

Influence of Fuel Bound Oxygen on Soot Mass and Polyaromatic Hydrocarbons during Pyrolysis of Ethanol, Methyl Acetate, Acetone and Diethyl Ether

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Abstract. Air pollution has reached critical levels in many major industrial cities, endangering public health, deteriorating the environment, and causing harm to property and landscape. The particulate emissions (PM) from propulsion which contribute to air pollution vary greatly in size and composition, conveying carcinogenic polyaromatic hydrocarbons (PAHs) present on the particle surface. Although it has been found that replacing fossil fuels with renewable oxygen-bearing fuels reduces the mass of PM released, not much is known on how this change in fuel composition affects soot levels, PAH production, and toxicity during the pyrolysis processes that occur in combustion engines. Biofuels such as alcohols, esters, ethers, and ketones are considered to be potentially sustainable alternative fuels and can be produced by various biological and thermochemical processes from a range of renewable feedstocks. The effects of these oxygenated functional groups on the soot mass and PAHs produced during pyrolysis in a laminar flow reactor were investigated quantitatively in this study. The 16 PAHs identified as priority pollutants by the US Environmental Protection Agency (EPA) were investigated in this research, with particular focus on the probable mechanisms for production of the most carcinogenic PAHs (group B). The oxygenated fuels were pyrolyzed at temperatures ranging from 1050 to 1350 °C under oxygen-free conditions with a constant carbon atom content in nitrogen of 10,000 ppm and at a consistent residence period. Both soot bound PAH collected on filter papers and gaseous PAHs collected on XAD resin were extracted using accelerated solvent extraction (ASE), with PAH identification and quantification carried out using gas chromatography combined with mass spectroscopy (GCMS). An effect of the oxygenated functional groups on soot mass was readily apparent, with consistently lower production of soot by methyl acetate, and which has a higher oxygen to carbon ratio than ethanol, acetone, and diethyl ether. At all temperatures except 1350 °C, methyl acetate pyrolysis yielded much lower GP PAH levels than acetone and diethyl ether, but somewhat higher than that from ethanol pyrolysis. The concentration of PP PAH per unit volume of gas is much lower than the corresponding GP PAH, which suggests that PP PAH that condensed onto particulate surface, subsequently experienced surface reaction and were therefore not recoverable during the extraction process. The production of pyrene via acenaphthylene was found to dominate at higher temperatures for all fuels, regardless of molecular structure. At 1150 °C the relative abundance of the soot particles was low, however, the toxicity of the soot particles formed was substantially higher at lower temperatures, particularly in the case of pyrolysis of methyl acetate soot.

1 Introduction

Air pollution due to combustion process has reached critical levels in many major industrial cities, endangering public health and deteriorating the environment. The particulate emissions (PM) from combustion which contribute to air pollution vary greatly in size and composition, conveying carcinogenic polyaromatic hydrocarbons (PAHs) present on the particle surface. The resultant toxicity of particulate matter from internal combustion engines is therefore a topic of significant scientific and practical importance in the development of sustainable low emission propulsion systems. It is widely accepted that it is the presence of adsorbed PAHs on the surface of soot which are primarily responsible for the toxicity of these particles [1]. The link between polyaromatic hydrocarbons (PAHs) and soot generation has long been known, with PAHs being regarded as the primary soot precursors. Following the development of single aromatic rings, the rings expand into larger polyaromatic hydrocarbons and finally produce soot particles by a variety of processes.

Biofuels such as alcohols, esters, ethers, and ketones are regarded as possible sustainable alternative fuels since they can be produced from a range of potentially renewable feedstocks that can

be found all over the world. [2–6]. The combustion characteristics of biofuels containing oxygen in various forms, such as ethanol, methyl acetate, acetone, and diethyl ether, have been investigated in several experimental and numerical investigations. Ethanol and its blends with other fuels have been previously studied in different combustion systems, such as tube reactors, flames, and IC engines [7–13]. From these studies, it can be concluded that the addition of ethanol to fossil fuel suppressed the sooting tendency and PAHs formation. In recent years, Diethyl ether (DEE) has gathered the attention of many researchers as a potential alternative fuel as, unlike dimethyl ether, DEE is liquid at ambient temperature and thus relatively easy to store [14–16]. In the literature, several studies reported the use of DEE as a pure fuel or diesel additive in compression ignition engines and numerical simulation [14,15,17]. Long chain methyl ketones have been proposed as a possible alternative fuel as these exhibit relatively high cetane numbers. The simplest and the shortest methyl ketone is acetone, also known as dimethyl ketone and has potential as a renewable oxygenated fuel due to latent heat of vaporization similar to that of gasoline, addressing the issue of poor cold start behaviour of SI engines when utilising bioethanol, which has a higher heat of vaporization. The use of acetone in a spark-ignition engine has been reported in the literature [5,6,18], while Wu et al., 2015 [19] reported the effect of acetone fraction in acetone-butanol-ethanol-diesel blends and found that a high percentage of acetone reduced the mass of soot emitted and improved thermal efficiency. In recent years, methyl acetate and ethyl acetate have emerged as competitive alternative fuels as they are non-toxic, less volatile, easy handling, and low production cost as compared to alcohols and ethers. Furthermore, methyl and ethyl acetates have been found not to produce toxic emissions like aldehydes, ketones, and carbon monoxide due to a high proportion of carbon bonded to oxygen within the fuel [20,21]. Methyl acetate could also be used as potential biodiesel additive reducing viscosity [2].

While renewable fuels of various oxygenated functional groups have received interest for the potential of these to displace fossil fuel use, it remains unknown how the presence of oxygen impacts on PAH development during pyrolysis and thus the toxicity emitted particles. Therefore, four distinct oxygenated fuels, ethanol, methyl acetate, acetone and di-ethyl ether have been investigated in this study to increase knowledge of the impact of oxygenated fuel functional groups on soot and PAH production and relative toxicity.

2 Experimental methodology

2.1 Experimental setup and conditions

The high temperature flow reactor facility used in this study has been previously described in detail [22–25], therefore only a short explanation is provided. The laminar flow reactor tube used was electrically heated and vertically positioned with a tube length of 1440 mm and an inner diameter of 104 mm. The selected fuels were premixed with a heated nitrogen stream and pyrolyzed at temperatures ranging from 1050 to 1350 °C at atmospheric pressure. The fuel inlet concentration was fixed at 10,000 ppm based on a per carbon atom within the fuel. Pure nitrogen was used as a carrier gas with a fixed flow rate of 20 l/min. The soot and gaseous PAHs formed during the pyrolysis of oxygenated fuels were collected on a 70 mm glass microfibre filter paper and XAD-2 resin, respectively. The liquid fuel supply lines, soot and XAD-2 resin sample collection, and reactor tube temperature profiling have all been detailed in great detail before [22,23,25]. A gas residence time for all experiments of $t(s) = 4479/T$ was, and is defined as the ratio of reactor volume to gas flow at a certain temperature.

Particle and gas phases PAHs collected on the filter paper and XAD-2 resin were extracted with dichloromethane using an accelerated solvent extractor (ASE). The extraction process was repeated sequentially three times for each filter paper and resin, yielding a total of 60 ml extract which was subsequently placed on a heated block maintained at 40°C, with pure nitrogen blown over the top of the extraction vial to concentrate the extract to initially 15 ml and finally 1 ml.

The gas chromatography mass spectrometry (GC-MS) method used for the analysis of particulate and gas-phase PAHs has been detailed previously [22]. PAHs were quantified using the EPA Method TO-3A [26], with each of the 16 PAHs allocated to one or more of the deuterated PAHs in the internal standard. The tube reactor utilised in all of the tests is shown schematically in **Fig. 1**, replete with gaseous and liquid fuel supply lines and also sample paths for soot and XAD-2 resin collection.

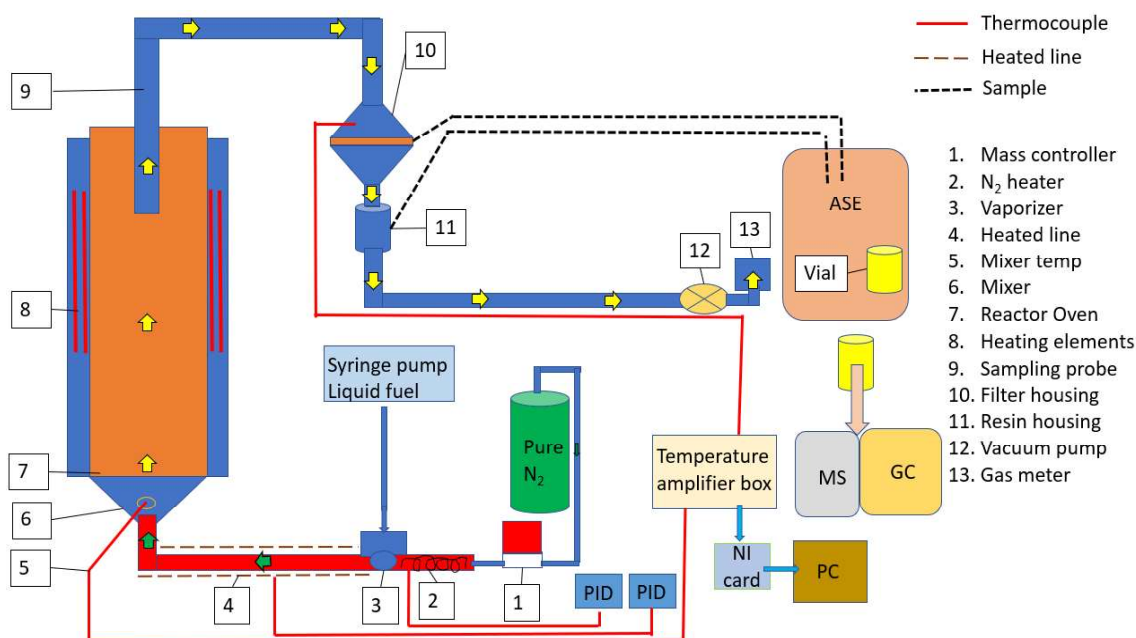


Fig. 1. Schematic diagram of laminar flow tube reactor facility

2.2 Fuels investigated

Ethanol, methyl acetate, acetone, and diethyl ether fuels were all obtained from Sigma Aldrich, at a purity of 99.6 % certified AR grade with the properties of each shown in **Table 1**. **Fig. 2** shows the molecular structure of each of the tests fuels.

Table 1. Tested oxygenated fuels and their properties [27,28]

Fuel	Molecular structure	Oxygen to carbon ratio	Molar mass (g/mol)	Density (Kg/m ³) at 25 °C	Boiling point (°C)
Ethanol	C ₂ H ₅ OH	0.5	46.07	789	78.37
Methyl acetate	CH ₃ COOCH ₃	0.66	74.08	934	57.1
Acetone	(CH ₃) ₂ CO	0.33	58.08	791	56
Diethyl ether	(C ₂ H ₅) ₂ O	0.25	74.12	706	34.6

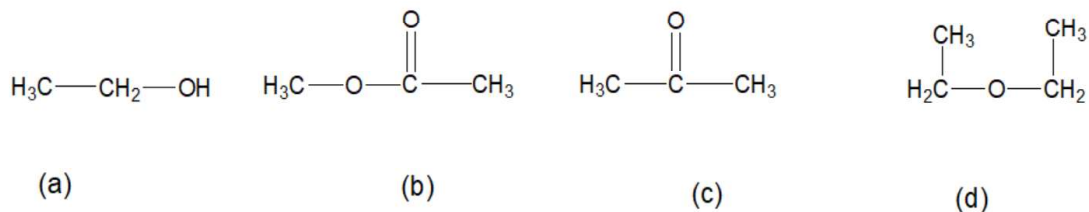


Fig. 2. Fuel molecular structure of (a) Ethanol, (b) Methyl acetate, (c) Acetone, and (d) Diethyl ether

The test fuels were selected so as to provide insight and understanding as to the following during pyrolysis:

- The influence of oxygen to carbon bond types and functional group within a fuel on soot and PAH formation.
- Consideration of the possible mechanisms that lead to individual PAH growth and the formation of the most toxic PAHs in the case of short chain oxygenates.

3 Results and discussion

3.1 Effect of oxygenated fuel on soot mass

The mass of soot extracted from the oxygenated fuels is depicted in **Fig. 3** at various temperatures, where the mass of soot extracted from the filter was normalised with the total volume of gas to have flowed through the filter during sampling. For determining experimental reproducibility, ethanol was employed as the reference fuel, with five repeat collections of soot mass and PAHs obtained. Where error bars are given in Figure 3, and subsequent figures, these show plus and minus one standard deviation from the mean value.

Fig. 3 shows that with the increase in the temperature of the tube reactor from 1050 to 1250°C, the mass of soot produced increased and subsequently decreased marginally at 1350°C for all fuels tested. This increase in the soot mass concentration with increasing temperature is in agreement with previous studies of various short chain hydrocarbon and alcohol fuels [7,10,22,23]. It is evident from **Fig. 3** that, compared to methyl acetate and ethanol, the pyrolysis of acetone and diethyl ether fuels produced a significantly greater soot mass, especially so at the lowest temperature at which soot was observed of 1150 °C. Methyl acetate produced the least mass of soot of all fuels tested and at all temperatures. It is important to note that methyl acetate contains one more oxygen than the other fuels tested (**Fig. 2**), as in the functional group of methyl acetate, a single carbon atom is attached to two oxygen atoms by a double bond and a single bond respectively. The carbon-oxygen double bond is very strong, and difficult to break [29], therefore, in the context of soot formation, it is important to understand whether the single-bonded oxygen atom will also remain bonded to the same carbon atom.

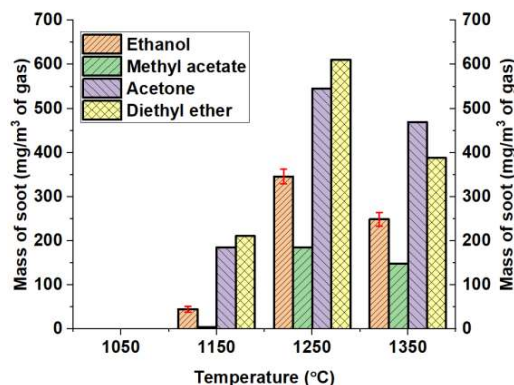


Fig. 3. Mass of soot collected during pyrolysis of oxygenated fuels at a temperature range of 1050 to 1350°C. The error bars denote standard deviation.

Fig. 4 shows two possible decomposition pathways of methyl acetate. Osswald et al. (2007) [30] suggested that ketene formation is more a prominent pathway for direct fuel decomposition. In this case, the carbon-oxygen double bond breaks, resulting in two of the three carbon atoms present remaining bonded to two different oxygens. Assuming that these two carbon to oxygen bonds do not subsequently break, these two carbon atoms might be considered reserved by the oxygen to which they are bonded and thus unable to participate in soot formation, reducing the overall soot tendency of methyl acetate. The methoxy radical upon unimolecular decomposition forms formaldehyde, which upon further dehydrogenation produces CO [31]. It has been also reported that the thermal decomposition of ketene produces allene and carbon dioxide, with the former further decomposing to methylene and acetylene [32].

Another possible explanation for the low mass of soot produced by methyl acetate might be the higher oxygen to carbon ratio, in a scenario whereby the carbon to oxygen bonds break the resulting free oxygen may subsequently oxidize intermediate species or soot, resulting in a higher concentration of CO and CO₂, thus reducing the carbon availability for soot formation. From **Fig. 3**, comparing the C3 oxygenated fuels, it can be seen that acetone produced a relatively higher mass of soot as compared to methyl acetate. This might be attributable to the low carbon to oxygen ratio for acetone as compared to methyl acetate.

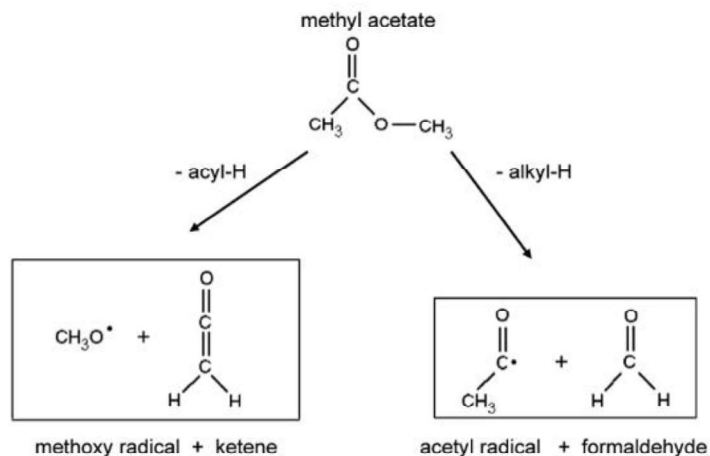


Fig. 4. Methyl Acetate fuel destruction pathways (Osswald et al., 2007 [30])

Agafonov et al. (2019) [33] studied experimentally, and through detailed simulation, the influence of acetone and propane on soot formation during pyrolysis in an acetylene flame behind a reflected shock wave, reporting that the thermal decomposition of acetone produced two methyl radicals and CO. This observation suggested that in acetone only one carbon atom is reserved and prevented from taking part in soot formation. The observed sooting propensity of acetone is in agreement with the study by Agafonov et al. (2019). The methyl radicals could be further consumed by first forming ethane molecules, before decomposition to form acetylene by the following reaction sequence (Eq 1):

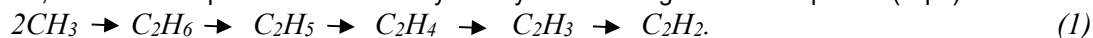


Fig. 3 shows that Diethyl ether formed the highest mass of soot of the four oxygenated fuels at 1150°C and 1250°C. In the functional group of diethyl ether, the oxygen atom is attached to two carbon atoms. It has been reported that the thermal decomposition of diethyl ether produces species including carbon monoxide, methane, ethylene, and acetaldehyde, with the two hydrocarbons able to undergo a progressive dehydrogenation to form soot [34]. Acetaldehyde could also potentially generate methyl radicals which could be consumed via ethane to form acetylene (Eq 1), an important soot precursor.

Fig. 3 shows that ethanol produced the second lowest mass of soot, after methyl acetate, at all temperatures. This can likely be attributed to ethanol possessing the second highest oxygen to carbon ratio (Table 1), potentially resulting in a higher concentration of CO and CO₂ as compared to acetone and diethyl ether. A further explanation for low soot mass formed during ethanol is that the C-O bond has been found to remain intact in a majority of instances under similar conditions, reserving a carbon atom and reducing the number available for soot formation [25].

The observed soot propensity trend of Ether > Ketone > Alcohol > Ester is in agreement with studies of the same functional groups during shock tube and jet flames experiments [35–37]. Furthermore, this is the first study to have observed the same trend of sooting tendency under purely pyrolytic conditions.

3.1.1 Effect of oxygenated fuel on gas-phase (GP) and particle-phase (PP) PAHs

Fig. 5 shows the total PAH measured (sum of the 16 US EPA priority PAH speciated) during pyrolysis of ethanol, methyl acetate, acetone, and diethyl ether at varying temperatures, collected from both gas and particle phases.

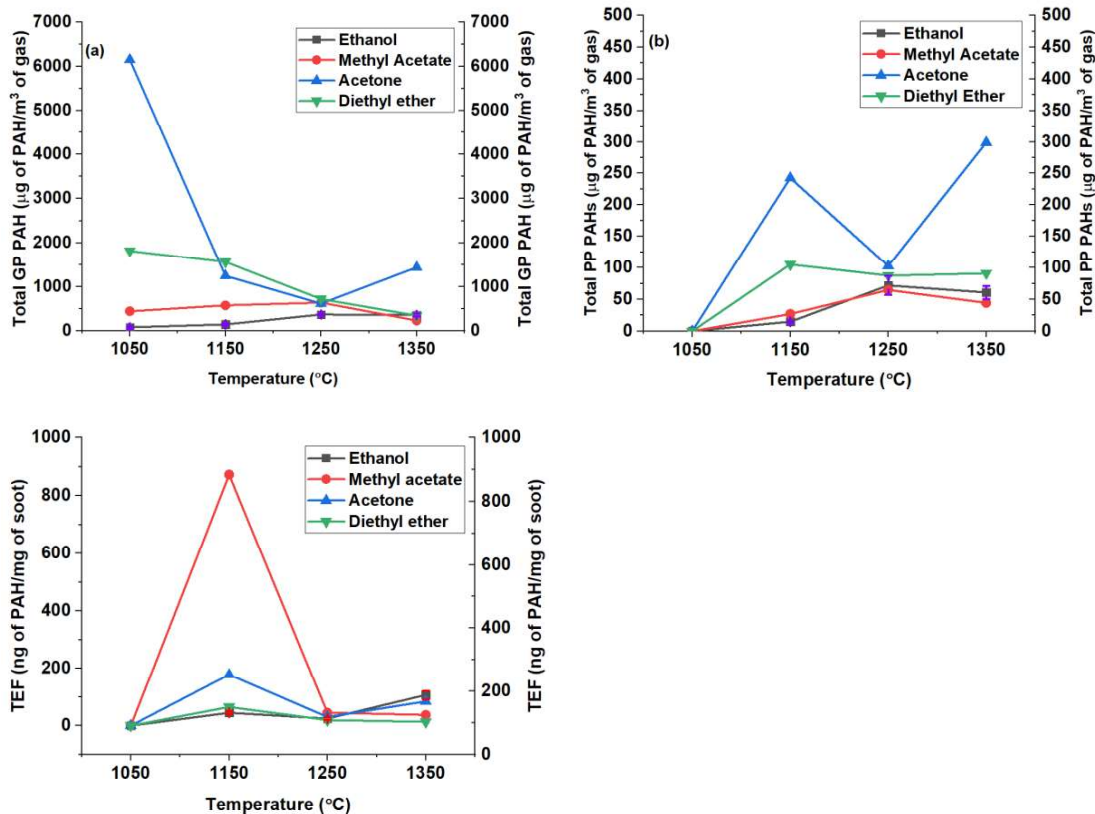


Fig. 5 (a) Total gas-phase PAH per m^3 of gas, (b) Total particle-phase PAH per m^3 of gas, and (c) Total particle-phase PAH per mg of soot during pyrolysis of ethanol, methyl acetate, acetone and diethyl ether at varying temperature. Error bars are for ethanol fuel repeatability

Fig. 5a shows that the concentration of gas-phase (GP) PAH produced during pyrolysis of diethyl ether and acetone decreased with an increase in temperature of the flow reactor from 1050 to 1250 °C. At lower temperatures of 1050 and 1150 °C, methyl acetate and ethanol pyrolysis produced much lower GP PAH concentrations than acetone and diethyl ether fuel (**Fig. 5a**), which is likely due to the delayed formation of intermediate PAH precursors (i.e., acetylene) from methyl acetate and ethanol decomposition due to unavailability of carbon as explained in Section 3.1. Despite the shorter carbon chain length and higher molecular oxygen content than diethyl ether, pyrolysis of acetone resulted in a larger concentration of GP PAH at the lowest and highest measured temperatures, as shown in **Fig. 5a**. A possible explanation for this is that during pyrolysis of diethyl ether the initial decomposition of DEE is slower than that of acetone, e.g. more unreacted DEE might remain at 1050 °C. produced two methyl radicals which readily formed acetylene and propargyl radicals, major precursors for benzene ring formation and PAHs growth.

It can also be seen from **Fig. 5a** that the relative effects of different functional groups on GP PAH concentration diminishes at 1250 °C and above, as was also observed in the case of short-chain alcohols fuels [22]. This can likely be attributed to the very fast reaction rates present at higher temperatures, and thus effects of temperature dominate those of fuel structure. It is interesting however that at 1350 °C the concentration of GP PAH is appreciably higher in the case of acetone relative to the other fuels, despite presumably faster rates, perhaps because of a new reaction regime is reached [22,23]. The decrease in the GP PAH concentration of during diethyl ether and acetone in the temperature range of 1050 to 1250 °C might be attributed to the increased rates of conversion of GP to heavier PAH, and then to soot particles, as can be observed in **Fig. 3**.

Fig. 5b shows that for the particle phase (PP) PAH concentration per unit volume of gas of the oxygenated fuels, there is a visible general trend of increasing PP PAH with temperature and a clear impact of DEE and acetone relative to methyl acetate and ethanol. **Fig. 5b** shows that the concentration of PP PAH for all fuels increased with an increase in temperature from 1050 to 1150 °C, while at 1250 °C all the fuels produced a comparable PP PAH concentration. The increase in PP PAH concentration for all four oxygenates in the temperature range of 1050 to 1150 °C, could be due to an increase in the collisions between the PAH which resulted in an increase in the heavier PAHs at higher temperatures

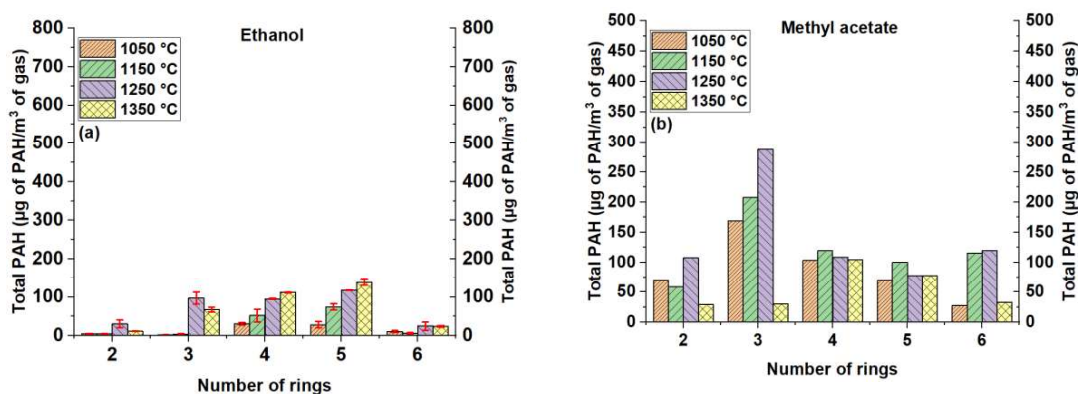
(Fig. 5b). It is also interesting to note that the concentration of PP PAH during ethanol and methyl acetate pyrolysis at different temperatures was very similar, despite different carbon numbers and oxygen to carbon ratios.

At a temperature of 1150°C, Fig. 5c indicates a peak PP PAH concentration per mass of soot during acetone and methyl acetate pyrolysis on a mass of soot basis, but that this concentration reduced when the temperature was increased to 1250°C. At a temperature of 1250°C, a further decrease in the PAH mass concentrations was observed. A similar effect was reported previously in the case of short-chain alcohols [22]. The small rise in PP PAH in the temperature range of 1250 to 1350°C shows that more PP PAHs were deposited on the soot surface, whereas the amount of soot decreased as the temperature rose (Fig. 3). In Fig. 5c an effect of the functional group on the PP PAH is most prominent at 1150°C. At a temperature of 1150°C methyl acetate produced approximately 9.8, 4.4, and 11.8 times more PP PAH concentration than ethanol, acetone, and diethyl ether respectively. This can likely be attributed to the very low mass of soot produced by methyl acetate at 1150°C as compared to acetone and diethyl ether (Fig. 3). It is interesting to note that methyl acetate produced the lowest PP PAH on a volume gas basis (Figure 5b) but the highest level on a per mass of soot basis (Figure 5c). It is tentatively suggested that during particle growth some surface adsorbed PAH becomes part of the soot structure and can no longer be extracted.

3.2 Influence of oxygenates on the PAH rings distribution

Fig. 6 shows the PAH concentration per volume basis of oxygenated fuels grouped according to the number of aromatic rings present. It can be observed from Fig. 6 that for all fuels, except ethanol, at the two lowest temperatures of 1050°C and 1150°C, the concentration of 3 ring PAH was greater than that of any other grouping of PAH by number of rings.

As observed from in Fig. 6 that the pyrolysis of acetone and diethyl ether fuels produced a greater amount of three-ring PAHs (for example, phenanthrene) than 2, 4, 5, or 6 rings in the temperature range of 1050 and 1150°C. At temperatures of 1050 and 1150°C, for example, diethyl ether produced a significant amount of three-ring PAH, but the concentration of three-ring decreased as the temperature increased, implying that three-ring PAHs are rapidly converted into larger species, such as soot particles, at higher temperatures (Fig. 6c). This observation supports the finding from Fig. 3 that the mass of soot increases with increasing temperature. The three-ring PAHs play an important role in the growth of 4-6 rings PAHs [22]. It can be seen that the concentration of 2 and 3 membered rings PAH formed during diethyl ether pyrolysis decreased with temperature from 1050 to 1350°C while in the case of acetone, between 1250 and 1350°C the concentration of 2, 4, and 5 rings PAH increases. Acetone produced a considerably higher concentration of 2, 3, and 4 member rings at 1350°C relative to the other tested fuels. Despite variations in fuel chemical structure, the concentration of four ring PAHs during pyrolysis of methyl acetate and diethyl ether were similar at all temperatures, as shown in Fig. 6b and Fig. 6c.



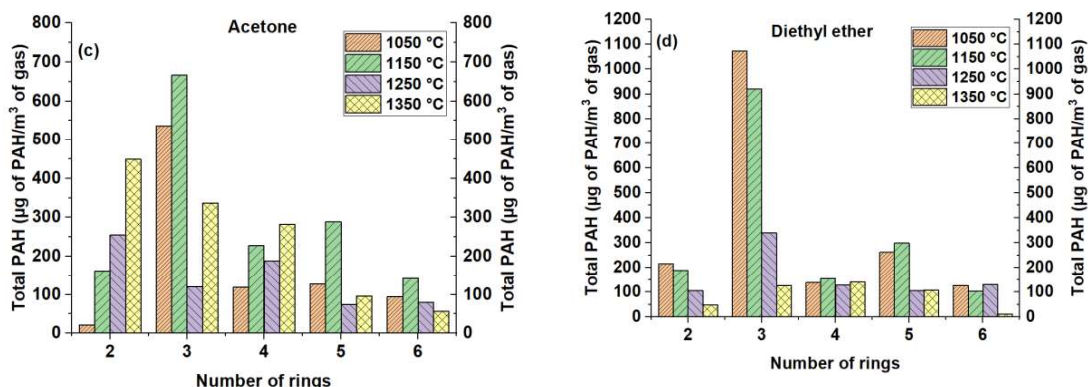


Fig. 6. PAH distribution according to the number of rings during pyrolysis at four different temperatures of 1050°C, 1150°C, 1250°C, and 1350°C (a) Ethanol (b) Methyl acetate (c) Acetone (d) Diethyl ether. Error bars denote standard deviation for ethanol fuel and note the extended y-axis necessary in the case of diethyl ether.

Fig. 6d demonstrates that the relative abundance of heavier ring PAHs in diethyl ether is higher than in methyl acetate and ethanol when considering the heavier ring PAHs (i.e., 5 and 6 rings) in the temperature range of 1050 and 1150°C. At temperatures of 1050 and 1150°C, the concentration of 5 ring PAHs in acetone and diethyl ether was higher than that of 6 ring PAHs, although methyl acetate had a slightly higher concentration of six member rings at 1150°C. The difference in concentration of the 5 and 6 ring PAHs might be attributed to the pace at which these rings convert to soot particles. The comparable ratios of 5 and 6 ring PAHs suggests that the formation rate of 5 rings PAHs and subsequent consumption to form 6 ring PAH is approximately equivalent for all fuels in the temperature range of 1250 to 1350°C.

In the temperature range of 1050 to 1150°C, the influence of the various functional groups on the ring distribution is clearly visible (**Fig. 6**). When compared to methyl acetate, ethanol, and acetone at 1150°C, diethyl ether generated 1.3, 211, and 4.4 times more three-ring PAHs. The larger quantity of three-ring PAHs during methyl acetate, acetone and diethyl ether pyrolysis implies that at lower temperatures the conversion rate of three-ring PAH to heavier-ring PAH was reduced and may have been a limiting step.

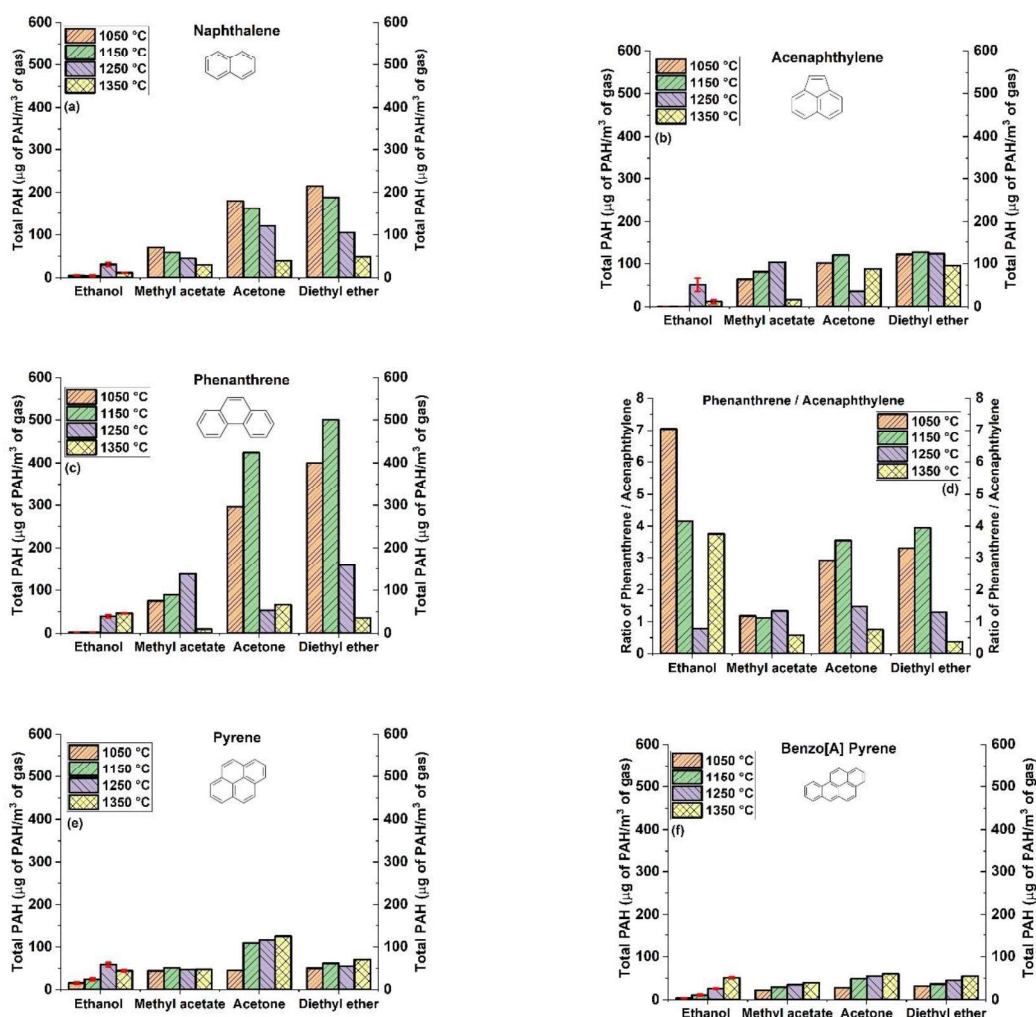
3.3 Influence of oxygenated structure on growth of individual PAHs

Fig. 7 shows the concentration of Naphthalene (NPH), Acenaphthylene (ACY), Phenanthrene (PHN), Pyrene (PYR), Benzo [a] Pyrene (B[a]P), and Benzo [k] fluoranthene (B[k]F) during the pyrolysis of ethanol, methyl acetate, acetone, and diethyl ether. These individual PAHs of varying size were chosen for further discussion on the basis of the PAH distribution by ring number presented in **Fig. 6**.

Fig. 7a shows that the concentration of naphthalene decreased with an increase in temperature from 1050 to 1350°C for all the oxygenates tested, except ethanol for which the total concentration of naphthalene increased up to 1250°C but then decreased at 1350°C. This decrease can likely be attributed to the rapid conversion of 2 ring naphthalene to higher ring PAHs, reaction rates of which can be expected to increase with temperature. A relatively low concentration of naphthalene was found at all temperatures during pyrolysis of methyl acetate and ethanol, and it is tentatively suggested that this can be attributed to slower rates of first ring formation, due to the high O: C ratio of methyl acetate and ethanol, which prevents accumulation of naphthalene. **Fig. 7a** shows that at the lowest temperatures of 1050 and 1150°C, diethyl ether produced an appreciably higher concentration of naphthalene than acetone. However, at 1250°C and 1350°C, diethyl ether and acetone produced an approximately equivalent concentration of naphthalene, suggesting a reduced influence of molecular structure at this condition.

As discussed in Section 3.1, C2 and C3 oxygenated fuels are expected to predominately decompose to methyl radicals which are consumed via ethane to form acetylene and subsequently propargyl radicals. Two propargyl radicals bond to form benzene, according to a mechanism proposed in the literature [38,39]. Following this, the benzene ring loses hydrogen atoms, yielding phenyl radicals that may readily generate two-ring naphthalene through the HACA mechanism [40,41]. Although the HACA method is most likely to produce naphthalene, cyclopentadienyl radicals might potentially be recombined to produce naphthalene as well [1], however, it is tentatively suggested that the formation of cyclopentadienyl radicals from the selected oxygenated is less likely. Once two-ring naphthalene has formed, it grows

further to the three ring species acenaphthylene and phenanthrene via the HACA mechanism. In **Fig. 7b**, it can be seen that acetone and diethyl ether produced a comparable concentration of acenaphthylene at 1050 and 1150 °C, despite the difference in the levels of naphthalene at these conditions (**Fig. 7a**). **Fig. 7c** shows that diethyl ether produced the highest concentration of phenanthrene in the temperature range of 1050 to 1250 °C. An effect of fuel molecular structure on phenanthrene formation is very evident at 1050 and 1150 °C. In comparison to acetone, ethanol, and methyl acetate, diethyl ether generated 1.2, 166, and 5.6 times the concentration of phenanthrene at 1150 °C, respectively. Pyrene can be formed by either the benzenoid phenanthrene or the three-ring acenaphthylene [42], as shown in **Fig. 7d**, which displays the ratio of acenaphthylene to phenanthrene at various temperatures. The concentration of phenanthrene was larger than that of acenaphthylene for all of the oxygenated fuels at the low-temperature range of 1050 to 1250 °C, as shown in **Fig. 7d**, while the converse is true at the maximum temperature.



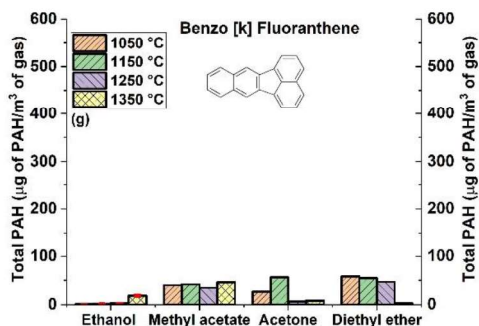


Fig. 7. Measured concentrations of (a) Naphthalene (NPH) (b) acenaphthylene (ACY) (c) phenanthrene (PHN) (d) ratio of acenaphthylene to phenanthrene (e) pyrene (PYR) (f) benzo[a] pyrene (B [A] P) (g) benzo[f] fluoranthene (B [K] F) and during pyrolysis of ethanol, methyl acetate, acetone, and diethyl ether. Error bars denote ethanol fuel repeatability.

It is hypothesised that for all fuels at lower temperatures, pyrene formation is dominated by growth from phenanthrene via the HACA mechanism, but at higher temperatures (except ethanol at 1350 °C, which exhibited a higher concentration of phenanthrene), pyrene formation is dominated by acenaphthylene due to the larger abundance of the smaller molecule. This hypothesis is in agreement with the previously suggested formation of PAH from alcohol fuels via the HACA mechanism [22]. A similar effect of temperature on pyrene formation was observed during the pyrolysis of a series of alcohol fuels [22]. **Fig. 7e** demonstrates that all oxygenated fuels formed a significant quantity of pyrene at all temperatures, and it is likely that various 2-ring and 3-ring PAHs expanded via pyrene to form heavier PAHs, particularly the B2 group, via HACA or HAVA (Hydrogen Abstraction/Vinylacetylene-Addition) [43]. It is interesting to note that, for all the tested fuels the concentration of pyrene is approximately constant at all temperatures, with the exception of acetone at 1050°C where the measured concentration of pyrene is significantly lower than for the same fuel at higher temperatures.

From **Fig. 7f**, it is interesting to note that for all oxygenated fuels the concentration of benzo[a] pyrene increased linearly with temperatures, which supports the assumption that at higher temperatures the low and medium molecular PAHs were more rapidly converted into heavier weight benzo[a]pyrene.

Fig. 7g shows that the measured concentration of benzo[f] fluoranthene was much less systematically influenced by temperature. It is also interesting to note that during ethanol and methyl acetate pyrolysis the concentration of benzo[f] fluoranthene increased at the highest tested temperature of 1350°C but only very low concentrations were detected in the case of acetone and di-ethyl ether.

3.4 PAH toxicity

This section assesses the potential carcinogenicity of particulate matter produced by oxygenated fuels of various functional groups at a range of temperatures, with a focus on PAHs from the B2 group because of their high toxicity. As indicated in Eq 2, a PAH toxicity index was computed for each particulate sample by adding the products of each PAH concentrations (C_i) and their toxicity equivalent factor (TEF). TEFs were proposed by Nisbet and Lagoy (1992) [44] and are commonly used to evaluate PAH toxicity.

$$\text{Toxicity index} = \sum_{i=1}^n (\text{TEF}_i * C_i) \quad (2)$$

Fig. 8 depicts the PAH toxicity of particulate matter formed during the pyrolysis of the test fuels on a mass basis. As seen in **Fig. 8**, the studied fuels had dramatically different degrees of toxicity at 1150°, however, it is interesting to see how close the TEF are at higher temperatures. At 1150°C, methyl acetate displays a maximum toxicity, 4.9 times that of acetone, 13.45 times that of diethyl ether, and 19.48 times that of ethanol, as shown in **Fig. 8**. The significant toxicity of soot from methyl acetate at 1150°C can be explained by a comparatively large concentration of toxic benzo [a] pyrene condensing onto the soot particles (**Fig. 3** and **Fig. 7d**). Further, it should be noted that methyl acetate produced very little mass of soot at this temperature, and so while the per volume of gas concentration of benzo[a]pyrene

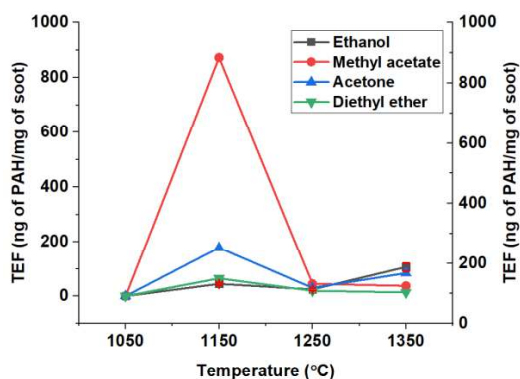


Fig. 8. Calculated toxicity equivalency factor of ethanol, methyl acetate, acetone, and diethyl ether fuels soot particle per mg of soot.

is not especially greater, it is much higher on a per mass of soot basis. Each step of PAH formation from acenaphthylene to benzo [a] anthracene and on to the most hazardous species, benzo[a] pyrene, raises the toxicity level of PAH by a factor of ten. At 1150°C, particulate matter from acetone is the most hazardous, while that from diethyl ether is the least harmful. Acetone has the maximum toxicity at the highest temperature measured, which is due to the presence of benzo[A]pyrene.

Finally, while the quantity of soot mass for all fuels is relatively low at 1150°C, as shown in **Fig. 3**, the toxicity of the extractable PAHs adsorbed on the soot particles was substantially higher than at higher temperatures, as shown in **Fig. 8**. It is also worth noting that at 1150°C, acetone produced the second highest PP PAH as shown in **Fig. 5**, which follows the same patterns as **Fig. 8**, implying that the PM toxicity is most influenced by the total concentration of PAH present rather than any dramatic change in the composition of those PAH when comparing the different fuels.

4 Conclusions

In summary, this paper investigated the sooting tendency and PAHs emissions from pyrolysis of ethanol, methyl acetate, acetone, and diethyl ether and the following conclusions can be drawn:

- Pyrene formation pathways appeared temperature dependent for all four oxygenates and were dominated by phenanthrene at 1050 and 1150°C, while at higher temperatures higher concentrations of acenaphthylene were found.
- At 1150°C the relative abundance of the soot particles was low, however, the toxicity of the soot particles produced was significantly higher than at higher temperatures, especially in the case of soot produced during pyrolysis of methyl acetate.
- An effect of different oxygenated functional groups on soot mass was evident, with consistently lower production of soot by methyl acetate, which has higher oxygen to carbon ratio than ethanol, acetone, and diethyl ether.
- Functional groups had an impact on the GP PAH concentration with methyl acetate pyrolysis resulting in a significantly lower GP PAH concentration relative to acetone and diethyl ether, but slightly higher than ethanol at all temperatures. However, the pyrolysis of acetone resulted in a higher concentration of GP PAH at the lowest and highest temperatures, despite the shorter carbon chain length and higher molecular oxygen content as compared to diethyl ether.
- The concentration of PP PAH per unit volume of gas is much lower than the corresponding GP PAH, which suggests that PP PAH that condensed onto the particulate surface, subsequently experienced surface reaction and were therefore not recoverable during the extraction process, contributing to the formation and emission of particulate matter.
- The concentration of four ring PAHs (which contribute to the formation of heavier molecular weight PAHs comprising 5 or 6 rings) during methyl acetate and diethyl ether pyrolysis were relatively similar, despite different molecular structures and carbon numbers.

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