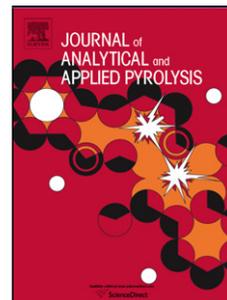


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Influence of unsaturation of hydrocarbons on the characteristics and carcinogenicity of soot particles

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Highlights

- Increasing unsaturation increased soot size, mass, and number concentrations
- Increasing unsaturation increased particle phase PAHs and soot particle carcinogenicity
- soot carcinogenicity decreased with the soot particle number.
- soot carcinogenicity decreased with soot particle mass and size
- Temperature increase from 1050 to 1350 °C decreased soot carcinogenicity

Abstract

This paper concerns the effect of unsaturation of hydrocarbons (single, double, and triple bonds) on soot particle characteristics (mass, number, and size) and on the carcinogenicity of soot particles. The soot particles were produced from oxygen-free pyrolysis of five hydrocarbons, namely: propane, propylene, ethane, ethylene, and acetylene. The characteristics of soot particles were measured with the aid of a differential mobility spectrometer

(Combustion-DMS-500) and measurement of soot mass concentration was confirmed using gravimetric filter measurements. The soot particle carcinogenicity was estimated from the emission quantities of total polycyclic aromatic hydrocarbons (PAHs) and the toxicity equivalent factor (TEF) of each PAH. Oxygen-free pyrolysis of the hydrocarbon fuels was conducted in a laminar tube reactor within the temperature range of 1050 – 1350°C at a constant nitrogen flow rate of 20L/min and constant fuel flow rate of 1% (vol) on carbon-1 basis. The experimental results showed that increasing unsaturation of fuels from single to double and to triple bonds increased the mass concentration, particle size, number concentration, and carcinogenicity of soot particle notably at the initial temperature of 1050 °C. Increase in the pyrolysis temperature of the tube reactor from 1050 – 1350°C, increased the mass concentration and sizes of the soot particle while the number concentration and carcinogenicity of the soot particle decreased. There was a positive correlation between the soot particle number and the corresponding soot particle carcinogenicity, while a negative correlation was observed between the soot particle mass and size with soot particle carcinogenicity regardless of the pyrolysis temperature examined. The potential implication of these observations is that, low-temperature combustion (LTC) applications, aimed at reducing emissions of soot and NO_x, could produce higher soot particle number concentration of higher carcinogenicity.

Keywords: unsaturation, soot particles, soot characteristics, PAHs, soot carcinogenicity

1.0 INTRODUCTION

Inhalation of atmospheric air contaminated with soot particles has led, and is still leading to the rising global human morbidities and mortalities [1]. The correlation between human exposure to atmospheric air contaminated by soot emissions and recent fatalities due to COVID-19 in the United States has been established [2]. While Poly-cyclic aromatic hydrocarbons (PAHs) are known as the primary precursors of soot particles; they also constitute some sizable noxious components deposited onto soot particles [3]. PAHs are carcinogenic and mutagenic and can be found both attached onto the surfaces of particulates and as inhalable gaseous substances available in the atmosphere.

Large atmospheric soot particles of diameter lower than $10\mu\text{m}$ emitted from various combustion sources could be accumulated into the superior airways of respiration [4],[5]. Inhalable soot particles of diameter lower than $1\mu\text{m}$ and ultrafine particles of diameter less than 100nm , carrying toxic PAHs, are possibly deposited into the lung of a human being, leading to health complications such as lung cancer, cardiovascular diseases and ultimately premature death [6]. Incidences of human mortality related to air-borne soot particles carrying PAHs have been revealed in many global cities [7],[8] [9],[10]. There are presently several hundreds of PAHs in nature, but only 16 of them have been categorised as potentially toxic by the United States (US) Environmental Protection Agency (EPA). The 16 prioritised PAHs with their toxicity equivalent factors (TEF) are shown in Table 1. The toxicity equivalence factors (TEF) designates potential carcinogenicity of each of the US EPA16 priority PAH relative to benzo(a)pyrene. Benzo(a)pyrene and dibenz[a,h]anthracene were assigned a TEF of unity by Nisbet and Lagoy assigned, while benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene were assigned a TEF value of 0.1. The remaining 10 PAHs of the US EPA were either 1000 or 100 times less toxic than the aforementioned six PAHs, hence their values of TEF of 0.01 and 0.001 [10].

Carcinogenicity of particulates bearing adsorbed PAHs is affected by the molecular configuration of the fuel [10], pyrolysis/combustion temperature [11] and particle characteristics of the exhaust soot formed. For example, Sánchez *et al.*, [11] investigated acetylene pyrolysis in a tube-reactor. They reported that the concentration and toxicity of both PAHs and soot depend on the pyrolysis temperature. Dandajeh *et al.* [12] researched the effect of the unsaturation of hydrocarbons having carbon numbers of 2 and 3 on the PAHs formed by those hydrocarbons. They concluded that increasing the unsaturation of fuels increased the type and concentration of PAHs formed depending on the pyrolysis temperature. In a related study, Dandajeh *et al.* [13] experimentally investigated the effect of increasing

carbon number of fuels from 1 to 7 in forming PAHs in a pyrolysis tube reactor. They reported that increasing the carbon number of fuels from 1 to 7 increased the propensity of fuel molecules to soot depending on the pyrolysis temperature. Mei *et al.*, [14] recently studied the experimental effects of adding CO₂ in the pyrolysis of ethylene. Their results revealed that adding CO₂ in small quantities (up to 10%) promoted the quantity of soot formed while also increasing the soot particle volume, soot particle number concentrations and, decrease in soot induction time. However, increasing CO₂ proportion beyond 10%, Mei *et al* reported a decrease in the rates of soot nucleation and soot mass growth. Kashiwa et al. [15] investigated the influence of oxygen on PAH and particulate formation in benzene pyrolysis at low temperatures. They reported forming small fraction of particulates at a low temperature of 900°C and zero oxygen and particulate formation increased with increasing oxygen level.

Despite these remarkable contributions by numerous researchers on hydrocarbon pyrolysis, investigating the influence of unsaturation of hydrocarbon fuels on soot particle characteristics (mass, number, size, and surface area) and soot particle carcinogenicity has been rarely studied. The interdependence of soot particle mass, size, number, and surface area on the carcinogenicity of soot particles was, to the best of our knowledge, also not investigated.

The paper herein, therefore, describes an experimental analysis on the influence of unsaturation of hydrocarbons on soot particle carcinogenicity and the interdependence of soot particle characteristics on soot carcinogenicity. The study was carried out in a pyrolysis furnace at a temperature range of 1050 -1350°C. PAHs in the gas phase and those attached to soot particles were trapped on XAD-2 resin and a glass microfibre filter, respectively. These PAHs were extracted using an accelerated solvent extraction system. The extracts of the PAHs were later analysed using Gas Chromatography (GC) coupled to Mass Spectrometry (MS). The carcinogenic equivalent sum of the soot particles produced by each fuel was calculated from the total PAH concentration and the toxicity equivalent factors (TEFs) shown in Table 1. Soot

particle characteristics (particle mean diameter, number concentrations, surface area and mass concentrations) were measured and analysed using Cambustion-DMS 500 instrument.

2.0 EXPERIMENTAL

2.1 Fuel Molecules Investigated

Five gaseous hydrocarbon molecules are propane, propylene, ethane, ethylene, and acetylene. Each of the hydrocarbon fuel had a purity of over 99 %. Table 2 shows the properties of the hydrocarbons.

The objective of this study is to analyse the influence of unsaturation of fuels listed in Table 2 as follows:

- I. Determine the effect of unsaturation of fuels on the gravimetric filter measurements of mass concentration
- II. Characterise the soot particles based on size, mass and number concentration
- III. Confirm the soot mass concentration measurements from the gravimetric filter values and those obtained from DMS 500.
- IV. Investigate the interdependence of soot particle characteristics on the soot particle carcinogenicity
- V. Investigate temperature influence on the characteristics and carcinogenicity of soot particles

2.2 Soot particle generation

Samples of soot particles were generated by pyrolysis within the temperature range of 1050 to 1350 °C. The pyrolysis was conducted at temperature intervals of 100 °C using a tube reactor

shown in Figure 1. The carrier gas (nitrogen) was measured at a fixed flow rate of 20 L/min. All the five fuel molecules had a fixed flow rate of carbon of 1% on C₁ basis. Example, the flow rate of ethylene, with 2 carbon number, was about 1.5 times higher than that for propylene, a fuel with a carbon number of 3. To check daily repeatability and to detect any potential change in the experimentation, ethane pyrolysis was used as a baseline data. Gas-phase PAHs were also sampled under the same conditions.

The oxygen-free pyrolysis conditions in the tube reactor and the selected range of temperatures (1050 to 1350 °C) resemble a significant extent, the conditions in the core of the fuel spray of a diesel engine, where, in the early stages of combustion, there is little oxygen available.

The hydrocarbons were supplied to a heated stream of nitrogen through solenoid valves. The combined stream of heated nitrogen gas and fuel passed through a static mixer (3) which ensured adequate homogenous mixing. A type K thermocouple maintained the mixer's temperature at ~180 °C. The alumina tube reactor has a diameter of 10.4 cm and a length of 144 cm. Detailed soot generation procedure can be found in [10].

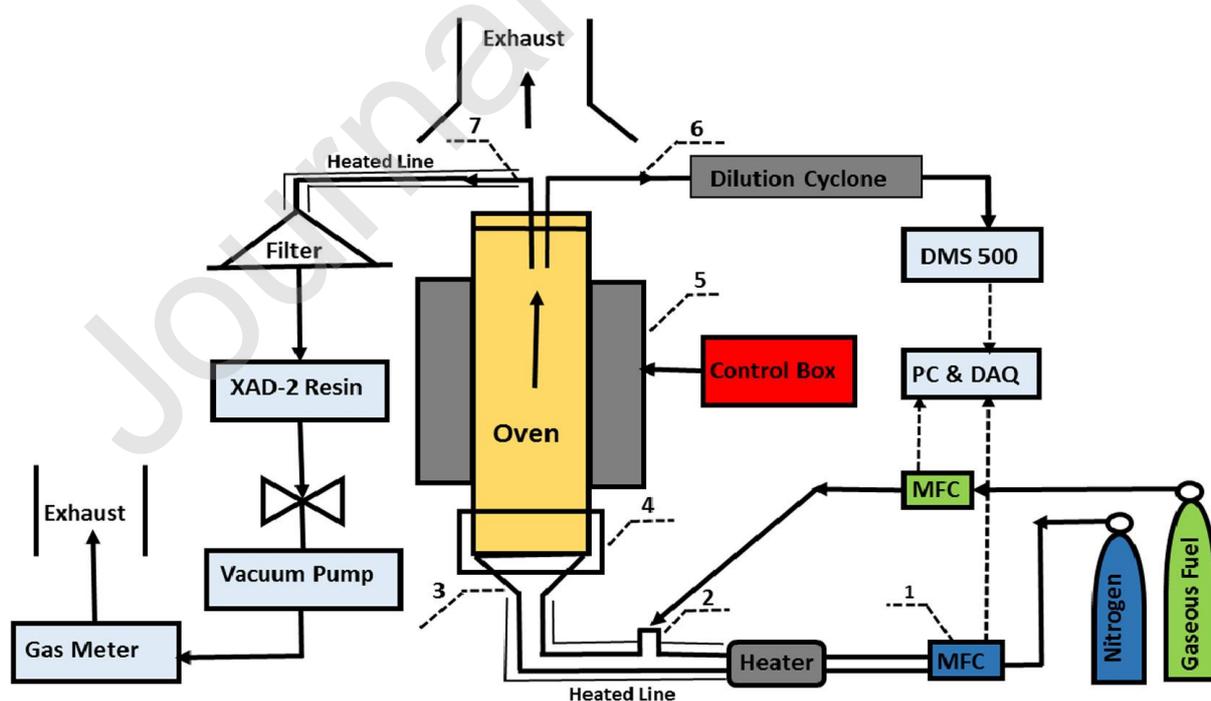


Figure 1: Schematics of the experimental set-up: (1) mass flow controller (MFC), (2) fuel inlet, (3) static mixer, (4) circulating cooling water, (5) tube furnace, (6) DMS 500 sampling probe, and (7) soot sampling probe [12].

The Alumina tube was put in a vertical form in an electrically controlled furnace and 60 cm of the tube central length was heated between 1050 – 1350 °C. The axial temperature distribution profile in the tube reactor over this 60 cm length axis was uniform as reported in earlier published works [16]. The gas average residence time (t_r) was evaluated using equation 1.

$$t_r(s) = \frac{V_r(L)}{Q(L/s)} \quad (1)$$

Where V_r (L) is the volume (in litres) of the 60 cm heated portion of the tube.

Q is the flow rate (litres/second) at the test temperatures. The average residence time was temperature (T) dependent.

2.3 Sampling of soot particles

Soot particles and gaseous PAHs were captured from the reactor's outlet using a stainless-steel probe. The probe was attached to a vacuum-pump and soot samples were drawn at a temperature of 100 °C intervals. The sampling probe leading to where the microfibre filter is housed was heated and sustained at a temperature of 120 °C. This was done primarily, to avoid gas phase PAHs condensing within the sampling line. The sampling probe was installed at the outlet of the reactor and was also connected to the filter by a 12.5 mm stainless-steel tube. A control valve was used to maintain the vacuum pump's flow rate always at less than 18 L/min. A filter and XAD-2 resin systems were placed in tandem, to collect soot particles and gas phase PAHs, respectively.

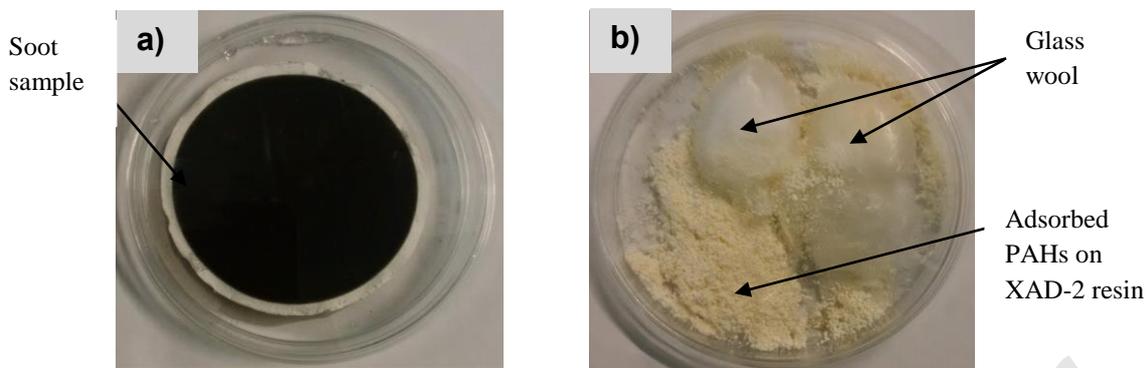


Figure 2: Samples of: a) soot collected on a glass micro fibre filter b) gas phase PAHs collected on an XAD-2 resin; samples were collected during ethane pyrolysis at a temperature of 1150 °C

Before sampling, the glass micro-fiber filter was baked to 120 °C in an electrical oven for a period of 8 hours in order to reduce moisture on the filter. The baked filter was used immediately after removal from the oven. The filter is 70 mm in diameter, 700 nm pore size, and has 310 seconds filtration speed. The filter was selected since it can withstand high temperatures and was also found suitable by many other studies [11,17]. Soot samples were measured on a mass balance having 0.001 mg resolution. Figure 2a and b show samples of soot and gas-phase PAHs collected during ethane pyrolysis at a temperature of 1150 °C.

The XAD-2 resin, onto which the gas phase PAHs were collected, had a surface area of ~300 m²/g, 90 Å average pore size and 1.02 g/mL density at a temperature of 25 °C. XAD-2 resin was chosen due to its superior retention and trapping of gaseous PAHs compared with other materials [17]. To capture the gas phase PAHs effectively, a 5g of XAD-2 resin, embedded within two pieces of glass wool, was initially put into a glass cartridge. The cartridge was loaded into a customized housing made from stainless steel. The XAD-2 resin housing system was coupled in tandem with the glass microfiber filter system.

The volume of gas (V_g), passing through the microfiber filter and the XAD-2 resin was metered using a volumetric diaphragm gas meter. The gas meter has a maximum volumetric flow (Q_{max}) rate of $6 \text{ m}^3/\text{h}$.

The duration of sampling the soot particles and gaseous PAHs were kept at 15 min for all the test temperatures. The sampling duration was optimised to collect a satisfactory mass of soot that can yield visible PAH peaks on the GC-MS. The filter gravimetric soot mass (M_s) and the cumulative volume of gas (V_g) were measured for each test duration.

2.4 Sample Preparation and Analysis

PAH extraction from the samples of the soot and XAD-2 resin, shown in Figure 2a and 2b respectively, was conducted using Dionex-150 Accelerated Solvent Extracting Machine (ASE). All the samples were extracted in dichloromethane (DCM) solvent. The optimised extraction conditions are shown in Table 3. The DCM in the extracted PAH sample was evaporated by bubbling nitrogen gas into the PAH-DCM solution; thereby leaving concentrated PAH extracts.

The concentrated PAH extracts were identified using Gas chromatograph (GC) and quantified using the Mass Spectrometer (MS). The GC was first calibrated using a standard QTM PAH Mix Standard prior to the PAH quantification. Details of the calibration procedure can be found in the supplementary material. The PAH standard contained the 16 EPA PAHs (see Table 1). The optimised GC-MS operating conditions are shown in Table 4 and detailed PAH extraction and analysis procedures can be found in [12],[13].

3.0 RESULTS AND DISCUSSION

3.1 Effect of unsaturation on gravimetric soot mass concentration

Soot masses (M_s) and gas volume (V_g) were recorded during the pyrolysis of each of the five hydrocarbons at different temperatures of 1050, 1150, 1250 and 1350 °C. These measurements of M_s and V_g are shown in Table 5. Figure 3, therefore, shows the calculated gravimetric filter mass concentration (M_s/V_g) emanating from Table 5. The error bars on the ethane data in Figure 3 denotes standard deviation derived from the repeat tests with ethane. It can be deduced from Table 5 that, for all the hydrocarbons pyrolysed, increasing temperature of the reactor from 1050 – 1350 °C resulted in an increase in the mass of soot collected (M_s) and a decrease in the corresponding volume of gas (V_g). The temperature increase in the reactor also led to the increase in the calculated soot mass concentration as shown in Figure 4 regardless of the unsaturation of the hydrocarbon. This trend of increasing soot mass concentration and a decrease in gas volume with temperature rise is in line with those reported previously in the literature [18,19].

It can also be seen from Table 5 and Figure 3 that the filter soot mass and mass concentration increased with increasing the degree of unsaturation from single-bonded ethane to double-bonded ethylene and to the triple bonded acetylene at temperatures of 1050 °C, 1150 °C and 1350 °C. Likewise, increasing mass concentration from single to double bond in the case of propane to propylene. This also corresponds to the increasing density and carbon to hydrogen ratio of the hydrocarbons (see Table 2). However, at a temperature of 1250 °C, ethane (single-bonded) and ethylene (double-bonded) generated practically the same soot mass concentrations, showing that at this test temperature, the existence of a double-bond was not considerable in deciding the rates at which soot is formed.

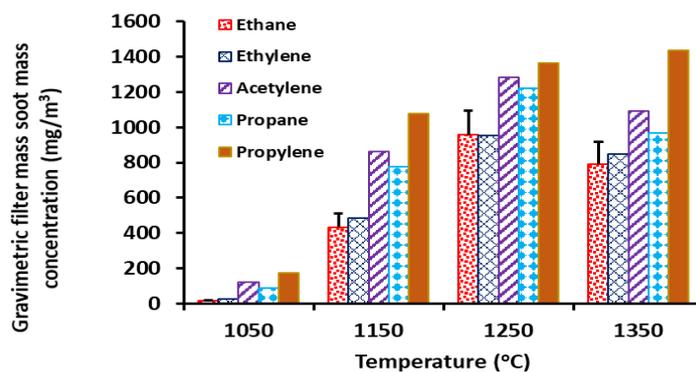


Figure 3: Gravimetric filter mass at different temperatures

Comparing ethane, ethylene, and acetylene, all having a carbon number of 2, it can be deduced from Figure 3 that pyrolysis of acetylene (triple-bonded) increased the soot formation considerably in comparison to ethane (single-bonded) and ethylene (double-bonded). For example, the soot mass concentrations measured in pyrolysis of acetylene at the initial temperature of 1050 °C were, approximately, 7 and 5 times those for ethane and ethylene respectively. These observations are supported by the works of other investigators. For instance, in a similar tube reactor, Ruiz *et al.*, [20] studied ethylene and acetylene pyrolyses within the temperature range of 1000 – 1200 °C. Ruiz *et al* reported that the concentration of soot recorded from triple-bonded acetylene was significantly in excess of that from double-bonded ethylene pyrolysis at all test temperatures.

Similar observations can be made from Figure 3 between single-bonded propane and double-bonded propylene, each of the same carbon number of 3. Propylene generated a much higher amount of soot when compared to propane at all test temperatures. This trend was explained by Dandajeh *et al.* [12] that propylene is a C₃ hydrocarbon that could generate propargyl radicals (C₃H₃) during its pyrolysis [21]. These radicals are key in accelerating PAH growth and subsequent production of incipient soot [3]. Significant soot formation for propylene over propane was also described by Wang and Chung [22] in diffusion flames. From Table 5 and

Figure 3, it can be finally deduced that the propensity of a hydrocarbon to soot increases when the degree of unsaturation and carbon to hydrogen ratio increases.

3.2 Effect of unsaturation on soot particle characteristics

Figure 4 shows the size distribution of soot particles (on number basis) produced from pyrolysis of the five hydrocarbons as measured with the DMS 500 instrument. Figures 4a, b, c and d show the size and number spectra for the five hydrocarbons at temperatures of 1050, 1150, 1250, and 1350 °C respectively.

It can be seen from Figures 4a, b, c, and d that the soot particle size spectra shifted toward larger sizes of soot particles with increasing pyrolysis temperature from 1050 to 1350 °C irrespective of the degree of unsaturation of the fuels, but ethylene pyrolysis was an exception. For example, pyrolysis of ethane at a temperature of 1050 °C resulted in particles with size range between 13 to 86 nm, whereas at the higher temperature of 1350 °C, particles were distributed, predominantly, in the size range of 86 to 562 nm. As the degree of unsaturation of the hydrocarbons was increased, it appeared in Fig.4 that the ranges of soot particle sizes also become broader regardless of the pyrolysis temperature.

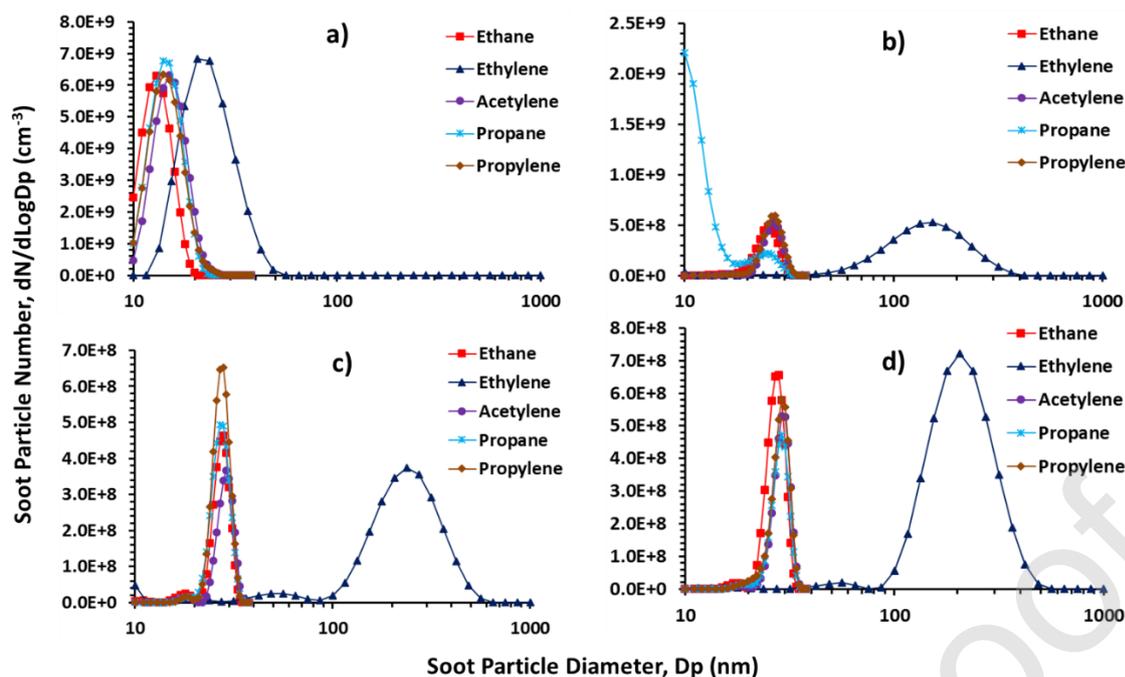


Figure 4: Soot number distribution of particles produced from the pyrolysis the five hydrocarbons at 4 different temperatures a) 1050 °C b) 1150 °C c) 1250 °C d) 1350 °C

Similar observations of broadening particle size range with temperature increase have been reported by Eveleigh, (2015) using a similar tube reactor during pyrolysis of ethane, ethylene and ethanol. From figures 4a, b, c, and d as a whole, there appeared to be a massive decrease in the soot particle number concentration when the pyrolysis temperature was raised from 1050 (Figure 4a) to 1350 °C (Figure 4c) primarily by the reason of faster agglomeration of soot particles at high temperatures.

Figure 5 summarises the DMS data for the five hydrocarbons in terms of effect of temperature on soot particle mean diameter (SPMD) (5a), soot mass concentration (SMC) (5b) per unit volume of N₂ carrier gas and soot particle number concentration (SPNC) (5c).

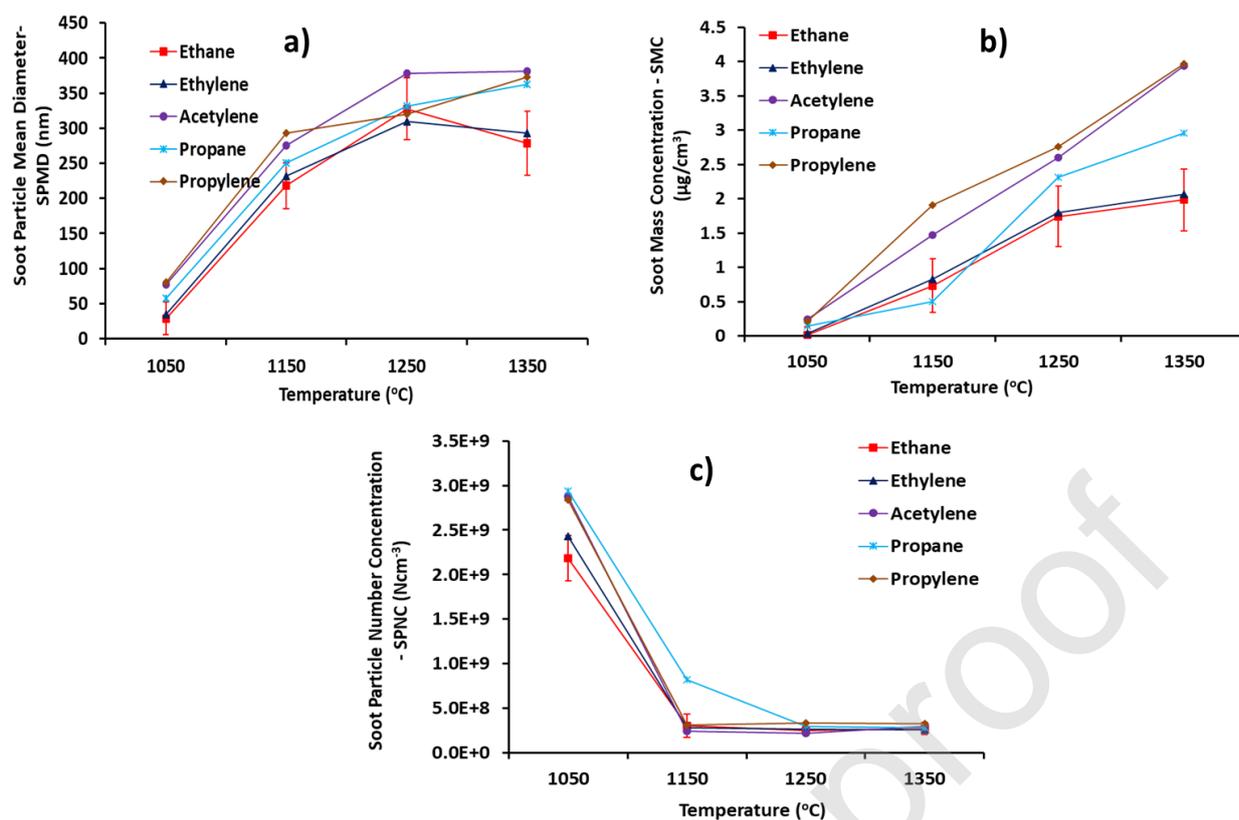


Figure 5: Temperature Variations of soot particles produced from pyrolysis of the five hydrocarbons with a) Soot particle mean diameter - SPMD (nm) b) soot mass concentration – SMC ($\mu\text{g}/\text{m}^3$) c) soot particle number concentration - SPNC (cm^{-3})

Figure 5a shows that the soot particle mean diameter increased with temperature increase, irrespective of the unsaturation of the hydrocarbon. It is apparent from Figure 5a that the average soot particle size of acetylene increases from 77 to 378 nm when the temperature increases from 1050 to 1350 °C and thereafter levelled-off up to 1350 °C. A similar observation can be made in the same temperature range of 1050–1350 °C, for ethane and ethylene in terms of trends, although the particle size range was somewhat lower at 40 to 305 nm. Apparent from Figure 5a is the trend for larger soot particle mean diameter with an increase in the degree of unsaturation of the five hydrocarbons within the temperature range of 1050 to 1150 °C. For instance, at the temperature of 1050 °C, the mean soot particle size increased from 29 nm to 34 nm and to 77 nm when the degree of unsaturation was increased from ethane to ethylene and to

acetylene, respectively. In Figure 5a, propylene formed slightly bigger soot particles than propane within the temperature range of 1050 to 1250 °C.

Comparing Figure 5b and Figure 3, similar variations can be observed for the degree of unsaturation of the five hydrocarbons for soot particle mass concentrations respectively measured by the DMS 500 and gravimetric filter mass concentration measurements at all temperatures. Figure 5c shows that the soot number concentrations of ethane, ethylene and acetylene increased with increasing unsaturation of the fuels only at a temperature of 1050 °C. Ethane, ethylene, and acetylene can be observed from Figure 5c to have approximately the same particle number in the temperature range of 1150 to 1350 °C regardless of the unsaturation of the hydrocarbon. This result suggests that within this temperature range, soot particle agglomeration may not be dependent on the fuel molecular structure. Increasing unsaturation from propane to propylene decreased the total number concentration within the temperature range of 1050 to 1350 °C.

Considering now Figures 5a and c together, it is clear that as the pyrolysis temperature was increased from 1050 to 1350 °C, the particles became bigger (Figure 5a – larger diameter) and also the total number of particles became fewer (Figure 5c – smaller particle number), irrespective of the degree of unsaturation of the fuels. This trend can be attributed to the primary particles agglomerating into larger, fewer, particles of several hundred nm in size [24],[25] as the reactor's temperature was raised.

Therefore, from Figure 5, it could be summarised that as the temperature was increased, the particles agglomerated into fewer bigger particles, but with the bigger particles still growing, with the target that the total mass of the particles increases. So, although agglomeration yielded fewer bigger particles, the fewer particles continued to grow through agglomeration but also new soot deposition on them.

Figure 5c also shows that this observation applies mainly to the temperature increase from 1050 to 1150 °C, beyond which soot particle agglomeration may be less significant within the temperature range of 1150 to 1350°C. Nevertheless, Figure 5a shows that in the temperature range of 1150 to 1350 °C, agglomeration may have ceased, but particle growth continues through new soot deposits on the particles already formed.

Figures 5a, b and c showed that the total soot mass concentration measured by the DMS-500 is influenced by the larger soot particle sizes of a smaller number, than the much smaller particles of smaller sizes. It is also important to note that changing the bond of the hydrocarbons shown in Table 1 from single to double and to triple bonds, increases the propensity of the hydrocarbons to produce soot particles of bigger sizes.

3.3 Effect of unsaturation on soot particle carcinogenicity

3.3.1 PAHs adsorbed on soot particles

Fig.6 shows the particle-phase PAH concentrations found by summing-up the total 16 PAHs (see Table 1) extracted from the surfaces of the soot particles of the hydrocarbons examined. Complete characterisation of these PAHs have been presented in the supplementary material and was discussed more extensively in [12]. Fig.6a and b show particle-phase PAH concentration normalised with gas volume and soot mass, respectively. It is obvious that at the lowest temperature of 1050 °C, both figure 6a and b show a high concentration of PAHs for all the hydrocarbons and this concentration, decreased markedly when the pyrolysis temperature was raised to 1350 °C. This trend is consistent with those shown in Fig.5c of soot particle number concentration with rising pyrolysis temperature to 1350 °C. The trend was based on the increased agglomeration of soot particles, leading to fewer but larger particles of reduced surface area [12]; so lower PAH concentration was found on those larger soot particles.

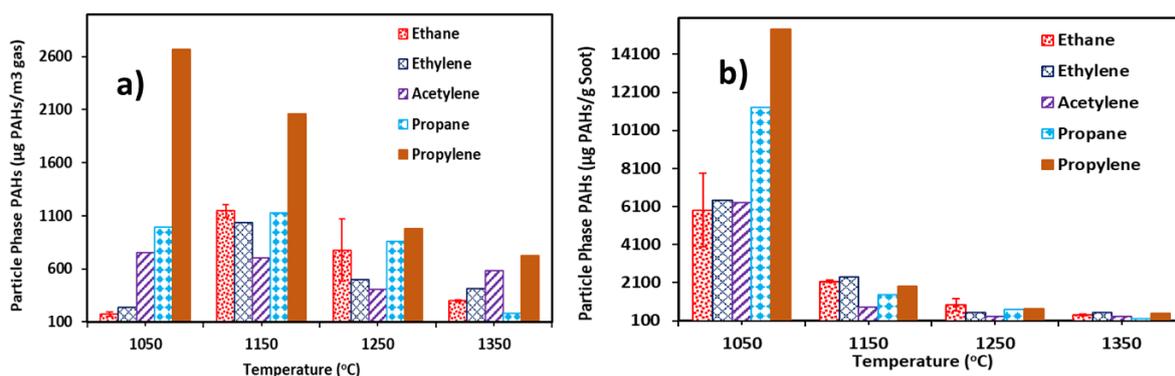


Fig.6: particle phase PAHs concentration a) normalised with gas volume ($\mu\text{g PAHs/m}^3$ of gas) b) normalised with soot mass ($\mu\text{g PAHs/g}$ of soot)

For example, it was found with the DMS 500 particle size spectrometer that at the lowest temperature of 1050 °C, the surface area of the soot particles normalised with the volume of gas was considerably high for ethane pyrolysis ($6 \times 10^{12} \mu\text{m}^2\text{m}^{-3}$ of soot) and this soot area onto which the PAHs were adsorbed decreased substantially to $7 \times 10^8 \mu\text{m}^2\text{m}^{-3}$ with rising pyrolysis temperature to 1350 °C. It can also be observed from Fig.6 that increasing the unsaturation of the hydrocarbons examined increased their propensity of producing soot with notably adsorbed PAHs. For example, it can be deduced from Fig.6a that the particle phase PAH concentrations for ethane (single-bond) at the temperature of 1050°C is 173 μg of PAHs/ m^3 of gas and this PAH concentration increased by 38% and 333% when the degree of unsaturation was increased respectively, to double-bond for ethylene and triple-bond for acetylene. A similar trend can be seen in Fig.6a for propane and propylene. It can be observed from Fig.6a that the particle phase PAH concentrations for propane (single-bond) at a temperature of 1050°C is 996 μg of PAHs/ m^3 of gas and the concentration increased by 168% for propylene (double-bond).

3.3.2 soot particle carcinogenicity

This section presents the relationship between the soot particle characteristics (mass, size, and number) and the potential carcinogenic equivalent sum of soot particles at four different temperatures (1050, 1150, 1250 and 1350°C). The carcinogenic equivalent sum of PAHs (CES-PAHs) adsorbed on soot particles is defined in equation 2. CES-PAHs is the sum of the product of concentration (C_i) of each of the EPA16 priority PAHs on each soot particle sample and the corresponding toxicity equivalent factors (TEFs) of the PAHs. The TEFs adopted are shown in Table 1 and were those proposed by Nisbet and Lagoy [26]. These factors are widely used by investigators worldwide to assess the toxicity of PAHs. The CES-PAHs has a unit of concentration, since TEF is a dimensionless relative factor.

$$\text{CES - PAHs adsorbed on soot particles} = \sum_{i=1}^{16} (\text{TEF}_i * C_i) \quad 2)$$

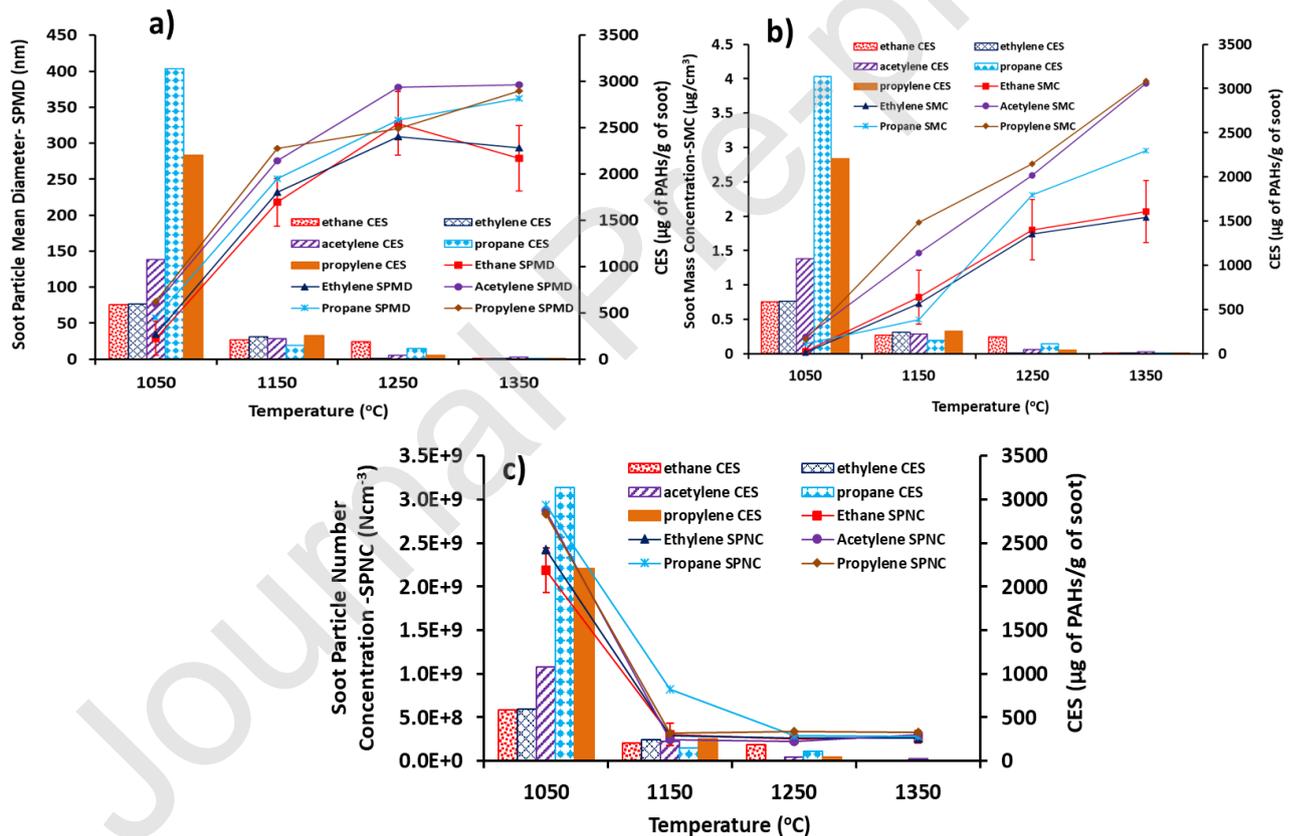


Figure 7: Interdependence of carcinogenic equivalent sum (CES) during acetylene pyrolysis at temperature range of 1050 – 1350 °C with a) Soot particle mean diameter - SPMD (nm) b) soot mass concentration – SMC ($\mu\text{g}/\text{m}^3$) c) soot particle number concentration - SPNC (cm^{-3}).

Figures 7a, b and c show the variation of carcinogenic equivalent sum (CES) with temperature, of soot particle mean diameter (SPMD), soot mass concentration (SMC) and soot particle number concentration (SPNC) respectively. Figure 7 designates these variations in the case of pyrolysis of the five hydrocarbons examined. Figure 7a, b and c show on the secondary axis that increasing pyrolysis temperature from 1050 – 1350°C of the hydrocarbons investigated lead to the decrease in CES of PAHs adsorbed on soot particles. While Figure 7a shows that the CES decreased with temperature increase, the soot particle mean diameter on the primary axis also increased with a rise in temperature. In other words, soot particles of smaller mean diameters (29 -77nm) bearing adsorbed PAHs have significant carcinogenic potential and these ultrafine particles are likely inhalable by humans [5], passing through the bloodstream. Fig.7a also shows that increasing the unsaturation of the hydrocarbons, especially from ethane to ethylene and to acetylene at a temperature of 1050°C also increased the CES. Figure 7b shows that while soot particle mass concentration increased due to increasing pyrolysis temperature of the reactor, there was also corresponding decrease in the CES of PAHs. That is, the carcinogenic potential of PAHs is higher on soot particles of lower mass concentrations. However, Figure 7c shows a decreasing trend of both CES of PAHs and soot particle number concentrations with increasing pyrolysis temperature. That is, while the particle size increase (see Figure 7a) and particle number decrease (see 7c) due to agglomeration, the carcinogenic potential of soot particles carrying PAHs also decreased. These results further confirm that a high number of ultrafine particles (soot particles of high SPNC) could potentially pose allergic inflammations of the lungs [27] and cardiovascular disease [28] than fewer numbers of large coarse particles (soot particles of high SPMD).

4.0 CONCLUSIONS

- Increasing unsaturation of fuels from single to double and to triple bonds increased the soot mass concentration, soot particle size, soot number concentration, particle phase PAHs and soot particle carcinogenicity particularly at the initial temperature of 1050°C.
- As the degree of unsaturation of the hydrocarbons was increased, it was also observed that the ranges of soot particle mean diameter become broader and bigger regardless of the pyrolysis temperature.
- Increasing the pyrolysis temperature of the reactor from 1050°C – 1350°C, increased the soot mass concentration and soot particle size while the soot particle number concentration, soot surface area concentration, particle-phase PAHs and associated soot carcinogenicity decreased substantially.
- There was a positive correlation between the soot particle number concentration and the corresponding soot particle carcinogenicity, while a negative correlation was observed between the soot particle mass and size with soot particle carcinogenicity regardless of the pyrolysis temperature examined
- The decreasing trend of PAH concentration and associated soot carcinogenicity with rising temperature was believed to be due to the increased agglomeration of soot particles, leading to fewer but larger particles of reduced surface area

- The potential implication of these observations is that, low-temperature combustion (LTC) applications, aimed at reducing emissions of soot and NO_x, could produce higher soot particle number concentration of higher carcinogenicity

CRedit author statement

Hamisu Adamu Dandajeh, Nicos Ladommatos and Paul Hellier: Conceptualization, Methodology. **Hamisu Adamu Dandajeh:** formal analysis, investigation. **Hamisu Adamu Dandajeh, Nicos Ladommatos:** Data Curation, Resources, writing—original draft preparation. **Hamisu Adamu Dandajeh, Nicos Ladommatos and Paul Hellier:** writing—review and editing. **Nicos Ladommatos and Paul Hellier:** supervision

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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References

- [1] S. Sanyal, T. Rochereau, C.N. Maesano, L. Com-ruelle, I. Annesi-maesano, Long-Term Effect of Outdoor Air Pollution on Mortality and Morbidity: A 12-Year Follow-Up Study for Metropolitan France, (2018) 1–8. <https://doi.org/10.3390/ijerph15112487>.

- [2] D. Liang, L. Shi, J. Zhao, P. Liu, J. Schwartz, S. Gao, J. Sarnat, Y. Liu, S. Ebel, N. Scovronick, H. H. Chang Urban Air Pollution May Enhance COVID-19 Case-Fatality and Mortality Rates in the United States, (2020).
- [3] H. Richter, J.. Howard, Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways, 2000. [https://doi.org/10.1016/S0360-1285\(00\)00009-5](https://doi.org/10.1016/S0360-1285(00)00009-5).
- [4] H.A. Dandajeh, M. Talibi, N. Ladommatos, P. Hellier, Influence of Combustion Characteristics and Fuel Composition on Exhaust PAHs in a Compression, *Energies*. (2019) 1-19. <https://doi:10.3390/en12132575>
- [5] P.S. Pedersen, J. Ingwersen, T. Nielsen, E. Larsen, Effects of fuel, lubricant, and engine operating parameters on the emission of polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.* 14 (1980) 71–79. <https://doi.org/10.1021/es60161a011>.
- [6] D.W. Dockery, C. A I. Pope, Acute respiratory effects of particulate air pollution, *Ann.Rev.Public Heal.* 15 (1994) 107–132.
- [7] A M. Gowers, B.G. Miller, J.R. Stedman, Estimating Local Mortality Burdens associated with Particulate Air Pollution, 2014. http://www.hpa.org.uk/webc/HPAwebFile/HPAweb_C/1317141074607.
- [8] H. Richter, W.J. Grieco, J.B. Howard, Formation mechanism of polycyclic aromatic hydrocarbons and fullerenes in premixed benzene flames, *Combust. Flame.* 119 (1999) 1–22. [https://doi.org/10.1016/S0010-2180\(99\)00032-2](https://doi.org/10.1016/S0010-2180(99)00032-2).
- [9] J. Nriagu, E.A. Udofia, I. Ekong, G. Ebuk, Health Risks Associated with Oil Pollution in the Niger Delta , Nigeria, *Int. J of Env. Res. and Pub. Health.* (2006) 1–23. <https://doi.org/10.3390/ijerph13030346>.

- [10] H.A. Dandajeh, Effect of molecular structure of liquid and gaseous fuels on the formation and emission of PAHs and soot, PhD Thesis Submitted to the University College London (UCL) (2018).
- [11] N.E. Sánchez, Á. Millera, R. Bilbao, M.U. Alzueta, Polycyclic aromatic hydrocarbons (PAH), soot and light gases formed in the pyrolysis of acetylene at different temperatures: Effect of fuel concentration, *J. Anal. Appl. Pyrolysis*. 103 (2013) 126–133. <https://doi.org/10.1016/j.jaap.2012.10.027>.
- [12] H.A. Dandajeh, N. Ladammatos, P. Hellier, A. Eveleigh, Effects of unsaturation of C₂ and C₃ hydrocarbons on the formation of PAHs and on the toxicity of soot particles, *Fuel*. 194 (2017) 306–320. <https://doi.org/10.1016/j.fuel.2017.01.015>.
- [13] H.A. Dandajeh, N. Ladammatos, P. Hellier, A. Eveleigh, Influence of carbon number of C₁ – C₇ hydrocarbons on PAH formation, 228 (2018) 140–151. <https://doi.org/10.1016/j.fuel.2018.04.133>.
- [14] J. Mei, X. You, C.K. Law, Effects of CO₂ on soot formation in ethylene pyrolysis, *Comb. Flame* 215 (2020) 28–35. <https://doi.org/10.1016/j.combustflame.2020.01.015>
- [15] K. Kashiwa, M. Arai, Y. Kobayashi, Oxygen effect on PAH and PM formation in low temperature benzene pyrolysis, *Fuel*, 262 (2020). <https://doi.org/10.1016/j.fuel.2019.116429>
- [16] P. Glarborg, M. Østberg, J.T. Johannessen, H. Livbjerg, A.D. Jensen, T.S. Christensen, Formation of polycyclic aromatic hydrocarbons and soot in fuel-rich oxidation of methane in a laminar flow reactor, 136 (2004) 91–128. <https://doi.org/10.1016/j.combustflame.2003.09.011>.
- [17] EPA Method TO, Method TO-13A: Compendium of Methods for the Determination of

- Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-13A Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography / Mass Spectrom, Epa. (1999).
- [18] M.P. Ruiz, A. Callejas, A. Millera, M.U. Alzueta, R. Bilbao, Soot formation from C₂H₂ and C₂H₄ pyrolysis at different temperatures, *J. Anal. Appl. Pyrolysis*. 79 (2007) 244–251. <https://doi.org/10.1016/j.jaap.2006.10.012>.
- [19] O. Mathieu, G. Frache, N. Djebaili-Chaumeix, C.E. Paillard, G. Krier, J.F. Muller, F. Douce, P. Manuelli, Characterization of adsorbed species on soot formed behind reflected shock waves, *Proc. Combust. Inst.* 31 I (2007) 511–519. <https://doi.org/10.1016/j.proci.2006.07.190>.
- [20] M.P. Ruiz, A. Callejas, A. Millera, M.U. Alzueta, R. Bilbao, Soot formation from C₂H₂ and C₂H₄ pyrolysis at different temperatures, *J. Anal. Appl. Pyrolysis*. 79 (2007) 244–251. <https://doi.org/10.1016/j.jaap.2006.10.012>.
- [21] K. Norinaga, O. Deutschmann, Detailed Kinetic Modeling of Gas-Phase Reactions in the Chemical Vapor Deposition of Carbon from Light Hydrocarbons, *Ind. Eng. Chem. Res.* 46 (2007) 3547–3557. <https://doi.org/10.1021/ie061207p>.
- [22] Y. Wang, S.H. Chung, Effect of strain rate on sooting limits in counterflow diffusion flames of gaseous hydrocarbon fuels: Sooting temperature index and sooting sensitivity index, *Combust. Flame*. 161 (2014) 1224–1234. <https://doi.org/10.1016/j.combustflame.2013.10.031>.
- [23] A. Eveleigh, The influence of fuel molecular structure on particulate emission investigated with isotope tracing, PhD Thesis Submitted to the University College London (UCL) (2015).

- [24] Heywood, J.B, *Internal Combustion Engine Fundamentals*, 39. Mcgraw-hill New York, 1988.
- [25] R.J. Samson, G.W. Mulholland, J.W. Gentry, Structural Analysis of Soot Agglomerates *, *Langmuir* (1987) 272–281. <https://doi.org/10.1021/la00074a022>.
- [26] I.C.T. Nisbet, P.K. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regul. Toxicol. Pharmacol.* 16 (1992) 290–300. [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X).
- [27] F. Alessandrini, H. Schulz, S. Takenaka, Effects of ultrafine carbon particle inhalation on allergic inflammation of the lung, *J Allergy and Clin Immunol.* (2006) 824–830. <https://doi.org/10.1016/j.jaci.2005.11.046>.
- [28] D.I. Stefano, V. Conti, E. Graziani, A. Petroianni, Air pollution ultrafine particles : Toxicity beyond the lung, *European Review for Medical and Pharmacological Sciences.* (2010) 809–821.

Table 1: The 16 PAHs with their degree of toxicity [4]

Sn	PAHs	Carcinogenicity Group	Toxicity Factor	Molecular Weight(g/mole)	Structure
1	Naphthalene	D	0.001	128	
2	Acenaphthylene	D	0.001	152	
3	Acenaphthene	NA	0.001	154	
4	Fluorene	D	0.001	166	
5	Phenanthrene	D	0.001	178	
6	Anthracene	D	0.01	178	
7	Fluoranthene	D	0.001	202	
8	Pyrene	NA	0.001	202	
9	Benzo[a]anthracene	B2	0.1	228	
10	Chrysene	B2	0.01	228	
11	Benzo[b]Fluoranthene	B2	0.1	252	
12	Benzo[k]Fluoranthene	B2	0.1	252	
13	Benzo(a)pyrene	B2	1.0	252	
14	Indeno[1,2,3-cd]pyrene	B2	0.1	276	
15	Dibenzo[a,h]anthracene	B2	1.0	278	
16	Benzo[g,h,i]perylene	D	0.01	276	

Group B2 are 'possibly carcinogenic to humans' while Group D are 'unclassifiable as to carcinogenicity' NA –

Not available.

Table 2: Properties of the test hydrocarbons at 1.013 bar and 15 °C [12].

Sn	Fuel Molecules	Molecular Structure	C/H	Bond Type	Carbon number	Boiling point(°C)
1	Ethane	$\text{H}_3\text{C}-\text{CH}_3$	0.33	single	2	-88.6
2	Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	0.5	double	2	-103.7
3	Acetylene	$\text{HC}\equiv\text{CH}$	1	triple	2	-84.7
4	Propane	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$	0.375	single	3	-42.1
5	Propylene	$\text{H}_3\text{C}-\text{CH}=\text{CH}_2$	0.5	double	3	-47.6

Table 3: ASE optimised conditions for PAH extraction [13]

Accelerated Solvent Extraction (ASE)	
ASE (Dionex-150, Thermo-Scientific)	
Solvent = Dichloromethane (20 mL)	
Duration for single extraction = 15 min	
Temperature	125 °C
Pressure	1500 bar
Static Cycle	1 (at 5 min)
Extraction Cell	10 mL
Purge Time	60 s
Rinse Volume	40 %
Extraction Repeats	3
Final Volume of Extracts	60 mL

Table 4: Optimised conditions for GCMS analysis [13]

Gas Chromatography Mass Spectrometry (GC- MS)

GC (7890B GC), MSD (5977A)

Column (HP-5; 30 m x 250 μ m x 0.25 μ m)

Total Sample Run Time = 33 min

Ramp rate ($^{\circ}$ C/min)	Temperature ($^{\circ}$ C)	Hold -Time (min)
-	50	1
25	150	1
25	200	1
3	230	1
8	310	3

Carrier Gas = Helium at 1.2 L/min, Inlet temperature = 300 $^{\circ}$ C)

MS Source = 230 $^{\circ}$ C, MS quad =150 $^{\circ}$ C, Transfer line = 290 $^{\circ}$ C

Table 5: Filter measurements of soot mass (M_s) and gas volume (V_g) of the hydrocarbons

T (°C)	Ethane		Ethylene		Acetylene		Propane		Propylene	
	M_s (mg)	V_g (m ³)								
1050	5.1	0.319	8	0.311	36.3	0.305	31.4	0.356	45.9	0.265
1150	75	0.173	84.6	0.174	142.4	0.165	146.3	0.189	202	0.187
1250	153	0.16	155.4	0.163	202.6	0.158	202.9	0.166	221.4	0.162
1350	124	0.156	135	0.16	169.3	0.155	157.5	0.163	222.6	0.155