Predicting the Soot Emission Tendency of Real Fuels – A Relative Assessment Based on an Empirical Formula

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Abstract

Significant progress is going on in the development of non-fossil based alternative fuels which are designed to be sustainable, have potential to substitute (fully or partially) the fossil-based fuels and importantly are targeted to reduce emissions. Though soot emission characteristics has not been focus of fuel certification process yet, due to growing environmental concerns it is important to consider this aspect in the fuel design and understand its emission patterns.

It is known that soot formation in combustion is linked to the degree of branching, degree of unsaturation or the degree of cyclization of a fuel molecule. This information is used to extract soot emission properties of complex real fuel mixtures. To do so, we use the definition of hydrogen deficiency (HD) which gives information on the number of double bonds or cyclic structures present in a fuel. With the help of one measured emission property, the same property of different fuels is predicted using HD. This way, we obtain a relative assessment of fuels' sooting tendency compared to other known fuels. In this work, soot emission pattern of six jet fuels (reference fuels and synthetic fuels) is predicted based on HD and compared them with the recent ground-test measurements of V2527-A5 engine of an Airbus A320. In addition, two more test cases are provided: aviation fuels and diesel fuels, to predict sooting tendency using HD to support our concept. The prediction of the sooting propensity based on HD was found in excellent agreement with the measurements.

Keywords: Sooting tendency, fuel composition, alternative fuels, hydrogen deficiency

1. Introduction

Aviation kerosene is a multi-component complex mixture of hundreds of different hydrocarbons of varying molecular classes mainly categorized by four major classes namely n-paraffins, iso-paraffins, cy-paraffins, and aromatics [1]. The amount of n- and iso-paraffins dominates the fuel composition of most of the conventional fossil-based fuels [2]. Not only the composition varies among the different kerosenes (Jet A, Jet A-1, JP4, JP8), they also vary among the region, feedstock used, and variability in production processes [3]. This leads to a fuel of diverse chemical composition which is furthermore complicated by the new variety of alternative fuels being synthesized. The most notable impact of fuel composition variation is anticipated on the soot emissions where new fuels are paraffinic (Fischer-Tropsch FT-fuels) or are derived through hydro-processed esters and fatty acid (HEFA) [4-11]. See ASTM7566 [12] for a complete list of certified production paths.

Worldwide efforts are being undertaken to replace energy sources based on crude oil to fuels from alternative sources owing to the growing concerns about the security of supply, as well as negative effects on the environment and climate [13]. Alternative fuels have been of great interest due to their potential for reduction in net emissions. These fuels are synthesized from various alternative sources with an aim to produce fuel that emits lower emissions. The alternative fuels are still primarily hydrocarbons obtained from natural gas, coal or biomass as feedstock and their compositions can be typically dependent on the production process and the feedstock used. Since they are synthesized from different production technologies, they differ in their chemical composition. Synthetic fuels from FT-processes are mainly paraffinic in nature [14]. Due to the absence of aromatics, the density of synthetic fuels is lower compared to the existing jet fuels. In order to comply with specification limits one would require addition of components of higher densities such as cyclo-paraffins or aromatics [3]. Thus, alternative fuels may contain hydrocarbons of different molecular nature not present in conventional fuel. Therefore, an understanding of not only the physical and chemical process occurring during combustion but also the molecular structural effect on emissions is important. This can help to understand how the particular chemical structure of the fuel influences emission patterns. Understanding this influence can help us to better understand and design the fuels of future.

In this context, in the present work we aim to understand how the fuels' molecular structure influences the particulate emissions irrespective of the conditions they are burned. To this end, we present a simple correlation to predict the soot emissions of fuels at a given combustion condition. For this reason, we exploit the fact that soot emissions are linked to the unsaturation and cyclization of fuel molecules. Through this we can assess relatively the fuel emission pattern based on the fuels' molecular structure.

2. Background – Fuel Property Effects on Soot Emission

The presence of different molecular classes in different fuels has an influence on various physical and chemical processes occurring inside the combustor. Such differences may influence the ignition, spray characteristics such as atomization of droplets, fuel vaporization which may subsequently affect the combustion and soot emissions. Several reports are available in literature showing strong link between fuel properties and measured particulate matter (PM) emission from engines and gas turbines [4-7, 15-23], also supported by theoretical correlations [15, 19, 21-23]. The correlations on fuel effects are empirical in nature and links sooting tendency of fuel such as smoke point, smoke number, and particle emissions with fuels' chemical or physical properties such as the amount of aromatics or hydrogen, H/C ratio, viscosity, volatility, vapor pressure, distillation parameters or boiling range etc. [24].

There are numerous studies on the soot emissions involving varying scales of experiments and models starting from simple laboratory flames to complex engine tests. Based on the type of fuels studied, i.e. aviation fuels (conventional and alternative fuels), road transportation fuels (diesel and gasoline) and depending on the focus of these studies one can categorize these studies into: (a) relationship of fuel parameters to the emissions based on experimental observations, (b) theoretical fuel-property correlations to estimate the emissions, and (c) fundamental studies on sooting tendencies of individual fuel components in laminar flames. In this work, we focus on the second aspect using knowledge gained from aspect one and three.

(a) Emission Measurements

With increasing use, the performance of alternative fuels with respect to the soot emission has received considerable attention [25-27]. The particles emitted from aircraft engine are influenced by the fuel composition, fuel flows, as well as engine design/operating conditions and altitude [28]. The effect of fuel composition on emissions has been part of many studies. Compared to the aromatics present in fuel that has been identified as compounds that primarily influence the tendency to form soot [29-32, 4, 5, 17, 2, 23] the fuel hydrogen content has been considered a more fundamental parameter that is independent of molecular structure [33-35, 23]. Most of the studies identify the aromatic content of the fuel to be correlated to the emissions [4, 5, 8, 19, 18, 36]. However, many of these earlier studies are done on conventional kerosene or existing jet fuels [6, 18, 19, 22, 23]. With emerging demand of alternative fuels, it is important to expand our current knowledge/database on aircraft emission and increase knowledge towards influence of other fuel components on soot emissions [37, 18]. Recent measurements of soot emissions in aircraft engines using alternative fuels [11, 23] have shown that the aromatic content of fuel does not always explain the trends measured. The data presented by [23] who studied various blends of various conventional and alternative fuels could not differentiate the impact of aromatics and H/C ratio as both were varied simultaneously. They demonstrated that non-volatile particulate emission showed strong function of fuel composition, consistent with other similar studies [20, 19]. Other criteria that showed relationship to emissions are hydrogen content or H/C ratio of fuel [33-35, 4, 20, 11]. The H/C ratio criterion is disputed in the literature: It has been found to correlate in some studies [33-35] whereas the trend of PM emissions to H/C ratio was found to be inconsistent by others [38, 23]. This is not surprising as complexity of fuel composition also implies complexity in assessing their influence on the emissions.

However, these relationships are not widely applicable and are often valid only for specific fuel and the specific conditions investigated. For example, a few fuels present in this study showed no linear relation to the aromatics content mainly due to the presence of a significant amount of cy-paraffins. The soot emissions can be linearly related to the H/C ratio but this relationship is non-predictive, i.e. cannot be extended to predict soot emissions directly. Christie et al. [23] also reported

that the correlation between H/C ratio and aromatics content is poor and insufficient to define the fuel. Similarly, correlation based on hydrogen content can be influenced by molecular structure especially when large aromatics are present in fuel [30].

(b) Theoretical Correlations
Regarding aviation fuels, there are many scientific reports addressing the issue of emissions involving both conventional and synthetic fuels [4-7, 15-20, 39, 40, 22, 23]. Among them there are examples where fuel properties effects have been emphasized to correlate with the soot emissions of aviation fuels [15, 19]. Similar studies are also available for fuels used in road transport. Relevant to this work, among these fuel composition-property relationships, are the ones which emphasized the correlation of the fuel's chemical composition to the emission. These studies include correlations obtained from studies on jet and diesel fuels [15, 19, 21] as well as relations obtained in gasoline engines [41-45].

Cookson and Smith [15] provided a simple linear relationship of the fuel composition to the smoke point, aromatics content, H-content, and other physical properties. Their model requires the amount of n-alkane, branched plus cyclic saturates and aromatics content of fuel as well as three respective fitting coefficients determined from multiple linear regression analysis to predict the property of blends in question. They demonstrated their model validation through blends of verified jet and diesel fuel. Recently Brem et al. [19] obtained a correlation for emission indexes of conventional kerosenes using the hydrogen content of fuel as well as information on engine thrust whereas Speth et al. [21] predicted black carbon emissions as a function of the aromatic content and engine thrust. Both studies reported that the validity limit of their correlations is mainly restricted to similar technology or similar fuels respectively.

The influence of fuel composition on particulate emission in gasoline engines are also demonstrated in literature [41-45] using physical properties along with the chemical composition of the fuel to obtain particle number (PN) indexes. Aikawa et al. [41] obtained the PN index based on the vapor pressure and double bond equivalent (alias hydrogen deficiency) of each fuel component. Subsequent studies [42-45] have also presented correlations based on the fuel composition and fuel properties to predict the particulate emissions. All of these correlations use, along with fuel compositions, at least one physical property; like vapor pressure [41, 45] or distillation range parameter [43] and may employ up to fourteen properties [44] of each fuel component. Such correlations are cost intensive as they require specialized laboratory tests which also multiply with number of components present in a fuel.

(c) Fundamental Soot Investigations
On the fundamental level, a detailed description of soot formation and growth process is in itself a wide field of research originating from pioneering work of K.H. Homann, H.G. Wagner, B. Haynes, H. Bockhorn, M. Frenklach and a detailed discussion is beyond the scope of this work. In addition, a large body of work in terms of sooting tendencies of fuel components and their relation to the fuels' molecular structure has been reported in literature [46-51]. It has been demonstrated that the sooting tendencies of hydrocarbons are governed by the structure of the molecules [49, 31, 51]. Among them, aromatics are found to be most prolific sooters whereas fused aromatic-aliphatic compounds such as tetralin as well as cy-paraffins have higher sooting tendency compared to saturated hydrocarbons [31, 48]. The presence of unsaturation (double, triple bonds), position and length of branching also present a secondary influence on sooting tendency [49, 31, 47, 46]. Hai Wang and coworkers [52] identified that the high molecular weight components in a conventional jet fuel, which are usually multi-ring components, have a higher impact on the emissions. These components are seen at the high temperature end of the distillation curve. They suggested using this information as potential way to reduce emissions by designing fuels through tighter constraints on the distillation process [52].

The formation of soot in flames is described by formation, growth, and oxidation of polycyclic aromatic hydrocarbons (commonly known as PAHs) that are dependent on the temperature and on the combustion intermediates forming them [53, 54]. The formation of PAHs is initiated by the emergence of aromatic rings from smaller hydrocarbon intermediates such as C_2H_2, C_2H_4, C_3H_3 [53, 54], the routes are function of temperature [55]. It has been observed that soot levels in flames are proportional to benzene concentrations but not to acetylene levels [40]. Jet fuels already contain, by specification up to 20% (vol.) aromatics and studies have shown an increase in soot formation directly from the

fuel-bound aromatics [56, 57, 40]. Thus, it is possible to relate the fuel-bound aromatics and cyclic compounds to predict the soot. As pointed out by Speth et al. [21] the formation of PAHs and subsequently soot can be modeled as soot formed due to the presence of aromatics in the fuel as well as soot formed from intermediates that are independent of the fuels' aromatic content. To account for both of these effects we consider the definition of hydrogen deficiency which takes into account the presence of unsaturation (double, triple bonds) and ring formations (cy-paraffins, aromatics).

Thus, we use in this work the hydrogen deficiency as a measure of the total amount of unsaturation and cyclic structures present in fuel which is the key factor to predict soot emission at a given condition.

3. Sooting Propensity of Hydrocarbons and Real Fuels

In literature, the sooting propensity of a fuel or fuel component is discussed as a function of the smoke point (SP) or soot volume fraction (f_v). Earlier studies on sooting tendency, measured as a smoke point, revealed its dependence on several factors such as fuels' molecular structure, air flow, burner temperature, and molecular weight of fuel [58-60]. Thus, the actual values of the SP varied as they were dependent on the burner used as well as on the conditions studied. However, all measured SP showed a similar qualitative trend in sooting tendencies. Later, Threshold Sooting Index (TSI) was introduced by Calcote and Manos [61] to overcome the dependencies of smoke point measurements on molecular weight or mass flow rate. This was further refined by McEnally and Pfefferle [46, 48] who measured sooting tendency, in terms of Yield Sooting Index (YSI), by correlating soot volume fraction of fuel in methane-doped diffusion flames. They have provided impressive database on YSI of several chemical components of varying structural classes [46, 48] as well as recently of some real fuels [51, 62]. Their sooting tendency data were found in agreement with the smoke point data from literature. Since all these studies used different correlations one cannot simply use two different data sets directly for comparison.

The estimation of sooting propensity of a real fuel requires considerable experimental or modeling efforts. The real fuels, such as Jet A-1 shown in Fig. 1, are typically complex mixtures of compounds from several structural classes of varying carbon number. This makes the estimation of emission from the analysis of real fuel components very difficult. The fuel surrogate definition used for numerical studies of real fuels often ignores the sooting tendency as input parameter. There exists another difficulty on how to use individual sooting propensities measured (TSI, SP, YSI) for a fuel surrogate consisting of two or more components. Only limited studies are done so far; most of them are restricted to binary mixtures and demonstrate the validity of mixing rule based on linear combinations of individual TSI values [63-65]. Moreover, it is difficult to find a consistent definition of sooting tendency for all hydrocarbons present in a fuel.
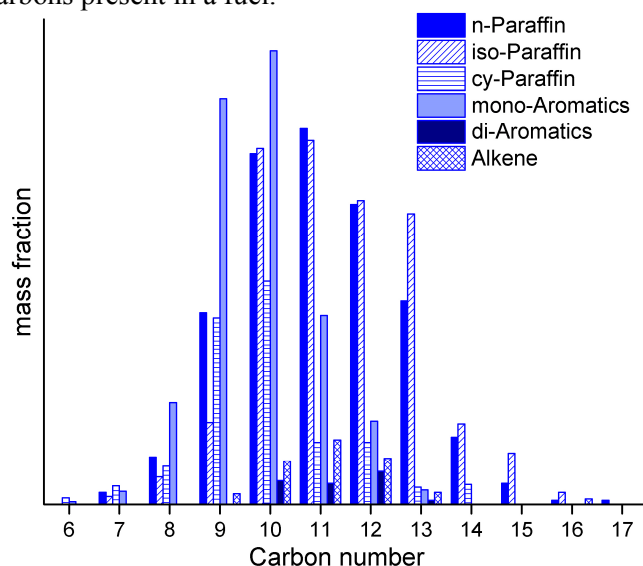

Figure 1. Chemical composition of Jet A-1, Stuttgart airport [66, 67].

4. Predicting Sooting Tendency of Fuels

It has often been revealed in different studies that soot emissions are highly dependent on the structure of the molecules especially on unsaturation (double bonds), cyclic structures and degree of branching [68-70, 51, 49]. It is generally known that the various structural classes have increasing sooting tendencies in the order: n-paraffins < iso-paraffins < olefins < alkynes < aromatics < polyaromatics [70]. Most importantly, cy-paraffins and aromatics are attributed as the class of compounds that primarily influence the tendency to form soot precursors and soot [31, 4, 40, 17, 2]. These two structural classes lumped as "total cyclic compound" can be distinguished by the presence of double bonds and/or ring structures. Each of these two structural classes has lower hydrogen to carbon ratio compared to paraffins.

4.1 Definition of Hydrogen Deficiency (HD)

To define a metrics for the total cyclic compound of a fuel we referred to the definition of hydrogen deficiency, long known in chemistry [71-73], which measures the degree of unsaturation (double bonds) and cyclization (ring structure) of a fuel. For a given fuel C_xH_y, the Hydrogen Deficiency is defined as

$$HD = (x+1) - (y/2).$$

By this definition, the HD of n- and iso-paraffins is zero as in both cases neither unsaturation nor cyclic structures are present. Figure 2 exemplifies typical values of the hydrogen deficiency, calculated using the above equation, for several hydrocarbons of different structural classes typically found in jet-fuels or in liquid fuels in general.
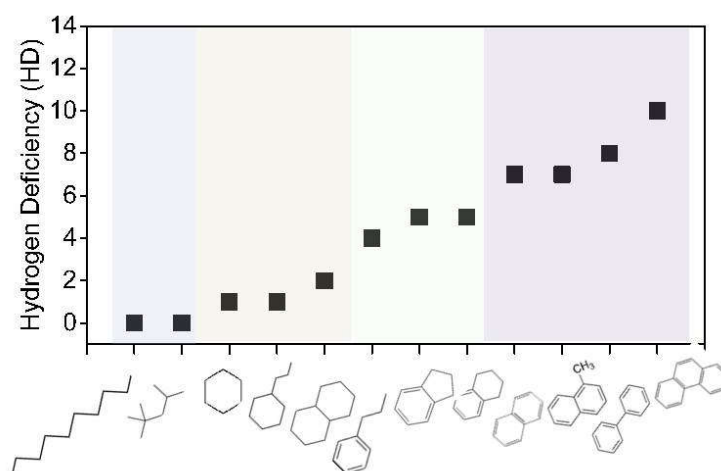

Figure 2. Hydrogen deficiency (HD number) of different hydrocarbons.

The HD provides a factor based on which the sooting tendency of a fuel can be estimated by linear extrapolation. As an example, for the prediction of emission of a given fuel, the emission of a reference fuel is multiplied by the relative factor of HD obtained from the ratio of $HD_{fuel}/HD_{ref-fuel}$. Thus the HD provides a factor for one point linear extrapolation. This is done at a given condition of temperature, pressure, or power setting and cannot be extrapolated between conditions. Thus, the extrapolation is applied to different fuel compositions and not between different combustion conditions.

4.2 Calculating the HD of Real Jet Fuel

A real fuel is often a multi-component complex mixture of hundreds of hydrocarbons [2]. The composition of complex mixtures can be estimated by employing methods such as Gas Chromatography (GCxGC/GCxMS analysis) or using Carbon-13 (C[13]) nuclear magnetic resonance (^{13}C NMR) spectroscopy. To estimate the HD of a fuel we use the fuels' empirical formula C_xH_y where the information on the fuel's C, and H number can be estimated by the methods mentioned above. Based on the information of the fuels' C, and H number, we estimate the hydrogen deficiency

of a fuel from its definition mentioned earlier. Please note that this empirical formula does not contain detailed information on the presence of the particular structural class but supplies information on summation of double bond and number of ring structure present. The influence of n- and iso-paraffins on soot formation, which by definition has a HD of zero, is included under model uncertainty. Since they possess little sooting tendency compared to aromatics this is not a disadvantage for predicting emission tendency of multi-component fuels. However, for accuracy an uncertainty factor for the influence of n- and iso-paraffins based on the sooting tendency database from Das et al. [51] is estimated. The YSI data [51] are available for n-paraffins from C_6 to C_{12} including various branched paraffins with varying degree of branching. We extrapolated these data up to C_{20}. Compared to most sooting aromatic compound measured (1,2-diphenylbenzene $C_{18}H_{14}$, YSI = 1340), we obtained the maximum deviation occurring from the presence of n-paraffin(+iso-paraffin) of 11%. This factor is considered as a conservative estimate of the HD model uncertainty accounting for the influence of its total n-/iso-paraffin content on soot in a multi-component fuel.

5. Predicting Soot Emission Pattern of Real Fuels from HD

We investigated three different test cases to obtain predicted sooting tendencies of fuels at different conditions in different combustion setups.

5.1 Case I: Predictions of Particle Emission Index of Alternative Fuels

The influence of the fuel composition on emission patterns - necessary for fuel quality assessment - was investigated with the help of six jet fuels. The simple correlation of predicting HD identifying the amount of the two structural classes (cy-paraffin, aromatics) in jet fuels is found to be correlated to the emission trends found in exhaust gas measurements of real jet engines. We assessed the soot emission pattern of real fuels measured at engine exhaust and contrasted this with their hydrogen deficiency.

In the present work we considered certified alternative jet fuels consisting of different compositions investigated within the framework of the DLR internal project "Emission and Climate Impact of Alternative Fuels" (ECLIF). These fuels are two reference kerosenes (100% Jet A-1), three semi-synthetic jet fuels consisting of reference fuel and Synthetic Paraffinic Kerosene (SPK) and one fully synthetic jet fuel. All six fuels are supplied and analyzed by Sasol. The nomenclature of these fuels is detailed in Table 1. For more information on fuels' composition and emission measurements, we refer to Schripp et al. [11].

Table 1. Alternative jet fuels studied in this work. Ref1 and Ref2: Reference kerosenes, SSJF: Semi-Synthetic Jet Fuel, FSJF: Fully Synthetic Jet Fuel, SPK: Synthetic Paraffinic Kerosene.

Fuels	Description
Ref1	100% Jet A-1 "Merox"
Ref2	100% Jet A-1 "Bitumen Run"
SSJF1	59% Ref1 + 41% SPK
SSJF2	55% Ref2 + 45% SPK
SSJF3	86% Ref1 + 14% SPK
FSJF	100% FSJF

Particles emissions were obtained for the above fuels in the ground-based test using Airbus A320 (V2527-A5 engines) [11]. We assessed the soot emission pattern of the above six real fuels calculating the hydrogen deficiency number. The prediction of fuels' HD was compared with the emission data obtained at engine exhaust in ground-tests [11] performed as part of the ECLIF project. The data are available for different power settings (fan speed, N1).

In the present case, we took the emission index of Ref1 as a reference data point for one-point linear extrapolation, which is multiplied by the relative ratio of the HD of the given fuel to the HD of the reference fuel used for extrapolation i.e. HD_{fuel}/HD_{Ref1}. This gives the predicted value of a given fuel at a given power setting. The extrapolation is done between different fuel compositions while keeping the physical condition constant, in this case fan speed. Figure 3 shows the extrapolated emission indexes of four different fuels based on Ref1, at five different power settings. The prediction

of the relative emission pattern of these fuels using the HD definition shows exactly the similar emission trend as observed in all ground test measurements at different power settings. Here one should note that the measurement uncertainty of Ref1 (reference extrapolation point) will also be carried forward to the predictions; the reason for the uncertainty bars shown together with the predicted values. In addition, the model uncertainty accounting the influence of n- and iso-paraffins, as discussed earlier, adds about 5-8% (based on 45-75% paraffins present in fuel) to the above uncertainty of reference extrapolation point. This total uncertainty is shown together with the predicted data points in Fig. 3. Four predicted data points of SSJF1 and SSJF2 are outside the range of measurement limits. This is however unclear due to multiple factors involved in the measurements and analysis of the complex measured data is beyond scope of this work. The trend of the relative variation in emissions dependent on the fuel composition is accurately predicted.
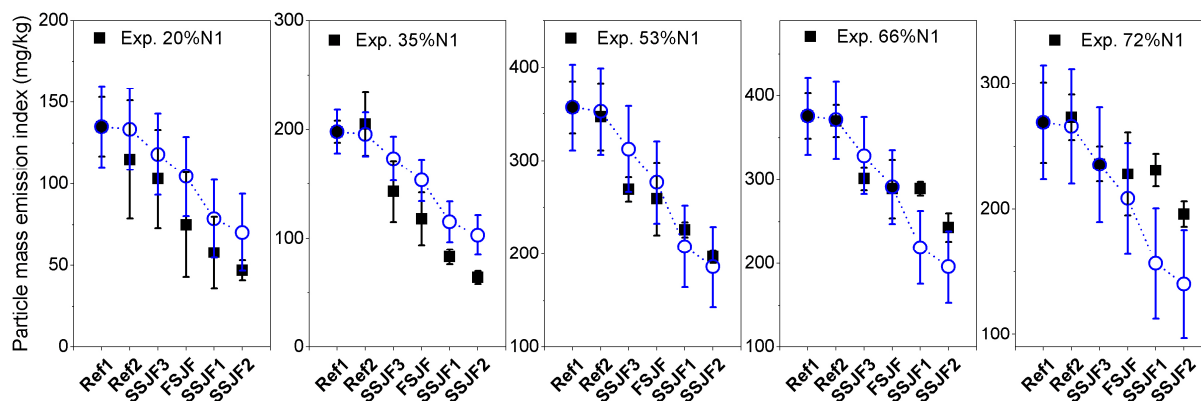

Figure 3. Comparison of measured particle mass emission index (mg/kg) of six alternative fuels in a ground-test at different power settings (N1) [11] with the predictions obtained using the hydrogen deficiency (HD) concept. Square: measurements, open circle: predictions.

The suitability of the HD concept to predict emission of complex fuel mixtures can be discussed based on the fuel structure. A detailed analysis of the six fuels' composition with respect to the presence of various structural classes is shown in Figure 4. The amount of n-paraffins among these fuels varies from 5-25% (wt.), whereas iso-paraffins are present in larger quantities (up to 60%). Both according to HD play no role in the prediction of soot emission pattern. The major deviation of fuel composition results from the amount of aromatics and cy-paraffins present. For both reference fuels (Ref1, Ref2) the aromatic- and cy-paraffinic- content are similar. Even to the smallest detail of slightly lower cy-paraffin in Ref2 is reflected in HD prediction. Similarly, the semi-synthetic fuels SSJF1 and SSJF2 have nearly similar total cyclic content (<5%); slightly lower in SSJF2, a trend also predicted by HD. Another point of interest here for both semi-synthetic fuels is, that both contain a high amount of iso-paraffins (~60%) with a difference of about 10% (lower) in SSJF1. This seems to have no effect on emissions. Whereas the amount of aromatics in SSJF2 is ~1% and cy-paraffins are ~4% lower, also reflected by HD.

An interesting observation is seen in the emissions of fully synthetic jet fuel (FSJF) that has aromatic content similar to SSJF1 and SSJF2 which however predicts much higher emissions compared to both semi-synthetic fuels. The main reason for such deviation is the high amount of cy-paraffins contained in FSJF. Since the concept of HD not only identify total cyclic compounds present in a fuel but also distinguish between their type and their impact on emissions (i.e. HD higher for aromatics compared to cy-paraffins), the deviation of FSJF emission pattern from SSJFs can be accurately estimated.
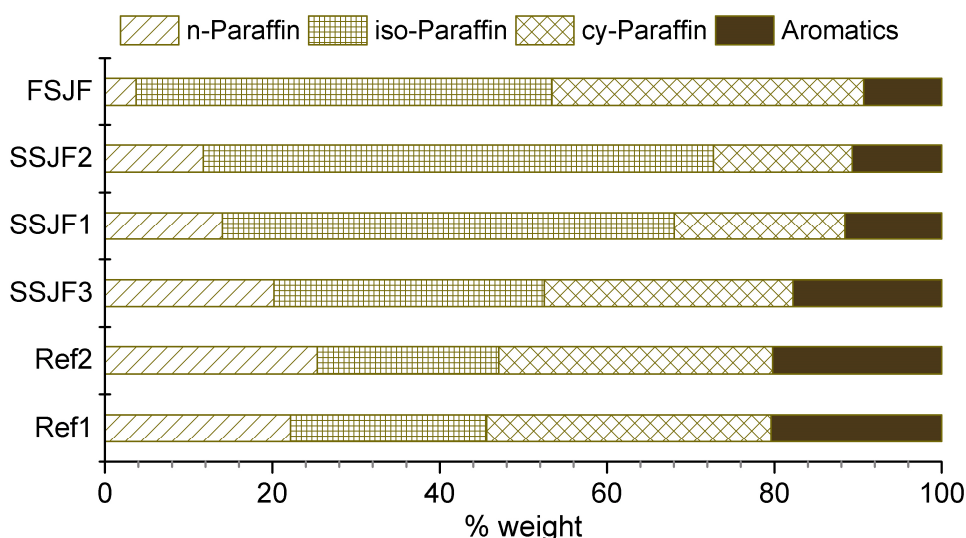
Figure 4. Composition of six fuels distinguished by structural classes present (Analysis supplied by Sasol).

This observation also strengthens the fact that considering only the aromatic content of a fuel would not be sufficient to explain the emission pattern and a more appropriate approach would be instead to identify the "total cyclic compounds" of a multi-component fuel. Secondly, the SSJF2 has the highest amount of iso-paraffins and lowest amount of "total cyclic compounds". The emissions in engine measurements for this fuel are also found to be lowest. This shows that influence of iso-paraffins on emissions is much lower compared to cyclic compounds. The SSJF3 fuel produces highest emissions among all four synthetic fuels which is a result of the high amount of aromatics and cy-paraffins in this fuel. The total cyclic compounds of SSJF3 is similar to FSJF however due to the presence of a higher amount of aromatics among the two, the emissions are higher. This is also viewed by its resulting HD value. This reflects why some fuels correlates to aromatics content and others not. In presence of high amount of cy-paraffins, those correlations would otherwise fail.

Thus, we found the predictions using the HD number are in excellent agreement with the ground tests of jet engine emission patterns. As outlined above, we expect this correlation to hold for a broad class of multi-component liquid fuels' compositions and not to be limited to jet fuels only.

5.2 Case II: Predictions of Sooting Tendency of Jet Fuels

In addition, we are able to obtain the fuel composition and YSI of four different jet fuels published in the literature. Das et al. [51] measured sooting tendencies of four jet fuels JP-5(10289), Jet-A(10325), JP-8(10264), and Jet-A(4658). The details of their fuel composition are available in [74, 75]. The measured and predicted yield sooting tendencies of these fuels are presented in Fig. 5. For the prediction of YSI, the sooting tendency of JP-5 is taken as a reference point to extrapolate the predictions using HD. The maximum uncertainty limits of YSI measurements are reported to be ±5% [51].

It can be seen that the sooting tendency of first three fuels (left to right in Fig. 5) decreases. This is consistent with their fuel composition shown in Fig. 6 where the total amount of cy-paraffin and aromatics decreases. Compared to them, the sooting tendency of Jet-A(4658) increases although the total cyclic compound is similar to JP-8. This is due to difference in the large amount of aromatics present in Jet-A(4658) compared to JP-8. Since the definition of HD not only captures the total cyclic compound but also distinguish their amount and thereby their varying influence through the presence of double bonds and/or rings, the sooting tendency of Jet-A(4658) is equally well captured by the predictions. The model uncertainty arising from the presence of n- and iso-paraffins is 3.5-7.5%, depending on their amount present in fuel.
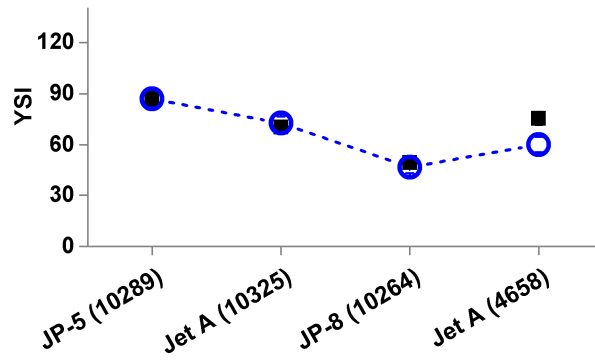
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Figure 5. Comparison of measured yield sooting index (YSI) of four jet fuels [51] with predicted YSIs obtained by the hydrogen deficiency (HD). Square: measurements, open circle: predictions. Dotted line in the figure is only guiding line.
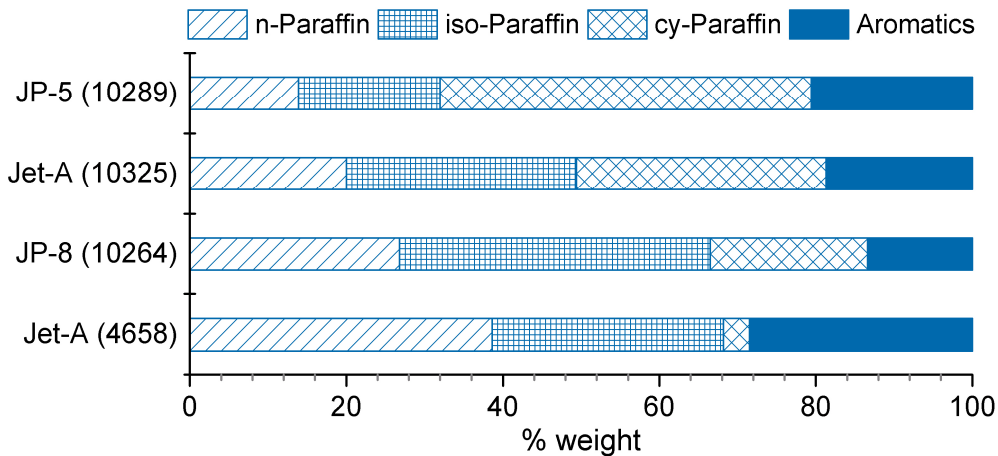

Figure 6. Composition of four different real jet fuels [74, 75].

5.3 Case III: Predictions of Sooting Tendency of Diesel

Since our predictions of the sooting tendency rely on the fuels' composition it can be extended to any hydrocarbon fuel (C_xH_y). As a third example, we present the smoke point and sooting tendency measured for certified diesel fuel (CF) along with its four fuel surrogates studied in Mueller et al. [76]. The information on the fuel composition and smoke point measurements are available in Mueller et al. [76] whereas their sooting tendencies are measured by Das et al. [51].

Figure 7 presents the measured smoke point and YSI in comparison with their predicted values. The predictions of sooting tendencies are obtained by extrapolation of CF values using again the HD concept. The predicted sooting tendencies of all five fuels are in excellent agreement with the measurements. The measurement uncertainties are less than 5% [51], whereas the model based uncertainty arising from the presence of n- and iso-paraffins are 3-8% for diesel fuel as shown in Fig. 7.
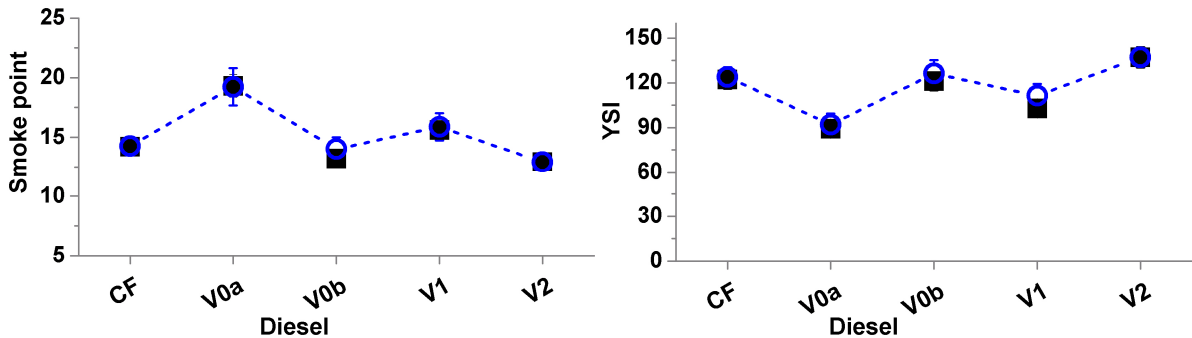
Figure 7. Comparison of measured smoke point [76] and YSI of Diesel fuels [51] with their respective predictions obtained using the HD concept. Square: measurements, open circle: predictions. Dotted line in the figure is only guiding line.

The trend of the sooting tendencies shown in Fig. 7 can be explained by analyzing the fuel compositions presented in Fig. 8. The fuel surrogate V0a has lowest amount of total cyclic compounds, and lowest sooting tendency. On the other hand the fuel surrogates V0b and V1 has same amount of total cyclic compounds, the V0b has a higher amount of aromatics compared to V1 which is reflected by higher sooting tendency of V0b. Among all fuels, the V2 fuel has not only highest aromatics content but also highest amount of total cyclic compounds and consequently also highest sooting tendency. Compared to V2, CF diesel has 50% more n- plus iso-paraffins but has no visible reduction in emission. This also supports the conclusion that the total cyclic components of a fuel have the dominant influence on the sooting tendency compared to n- and iso-paraffins.
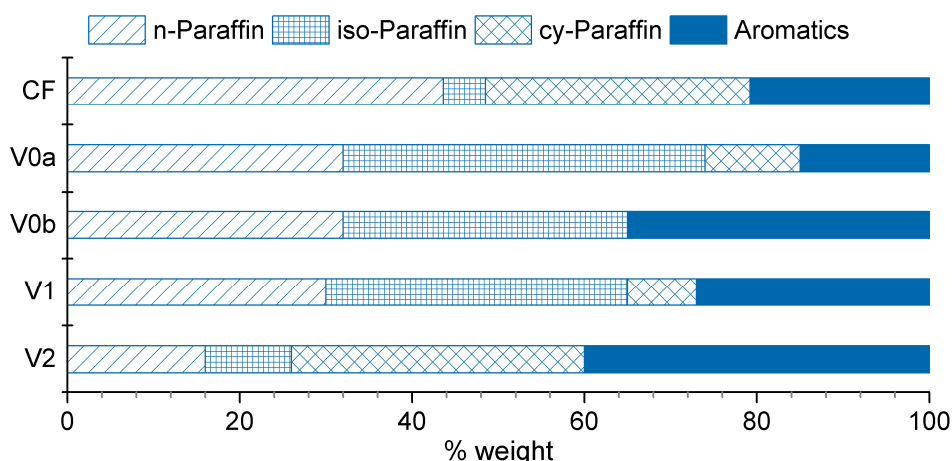

Figure 8. Composition of certified diesel fuel (CF) [76] and its surrogate fuels [51].

6. Comparison to Composition-Property Relationships from Literature

Similar correlations for predicting emission based on fuel composition and fuel properties are investigated in the literature. Among them, relevant to the present work are: smoke point correlated to fuel compositions by Cookson et al. [15], particle emissions correlated to hydrogen content and engine thrust from Brem et al. [19], the fuels' aromatic content and engine thrust used to predict emission reduction by Speth et al. [21].

Cookson et al [15] developed a correlation based on the fuel composition to predict different fuel properties (chemical and physical) for jet and diesel fuels of different boiling range. Their correlation requires mass fractions of n-alkanes, branched plus cyclic saturates, and aromatics, weighted by three fitting coefficients. With their correlation it is possible to predict the smoke point of fuels studied in case I and case II with accuracy of 10-20% and <11% respectively. In addition, we use their correlation to predict the aromatic content of fuels studied for these cases too. For case II, the fuels' aromatic content can be predicted within 5% accuracy. The reference fuels from case I, and the SSJF3 which also has fuel composition similar to the reference fuels, are predicted with <5% accuracy. However, the deviation of predicted aromatics in synthetic fuel increases from 18% (SSJF1) to 34%, (FSJF), although the fuel compositions are within the applicability limit of the correlation. The validity of this correlation, as they pointed out, is restricted to the aspect pertaining to the fuel composition, i.e. it may fail to predict fuel with composition outside the range of reference fuels, for example high n-alkane FT-fuels. This is however not the case, in fact the SSJF1, SSJF2, and FSJF have the lowest n-paraffins compared to other fuels. They also have lowest amount of aromatics and highest of total branched plus cyclic saturates. Thus the details on fuel structure i.e. presence of unsaturates or ring structure instead of fuel composition seems to be a more direct way of relating fuel composition and the emissions.

Engine studies of Brem et al. [19] on conventional jet fuels supplied a simple correlation to predict emission indexes of jet fuels based on the fuels' hydrogen content and engine thrust. The validity of

their correlation is proposed to be restricted for use in similar technology combustion concepts i.e. RQL combustors. In addition, the authors expect the extension of their correlation to the fuels that are compliant with Jet A-1 specifications. In general, they identify reductions in particulate matter related to higher H-content and aromatic content, which is consistent with our fuels (studied in case I) in terms of the H-content but inconsistent with the aromatic content as discussed earlier.

Similarly, Speth et al. 2015 [21] predicted changes in black carbon (BC) mass as a function of the aromatic content of the fuel and engine thrust; for alternative and conventional fuels. Their correlation predicts the relative reduction in emissions relative to engine setting and relative to the aromatic content. The predictions of this correlation is interpreted as: for fixed thrust setting, the reduction in BC emissions are proportional to reduction in the aromatic content of the fuel; which is the case for our fuels (studied in case I), except for FSJF which contains high cy-paraffins.

7. Discussion

To estimate the sooting propensity for any fuels in a practical system is not an easy task. The fuel accounts for many complex effects. The hydrogen deficiency explains the influence of the molecular structure on fuel emission. For many real fuels, n- and iso-paraffins are main component of the fuel mixture. Deriving information on soot emission based on individual compound present is a tedious task as real fuels comprise of hundreds of species and an individual assessment of each component requires high effort.

Using hydrogen deficiency concept, we link the soot formation to the degree of unsaturation, or the degree of cyclization of a fuel molecule. Here it should be noted that we do not intend to estimate absolute values of soot emissions rather focus on relative assessment compared to the sooting tendency of a known fuel (e.g. Jet A-1). According to our findings, prediction of soot emission using hydrogen deficiency is feasible for a number of reasons detailed below.

(1) Why the single component sooting tendency is not important: For many real fuels, n- and iso-paraffins make up large portion of the fuel mixture (see Fig. 1 and 4). The definition of HD neglects the contribution of n- and iso-paraffin to soot formation, whereas considers the fuel components which contribute to most soot are aromatics, and cy-paraffins. They are often present as a small fraction of total fuel, e.g. in aviation fuels aromatics are restricted up to 20% (vol.) by its standard specification. In a real fuel mixture, many individual fuel component, especially soot promoting bicyclic-paraffins and naphthalenes, are often in trace amount. For example, a detailed composition of reference fuel (Ref1) studied earlier is shown in Figure 9. It presents the variation of each structural class as well as variation of composition with respect to carbon number. The sooting tendency of 1-methylnaphthalene is about factor of 9 higher compared to bicyclic decalin; however its composition in reference fuel can be about 1-2%. Therefore, accuracy of individual component sooting tendency is not essential for multi-component fuel mixture.
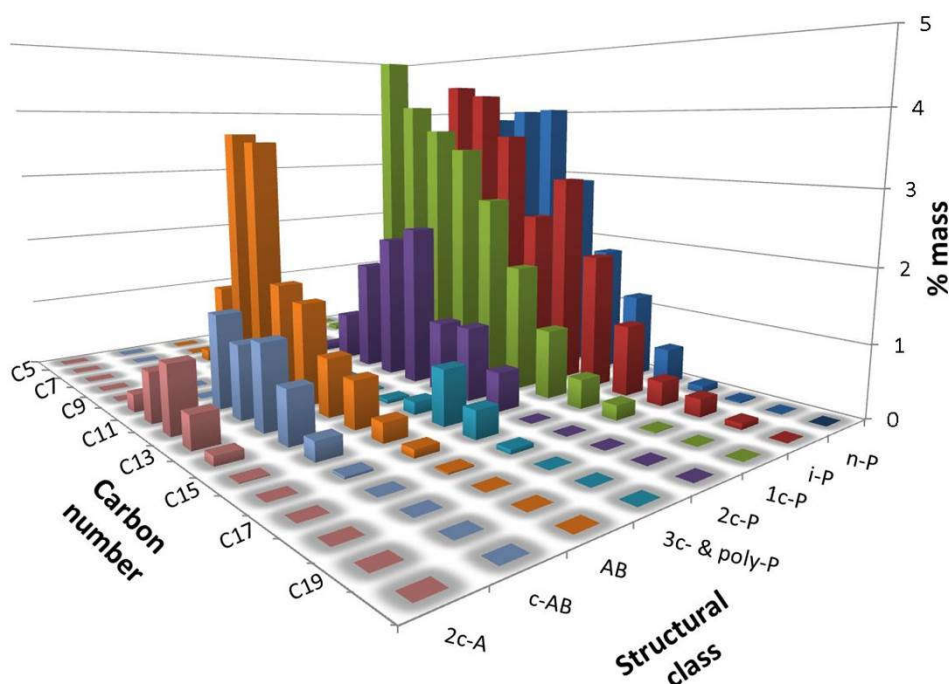
n-P: n-paraffin, i-P: iso-paraffin, 1c-P: monocyclo-paraffin, 2c-P: bicyclic-paraffin, 3c- &poly-P: tri-
& poly-cyclo-paraffin, AB: alkyl-benzenes, c-AB: cyclo-alkylbenzenes, 2c-A: bicyclic-aromatics

Figure 9. Classification with respect to carbon number and molecular structural classes present in the reference jet fuel "Ref1". Fuel composition data supplied by Sasol.

(2) Can one ignore the contribution of n-/iso-paraffins to emissions: The n- and iso-paraffins are often in abundance compared to ring-structured molecules. The iso-paraffins are considered to have a higher sooting potential compared to n-paraffins, but both classes do not contribute to the HD number, i.e. no contribution to soot. Although iso-paraffins have higher sooting tendency compared to n-paraffins, it is still much less compared to the sooting tendency of aromatics and most cy-paraffins (at least a factor of 4 or higher).

(3) Can one ignore highly branched iso-paraffins: As seen above, by definition, the HD number ignores iso-paraffins, irrespective of their degree of branching, as a contributor to soot emission. No major data on large, highly branched iso-paraffins are available to judge its influence on sooting tendency in a fuel mixture. In general, iso-paraffins are known the have higher sooting tendency compared to n-paraffin. Moreover, the sooting tendency of iso-paraffins varies depending on its degree of branching. Only sooting tendency predictions are available for C_6-C_{11} iso-paraffins from Crossley et al. [47]. As seen in Fig. 10, they provided sooting tendencies of iso-paraffins with different degree of branching as a function of carbon number. Data are presented for mono- and di-methyl substituted paraffins which contain one tertiary and one quaternary carbon respectively. Both iso-paraffins show linear increase in sooting tendency with increase in carbon number. For a given carbon number, the sooting tendency of di-methyl substituted paraffins is highest among the two types and is about twice as high as n-paraffins. Compared to these, the cy-paraffins exhibit an exponential increase in sooting tendency and at a carbon number 7 it is about 3 times higher. No sooting tendency data of aromatics are available from the same authors for a direct comparison. However, their study clearly elaborates that the sooting tendency of iso-paraffins, though higher compared to n-paraffins, is by far lower than the one of cy-paraffins and aromatics.
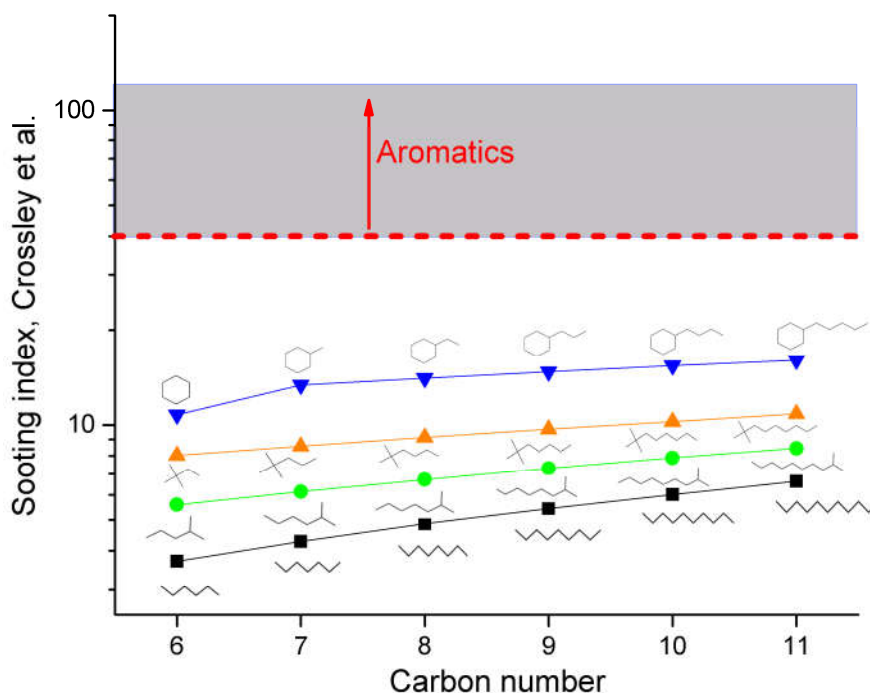
13

Figure 10. Comparison of the increase in sooting tendency of n-, iso-, and cy-paraffins as a function of carbon number – molecules with carbon number 6 to 11 (C_6-C_{11}). All data plotted are from Crossley et al. [47]. Projected sooting index of aromatics, no exact data available from the same reference for direct comparison.

In order to estimate the influence of the sooting tendency of iso-paraffins and to identify whether this might be a limitation on the importance of HD for real fuels, we considered two extreme cases. As a reference case, consider a highly branched iso-paraffin 2,2,4,4,6,8,8-heptamethylnonane (iso-cetane) which has sooting tendency YSI = 31 [51] and that of 1-methylnaphthalene with YSI of 471.2 [51]. Compared to the fuel containing 100% iso-cetane ($YSI_{100\%}$ = 31), a fuel mixture containing 20% 1-methylnaphthalene mixture ($YSI_{20\%}$ = 94.24) will still have higher sooting tendency by factor of three. Thus, the influence of iso-paraffins is still negligible compared to aromatics.

(4) Predicting emission of oxygenated hydrocarbons: The combustion of oxygenated hydrocarbons produces fewer soot particles compared to non-oxygenated hydrocarbons [77]. Though not approved for aviation, potential increase in the use of biofuels is expected (compared to the current level of biodiesel) and therefore it is important to understand the influence of the fuel-bound oxygen, present as additive or as a pure fuel, on the soot emissions. Numerous studies have observed that reduced soot emissions are dependent on both, molecular structure (different functional groups like aldehydes, alcohols, ketones, ethers, esters etc.) as well as on the oxygen content of the fuel, see [50] and references therein. The exact mechanism of soot reduction can be an effect of many factors debated in literature, which can be an entire review topic beyond scope of this work.

Our definition of HD does not take into account the presence of fuel-bound oxygen. The relationship between oxygenated fuels to soot emissions is complicated with the fact that the oxygen present in these fuels not only provides extra oxygen to react with carbon but also displaces and reduces the amount of carbon needed to burn. Stoichiometric air-to-fuel ratio of a hydrocarbon containing fuel-bound oxygen can be defined as C+H/4-O/2 [50]. We related this parameter to the sooting tendencies of more than 200 single components oxygenates measured by Das et al. [51]. As seen in Fig. 11, it shows that sooting tendencies of oxygenated fuels vary linearly with air-to-fuel ratio. Barrientos et al. [50] used this relation to represent the influence of oxygen on the sooting tendencies of oxygenated fuels. The Fig. 11(a) presents the complete data set which shows that except 6 data points all sooting tendencies can be correlated to the stoichiometric air-to-fuel ratio. The six data points with higher tendency to soot are significantly more aromatic in character. A close-up of the data except these 6 data points are shown in Fig. 11(b).
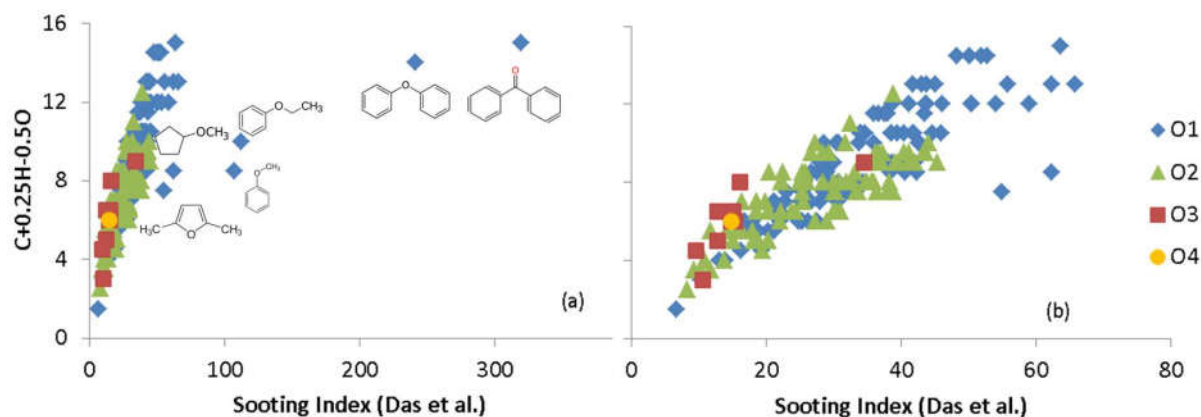
14

Figure 11. Stoichiometric air-to-fuel ratio compared against sooting tendencies of O_1-O_4 oxygenates from Das et al. [51].

Based on such relations one can modify the hydrogen deficiency, by adding a parameter that considers reduction in emission due to presence of fuel-bound oxygen, to predict the influence of oxygenates. However, at present we confine this study to the non-oxygenated hydrocarbon fuels until more relevant measurements are available.

(5) Synergistic effect of aliphatic-aromatic hydrocarbons: Studies focused on soot in hydrocarbon mixtures, especially binary mixtures, have observed synergistic effect of interaction between aliphatic and aromatic hydrocarbons on the soot formation [78-80]. The synergistic effect is defined as the increased tendency to form soot in a mixture due to the intensifying effect of one fuel component to another possibly due to the interaction of some pyrolysis products of these fuels [79]. The cause for the synergistic effect is long debated and several possible reasons are provided [78-84]. Many studies have identified synergistic effect of interaction of aliphatic (e.g. ethylene, butane isomers, propane, allene, butadiene) with aromatics (e.g. benzene, n-propylbenzene) present in fuel mixtures [78-80, 82]. Studies on dodecane or methane blended with aromatics [83, 84] have shown that the presence of small amount of aromatics in the fuel has considerable impact on the soot formation, which is consistent with our study. The synergistic effects have also found to cause change in the particle size distribution of soot particles formed [80].

Most of these studies provide evidence of synergistic effect of smaller aliphatic hydrocarbons present in fuel mixtures, exceptions being n-dodecane, n-heptane mixtures [81, 83]. This information is not sufficient for practical fuels where high molecular weight n-paraffins are present in the fuel. E.g. Jet A-1 (Fig. 1) contains nearly no paraffins below C_8, similarly fuels discussed in Fig. 4 also contains most paraffins in the range of C_9-C_{15}. To our best knowledge, it is not known in literature how emissions from a multi-component fuel would be influenced by such synergistic effect. Therefore, the influence of aliphatic-aromatic interaction is not considered in the present work but would be interesting to consider in future study.

8. Conclusion

In this work, we use the hydrogen deficiency (HD) to assess the relative soot emission of real fuels which are usually a complex multi-component mixture. To predict the soot emission pattern of a real fuel, the fuel's carbon and hydrogen number (C_xH_y) is required which can be estimated by gas chromatography. Further, we use the definition of hydrogen deficiency HD = (x+1) – (y/2), which gives information on the number of double bonds or cyclic structures present in a fuel, to estimate the total degree of cyclization and unsaturation from the obtained fuel's empirical formula C_xH_y. This approach of using HD does not provide quantitative data on soot emission, instead gives a relative assessment of fuels' sooting tendency compared to other known fuels. The evaluation of the fuels sooting tendency by this approach is tested for soot emission index of six jet fuels (reference fuels and synthetic fuels, supplied by Sasol). The calculated soot emission pattern based on HD number is compared with the ground test measurements of an Airbus A320 (V2527-A5 engines), carried out

within the DLR internal project ECLIF. We found that the predictions of emission levels based on HD are in excellent agreement with the ground tests of a jet engine. In addition, we applied our approach to predict the sooting tendencies of different jet fuels and diesel fuels from the literature which are excellently predicted by HD concept. Since our approach is based on the fuel's carbon and hydrogen number (C_xH_y), it can be applicable to any fuel used in the different modes of transportation.

Acknowledgment

References

[1] Shafer LM, Striebich RC, Gomach J, Edwards T. Chemical class composition of commercial jet fuels and other specialty kerosene fuels. 14th AIAA/AHI Space Planes and Hypersonic Systems and Technologies Conference 2006; AIAA Paper No 2006-7972.

[2] Dryer FL. Chemical kinetic and combustion characteristics of transportation fuels. Proc Combust Inst 2015;35:117-144.

[3] Edwards T, Moses C, Dryer F. Evaluation of combustion performance of alternative aviation fuels. 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit 2010; Paper No 2010-7155.

[4] DeWitt M, Corporan E, Graham J, Minus D. Effects of aromatic type and concentration in Fischer-Tropsch fuel on emissions production and material compatibility. Energy Fuels 2008;22:2411-2418.

[5] Timko MT, Yu Z, Onasch TB, Wong HW, Miake-Lye RC, Beyersdorf AJ, Anderson BE, Thornhill KL, Winstead EL, Corporan E, DeWitt MJ, Klingshirn CD, Wey C, Tacina K, Liscinsky DS, Howard R, Bhargava A. Particulate emissions of gas turbine engine combustion of a Fischer-Tropsch synthetic fuel. Energy Fuels 2010;24:5883-5896.

[6] Lobo P, Hagen DE, Whitefield PD. Comparison of PM emissions from a commercial jet engine burning conventional, biomass, and Fischer-Tropsch fuels. Environ Sci Technol 2011;45:10744-10749.

[7] Corporan E, Edwards T, Shafer L, DeWitt MJ, Klingshirn C, Zabarnick S, West Z, Striebich R, Graham J, Klein J. Chemical, thermal stability, seal swell, and emissions studies of alternative jet fuels. Energy Fuels 2011;25:955-966.

[8] Lobo P, Rye L, Williams PI, Christie S, Uryga-Bugajska I, Wilson CW, Hagen DE, Whitefield PD, Blakey S, Coe H, Raper D, Pourkashanian M. Impact of alternative fuels on emissions characteristics of a gas turbine engine - Part 1: Gaseous and particulate matter emissions. Environ Sci Technol 2012;46:10805-10811.

[9] Cain J, DeWitt MJ, Blunck D, Corporan E, Striebich R, Anneken D, Klingshirn C, Roquemore WM, Vander Wal R. Characterization of gaseous and particulate emissions from a turboshaft engine burning conventional, alternative, and surrogate fuels. Energy Fuels 2013;27:2290-2302.

[10] Beyersdorf AJ, Timko MT, Ziemba LD, Bulzan D, Corporan E, Herndon SC, Howard R, Miake-Lye R, Thornhill KL, Winstead E, Wey C, Yu Z, Anderson BE. Reductions in aircraft particulate emissions due to the use of Fischer-Tropsch fuels. Atmos. Chem. Phys. 2014;14:11-23.

[11] Schripp T, Anderson B, Crosbie E, Moore R, Herrmann F, Oßwald P, Wahl C, Kapernaum M, Koehler M, Le Clercq P, Rauch B, Eichler P, Mikoviny T, Wisthaler A. Impact of alternative jet fuels on engine exhaust composition during the 2015 ECLIF ground-based measurements campaign. Environ Sci Technol 2018;52:4969-4978.

[12] ASTM D7566-19, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, ASTM International, West Conshohocken, PA, 2019. www.astm.org

[13] IPCC, 2014: Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Edenhofer O, Pichs-Madruga R, Sokona Y, Farahani E, Kadner S, Seyboth K, Adler A, Baum I, Brunner S, Eickemeier P, Kriemann B, Savolainen J, Schlömer S, von Stechow C, Zwickel T,

Minx JC (eds.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. http://www.ipcc.ch/report/ar5/wg3/

[14] Kathrotia T, Oßwald P, Jürgens S, Selinsek M, Braun-Unkhoff M, Riedel U, Chemical kinetics investigation of combustion characteristics of a non-hydroprocessed Fischer-Tropsch fuel. 29. Deutscher Flammentag, 17.-18th Sept.2019, Bochum.

[15] Cookson DJ, Smith BE. Observed and predicted properties of jet and diesel fuels, formulated from coal liquefaction and Fischer-Tropsch feedstocks. Energy Fuels 1992;6:581-585.

[16] Anderson BE, Beyersdorf AJ, Hudgins CH, Plant JV, Thornhill KL, Winstead EL, Ziemba LD, Howard R, Corporan E, Miake-Lye RC, Herndon SC, Timko M, Wood E, Dodds W, Whitefield P, Hagen D, Lobo P, Knighton WB, Bulzan D, Tacina K, Wey C, Vander Wal R, Bhargava A, Kinsey J, Liscinsky DS. Alternative aviation fuel experiment (AAFEX). NASA/TM-2011-217059, Hanover, MD; February 2011.

[17] Christie S, Raper D, Lee DS, Williams PI, Rye L, Blakey S, Wilson CW, Lobo P, Hagen D, Whitefield P. Polycyclic aromatic hydrocarbon emissions from the combustion of alternative fuels in a gas turbine engine. Environ Sci Technol 2012;46:6393-6400.

[18] Moore RH, Shook M, Beyersdorf A, Corr C, Herndon S, Knighton WB, Miake-Lye R, Thornhill KL, Winstead EL, Yu ZH, Ziemba LD, Anderson BE. Influence of jet fuel composition on aircraft engine emissions: A Synthesis of aerosol emissions data from the NASA APEX, AAFEX, and ACCESS Missions. Energy Fuels 2015;29:2591-2600.

[19] Brem BT, Durdina L, Siegeris F, Beyerle P, Bruderer K, Rindlisbacher T, Rocci-Denis S, Gurhan Andac M, Zelina J, Penanhoat O, Wang J. Effects of fuel aromatic content on nonvolatile particulate emissions of an in-production aircraft gas turbine. Environ Sci Technol 2015;49:13149-13157.

[20] Lobo P, Christie S, Khandelwal B, Blakey S, Raper D. Evaluation of non-volatile particulate matter emission characteristics of an aircraft auxiliary power unit with varying alternative jet fuel blend ratios. Energy Fuels 2015;29:7705-7711.

[21] Speth RL, Rojo C, Malina R, Barrett SRH, Black carbon emissions reductions from combustion of alternative jet fuels. Atmos Environ 2015;105:37-42.

[22] Abrahamson JP, Zelina J, Andac MG, Vander Wal RL. Predictive model development for aviation black carbon mass emissions from alternative and conventional fuels at ground and cruise. Environ Sci Technol 2016;50:12048-12055.

[23] Christie S, Lobo P, Lee D, Raper D. Gas turbine engine nonvolatile particulate matter mass emissions: correlation with smoke number for conventional and alternative fuel blends. Environ Sci Technol 2017;51:988-996.

[24] Blevins L. Particulate matter emitted from aircraft engines. AIAA/ICAS International Air and Space Symposium and Exposition, 2003; Paper No 2003-2764.

[25] Moses C, Roet P. Properties, characteristics, and combustion performance of sasol fully synthetic jet fuel, J Eng Gas Turbines Power 2009;131:041502.

[26] Bulzan D, Anderson B, Wey C, Howard R, Winstead E, Beyersdorf A, Corporan E, DeWitt MJ, Klingshirn C, Herndon S, Miake-Lye R, Timko M, Wood E, Tacina KM, Liscinsky D, Hagen D, Lobo P, Whitefield P. Gaseous and particulate emissions results of the NASA alternative aviation fuel experiment (AAFEX). ASME Turbo Expo: Power for Land, Sea, and Air, 2010; Paper No GT2020-23524.

[27] Blakey S, Rye L, Wilson CW. Aviation gas turbine alternative fuels: A review. Proc Combust Inst 2011;33:2863-2885.

[28] Wayson RL, Fleming GG, Kim B. A Review of literature on particulate matter emissions from aircraft, DTS-34-FA22A-LR1, April 2002.

[29] Bittner J.D, Howard J.B. Role of aromatics in soot formation. Prog Astronaut Aeronaut. 1978;62:335-358.

[30] Naegeli D, Moses CA. Effect of fuel molecular structure on soot formation in gas turbine engines. ASME Turbo Expo: Power for Land, Sea, and Air, 1980; Paper No 80-GT-62.

[31] Ladommatos N, Rubenstein P, Bennett P. Some effects of molecular structure of single hydrocarbons on sooting tendency. Fuel 1996;75:114-124.

[32] Ebbinghaus A, Wiesen P. Aircraft fuels and their effect upon engine emissions. Air & Space Europe 2001;3:101-103.

[33] Martel C, Angello L. Hydrogen content as a measure of the combustion performance of hydrocarbon fuels. Technical Report AFAPLT P.-72-103, May 1973.

[34] Moses CA, Callahan TJ, Cuellar JP, Dodge LG, Likos WE, Naegeli DW, Valtierra ML. An alternate test procedure to qualify fuels for navy aircraft: Phase II. Report No. NAPC-PE-145C; Naval Air Propulsion Center: Trenton, NJ, 1984.

[35] Bowden TT, Pearson JH, Wetton RJ. The Influence of fuel hydrogen content upon soot formation in a model gas turbine combustor. J. Eng. Gas Turbines Power 1984;106:789-794.

[36] Moore RH, Thornhill KL, Weinzierl B, Sauer D, D'Ascoli E, Kim J, Lichtenstern M, Scheibe M, Beaton B, Beyersdorf AJ, Barrick J, Bulzan D, Corr CA, Crosbie E, Jurkat T, Martin R, Riddick D, Shook M, Slover G, Voigt C, White R, Winstead E, Yasky R, Ziemba LD, Brown A, Schlager H, Anderson BE. Biofuel blending reduces particle emissions from aircraft engines at cruise conditions. Nature 2017;543:411-415.

[37] Webb S, Whitefield PD, Miake-Lye RC, Timko MT, Thrasher TG. Airport Cooperative Research Program (ACRP) Report 6: Research needs associated with particulate emissions at airports; Transportation Research Board: Washington, DC, USA, 2008.

[38] Corporan E, Edwards T, Stouffer S, Hendershott T, DeWitt M, Klingshirn C, West Z, Bruening C, Striebich R. Impacts of fuel properties on combustor performance, operability, and emissions characteristics. 55th AIAA Aerospace Sciences Meeting, 2017; Paper No 2017-0380.

[39] Blazowski W. Future Jet fuel combustion problems and requirements. Prog Energy Combust Sci 1978;4:177-199.

[40] Saffaripour M, Zabeti P, Kholghy M, Thomson MJ. An experimental comparison of the sooting behavior of synthetic jet fuels. Energy Fuels 2011;25:5584-5593.

[41] Aikawa K, Jetter JJ. Impact of gasoline composition on particulate matter emissions from a direct-injection gasoline engine: Applicability of the particulate matter index. Int J Eng Res 2014;15:298-306.

[42] Chapman E, Winston-Galant M, Geng P, Latigo R, Boehman, A. Alternative fuel property correlations to the Honda Particulate Matter Index (PMI). SAE Technical Paper 2016; Paper No 2016-01-2250.

[43] Moriya H. Fuel property influence on exhaust emissions – Simplified PM index. SAE-China Congress & Exhibition, Shanghai; 2016.

[44] Wittmann JH, Menger L. Novel index for evaluation of particle formation tendencies of fuels with different chemical compositions. SAE Int J Fuels Lubr 2017;10:690.

[45] Leach F, Stone R, Fennell D, Hayden D, Richardson D, Wicks N. Predicting the particulate matter emissions from spray-guided gasoline direct-injection spark ignition engines. Proc Inst Mech Eng D: Int J Automot Eng, 2017;231:717-730.

[46] McEnally CS, Pfefferle LD. Improved sooting tendency measurements for aromatic hydrocarbons and their implications for naphthalene formation pathways, Combust Flame 2007;148:210–222.

[47] Crossley S, Alvarez W, Resasco D. Novel Micropyrolyis Index (MPI) to estimate the sooting tendency of fuels. Energy Fuels 2008;22:2455-2464.

[48] McEnally CS, Pfefferle LD. Sooting tendencies of nonvolatile aromatic hydrocarbons. Proc Combust Inst 2009;32:673-679.

[49] Olson DB, Pickens JC. The effects of molecular structure on soot formation, I Soot thresholds in premixed flames. Combust Flame 1984;57:199-208.

[50] Barrientos EJ, Lapuerta M, Boehman AL. Group additivity in soot formation for the example of C-5 oxygenated hydrocarbon fuels. Combust Flame 2013;160:1484-1498.

[51] Das D, McEnally CS, Kwan TA, Zimmerman JB, Cannella WJ, Mueller CJ, Pfefferle LD. Sooting tendencies of diesel fuels, jet fuels, and their surrogates in diffusion flames. Fuel 2017;197:445-458.

[52] Saggese C, Singh AV, Xue X, Chu C, Kholghy MR, Zhang T, Camacho J, Giaccai J, Miller JH, Thomson MJ, Sung C, Wang H. The distillation curve and sooting propensity of a typical jet fuel. Fuel 2019;235:350-362.

[53] Soot formation in combustion, Mechanisms and models. H. Bockhorn (Ed.) Berlin Heidelberg: Springer-Verlag; 1994.

[54] Richter H, Howard JB. Formation of polycyclic aromatic hydrocarbons and their growth to soot - A review of chemical reaction pathways. Prog Energy Combust Sci 2000;26:565-608.

[55] Kathrotia T, Oßwald P, Köhler M, Slavinskaya N, Riedel U. Experimental and mechanistic investigation of benzene formation during atmospheric pressure flow reactor oxidation of n-hexane, n-nonane, and n-dodecane below 1200 K. Combust Flame 2018;194:426-438.

[56] Dagaut P, Gail S. Chemical kinetic study of the effect of a biofuel additive on Jet-A1 combustion. J Phys Chem A 2007;111:3992-4000.

[57] Lemaire R, Therssen E, Pauwels J, Desgroux P. Experimental comparison of soot formation in turbulent flames of kerosene and surrogate model fuels. In: Bockhorn H, D'Anna A, Sarofim A, Wang H, eds. Combustion generated fine carbonaceous particles. Proc Inter Workshop 2009:Chapter 37, Villa Orlandi, Anacapri, Italy.

[58] Minchin ST, Luminous stationary flames: the quantitative relationship between flame dimensions at the sooting point and chemical composition, with special reference to petroleum hydrocarbons, J Inst of Petro Technol 1931;17:102-120.

[59] Clarke AE, Hunter TG, Garner FH. The tendency to smoke of organic substances on burning, Part I. J Inst of Petro 1946;32:627-642.

[60] VanTreuren KW. Sooting characteristics of liquid pool diffusion flames. MS Thesis, Department of Mechanical and Aerospace Engineering, Princeton Univ., Princeton, NJ, October, 1978.

[61] Calcote HF, Manos DM. Effect of molecular structure on incipient soot formation. Combust Flame 1983;49:289-304.

[62] Das D, St John PC, McEnally CS, Kim S, Pfefferle LD. Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale. Combust Flame 2018;190:349-364.

[63] Gill RJ, Olson DB. Estimation of soot thresholds for fuel mixtures. Comb Sci & Tech 1984;40:307-315.

[64] Yan S, Eddings EG, Palotas AB, Pugmire RJ, Sarofim AF. Prediction of sooting tendency for hydrocarbon liquids in diffusion flames. Energy Fuels 2005;19:2408-2415.

[65] Mensch A, Santoro RJ, Litzinger TA, Lee SY. Sooting characteristics of surrogates for jet fuels. Combust Flame 2010;157:1097-1105.

[66] Wahl C, Kapernaum M. EU FP5 G4RD-CT-00075 Final Report 2003, DLR-Stuttgart, Germany.

[67] Braun-Unkhoff M, Kathrotia T, Rauch B, Riedel U. About the interaction between composition and performance of alternative jet fuels. CEAS Aeronaut J 2016;7:83-94.

[68] Hanson MP, Rouvray DH. Novel applications of topological indices. 2. Prediction of the threshold soot index for hydrocarbon fuels. J Phys Chem 1987;91:2981-2985.

[69] Yang Y, Boehman AL, Santoro RJ. A study of jet fuel sooting tendency using the Threshold Sooting Index (TSI) model. Combust Flame 2007;149:191-205.

[70] Glassman I. Soot formation in combustion processes. Proc Comb Symp 1989;22:295-311.

[71] Pellegrin V. Molecular formulas of organic compounds: the nitrogen rule and degree of unsaturation. J Chem Educ 1983;60:626.

[72] 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 2001;41:889-893.

[73] McEnally CS, Pfefferle LD. Aromatic hydrocarbon growth mechanisms in flames: insights from sooting tendency measurements In: Bockhorn H, D'Anna A, Sarofim A, Wang H, eds. Combustion generated fine carbonaceous particles. Proc Inter Workshop 2009:Chapter 9, Villa Orlandi, Anacapri, Italy.

[74] Wang H. https://web.stanford.edu/group/haiwanglab/HyChem/.

[75] Dooley S, Won SH, Heyne J, Farouk TI, Ju Y, Dryer FL, Kumar K, Hui X, Sung C, Wang H, Oehlschlaeger MA, Iyer V, Iyer S, Litzinger TA, Santoro RJ, Malewicki T, Brezinsky K. The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena. Combust Flame 2012;159:1444-1466.

[76] Mueller CJ, Cannella WJ, Bays JT, Bruno TJ, DeFabio K, Dettman HD, Gieleciak RM, Huber ML, Kweon C, McConnell SS, Pitz WJ, Ratcliff MA. Diesel surrogate fuels for engine testing and chemical-kinetic modeling: Compositions and properties. Energy Fuels 2016;30:1445-1461.

[77] Kohse-Hoeinghaus K, Osswald P, Cool TA, Kasper T, Hansen N, Qi F, Westbrook CK, Westmoreland PR. Biofuel combustion chemistry: From ethanol to biodiesel. Angew Chem 2010;21:3572-3597.

[78] Frenklach M, Yuan T, Ramachandra K. Soot formation in binary hydrocarbon mixtures. Energy Fuels 1988;2:462-480.

[79] Karatas A, Commodo M, Gülder Ö. Soot formation in co- and counter-flow laminar diffusion flames of binary mixtures of ethylene and butane isomers and synergistic effects. Energy Fuels 2010, 24:4912-4918.

[80] Sirignano M, Ciajolo A, D'Anna A, Russo C. Particle formation in premixed ethylene-benzene flames: An experimental and modeling study. Combust Flame 2019;200:23-31.

[81] D'Anna A, Alfè M, Apicella B, Tregrossi A, Ciajolo A. Effect of fuel/air ratio and aromaticity on sooting behavior of premixed heptane flames. Energy Fuels 2007;21:2655-2662.

[82] Wang Y, Raj A, Chung SH. A PAH growth mechanism and synergistic effect on PAH formation in counterflow diffusion flames. Combust Flame 2013;160:1667-167.

[83] Zhang T, Zhao L, Thomson MJ. Effects of n-propylbenzene addition to n-dodecane on soot formation and aggregate structure in a laminar coflow diffusion flame. Proc Combust Inst 2017;36:1339-1347.

[84] Russo C, Giarracca L, Stanzione F, Apicella B, Tregrossi A, Ciajolo A. Sooting structure of a premixed toluene-doped methane flame. Combust. Flame 2018;190:252-259.