)—were prepared as well as one blend with a typical aromatic composition including all aromatic compounds (24.69 mol% toluene + 47.78 mol% *n*-propylbenzene + 19.55 mol% indane + 7.24 mol% 1-methylnaphthalene + 0.73 mol% biphenyl). In subsequent measurements, the concentration of the aromatics was increased from initially 8.0 vol%, to about 16.5 vol%, and to 25.0 vol% finally. An exception had to be made for biphenyl being only soluble in the SPK surrogate up to about 17 mol% (15.6 vol%) [13, 14].

An overview on the structure of the components (including aromatics) used for the preparation of the surrogate mixtures as well as short information on the composition of the studied aviation fuels is given in Table 1.

Table 1 Overview of the used aromatics, SPK surrogate components, and measured aviation fuels

| | | | | | |
|------------------------------------|---|--|---|---|--|
| Aromatics | Toluene  | <i>n</i> -Propylbenzene  | Indane  | 1-Methylnaphthalene  | Biphenyl  |
| SPK surrogate components (alkanes) | <i>n</i> -Dodecane  | | iso-Octane  | | <i>n</i> -Propylcyclohexane  |
| Real fuel drop-in | Jet A-1 15.1 vol% aromatics | ReadiJet 25.1 mas-% <i>n</i> + iso-alkanes 51.0 mas-% cycloalkanes 20.9 vol% aromatics | AtJ-SKA Predominant iso-alkanes 9.5 mas-% (8.7 vol%) mono-aromatics | AtJ-SPK  | Farnesane  |

AtJ alcohol to jet, SKA synthetic kerosene with aromatics, SPK synthetic paraffinic kerosene

2.2 Experimental setup

In present work, the sooting propensity as a threshold in equivalence ratio is measured instead of TSI/smoke point included in the standard ASTM 1766. The reason for this unusual selection has been to extend the use of existing burner setup, employed for determining the laminar burning velocities, for sooting propensity measurement using a prevaporised premixed fueled burner system, used so far for the measurement of the laminar burning velocity, see, e.g. [15, 16], providing well known and controllable boundary conditions with respect to mixture and flame. Whereas for the measurement of the burning velocity, a conical flame is used; here, a planar flame is stabilized by a nozzle with an outlet diameter of 12 mm containing a fine-pored sinter plate and confined by an air co-flow at preheat temperature. The scheme in Fig. 1 shows the experimental setup consisting of four parts: (I) the preparation of the fuel–air mixture, (II) the burner, (III) the sampling probe, and (IV) the soot particle detection unit. For the preparation of the fuel–air mixture, (I) the vaporized fuel is first mixed with preheated nitrogen (N_2) and conditioned to the set temperature of 473 K before 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. Part (I) preparation of the fuel–air mixture as well as part (II) the burner are both basically identical with the burner setup for the measurement of the burning velocity. For these details, the reader is referred to our previous publications [15, 16].

To avoid disturbance of the flame, the nozzle is surrounded by a laminar purified air co-flow and shielded by a cylinder made from quartz glass reducing the perturbation from the environment. The part (III), 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 central 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 part (IV) of the setup is the detection unit of soot particles. The sample (= exhaust gas containing soot particles) is measured by the particle number counter (CPC 3022A, TSI), operating with a total flowrate of 1500 ml/min. This leads to a low pressure of about 880 mbar in the sampling unit compared to an ambient pressure of about 965 mbar. Particles are detected upon a minimum size of $0.007 \mu\text{m}$.

Starting at $\varphi = 1.40$, the fuel fraction is increased during the measurement. As soon as the particle concentration starts to

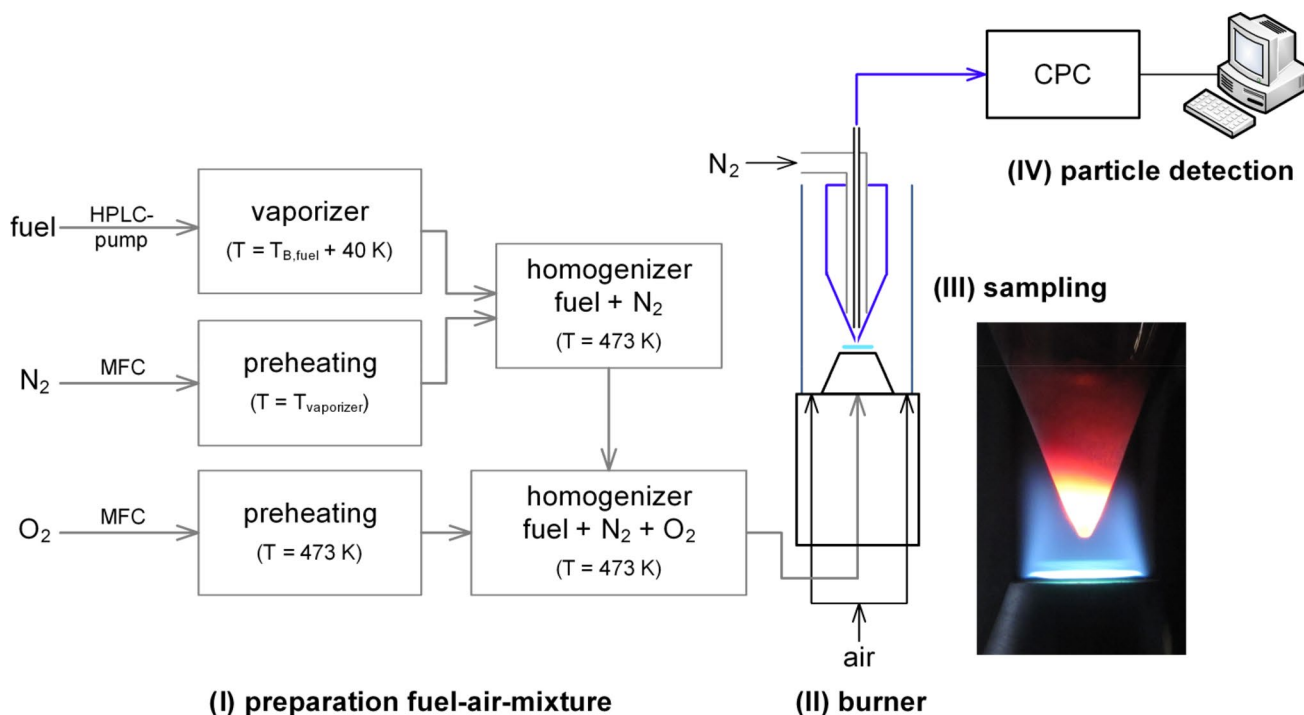


Fig. 1 Scheme of the experimental setup for the measurement of the particle concentration in the exhaust gas of a plane laminar flame; CPC condensation particle counter, HPLC high performance liquid

chromatography, MFC mass flow controller, T_B boiling temperature/final boiling point

rise, each set φ -value is kept constant for 15 min. The particle concentration is measured by the particle counter at a sampling rate of 1 s^{-1} and recorded with an averaging over 10 s by the Aerosol Instrument Manager[®] Software (TSI) during the whole experiment. In the evaluation, the particle counts from the first 3 min were excluded in order to respect the slight time delay between the increase in the fuel volume flow and the adjustment of the φ -value.

2.3 Determination of the sooting propensity

As a measure for the sooting propensity, the φ -value is defined as soot threshold (φ_{ST}) obtained from the maximum gradient of the normalized particle concentration by extrapolation to the baseline. For the determination of φ_{ST} , the φ -value is increased during the measurement until an average particle number density (N) of minimum $10^5 \text{ particles/cm}^3$ over 15 min is obtained. In the evaluation, the φ -value at $10^4 \text{ particles/cm}^3$ ($=N_0$) is determined by an appropriate interpolation. Thereon the particle number density N_0 is used to normalize the measured particle number densities leading to the value 1 for the φ -value at $10^4 \text{ particles/cm}^3$ determined by interpolation. As an example, Fig. 2 shows the comparison of the normalized particle concentrations for the neat SPK surrogate and the respective surrogates with *n*-propylbenzene added.

Taking the first derivative at $N/N_0=1$, corresponding to the maximum gradient, the soot threshold (φ_{ST}) can be calculated by extrapolation to the baseline using the equation:

$$\varphi_{\text{ST}} = \varphi_{10000} - \frac{N_{\text{norm}}}{N'_{\text{norm}}} = \varphi_{10000} - \frac{1}{N'_{\text{norm}}}, \quad (1)$$

with the φ -value at a particle number density of $10^4 \text{ particles/cm}^3$ (φ_{10000}), the normalized particle number density

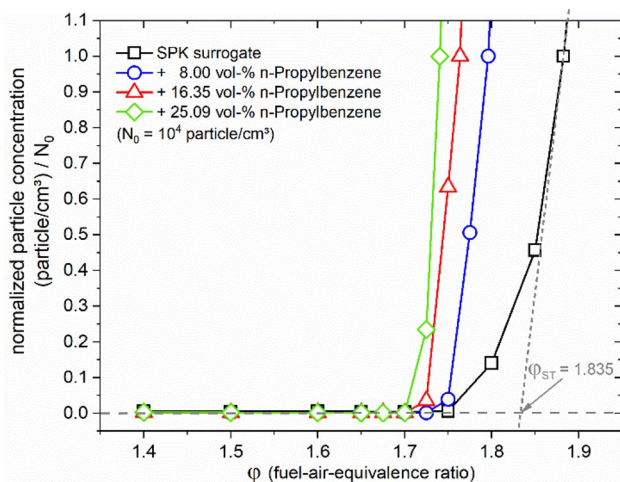


Fig. 2 Normalized particle concentrations for the SPK surrogate and the mixtures with *n*-propylbenzene

(N_{norm}), and its first derivative (N'_{norm}). In Fig. 2, the determination of φ_{ST} is graphically demonstrated for the SPK surrogate. The uncertainty of the calculated soot thresholds is ± 0.01 determined from repeated measurements of the neat fuel components.

2.4 Results

The results for the soot threshold (φ_{ST}), depending either on the concentration of aromatics or the amount of Hatoms, of all the studied surrogates and fuels are summarized in Fig. 3. For a better clarity, error bars are only drawn for a few data points. In general, the uncertainty of the experiment amounts to ± 0.01 in the determined soot threshold. Since with an increasing aromatic content, the amount of H-atoms in a fuel mixture is reduced and the results are more or less mirrored. The different spread of the data points between the dependence on aromatic concentration and hydrogen content is attributed to the consideration of the SPK surrogate in the hydrogen content. Whereas the detail on the volumetric concentration of the aromatics is independent of the SPK surrogate, the amount of hydrogen atoms is calculated for each surrogate mixture consisting of SPK surrogate and aromatics.

Regarding the different concentrations of aromatics in the surrogates, it is shown that the addition of 8.0 vol% aromatic to the SPK surrogate has a considerably greater impact on the sooting propensity than the increase in the aromatic concentration from 8.0 to 16.5 vol% or to 25.0 vol%, respectively. Similar results regarding the sooting behavior of aromatic mixtures were also found by Crossley et al. [17]. Comparing the influence of the different aromatics, it is obvious that the individual molecular structure of the aromatics is more important for the soot formation than their concentration. In general, the increase in the sooting propensity follows the order mono-aromatics < cyclo-aromatics < bi-aromatics which was also shown by Ladommatos et al. [18], who investigated the structural effects of various hydrocarbons on the sooting propensity.

In this study, the mono-aromatics toluene and *n*-propylbenzene have nearly identical sooting propensities due to their similar molecular structure (see Table 1). Even a difference between these two mono-aromatics is to discern with a constant slightly higher sooting propensity (or lower soot threshold (φ_{ST})) for *n*-propylbenzene. Although this difference lies within the experimental uncertainty of ± 0.01 , it is to suppose that this finding is caused by the longer side chain of *n*-propylbenzene. Whereas Crossley et al. [17] have made the same observation; Ladommatos et al. [18] have reported a sooting propensity for *n*-propylbenzene even slightly lower than for toluene. But in total ignoring *n*-propylbenzene, they show also an increasing sooting propensity with growing side chain as well. Similarly, the sooting

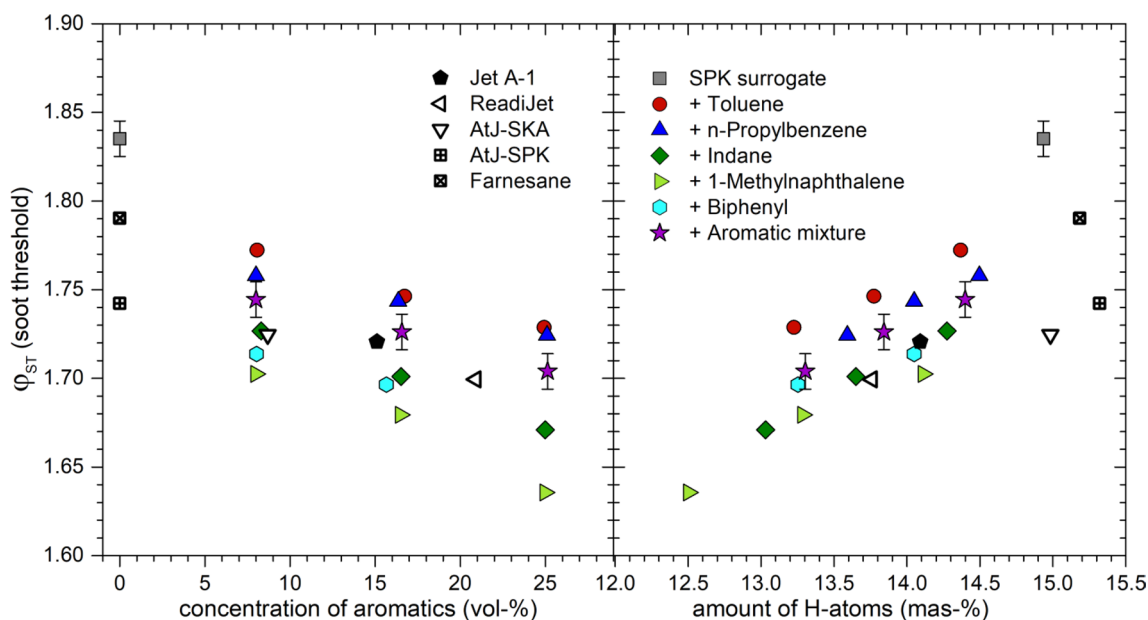


Fig. 3 Soot thresholds as measure for the sooting propensity; composition of the initial SPK surrogate (in mol%): 11.72% *n*-dodecane + 30.02% iso-octane + 58.26% *n*-propylcyclohexane, composition of the aromatic

mixture (in mol%): 24.69% toluene + 47.78% *n*-propylbenzene + 19.55% indane + 7.24% 1-methylnaphthalene + 0.73% biphenyl; *AtJ* alcohol to jet, *SKA* synthetic kerosene with aromatics, *SPK* synthetic paraffinic kerosene

tendencies measured by McEnally and Pfefferle group [19] reported higher sooting tendency of propylbenzene compared to toluene.

As also already shown by Ladommatos et al. [18], the sooting propensity of indane, a monocyclo-aromatic with nine carbon-atoms, is found between that of the mono- and bi-aromatics. Indeed, indane and propylbenzene have the same number of carbon atoms, but the entire cyclic structure of indane leads to a smaller H/C ratio of 1.11 for indane (compared to 1.3 for *n*-propylbenzene) and therefore to a distinct higher sooting propensity.

Regarding mixtures containing the bi-aromatics, 1-methylnaphthalene or biphenyl soot particles are formed at distinctly lower φ -values being expected due to H/C ratios of < 1 for 1-methylnaphthalene (H/C = 0.91) as well as for biphenyl (H/C = 0.83).

For the aromatic mixture, the sooting propensity is found closer to *n*propylbenzene and toluene than to indane or the bi-aromatics since the mono-aromatics are the main components.

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 ReadiJet fuel shows a slightly higher sooting propensity than Jet A-1. In contrast, AtJ-SKA has only mono-aromatics at a lower concentration, but the value of the sooting threshold is nearly identical to that of Jet A-1.

To explain this behavior, the complete composition of the fuel should be considered. As listed in Table 1, AtJ-SKA consists predominantly of iso-alkanes, having a branched structure, whereas a conventional jet fuel contains typically a significant amount of straight *n*-alkanes. Since it is already known that the sooting propensity raises with the degree of branching in alkanes [17, 18], the similar soot threshold of AtJ-SKA compared to Jet A-1 may be attributed to the iso-alkanes. The influence of branching arises also from the comparison of 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 soot threshold for AtJ-SPK as high as determined for the surrogates with 8.0 vol% aromatic mixture or 16.5 vol% mono-aromatics. Unfortunately, no sooting propensity data on highly branched iso-alkanes are available for comparison. Only information on 2,2,4,4,6,8,8-heptamethylnonane (isocetane) showing a sooting tendency more than one order of magnitude lower than that of 1methylnaphthalene was found in the literature [20]. So at present, it is not possible to explain satisfactorily the sooting tendency of AtJ-SPK or other highly branched alkanes.

3 The hydrogen deficiency approach

To understand the above measured sooting propensity from the molecular structure point of view, we considered employing hydrogen deficiency (HD) as a measure for the presence of unsaturation and cyclic structure present in a molecule. This is to the extension of our earlier study [10] where we showed that the particle emissions measured in a ground-based V2527-A5 engine of an Airbus A320 can be extrapolated to other fuels using their HD and one reference measurement. This assessment was also observed to be extended to the smoke point and sooting tendency measurements from the literature.

3.1 Definition

A useful correlation to compare the sooting propensity of any multicomponent fuel arises from the definition of the ‘Hydrogen Deficiency’ (HD) [10]. Indeed, the hydrogen deficiency does not provide data to quantify the soot emission but is beforehand a measure for the amount of cyclic and unsaturated molecular structures being present in a fuel. Since the cyclic and especially aromatic (cyclic and unsaturated) components in a jet fuel account for most of the soot formation, the hydrogen deficiency therefore correlates with the sooting propensity of jet fuels. Thus, the HD-number provides an easy way to assess the sooting behavior of a jet fuel knowing its molecular composition. The hydrogen deficiency as a measure for the degree of unsaturation (double bonds) and cyclization (ring structure) of a fuel has long been known in chemistry [21, 22] and is defined as:

$$\text{HD} = (x + 1) - \left(\frac{y}{2}\right). \quad (2)$$

According to the general fuel formula C_xH_y , x and y are the number of C- and H-atoms. By this definition, the HD of n - and iso-alkanes is zero as in both cases neither unsaturation nor cyclic structures are present. To estimate the HD of a real fuel, the molecular formula in the form of C_xH_y needs to be known. The information on the fuel’s C and H number can be estimated by the combined use of different analytical and spectroscopic methods such as gas chromatography (GC), mass spectroscopy (MS), $^1\text{H-NMR}$ or $^{13}\text{C-NMR}$ spectroscopy.

3.2 Calculation of the hydrogen deficiency

For the calculation of the hydrogen deficiency, a theoretical formula for each fuel and fuel mixture has to be determined. In case of the SPK surrogate and aromatic surrogate mixtures, the formula is known from the initial weight of

the pure components. The H/C-ratio of Jet A-1, ReadJet, and AtJ-SKA was determined to 1.95, 1.90, and 2.10. Using these values, the theoretical formula of the real fuels was calculated assuming an average number of C-atoms of 11 in each of the fuels. Since AtJ-SPK and farnesane contain neither cyclic nor unsaturated structures, their hydrogen deficiency is zero, so they are excluded from the comparison with experimentally determined sooting propensities. Table 2 gives an overview about the calculated hydrogen deficiencies including the theoretical formula of each tested fuel and fuel mixture. Regarding the HDs for the SPK surrogate and AtJ-SKA, the reader is reminded that more than half of the SPK surrogate is n -propylcyclohexane—a cyclic component. This leads to a higher HD than for the AtJ-SKA fuel containing aromatics.

3.3 Comparison with the experimental sooting propensity

The results of the estimated hydrogen deficiency (HD) are presented in Fig. 4 as correlation with the soot threshold (φ_{ST}) as well as in Fig. 5 together with the results of the experimentally determined sooting propensity. Since in Fig. 5, the amount of hydrogen atoms is chosen as abscissa

Table 2 Theoretical formula and hydrogen deficiency (HD) of the investigated fuels and fuel mixtures

| Fuel | | | HD |
|-----------------------|-----------|---------------------|------|
| SPK surrogate | | $C_{9.05}H_{18.94}$ | 0.58 |
| + Toluene | 8.0 vol% | $C_{8.80}H_{17.59}$ | 1.00 |
| | 16.5 vol% | $C_{8.55}H_{16.28}$ | 1.41 |
| | 25.0 vol% | $C_{8.34}H_{15.15}$ | 1.77 |
| + n -Propylbenzene | 8.0 vol% | $C_{9.05}H_{18.28}$ | 0.91 |
| | 16.5 vol% | $C_{9.04}H_{17.61}$ | 1.24 |
| | 25.0 vol% | $C_{9.04}H_{16.94}$ | 1.57 |
| + Indane | 8.0 vol% | $C_{9.05}H_{17.95}$ | 1.07 |
| | 16.5 vol% | $C_{9.04}H_{17.03}$ | 1.53 |
| | 25.0 vol% | $C_{9.04}H_{16.13}$ | 1.97 |
| + 1-Methylnaphthalene | 8.0 vol% | $C_{9.24}H_{18.09}$ | 1.19 |
| | 16.5 vol% | $C_{9.43}H_{17.21}$ | 1.82 |
| | 25.0 vol% | $C_{9.61}H_{16.37}$ | 2.43 |
| + Biphenyl | 8.0 vol% | $C_{9.31}H_{18.14}$ | 1.24 |
| | 16.5 vol% | $C_{9.56}H_{17.40}$ | 1.86 |
| + Aromatic mixture | 8.0 vol% | $C_{9.01}H_{18.07}$ | 0.98 |
| | 16.5 vol% | $C_{8.97}H_{17.18}$ | 1.38 |
| | 25.0 vol% | $C_{8.94}H_{16.34}$ | 1.77 |
| Jet A-1 | | $C_{11}H_{21.5}$ | 1.25 |
| ReadJet | | $C_{11}H_{20.9}$ | 1.55 |
| Alcohol to Jet SKA | | $C_{11}H_{23.1}$ | 0.45 |

SPK synthetic paraffinic kerosene, SKA synthetic kerosene with aromatics

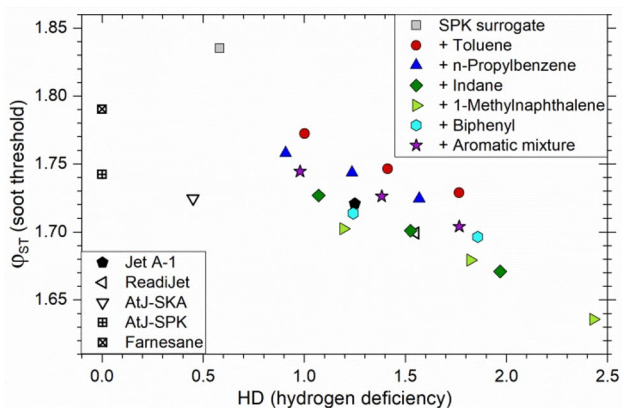


Fig. 4 Direct correlation between soot threshold and hydrogen deficiency

and the results of the hydrogen deficiency lead to a linear correlation: with decreasing hydrogen content the hydrogen deficiency increases. Furthermore, to allow an easier comparison with the sooting propensity, the ordinate for the hydrogen deficiency is reversed.

As the threshold for the soot formation is reduced with a decreasing amount of hydrogen atoms in the fuel, the

results illustrate that the hydrogen deficiency correlates with the sooting propensity: the higher the hydrogen deficiency, the higher the sooting propensity corresponding to a lower soot threshold (φ_{ST}) as shown in Fig. 4. Regarding the consideration of the aromatics, the results lead to the same finding as already obtained from the experiment: the structure of the aromatics has a greater influence on the soot formation than its concentration with the order of increasing impact on the sooting propensity mono-aromatics < cyclo-aromatics < bi-aromatics.

These results show that the hydrogen deficiency is a simple tool to gain information about the sooting propensity of fuels without doing extensive experiments or calculations. Furthermore, it was already shown in our recent publication in Kathrotia and Riedel [10] that though HD is merely the subset of H-content or H/C ratio of hydrocarbon molecule, it provides extrapolation of the known soot emissions. Compared to it, H/C ratio of the fuel can be linearly related to the emission, but this relationship is non-predictive, i.e., cannot be extended to predict soot emissions directly. This is mainly because, the bulk of fuel contains *n*- and iso-alkanes which has no major impact on soot emissions (compared to cyclo-alkanes and aromatics) and which makes also the H-content of the fuels similar for fuels. In contrast, the HD considers

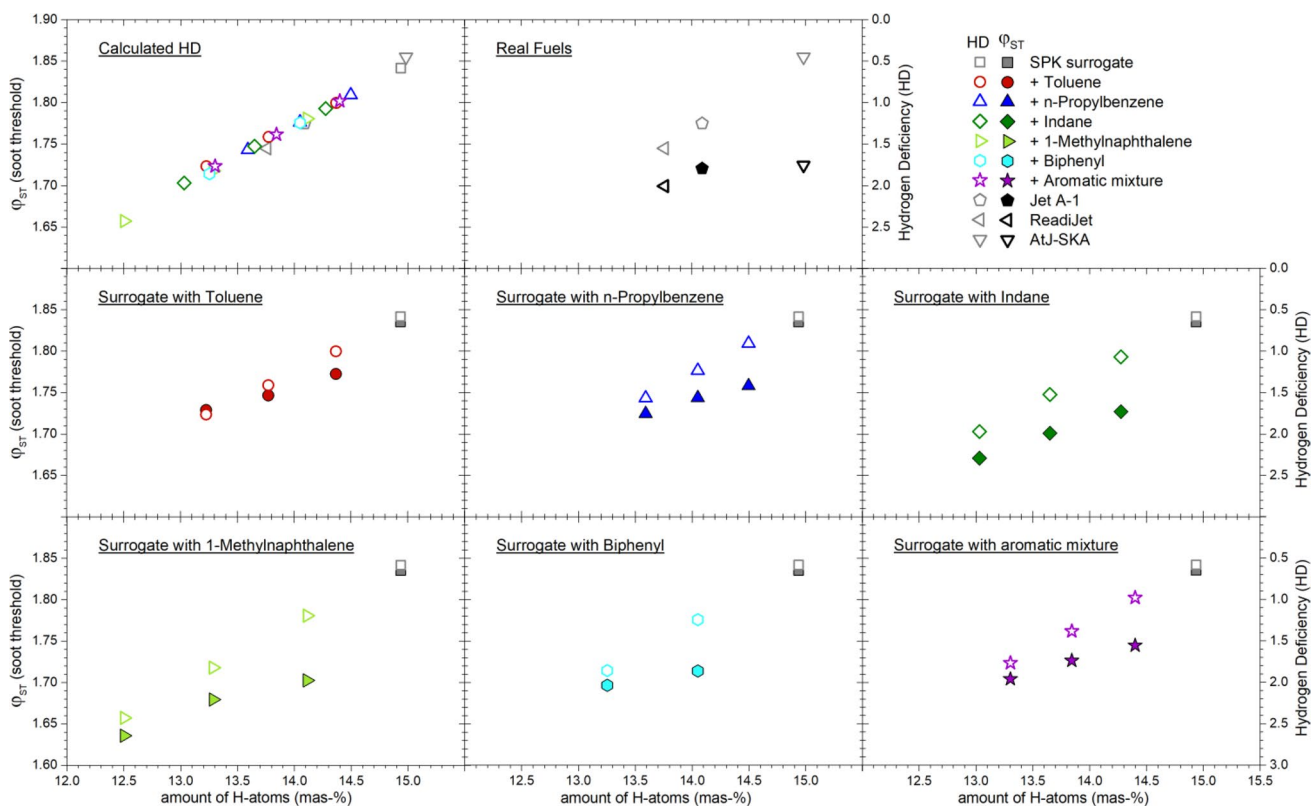


Fig. 5 Calculated hydrogen deficiency (HD) and comparison with experimentally determined soot threshold; *AtJ* alcohol to Jet, *SKA* synthetic kerosene with aromatics, *SPK* synthetic paraffinic kerosene

only the small but important aspect of the fuel components, namely, the cyclo-alkanes and aromatics which vary among the fuels and makes extrapolation possible. So with the use of the HD, the sooting propensity of various fuels can be predicted using information about the sooting propensity of only one reference fuel is available. Using the ratio $HD_{\text{fuel}}/HD_{\text{reference-fuel}}$, one can extrapolate the values of soot parameters like particle mass emission index, yield sooting index, and smoke point, each based on the known value of a reference fuel. But, whereas the values of different soot parameters and to some extent even of the same parameter obtained from different experiments are not comparable, the HD enables an easy comparison of the sooting behavior of different fuels.

A deviation between the measured sooting propensities and the correlation to the hydrogen deficiency occurs only for fuels with a considerable content of branched iso-alkanes. According to the hydrogen deficiency, AtJ-SPK and Farnesane (both with $HD=0$) as well as AtJ-SKA ($HD=0.45$) should have a sooting propensity being smaller (respectively, a higher φ_{ST}) than the SPK surrogate ($HD=0.58$). But actually their sooting behavior is similar compared to fuels containing aromatics between 8 and 16 vol% as visible from Fig. 4 (see Fig. 3 for aromatic concentration). Since it is not fully understood why the sooting propensity of these fuels is higher than expected, more detailed studies on the sooting propensity of highly branched alkanes as well as on the kinetics of the formation of the first aromatic ring are necessary.

In general, hydrogen deficiency provides valuable initial hint on the sooting tendency of potential fuels compared to a reference fuel without a need of experimental investigations. This is important for new fuels which are investigated for the fuels of future aviation where their potential emission tendencies can be estimated beforehand, an important aspect when the focus of the fuel design is the emission reduction.

4 Conclusion

Within this work, the sooting propensity of different surrogates and jet fuels was determined experimentally. The various surrogate mixtures were prepared to investigate the influence of aromatic structures and concentration on the sooting behavior of fuels. This study shows that the structure of the aromatics plays a larger role in soot formation than their concentration. In detail, the increase in the sooting propensity follows the order mono-aromatics < cyclo-aromatics < bi-aromatics. These conclusions were also obtained when the hydrogen deficiency is used as a parameter to correlate the sooting propensity. From these results follow that for a reduction in the soot emissions, it is more important to reduce the content of cyclo- and bi-aromatics in jet fuels

than to minimize the amount of aromatics, e.g., by adding alkanes. Alternatively, this can also be achieved by carefully selecting aromatic fuel components that have less sooting tendency. This is not only important for the blending of a conventional jet fuel with simple alternative jet fuels consisting of *n*- and iso-alkanes but also for the development of advanced sustainable aviation fuels (SAF) already containing aromatics.

The results for the tested jet fuels indicate that fuels consisting only or predominantly of highly branched iso-alkanes have an increased sooting propensity as it is the case for AtJ-SPK and AtJ-SKA. In detail, compared to the SPK surrogate and the surrogate with 8 vol% of aromatic mixture, respectively, both AtJ fuels exhibit a higher sooting propensity than expected. Up to now, it is not fully understood why the sooting propensity of these fuels is higher than expected. Ultimately, more studies on the sooting propensity of highly branched alkanes are necessary. Hence, the correlation of the hydrogen deficiency with the sooting propensity failed for AtJ-SPK and AtJ-SKA since according to the definition iso-alkanes as well as n-alkanes do not contribute to the hydrogen deficiency. Despite such special cases—conventional (Jet A-1) as well as alternative jet fuels (e.g., ReadiJet) consist typically of several kinds of components—the hydrogen deficiency is a useful tool assessing the sooting propensity of various fuels using their chemical composition only, thus eliminating the need to perform time intensive experiments or model calculations.

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Availability of data and material All data and information being necessary to understand the study are given in the manuscript.

Code availability Not applicable.

Compliance with ethical standards

Conflict of interest Not applicable.

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References

1. Lee, D.S., Fahey, D.W., Forster, P.M., Newton, P.J., Witt, R.C.N., Lim, L.L., Owen, B., Sausen, R.: Aviation and global climate change in the 21st century. *Atmos. Environ.* **43**, 3520–3537 (2009)
2. Braun-Unkhoff, M., Riedel, U., Wahl, C.: About the emissions of alternative fuels. *CEAS Aeronaut. J.* **8**, 167–180 (2017)
3. Burkhardt, U., Bock, L., Bier, A.: Mitigating the contrail cirrus climate impact by reducing aircraft soot number emissions. *NPJ Clim. Atmos. Sci.* **1**, 37 (2018). <https://doi.org/10.1038/s41612-018-0046-4>
4. Braun-Unkhoff, M., Riedel, U.: Alternative fuels in aviation. *CEAS Aeronaut. J.* **6**, 83–93 (2015)
5. Zschocke, A., Scheuermann, S., Ortner, J.: High Biofuel Blends in Aviation (HBBA), ENER/C2/2012/420-1, Final Report (2017). <https://ec.europa.eu/energy/en/studies/high-biofuel-blends-aviation>. Accessed 5 Feb 2020
6. ASTM D7566-19.: Standard specification for aviation turbine fuel containing synthesized hydrocarbons. <https://www.astm.org>. Accessed 18 Aug 2020
7. Calcote, H.F., Manos, D.M.: Effect of molecular structure on incipient soot formation. *Combust. Flame* **49**, 289–304 (1983)
8. McEnally, C.S., Pfefferle, L.D.: Improved sooting tendency measurements for aromatic hydrocarbons and their implications for naphthalene formation pathways. *Combust. Flame* **148**, 210–222 (2007)
9. McEnally, C.S., Pfefferle, L.D.: Sooting tendencies of nonvolatile aromatic hydrocarbons. *Proc. Combust. Inst.* **32**, 673–679 (2009)
10. Kathrotia, T., Riedel, U.: Predicting the soot emission tendency of real fuels—a relative assessment based on an empirical formula. *Fuel* **261**, 116482 (2020). <https://doi.org/10.1016/j.fuel.2019.116482>
11. Richter, S., Kathrotia, T., Naumann, C., Scheuermann, S., Riedel, U.: Measurement of the sooting propensity of aviation fuel mixtures. In: 9th Eur. Combust. Meet. Paper_S1_R1_74 (2019); full text available at <https://elib.dlr.de>
12. Scheuermann, S.S., Forster, S., Eibl, S.: In-depth interpretation of mid-infrared spectra of various synthetic fuels for the chemometric prediction of aviation fuel blend properties. *Energy Fuel* **31**, 2934–2943 (2017)
13. Acree, W.E., Jr.: Solubility of biphenyl in binary solvent mixtures. *Int. J. Pharm.* **18**, 47–52 (1984)
14. Acree, W.E., Jr., Pontikos, N.M., Judy, C.L.: Solubility in binary solvent systems. 6. Predictions of naphthalene and biphenyl solubilities based on the Wilson model. *Int. J. Pharm.* **31**, 225–230 (1986)
15. Richter, S., Kathrotia, T., Naumann, C., Kick, T., Slavinskaya, N., Braun-Unkhoff, M., Riedel, U.: Experimental and modeling study of farnesane. *Fuel* **215**, 22–29 (2018)
16. Methling, T., Richter, S., Kathrotia, T., Braun-Unkhoff, M., Naumann, C., Riedel, U.: An investigation of combustion properties of butanol and its potential for power generation. *J. Eng. Gas Turbines Power* **140**(9), 091505 (2018)
17. Crossley, S.P., Alvarez, W.E., Resasco, D.E.: Novel micropyrolysis index (MPI) to estimate the sooting tendency of fuels. *Energy Fuels* **22**, 2455–2464 (2008)
18. Ladommatos, N., Rubenstein, P., Bennett, P.: Some effects of molecular structure of single hydrocarbons on sooting tendency. *Fuel* **75**(2), 114–124 (1996)
19. Das, D., St John, P.C., McEnally, C.S., Kim, S., Pfefferle, L.D.: Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale. *Combust. Flame* **190**, 349–364 (2018)
20. Das, D., McEnally, C., Kwan, T., Zimmerman, J., Cannella, W., Mueller, C., Pfefferle, L.: Sooting tendencies of diesel fuels, jet fuels, and their surrogates in diffusion flames. *Fuel* **197**, 445–458 (2017)
21. Pellegrin, V.: Molecular formulas of organic compounds: the nitrogen rule and degree of unsaturation. *J. Chem. Educ.* **60**(8), 626–633 (1983)
22. Badertscher, M., Bischofberger, K., Munk, M., Pretsch, E.: A novel formalism to characterize the degree of unsaturation of organic molecules. *J. Chem. Inf. Comput. Sci.* **41**, 889–893 (2001)

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