Identification and Quantification of Aromatic Hydrocarbons Adsorbed on Soot from Premixed Flames of Kerosene, Synthetic Kerosene, and Kerosene-Synthetic Biofuels

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ABSTRACT

In the current study, the chemical characterization of Polycyclic Aromatic Hydrocarbons (PAHs) adsorbed on soot from premixed flames of synthetic paraffinic kerosene (SPK), conventional kerosene (Jet A-1) and Jet A-1/synthetic biofuels blends was performed. Jet A-1 and SPK liquid fuels were analyzed with Nuclear Magnetic Resonance (NMR) to provide supplementary information on their chemical composition. The analytical procedure used to characterize PAHs fraction in soot samples includes: (i) filtration of the soot samples diluted into n-hexane through PTFE filters, (ii) Automated Solid Phase Extraction (A-SPE) for fractioning and cleaning-up the soot extracts and (iii) chromatographic analysis of every fraction by Reverse-High Performance Liquid Chromatography (RPLC) with photodiode array (PDA) detection. Application of the aforementioned methodology allowed the identification of 78 compounds including indene, toluene, and 76 PAHs. Moreover, the relative abundance of five-membered ring PAHs and alkyl-PAHs was evaluated and 19 PAHs (16 EPA PAHs, 1-methylnaphthalene, 2-methylnaphthalene and coronene) were quantified. The PAH characterization should contribute to improve our understanding of atmospheric reactivity of soot, and other environmental aspects of aromatic compounds adsorbed on soot.

KEYWORDS: PAHs, soot, kerosene, 1-butanol, 2,5-dimethylfuran, methyloctanoate, diethylcarbonate.

1. INTRODUCTION

Important human activities such as transportation, manufacturing, heating, cooling, electricity generation and other applications are highly dependent on the combustion of fossil fuels (coal, natural gas, petroleum). However, peak oil threat and greenhouse effect mostly caused by burning fossil fuels (up to 80-85% of CO_2 emitted to the atmosphere) make recommendable moving towards more renewable and sustainable fuels.[1-2] Biofuels seem to represent a viable alternative to conventional fuels in order to reduce the greenhouse effect and get around the peak oil. However there is not enough information on the chemical characterization of soot from synthetic and reformulated fuels, in spite of the huge growth in biofuels consumption, and although it is known that PAHs are produced at high concentrations from the combustion of fossil fuels and biofuels, frequently associated to soot particles,[3-4]. PAHs, which are considered to be soot precursors, have a great environmental importance. Upon their emission to the atmosphere, PAHs can undergo chemical transformation in both gas and particulate phases often leading to the formation of even more toxic and mutagenic compounds than primary PAHs. In our recent studies,[5-6] we have demonstrated that PAH content existing in aerosol particles significantly influences their photochemical reactivity.

Biofuels and synthetic fuels are of interest for both air and ground transportation. Nevertheless, for laboratory studies, jet fuels are easier to study because their composition is simpler, which facilitates chemical analyses. To date, little information is available for several biofuels of interest whereas others have received more attention.[7-15]

The aim of the present study is to probe the effect on soluble fraction of soot of blending a conventional fuel with biofuels. A similar study involving pure biofuels

71 would be difficult to interpret because the flames conditions will differ significantly due

72 to the range of molecular size (C_4 to C_9 here), the oxygen content to burn the fuels, the

73 adiabatic flame temperature, the flow rates above the burner.   Therefore, we

74 characterized PAHs content on soot from conventional kerosene (Jet A-1), synthetic

75 paraffinic kerosene (SPK), and Jet A-1/biofuels blends (80/20% v/v) burned using a

76 pre-mixed flame burner. Soot samples from 6 premixed flames were produced and

77 analyzed following the analytical methodology described in detail in a recent paper.[16,17]

78   This work complements previous investigations using a simple main fuel doped

79 with oxygenates in flames or in reactors.[8-9] The originality of the present work is the

80 blending of a complex commercial fuel with reasonable amounts of a variety of biofuels

81 in order to probe the effect of the blending without greatly modifying the flame

82 conditions. For interpreting the results, presently determined soot tendencies and atomic

83 C/O ratios in the fuels are used in place of more sophisticated approach[18] requiring

84 missing smoke point data.

85

86 **2. Material and methods**
87
88   **2.1 Material and reagents**

89   All the chemicals used in the current study were commercially available (Sigma

90 Aldrich/Carlo Erba). A mixture of 18 PAHs (2000 μgmL^{-1} each component in

91 methylene chloride:benzene (1:1)) was used for preparation of standards by dilution.

92 Components in the mixture were: 1-methylnaphthalene, 2-methylnaphthalene,

93 acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene,

94 benzo[k]fluoranthene,   benzo[g,h,i]perylene,   benzo[a]pyrene,   chrysene,

95 dibenzo[a,h]anthracene, fluorene, fluoranthene, indeno[1,2,3-cd]pyrene, naphthalene,

96 phenanthrene and pyrene. Coronene used for quantification was purchased 98% pure.

97 HPLC-grade n-hexane, water, and 2-propanol, supplied from Sigma-Aldrich and

98 acetonitrile and acetic acid glacial from Carlo Erba, were used for fractioning,

99 chromatographic analysis and pre-treatment of the fractions.

100 We used 0.2 µm sealed hydrophobic PTFE membrane filters with PTFE housing

101 from Grace-Alltech and Durobax glass syringes of 5 mL from Poulten & Graf for

102 filtering soot samples before A-SPE. A silica column (25 cm x 2.1 mm ID, 5µm) from

103 Supelco was used for A-SPE. An analytical balance Sartorius CP124S (precision +/-

104 0.1mg) was used for weighing the soot samples.

105 The biofuel blends were prepared by mixing Jet A-1 with 20% vol. of each

106 additive (80/20 v/v). The additive compounds used were (i) 1-butanol ($CH_3(CH_2)_3OH$),

107 (ii) methyloctanoate ($CH_3(CH_2)_6COOCH_3$) (iii) anhydrous diethyl carbonate

108 $(C_2H_5O)_2CO$ (DEC) and (iv) 2,5-dimethylfuran $(CH_3)_2C_4H_2O$ (2,5-DMF), with stated

109 purity ≥99%. The SPK (Sasol, ETSP) had a density of 0.7606 kg/L at 15°C, a derived

110 cetane number of 23 (ASTM D7668), and contained <1% vol. of aromatics. The Jet A-1

111 had a density of 0.805 kg/L at 15°C and a derived cetane number of 44.7 (ASTM

112 D7668).

113
114 **2.2 Production of soot samples**

115 A flat-flame burner was used for the combustion of Jet A-1/biofuels blends, Jet A-

116 1 and SPK under well characterized and controlled conditions. A simplified scheme and

117 a detail description of the soot production and collection system have been presented

118 elsewhere.[5, 19] Soot samples were generated under fuel-rich conditions, φ≈2.3, and

119 deposited on the outer surface of a Pyrex rod tube at 4 cm above the surface of the

120 burner which was isolated using a "cross type" cylindrical Pyrex tube, in order to

121 prevent flame perturbations from external air streams. At this point it should be noted

122 that soot collection experiments were performed at different heights (1, 2.5, 4, and 7

123   cm), however no systematic trend was observed in EPA PAH concentrations. This issue

124   has been also addressed in a previous publication from this laboratory.[20] The collection

125   tube was introduced perpendicular to the flame vertical axis, rotated and moved through

126   the flame. The sampling Pyrex rod was thermostated at $45°C$ by circulating water in

127   order to avoid temperature gradients and to ensure the homogeneous distribution of

128   PAHs along the sample tube.[21] The deposited soot was weighted upon mechanical

129   removal from the glass tube, diluted in 2 mL of n-hexane and driven for storage and

130   further analyses.

131   The thickness of soot coverage was determined directly by means of a universal

132   optical microscope (Reichert meF2).[19] The microscope was sequentially focused on the

133   support Pyrex surface and the surface of the soot. The soot coverage thickness was

134   determined as the difference between two readings. By repeating this operation in

135   several points along the soot samples, it was found that the procedure of soot deposition

136   used in this study provided homogeneous soot coverage (within 10%). The thickness of

137   soot samples used was varied in the range 50–300 μm depending on the soot collection

138   time.

139
140   **2.3 Extraction procedure**
141
142   Regarding the extraction of the target analytes from soot, although literature refers

143   to PAHs as material strongly adsorbed on soot surfaces[22] and consequently efficient

144   extraction procedures should be used,[23] this requirement seems to depend on the nature

145   of soot. Thus, whereas soot from power generators requires Accelerated Solvent

146   Extraction (ASE),[24] other soot samples, like those analyzed in this work, do not.[16] In

147   particular, we found in our recent study[16-17] (see supporting information, Table S1) that

148   an ultrasound-assisted extraction procedure destroys up to ca. 20% of some PAHs that

149   could be collected via simply filtrating twice through a PTFE filter. Therefore, the

150 extraction procedure was simplified and only two filtrations through a PTFE membrane

151 were performed in order to remove the soot particles and extract the aromatic material.[16]

152
153   **2.4 Cleaning-up and fractioning procedure**

154   A-SPE was carried out through a silica column (25 cm x 2.1 mm I.D., 5 µm size

155 particles) as detailed earlier.[16] Briefly, the fractioning was carried out using an HPLC

156 pump for passing n-hexane mobile phase against gravity through a commercial silica

157 column with stainless steel case pipe, at very low flow rate (0.05 mL/min). The

158 fractions were collected using a Shimadzu fraction collector (FRC-10A). This procedure

159 has demonstrated high performance and efficiency.

160
161   **2.5 Pretreatment of the fractions collected in the A-SPE procedure**
162
163   The appropriate pre-treatment of the collected fractions depends on the fuel

164 burned. The combustion of methyloctanoate yielded soot rich in unburned ester,

165 aromatic acids, aromatic hydroxy-acids, and aromatic diacids.[16] As the unburned ester

166 co-elutes with the aromatic fraction from the silica column during the A-SPE procedure,

167 the collected fractions should be pre-treated before injection into the RPLC column by

168 adding some µL of acetic acid glacial. In acidic medium, esters undergo hydrolysis and

169 convert into acids and alcohols, which easily elute from the C_{18} column. If esters are

170 injected along with PAHs into the C_{18} column, a quenching of the PAHs spectroscopic

171 signals occurs, preventing efficient identification and quantification of PAHs.

172   In the case of 2,5-dimethylfuran, the collected fractions from the silica column

173 were pre-treated with sodium hydroxide, NaOH, before injection into the RPLC

174 column. Furan and derivatives are abundant in this soot sample and can co-elute with

175 aromatic compounds on the silica column; hence they should be degraded before re-

176 injection of the sample into the HPLC column. As furan and derivatives are not stable in

177   presence of base, NaOH was used as degradation reagent. SPK fractions were submitted

178   to the same pre-treatment due to the abundance of hydroxy-acids. Pre-treatment of the

179   A-SPE fractions from Jet A-1, Jet A-1/diethylcarbonate and Jet A-1/1-butanol

180   fractioning was not required.

181

182   **2.6 Chromatographic analyses**
183

184   Chromatographic analyses were performed by using a HPLC system from

185   Shimadzu. The instrument consisted of a system controller CBM-20A/20Alite

186   Prominence, a solvent delivery module LC-20AB Prominence, an auto sampler SIL-

187   20A/20AC Prominence, a column oven CTO-20A/20AC Prominence, and a UV/Visible

188   photodiode array detector SPD-M20A Prominence. A Vydac column 201TPC18, 5 µm,

189   250 mm length x 4.6 mm ID (Grace Davison Discovery Sciences) was used for the

190   analyses. Acetonitrile and water were used as mobile phases and the flow rate was set

191   up at 0.5 mL min^{-1}. The detailed procedure has been described and validated

192   previously.[16]

193
194   **2.7 Liquid State NMR Spectroscopy of Jet A-1 and SPK fuels**
195

196   In order to obtain extra information about the chemical composition of the

197   "reference fuel" used (i.e., Jet A-1) and of SPK, a small amount (5-10 mg) of each of

198   them was dissolved into 0.8 mL of $CDCl_3$. The mixture was sonicated for 40 minutes at

199   room temperature in an ultrasonic bath and then transferred into a 5 mm NMR tube.

200   NMR spectra were obtained on a Bruker Avance III 500 spectrometer using a BBO

201   probe. ^{1}H 1D NMR spectra were obtained using 32 K data points and a 90° pulse of 12

202   µs. The number of scans was 2048 and the relaxation delay before each pulse sequence

203   was 5 s. After Fourier transformation, the NMR spectra were phase-corrected and a

204　polynomial fifth-order baseline correction was applied before manual integration using

205　the WINNMR software by Bruker.

206　　　　Comparison of ^{1}H 1D NMR spectra obtained from conventional Jet A-1 and

207　SPK in CDCl$_3$ indicates that in both spectra there is a clear preponderance of signals in

208　the aliphatic region δ 0.5–2.0, indicating the presence of high amounts of alkanes and

209　cycloalkanes in both fuels (Figure S1). Table 1 reports the different types of hydrogen

210　groups observed in the NMR spectra, and the relative amount of each type. Integration

211　of the methyl (-CH$_3$) and methylene (-CH$_2$-) signals shows that in SPK the relative

212　amount of methyl protons is much higher than that of methylene protons. After taking

213　into account the different number of protons in each group, the relative ratio of

214　CH$_2$/CH$_3$ groups (termed branching ratio, because it decreases with branching) is

215　calculated as 0.27, indicating that SPK consists mostly of branched alkanes with high

216　amount of methyl substituent per molecule. Conversely, Jet A-1 has higher amount of

217　methylene protons than methyl protons (the ratio of CH$_2$/CH$_3$ equals to 1.6) which

218　indicates that Jet A-1 contains mostly straight chain alkanes and cycloalkanes and

219　smaller amounts of iso- alkanes.

220　　　　Another important difference between the two fuels is that Jet A-1 ^{1}H NMR

221　spectrum has several large signals in the aromatic carbon region δ 6.5–8.5, while that of

222　SPK contains almost none. The NMR spectra verify that 4.4 % and 0.4 % of the total

223　protons are aromatic in Jet A-1 and SPK, respectively (Table 1). Furthermore, the

224　strong peaks at δ 7.4 and δ 7.7 in the Jet A-1 spectrum indicates the presence of

225　naphthalene, which is the major aromatic component of this fuel. The ratio of

226　aliphatic/aromatic protons is about an order of magnitude larger in SPK, compared to

227　Jet A-1 (Table 1). Finally, the absence of signal with chemical shift δ > 8.5 indicates

228　that heavy PAHs, (i.e., coronene, anthracene, phenathrene, triphenylene, chrysene,

229 dibenzanthracene, and benzo(a)pyrene) can be discarded as significant components of

230 both fuels.

231   It is worth noting that several signals in the region between δ 2.0–2.8 of the NMR

232 spectra are assigned to the presence of methyl and ethyl-substituted aromatic

233 compounds in conventional Jet A-1 kerosene, as expected. The amount of such

234 compounds in the SPK sample is much lower, as can be seen from the

235 Aromatic/Aliphatic ratios reported in Table 1. Finally, both fuels have very low signal

236 intensity in the alkenes region δ 4.6–6.2 indicating the fuels contain a very small

237 amount of alkenes.

238
239 **3   Results and discussion**
240
241   For fractioning of the organic material of the soot extracts, A-SPE was performed

242 as described in a previous work.[16] After collection and pre-treatment (when required),

243 fractions containing PAHs were dissolved into iso-propanol and injected into the

244 HPLC-C_{18} column under the conditions detailed in Section 2.

245

246 **3.1 PAHs**
247
248   Table 2 and Tables S1 (a-c) of supplementary material summarize all the PAHs

249 compounds identified in kerosene and bio-kerosene soot samples. The chromatographic

250 analyses showed a wide variety of PAHs present in Jet-A1 soot extract, 64 compounds,

251 which is significantly higher than in bio-soot samples. The soot sample with less PAHs

252 is that derived from the combustion of Jet A-1/1-butanol biofuel which contain only 36

253 out of the 78 PAHs characterized (toluene and indene are included although they only

254 have one aromatic ring).

255   As can be seen from Table 2, the concentrations of the 19 PAHs quantified are

256 within the range of 320-4900 ng/mg of soot, according to the following descending

10

257　concentration order: Jet A-1/ 2,5-dimethylfuran (4883 ng/mg of soot) > Jet A-1 (3681

258　ng/mg of soot) > SPK (3632 ng/mg of soot) > Jet A-1/ diethylcarbonate (2041 ng/mg of

259　soot) > Jet A-1/ methyloctanoate (847 ng/mg of soot) > Jet A-1/ 1-butanol (321 ng/mg

260　of soot). We can conclude that blending kerosene with biofuels reduces the emissions of

261　PAHs except in the case of 2,5-dimethylfuran. Regarding Jet A-1/methyloctanoate

262　blends, similar conclusions have been reported in a previous work on the combustion of

263　kerosene blended with rapeseed methyl esters.[3] Furthermore, it should be noted that

264　these relatively high concentrations were obtained through immediate analysis of the

265　soot samples, in order to recover the highest amount of light PAHs (due to their

266　volatility they can rapidly move to the gas phase) and prevent any oxidation of the other

267　medium/heavy PAHs. In real atmospheric samples, the PAHs concentrations are

268　expected to be lower either due to atmospheric oxidation, or due to their photolysis.

269　　The most abundant PAHs in all the soot samples analyzed here were

270　phenanthrene, fluoranthene, pyrene, benzo[g,h,i]perylene, and coronene (Table 2). In

271　addition, thorough reading of Tables 1 and S1 can lead to some other interesting

272　conclusions:

273　　1　Sooting tendency[a] as determined here with 20% of uncertainty (Table 3) is

274　　　　not exactly related to the concentration of PAHs adsorbed on soot. For

275　　　　instance, soot from the Jet A-1/ 2,5-dimethylfuran blend (highly sooting

276　　　　fuel) is rich in PAHs, but also soot from SPK (low sooting tendency fuel).

277　　　　In addition, although it has been proposed in the literature that fuels with

278　　　　high oxygen content tend to produce less soot,[25] we did not observed exactly

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[a] Here we define fuel tendency based on our soot mass measurements. The relative fuel tendencies were: 1 for Jet A-1, 0.33 for SPK, 1.77 for Jet A-1/2,5-Dimethylfuran blend, 1.17 for Jet A-1/Methyloctanoate mixture, 0.5 for Jet A-1/Diethylcarbonate blend, and 0.37 for Jet A-1/n-Butanol blend.

this trend. In fact, SPK, that contains no oxygenates and almost no aromatic hydrocarbons, produces much less soot than Jet A-1. Except Jet A-1/2,5-DMF, all the oxygenated fuel mixtures, containing different oxygenated structures (Table 3) tend to produce less soot than the reference fuel. Recent research on combustion of fuels containing oxygen atoms accomplished by other authors lead to the conclusion that sooting tendencies increase with the number of aromatic carbon atoms per molecule.[26] However, we found that Jet A-1/methyloctanoate (containing a lower number of aromatic hydrocarbons than Jet A-1, by dilution effect) exhibits a sooting tendency similar to that of Jet A-1, confirming the minor effect of esters on soot formation.[27] Soot production is related to the atomic ratio C/O in the fuel; it is given for fuels 3 to 6 in Table 2. From these ratios, one can expect to get increasing soot production from mixtures containing DEC < butanol < methyloctanoate < 2,5-DMF. Our determinations are close to these expectations: butanol ≤ DEC < methyloctanoate < 2,5-DMF. The relative impact of DEC and n-butanol on soot differ in the literature[9, 28] which might indicate similar efficiency to reduce soot formation, as observed here. Among the 4 fuels blended with oxygenates, 2,5-DMF (aromatic ether) is always yielding more light, medium, and heavy PAHs. For fuels with C/O of ca. 25, no clear trends can be delineated, probably due to the small C/O change combined with experimental errors. Oxidation experiments performed in our laboratory with pure fuels (1-butanol, methyloctanoate, diethylcarbonate) in a jet-stirred reactor[29-31] operating at atmospheric pressure in fuel-rich condition (Table 3) showed that methyloctanoate (MO) is the fuel producing the highest concentrations of intermediates involved in

soot formation, namely ethylene, propene, and 1,3-butadiene. The production of acetylene at 1220 K was 50% higher with MO or DEC than for 1-butanol. 2,5-DMF oxidizes slower under these conditions, making comparison difficult. However, it was noted that the maximum peak concentration of 1,3-butadiene was much higher with 2,5-DMF (68 ppm) than with MO (32 ppm) and 1-butanol (18 ppm). The formation of these intermediates is relatively well understood. Alkyl groups decompose to yield ethylene that follow the sequence of reactions: $C_2H_4 \rightarrow C_2H_3 \rightarrow C_2H_2$ and $1,3\text{-}C_4H_6$. However, here in most cases, oxygenates contribute to form less soot when blended with Jet A-1 because of dilution effect if they are not aromatic and through production of radicals yielding CH_2O, CO and CO_2 and not higher molecular weight hydrocarbons, as recognized in the literature.[10]

2 Light PAHs (2 aromatic rings) represents <3% of the total mass of the PAHs quantified (Table 2). On the contrary medium size PAHs (3-4 aromatic rings) constitute >54%. The mass fraction for SPK and Jet A-1/1-butanol soot samples were 54 and 58%, respectively, while for the others it exceeded 67%.

3 Soot from the combustion of SPK, a low sooting tendency fuel, had the highest mass percentage of heavy PAHs (>5 aromatic rings) with nearly 46%. For the other fuels, the mass percentage was <32%. However, it should be noted that no clear trend between sooting tendency and production of heavy PAH could be found here. The investigation of such trends would require the quantification of all PAHs compounds present on soot, which is probably impossible with the available/accessible

13

329   experimental techniques. Nevertheless, among the biofuels mixtures, this is

330   the 2,5-DMF blend which produces the largest amounts of PAHs (light,

331   medium, heavy, and total measured) which is expected to be due to its

332   aromatic structure and tendency to yield the soot precursor 1,3-

333   cyclopentadiene.[11, 14]

334 4 Regarding the mass percentage of pyrene (the most abundant EPA PAH),

335   one can distinguish two groups of soot:

336   a. Group A, with higher pyrene concentration: it concerns soot from Jet

337   A-1/ methyloctanoate and Jet A-1/ diethylcarbonate blends with mass

338   percentages 40.97% and 43.63%, respectively.

339   b. Group B: it concerns soot from Jet A-1, Jet A-1/ 2,5-dimethylfuran

340   blends, SPK and Jet A-1/ 1-butanol blends with 34.43%, 31.92%,

341   30.89% and 29.40% in mass of pyrene, respectively.

342 5. The soot sample containing the highest mass percentage of the fluoranthene

343   family EPA PAHs (i.e. fluoranthene + benzo[b]fluoranthene +

344   benzo[k]fluoranthene) is that from the Jet A-1/ 2,5-dimethylfuran blend

345   (28.04%)   followed by that from the Jet A-1/ diethylcarbonate blend

346   (26.20%). Similar mass percentages were obtained for Jet A-1 and the Jet

347   A-1/ methyloctanoate blend (23.83% and 24.16% respectively). Finally, the

348   lowest quantities were obtained upon the combustion of SPK and the Jet A-

349   1/ 1-butanol fuels for which soot samples contained 13.58% and 17.53%

350   respectively.

351 6. Excluding pyrene and fluoranthene, which were the most abundant PAHs

352   compounds, PAHs with a high degree of peri-condensation are much more

353   abundant in soot from very low sooting tendency fuels (SPK and Jet A1/ 1-

butanol blend). As a matter of fact, in soot from SPK and the Jet A-1/1-butanol blend, the sum of the aforementioned PAHs are respectively 45% and 39% of the total 19 PAHs analyzed, whereas for fuels with higher sooting tendency such as Jet A-1/ 2,5-dimethylfuran and Jet A-1/methyloctanoate blends, soot contains less peri-condensed PAHs (<32%).

3.2 Alkyl-PAHs

Eleven alkyl-PAHs were identified in the soot samples analyzed (Table 4). Due to the absence of commercially available standards their absolute concentrations were not determined (except the alkyl- EPA PAHs of Table 2), thus only their relative abundances are presented. Consequently, a direct comparison of the sums of the relative abundance cannot be achieved, because the molar absorptivity for each compound is different. Nevertheless thorough reading of Table 4, leads to the following observations:

1. Lower concentrations of alkyl PAHs were observed in soot from Jet A-1/ diethylcarbonate and Jet A-1/ 1-butanol blends than in soot from Jet A-1. One should recall that these fuels appeared to have lower sooting tendency that Jet A-1.

2. The most abundant alkyl-PAHs in the soot samples analyzed are isomers of methyl-pyrene and of methyl-naphthalene. Excluding these compounds, we can safely state that the Jet A-1/ 2,5-dimethylfuran fuel produces the highest concentrations of alkyl-PAHs identified among the biofuels blends and the reference Jet A-1 fuel.

3. It seems that heavy alkyl-PAHs are much more abundant in soot from SPK and Jet A-1/ 2,5-dimethylfuran than in the other soot samples analyzed

380   (Table 4). This trend could be expected because these samples had the

381   highest concentrations of the heavy EPA PAHs.

382   4. The only di-methyl PAH compound identified, 2,5-dimethylphenanthrene,

383   was found exclusively in soot from SPK (Table 4) which has the highest

384   fraction of branched paraffins. Other methyl-PAHs like 1-methylpyrene, 2-

385   methylpyrene and 3-methylpyrene are present in all the samples analyzed

386   whereas 4-methylpyrene is present only in soot from SPK and the Jet A-1/

387   methyloctanoate blend.

388

389   **3.3 Five-membered ring PAHs**

390   24 five-membered ring PAHs were identified in the soot samples analyzed, and

391   the results are shown in Table 5. Similar to the alkyl-PAHs results presented in

392   paragraph 3.2, due to the absence of commercially available standards only their relative

393   abundances are given (except for the five member EPA PAHs where their absolute

394   concentrations are presented in Table 2). However, from the data of Table 5 some

395   interesting conclusions can be drawn:

396   1. The relative abundance of five-membered ring PAHs was significantly

397   lower for Jet A-1/ methyloctanoate, Jet A-1/ diethylcarbonate and Jet A-1/

398   1-butanol blends than for the reference Jet A-1. On the contrary Jet A-1/

399   2,5-dimethylfuran soot sample has the highest concentrations of five-

400   membered ring PAHs. This is in line with that reported above for EPA and

401   alkyl PAHs formation.

402   2. The sum of the concentrations of the five-membered ring EPA PAHs

403   (acenaphthylene, acenaphthene, fluoranthene, benzo[b]fluoranthene,

404   benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene) are: 1080.6, 783.4,

16

1539.5, 244.6, 573 and 65.5 ng/mg soot for, Jet A-1, SPK, Jet A-1/ 2,5-dimethylfuran, Jet A-1/ methyloctanoate, Jet A-1/ diethylcarbonate and Jet A-1/ 1-butanol blends respectively. Therefore, the addition of 2,5-dimethylfuran caused ~50% increase of the concentrations of five-membered ring EPA PAHs while for the other biofuels a decrease greater than 50% was observed (in the case of Jet A-1/ 1-butanol blend, a decrease by a factor of 17 was observed).

3. Significant concentrations of five-membered ring PAHs were observed also in SPK soot. From the 23 five-membered ring PAHs identified, 13 of them appear to have maximum concentrations in SPK soot. In addition, SPK produced the highest concentrations of heavy (≥ 5 aromatic rings) five-membered ring PAHs (Table 5).

4. Benzo[a]fluorene was found only in soot samples from Jet A-1/ biofuels blends and dibenzo [a,i]fluorene was observed only in Jet A-1/ methyloctanoate blends. Other derivatives of fluorene such as naphtho[1,2-a]fluorene were found in all the soot samples studied here. Benzo[ghi]fluoranthene and dicyclopenta[cd,jk]pyrene were found exclusively in soot from SPK whereas dibenzo[j,l]fluoranthene was found in soot from Jet A-1, SPK and Jet A-1/ methyloctanoate at lower concentrations.

3.4 Atmospheric Implications

It is well known that PAHs upon their emission to the atmosphere are involved in many chemical reactions which will define their lifetime. The nature of these chemical reactions depends on the vapor pressure of the PAHs compounds. The major

430   sink of light PAHs is the gas phase reaction with atmospheric oxidants, HOx, NOx, Cl.

431   On the other hand, the semi-volatile and heavy PAHs are mainly removed from the

432   heterogeneous reaction of soot samples with atmospheric oxidants. However the

433   efficiency of this process significantly depends on the particle matrix, which can limit

434   the accessibility to the aforementioned oxidants. Photolysis of the PAHs on soot surface

435   is also considered as an important removal process. The oxidation of PAHs leads to the

436   formation of ring-opened or ring-retaining oxy- (e.g. ketones/quinones) and nitro-

437   compounds. Consequently, in order to assess the atmospheric impact and the health risk

438   that might arise, chemical and physical properties of the derived soot particles should be

439   considered and its chemical reactivity towards the oxidants of the atmosphere should be

440   evaluated. Some of these processes have been studied recently in our laboratory.[5]

441   In our latest study, we have investigated the chemical reactivity of the

442   conventional Jet A-1 and Jet A-1/biofuels studied herein, employing a low pressure

443   flow tube reactor coupled with a mass spectrometer.[6] NO_2 was used as reference

444   pollutant molecule of the NOx family, because it is known for participating in several

445   heterogeneous reactions producing HONO and acting as regulating agent for O_3

446   formation. The results showed that soot chemical reactivity strongly depends on the

447   additive compound used. In particular, the reactivity measured on freshly emitted Jet A-

448   1/1-Butanol and Jet A-1/Diethyl carbonate bio-soot surfaces was approximately 2, 3 and

449   10 times lower than for soot from Jet A-1, Jet A-1/Methyloctanoate and Jet A-1/2,5-

450   Dimethyl furan respectively. This observation was mainly attributed to a) the heavy

451   aromatic/olefinic ratio and b) to the Nitro-PAHs content existing in soot samples prior

452   to their reaction with the oxidant, revealing the crucial role of PAHs in the chemical

453   reactivity of aerosol particles.

454

3.5 Summary and Conclusions

In the current study, the chemical characterization of the PAHs fraction adsorbed on soot from premixed flames of synthetic paraffinic kerosene (SPK), conventional kerosene (Jet A-1) and Jet A-1/synthetic biofuels blends has been performed. The chromatographic analyses were conducted employing a HLPC system from Shimadzu coupled to an UV-Vis photodiode array detector. 78 PAHs were identified in the soot samples analyzed employing a novel methodology recently developed in our laboratory.[16] Due to absence of commercially available standards, only the absolute concentrations of the EPA PAHs, 1-methyl, 2-methylnaphthalene, and coronene were quantified. For alkyl PAHs and five-membered ring PAHs only the relative abundances were determined. Thorough examination of the results of the current study leads to the following conclusions:

1. The oxygen content of the fuel tends to be correlated to its sooting tendency, even if the effect of 1-butanol is higher than expected. For Jet A-1/biofuels mixtures, the data indicate that 2,5-DMF, which has the higher C/O ratio and an aromatic structure, favors large PAHs and soot formation. For the other oxygenated mixtures, no clear trend was observed among them in terms of PAHs production, besides the fact these fuels produce less PAHs that Jet A-1. On should note that a recent study conducted in our laboratory, did not show the fuel oxygen content being an indicative parameter for soot reactivity towards NO_2.[6]

2. Based on the absolute concentrations of the 19 PAHs quantified, and excluding 2,5-dimethylfuran soot sample, we can safely state that PAHs concentrations in the other biofuels studied significantly decreased compared

479   to the reference Jet A-1. Similar trend was observed for alkyl and five-

480   membered ring PAHs.

481   3. Light PAHs (2 aromatic rings) represent <3% of the total mass of the PAHs

482   quantified while medium size PAHs (3-4 aromatic rings) constitute >54%.

483   Therefore, the heterogeneous photo-oxidation is expected to be the major

484   atmospheric removal process of the PAHs content in our samples.

485   4. The most abundant PAHs compounds in the soot samples analyzed were

486   pyrene and fluoranthene.

487   5. Because light PAHs represent a small fraction of the PAHs identified (<3%)

488   and based on the results presented in Table 4 it seems that SPK produces

489   higher concentrations of alkyl PAHs than Jet A-1. Considering that SPK and

490   Jet A-1 fuels contain mostly branched and straight chain alkanes respectively

491   (as indicated by NMR analyses), it seems that there is a correlation between

492   branching and the abundance of alkyl PAHs in soot samples (i.e. fuel with

493   high concentrations of branched alkanes produce higher concentrations of

494   alkyl PAHs). However, thorough studies should be conducted with different

495   alkanes branching ratios to further asses such a trend.

496   6. SPK produces the highest concentrations of heavy (≥5 aromatic rings) five-

497   membered ring PAHs (Table 5).

498   7. Fuels with low sooting tendency produce a high concentration of peri-

499   condensed PAHs. In particular, in soot from SPK and the Jet A-1/1-butanol

500   blend, the sum of the peri-condensed PAHs is ≥39% of the total 19 PAHs

501   quantified. On the contrary, for the other soot samples studied, which

502   appears to have higher sooting tendency, soot contains less peri-condensed

503   PAHs (<32%).

504

Acknowledgements

510

Abbreviations

PAHs, Polycyclic Aromatic Hydrocarbons; SPK, synthetic paraffinic kerosene; Jet A-1, conventional kerosene; NMR, nuclear magnetic resonance; RPLC, reverse-high performance liquid chromatography; HPLC, high-performance liquid chromatography; PTFE, polytetrafluoroethylene; A-SPE, automated-solid phase extraction.

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519

520   Table 1. The ^{1}H chemical shifts in NMR spectra and the relative number of protons in

521   synthetic and conventional kerosene.

522

δ(ppm)	Hydrogen groups	Integration % Synthetic Kerosene	Integration % Conventional Kerosene
6.5 - 9.4	Ar	0.4	4.4
4.6 - 6.2	=CH	0.2	0.0
2.8 - 4.6	O-CH/N-CH	0.1	0.2
2.0 - 2.8	Ar-CH	0.3	5.4
1.0- 1.4	CH$_2$	15.0	47.0
0.5 -1.0	CH$_3$	84.0	43.0
CH$_2$/CH$_3$ (branching ratio)		0.27	1.6
Aromatic/Aliphatic ratio		0.01	0.1

523 Table 2.Concentration of 1-methylnaphthalene, 2-methylnaphthalene, EPA PAHs and
524 Coronene in each soot sample analyzed (in ng/mg of soot; n=3, SD within the range 3-
525 7%). UV identification according to literature spectra.[24, 32-45] In parenthesis, the
526 wavelength at which measurements were carried out is given.

Compound	Soot Sample *					
	1	2	3	4	5	6
	C/O					
	-	-	30.3	25.1	10.9	24.9
Naphthalene[i](λ=220 nm)	13.2	0.9	5.5	3.2	8.5	1.5
1-Methylnaphthalene[i](λ=222 nm)	11.2	n.o[#]	n.o	1.7	1.5	5.5
2-Methylnaphthalene[i](λ=223 nm)	18.2	<LOQ[‡]	3.4	2.4	3.5	n.o
Acenaphthylene[i](λ=229 nm)	52.7	8.20	19.1	3.8	7.7	n.o
Acenaphthene[i](λ=226 nm)	10.9	3.59	2.37	0.57	1.1	n.o
Fluorene[i](λ=260 nm)	n.o	n.o	n.o	<LOQ	n.o	n.o
ΣPAH (light)	**106.2**	**12.7**	**30.4**	**11.7**	**22.4**	**7**
Phenanthrene[i](λ=250 nm)	497	290	286	24.0	256	37.1
Anthracene[i](λ=250 nm)	106	29.7	178	12.8	27.5	3.6
Fluoranthene[v](λ=235 nm)	781	489	1146	194	514	51.5
Pyrene[v](λ=236 nm)	1267	1122	1559	347	891	94.3
Benzo[a]anthracene[i](λ=287 nm)	18.6	22.1	57.2	14.0	12.6	0.4
Chrysene[i](λ=267 nm)	19.3	11.3	85.9	8.69	20.0	1.3
ΣPAH (medium)	**2688.9**	**1964.1**	**3312.1**	**600.5**	**1721.1**	**188.2**
Benzo[b]fluoranthene[v](λ=300 nm)	83.5	1.8	171	5.0	12.7	3.7
Benzo[k]fluoranthene[v](λ=306 nm)	12.5	2.8	53.0	5.4	7.8	1.0
Benzo[a]pyrene[v](λ=295 nm)	146	310	269	64	11.5	1.4
Dibenzo[a.h]anthracene[i](λ=296 nm)	2.9	n.o	n.o	n.o	n.o	n.o
Benzo[g,h,i]perylene[v](λ=297 nm)	371	843	679	96.3	173	42.8
Indeno[1,2,3-cd]pyrene[v](λ=249 nm)	140	278	148	35.8	29.7	9.2
Coronene[v](λ=301 nm)	130	220	221	28.5	63.3	67.2
ΣPAH (heavy)	**885.9**	**1655.6**	**1541**	**234.9**	**298**	**125,3**
EPA PAHs+1-methyl,2-methylnaphthalene	**3551**	**3412**	**4662**	**819**	**1978**	**253**
EPA PAHs+1-methyl,2-methylnaphthalene+Coronene	**3681**	**3632**	**4883**	**847**	**2041**	**321**

527 Notes: *1: Kerosene Jet A-1, 2: SPK, 3: Jet A-1/2,5-Dimethylfuran, 4: Jet A-1/Methyloctanoate,
528 5: Jet A-1/Diethylcarbonate, 6: Jet A-1/n-Butanol; [‡] limit of quantification; [#] n.o: not observed; [i]
529 cata-condensed PAHs; [v] peri-condensed PAHs

530

531

532   Table 3a. Biofuels mixtures properties

Biofuel component	C/O in fuel mixture	sooting tendency relative to Jet A-1	type of oxygen
diethylcarbonate	10.9	0.49 ± 0.1	$(C\text{-}O)_2\text{-}C\text{=}O$
Butanol	24.9	0.39 ± 0.08	$C\text{-}O\text{-}H$
Methyloctanoate	25.1	1.17 ± 0.23	$C\text{-}C(\text{=}O)\text{-}O\text{-}C$
2,5-dimethylfuran	30.3	1.77 ± 0.36	$C\text{-}O\text{-}C$ aromatic

533

534   Table 3b. Formation of intermediates during the oxidation of 1000 ppm of pure

535   oxygenated fuels in a jet-stirred reactor (atmospheric pressure; residence time = 70 ms;

536   equivalence ratio = 2). Peak concentrations (in ppm) or maximum concentration

537   observed at a given temperature are reported.

Intermediate	1-butanol	methyloctanoate	diethylcarbonate	2,5-DMF
C_2H_4	884	<u>1910</u>	1170	214[‡]
C_3H_6	132	<u>225</u>	6	12
C_2H_2*	232[‡]	<u>324</u>[‡]	<u>327</u>[‡]	224[‡]
1,3-C_4H_6	18	32	1	<u>68</u>

538   * measured at 1220 K

539   [‡] maximum not reached

540

541

542

543 Table 4.Relative abundances of alkyl-PAHs in the soot samples analyzed (n=3, SD

544 within the range 3-7%). UV identification according to literature spectra. [24, 32-45] In

545 parenthesis, the λ at which measurements were carried out.

Compound	Soot Sample*					
	1	2	3	4	5	6
1-Methylnaphthalene (λ=222 nm)	1.0	n.o[#]	n.o	0.2	0.1	0.5
2-Methylnaphthalene (λ=223 nm)	1.0	<LOQ[‡]	0.2	0.1	0.2	n.o
1-Ethynylnaphthalene (λ=234 nm)	<LOQ	0.1	1.0	0.1	<LOQ	<LOQ
2,5-Dimethylphenanthrene (λ=253 nm)	n.o	1.0	n.o	n.o	n.o	n.o
1-Methylpyrene (λ=241 nm)	0.8	1.0	0.4	0.4	0.5	0.1
1.2.3.4-Tetrahydrochrysene (λ=258 nm)	0.3	0.2	1.0	0.1	0.1	0.1
3-Methylpyrene (λ=242 nm)	0.3	0.2	1.0	0.1	0.1	<LOQ
4-Methylpyrene (λ=241 nm)	n.o	1.0	n.o	0.9	n.o	n.o
1-Methylbenz[a]anthracene (λ=290 nm)	0.1	n.o	1.0	n.o	n.o	n.o
8-Methylbenz[a]anthracene (λ=290 nm)	0.1	1.0	n.o	<LOQ	n.o	n.o
Methylcoronene (λ=301 nm)	0.1	1.0	0.6	0.1	0.1	<LOQ

546 Notes: *1: Kerosene Jet A-1, 2: SPK, 3: Jet A-1/2,5-Dimethylfuran, 4: Jet A-

547 1/Methyloctanoate, 5: Jet A-1/Diethylcarbonate, 6: Jet A-1/n-Butanol

548 [‡] limit of quantification (for relative abundances <0.1)

549 [#] n.o: not observed

550

551 Table 5. Relative abundances of PAHs containing a five-membered ring in each soot

552 sample analyzed (n=3, SD within the range 3-7%). UV identification according to

553 literature spectra. [24, 32-45] In parenthesis, the λ at which measurements were carried out.

Compound	MW (Da)	Soot Sample*					
		1	2	3	4	5	6
Indene (λ=250 nm)	116.160	<LOQ[‡]	0.3	1.0	0.2	0.1	n.o[#]
Acenaphthylene (λ=229 nm)	152.192	1.0	0.2	0.4	0.1	0.1	n.o
Acenaphthene (λ=226 nm)	154.208	1.0	0.3	0.2	0.1	0.1	n.o
Benzo[f]indene (λ=240 nm)	166.218	0.2	0.2	1.0	0.1	0.3	0.1
4,5-Methylenephenanthrene (λ=252 nm)	190.240	0.7	0.2	1.0	0.1	0.2	<LOQ
Acephenanthrylene (λ=254 nm)	202.251	0.3	0.2	1.0	0.1	0.1	<LOQ
Fluoranthene (λ=235 nm)	202.251	0.7	0.4	1.0	0.2	0.4	<LOQ
Cyclopenta[hi]acephenanthrylene (λ=254 nm)	226.272	0.8	1.0	n.o	0.1	n.o	n.o
Benzo[a]fluorene (λ=261 nm)	216.277	n.o	n.o	1.0	0.1	0.1	<LOQ
Cyclopenta[cd]pyrene (λ=238 nm)+ 3.4-Dihydrocyclopenta[c,d]pyrene (λ=244 nm)	226.272 228.228	0.6	1.0	0.5	0.1	0.1	<LOQ
Dibenzo[a,i]fluorene (λ=265 nm)	266.336	n.o	n.o	n.o	1.0	n.o	n.o
Naphtho[1,2-a]fluorene (λ=265 nm)	266.336	0.2	0.2	1.0	0.1	0.1	<LOQ
Dicyclopenta[cd,jk]pyrene (λ=287 nm)		n.o	1.0	n.o	n.o	n.o	n.o
Benzo[g,h,i]fluoranthene (λ=297 nm)	226.272	n.o	1.0	n.o	n.o	n.o	n.o
Benzo[b]fluoranthene (λ=300 nm)	252.309	0.5	<LOQ	1.0	<LOQ	0.1	<LOQ
Benzo[k]fluoranthene (λ=306 nm)	252.309	0.2	0.1	1.0	0.1	0.1	<LOQ
Indeno[1,2,3-cd]fluoranthene (λ=292 nm)	276.331	0.6	1.0	n.o	0.2	n.o.	n.o
Naphtho[2,3-b]fluoranthene (λ=284 nm)	302.368	n.o	n.o	n.o	1.0	n.o	n.o
11-H-Indeno[2,1,7-cde]pyrene (λ=290 nm)	264.320	0.8	1.0	0.4	0.3	0.1	0.1
Dibenzo[j,l]fluoranthene (λ=247 nm)	302.368	0.4	1.0	n.o	0.1	n.o	n.o
Corannulene (λ=259 nm)	250.293	0.8	1.0	1.0	0.1	0.2	0.1
Indeno[1,2,3-cd]pyrene (λ=249 nm)	276.331	0.5	1.0	0.5	0.1	0.1	<LOQ
Cyclopenta[c,d]benzo[g,h,i]perylene (λ=290 nm)	300.352	0.6	1.0	n.o	n.o	n.o	n.o
Cyclopenta[b,c]coronene (λ=322 nm)	324.374	0.2	1.0	0.9	0.1	<LOQ	<LOQ

554 Notes: *1: Kerosene Jet A-1, 2: SPK, 3: Jet A-1/2,5-Dimethylfuran, 4: Jet A-

555 1/Methyloctanoate, 5: Jet A-1/Diethylcarbonate, 6: Jet A-1/n-Butanol; [‡] limit of

556 quantification (for relative abundances <0.1); [#] n.o: not observed.

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