The effect of poly(oxymethylene) dimethyl ethers (PODE₃) on soot formation in ethylene/PODE₃ laminar coflow diffusion flames

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Abstract

This paper investigates the effect of poly(oxymethylene) dimethyl ether (PODE₃) on soot formation in atmospheric pressure ethylene/PODE₃ laminar coflow diffusion flames. The flames were fuelled using ethylene/PODE₃ mixtures, where up to 20% of the total carbon in the mixture was substituted with $PODE_3$. Flame temperature measurements suggest that differences in the soot formation in the flames are more likely due to a chemical effect rather than a temperature effect. Colour ratio pyrometry and differential mobility spectrometry were used to measure the soot volume fraction (SVF) and the particle size distribution (PSD) of the flames. $PODE_3$ was observed to be effective in reducing soot formation due to its high oxygen content and the absence of carbon-carbon bonds as per previous engine studies. However, for the laboratory flames studied in this work, it was observed that introducing low levels of PODE₃ actually increased the amount of soot. When PODE₃ was blended with ethylene at 5%, there was an increase of about 10% in the SVF and about 6% in average particle size compared to the pure ethylene flame. Consideration of the chemical pathways suggests that this interaction is specific to C2 chemistry. Only when the amount of PODE₃ was increased to 10% did the SVF decrease. A further increase in PODE₃ to 20% was observed to inhibit the particle growth, with the maximum average particle size decreasing by about 73%. The results suggest that blending sufficient amounts of $PODE_3$ with fuels could reduce soot formation, but that the use of too little PODE₃ could increase soot formation in the cases of fuels that produce a substantial amount of C2 species in fuel-rich regions of an engine. The data set reported with this paper includes, for the first time, PSD data for the International Sooting Flame Workshop coflow laminar diffusion flame (ISF-4 coflow 3).



Highlights

- Soot formation investigated in ethylene/PODE₃ laminar diffusion flames
- Increasing PODE₃ showed non-monotonic trend in soot volume fraction (SVF)
- SVF and average particle size increased with small addition of PODE₃
- · Fuel-specific pathways likely contribute to the difference in soot growth
- PSDs for ISF-4 ethylene coflow diffusion flame were reported for the first time

Contents

1	Intr	oduction	3	
2	Materials and methods			
	2.1	Laminar coflow diffusion flame	4	
	2.2	Flame temperature	5	
	2.3	Soot temperature and soot volume fraction	6	
	2.4	Soot particle size distribution	6	
3	Results and discussion			
	3.1	Visible flame lengths	8	
	3.2	Flame temperatures	9	
	3.3	Soot volume fraction and soot temperature	10	
	3.4	Particle size distribution	12	
	3.5	Effect of $PODE_3$ on soot formation	15	
4 Conclusions				
A	Appendix			
	Refe	erences	23	

1 Introduction

Rapidly rising energy demand has prompted much research into alternative energy resources for the transport sector [1, 2]. In addition, the use of fossil-based fuels for transport releases pollutants [3] such as soot and particulate matter (PM) [4, 5] which are detrimental for human health [6] and the environment [7, 8].

Despite the increasing market share of electric vehicles, the internal combustion engine is expected to remain relevant in the transportation sector for the foreseeable future [9–11]. This is particularly evident in the heavy and long-range ground, aviation and maritime transportation sectors, where electrification is difficult, leaving compression ignition (CI) engines as the near exclusive solution [12]. As part of efforts to reduce the impact of CI engine technology, it is necessary to search for alternatives to fossil diesel fuels to ensure energy security and reduce pollution [13–16].

A simple yet attractive strategy to decrease the use of fossil-based fuels and achieve cleaner combustion in CI engines is to blend bio-based alternative fuels (biofuels) with fossil-based fuels [17]. Poly(Oxymethylene) Dimethyl Ethers (CH₃O(CH₂O)_nCH₃, $n \ge 1$), referred to as PODE_n, have been identified as a biofuel additive for CI engines that can be sourced from biomass or CO₂ capture, making them a promising alternative fuel [18]. The molecular structure PODE₃ is shown in **Figure 1**.



Figure 1: Molecular structure of PODE₃.

PODE_n have high cetane numbers and physio-chemical properties (*e.g.* viscosity, flash point and boiling point) that are close to those of diesel. In addition, PODE₃₋₅ have been shown to be able to be used in CI engines, either neat or blended with diesel, and are of significance interest in the context of current alternative fuel research [19]. The PODE_n-diesel blends require minimal modification to standard CI engines and have been shown to achieve significant reduction in soot, NO_x, hydrocarbons and CO emissions [20, 21]. Barro et al. [22] have even reported that neat PODE_n can be used in a diesel engine with exhaust gas recirculation to meet EURO 6 emissions limits for NO_x and PM emissions.

The soot reducing effect of PODE_n observed in engines is often attributed to the absence of carbon-carbon bonds and the high percentage of oxygen content (*ca.* 50% by mass) in the PODE_n. The effect of these two factors has been investigated using dimethyl ether (DME) under both premixed [23–25] and non-premixed [24, 26–31] conditions. DME is essentially PODE₀, a PODE_n monomer, and has a high oxygen content (*ca.* 35% by mass). The isomeric effect of DME and ethanol has been studied using laminar coflow diffusion flames with up to 9 mol% of the additives [27]. Both DME/ethylene and ethanol/ethylene fuel mixtures exhibited synergistic effects in soot formation, where both mixtures produced more soot than pure ethylene. Based on species measurements, it was concluded that the rate of formation of propargyl radicals ($^{\circ}C_3H_3$) was enhanced due to the presence of methyl radicals ($^{\circ}CH_3$) from the oxygenated fuels. This enhanced the rate of formation of benzene via propargyl self-recombination [27]. The choice base fuel plays an important role in this synergistic effect. Yoon et al. [28] studied the effect of the base fuel by mixing DME with methane, ethane, propane and ethylene. They only found a synergistic effect on soot formation with ethylene, where they observed a 25% increase in soot volume fraction at 10 vol% blending. Methane, ethane and propane instead showed a monotonic decrease in soot formation when the proportion DME was increased, with propane showing up to 20% reduction in soot volume fraction at 10 vol% blending. It was proposed that the synergistic effect was a consequence of the interaction between the ethylene (which does not readily produce methyl radicals) and methyl radicals from the DME, leading to enhanced benzene formation via propargyl recombination. The synergistic effect is not seen with the other base fuels because they readily produce methyl radicals; increasing the proportion of DME leads to a reduction in soot formation because the DME is less sooting than the fuel it displaces. Comparison of studies under premixed and non-premixed conditions shows that the synergistic effect only occurs under non-premixed conditions [24–26], where there exist fuel-rich regions.

The production of soot by the combustion of $PODE_n$ in engines has been the topic of several studies [32–34], but the composition of the soot varies with both the type and operating parameters of the engine. This makes it is difficult to evaluate the emission properties of $PODE_n$ from engine studies alone. Laboratory studies using flames offer a controlled environment to study the emissions from the combustion of $PODE_n$. Laminar diffusion flames are of particular interest because they allow the controlled investigation of the chemistry occurring in fuel-rich regions, which is relevant to full-scale practical combustion devices such as gas turbines, furnaces and internal combustion engines [35]. Initial work in this direction has investigated the sooting propensity of $PODE_n$ -diesel blends using a smoke point lamp [36]. The dilution of the fuel with the $PODE_n$ was shown to have an important effect on the reduction of $PODE_n$ has not yet been investigated using a laminar coflow diffusion flame burner. Such burners enable better control of the flame, enabling more insight into the effect of $PODE_n$ in soot formation.

The **purpose of this paper** is to understand the link between the molecular structure and sooting behaviour of $PODE_3$ when blended with ethylene fuel in a laminar coflow diffusion flame. The sooting behaviour is investigated via particle size distribution (PSD) and soot volume fraction measurements. The impact of the molecular structure of $PODE_3$, which like DME does not have any carbon-carbon bonds, on soot formation is critically assessed.

2 Materials and methods

2.1 Laminar coflow diffusion flame

Atmospheric-pressure laminar coflow diffusion flames were generated using a Yale coflow burner [37]. The Yale coflow burner was chosen because it is one of the accepted target flame platforms adopted by the International Sooting Flame Workshop (ISF) for the study of soot formation [38]. The burner has a central fuel tube with an inner diameter of 4.0 mm and a concentric coflow tube with an inner diameter of 74.0 mm, fitted with a stainless

steel honeycomb mesh (0.43 mm wall thickness, 18×18 mesh) for a laminar coflow of air. The movement of the Yale burner was performed by mounting it on a motorised Festo vertical translational stage, with a positioning accuracy of 0.1 mm.

In this study, four flames have been investigated, one of which was a pure ethylene flame and the other three of which were PODE₃-doped ethylene flames. PODE₃ was selected as the representative PODE_n because it has practical value as a fuel additive in CI engines [19] and kinetics studies are available to help interpret the sooting behaviour observed in the current investigation [39, 40]. The following naming convention has been adopted for this investigation: The fuel type is specified as 'E' (ethylene) or 'P' (PODE₃), followed by the percentage of carbon contributed to the fuel mixture. **Table 1** shows the fuel flow rates for the flames studied in this work, along with the visible flame lengths, which will be discussed further in **Section 3.1**.

Flame	C ₂ H ₄ flow rate (L _n /min)	PODE ₃ flow rate (g/h)	Visible flame length (mm)
E100	0.147	0.00	48.4 ± 0.3
P5	0.140	1.08	49.2 ± 0.4
P10	0.133	2.15	47.4 ± 0.3
P20	0.118	4.30	42.4 ± 0.1

Table 1: Flame conditions and visible flame lengths for the flames investigated.

The E100 base flame is an atmospheric pressure ethylene flame diluted with nitrogen (60% C_2H_4 : 40% N_2). It corresponds to the ISF-4 coflow 3 (Condition C) laminar diffusion flame that was identified as a target system for the study of soot formation at the International Sooting Flame (ISF) workshop in 2018 [38]. The PODE₃ was doped into the fuel in different proportions whilst maintaining a constant 0.79 g_c/h carbon flow rate and a constant 35 cm/s cold gas coflow velocity for all flames. The ethylene fuel, nitrogen and air flow rates were controlled by Bronkhorst EL-FLOW[®] Mass Flow Controllers. The gases were supplied from 99.99+% purity cylinders (ethylene, nitrogen) and an inhouse compressor (air). The PODE₃ was procured from ASG Analytik-Service GmbH in Germany with guaranteed purity of 95% and used without any purification. The PODE₃ was dosed via a New Era NE-500 syringe pump with dispensing accuracy of $\pm 1\%$. The liquid fuel was evaporated and mixed with the ethylene and carrier gas in an in-house nebuliser heated to 423 K. The fuel/carrier gas mixture was then fed to the burner via heated lines at 443 K. The flames were given 30 minutes to reach stability before performing any measurements.

2.2 Flame temperature

The flame temperature was measured using an uncoated Type-R thermocouple (Pt/Pt-13%R) with a wire diameter of 125 μ m. The constant-tension thermocouple design of

Cundy et al. [41] was used as a reference for the thermocouple holder. The thermocouple holder was mounted on a push-pull-action computer-controlled solenoid (RS Components, RS-533-7048), to perform fast insertion and withdrawal of the thermocouple into and out of the flame. Each temperature measurement was performed for 15 seconds in the flame. After each measurement at a given HAB, the thermocouple was moved to the flame tip to burn off any soot deposition. The temperature profile at each HAB was then extrapolated to t = 0 s to determine the thermocouple junction temperature, as detailed in the literature [42]. The gas temperature was then obtained by applying a suitable radiation correction to the thermocouple data [43].

2.3 Soot temperature and soot volume fraction

The soot volume fraction, f_v , and the soot temperature, T_{soot} were measured using colourratio pyrometry [44, 45]. The measurement system has been described in detail previously [45]. In brief, a Blackfly S colour camera (BSF-U3-32S4C-C, FLIP Integrated Imaging Solutions Inc.) was paired with a Thorlabs MVL25M23 Lens to image the flames. The camera was placed 250 mm from the flame at the same height as the flame. The assumption of parallel ray acquisition (orthographic imaging) was taken as a valid assumption given that the flame has a small radius of about 4 mm as compared to the camera which was 250 mm away [45].

A BG-7 filter from Thorlabs was used to balance the intensity ratios of the blue, green and red colour channels for the flame imaging [44]. For each flame, the captured images were then demosaiced and reconstructed, followed by the calculation of soot temperature and soot volume fraction through an in-house developed Python code [45] which is available online [46]. The calibration of the signal intensities as a function of soot temperature was based on the thermocouple measurements reported previously [45].

The fitting the line-of-sight projection of a predefined intensity distribution (FLiPPID) method was employed to perform the reconstruction of the images (Abel inversion) [45]. The benefits of the FLiPPID method are that it produces a smooth Abel inversion close to the flame centre-line and avoids non-physical negative light intensities [45]. Upon obtaining the soot temperature, the soot volume fraction for each flame was calculated as detailed in the literature [44]. The soot emissivity was assumed to vary as $\lambda^{-1.38}$ and the dimensionless extinction coefficient have a value of 8.6 as per [44].

2.4 Soot particle size distribution

The measurement of the soot particle size distribution (PSD) was performed using a DMS500 Differential Mobility Spectrometer from Cambustion Ltd. The experimental setup for the PSD measurement is shown in **Figure 2**. The flame was sampled using a quartz probe. The probe was based on the design by Hepp and Siegmann [47] and a similar design of probe has been used to extract samples from laminar coflow diffusion flames in other investigations [48, 49]. The probe was manufactured by Aachener Quarzglas-Technologie Heinrich GmbH & Co. KG, Germany. The tip of the probe has an inner diameter of 0.4 mm and outer diameter of 0.8 mm with a straight length of 3 mm, which

is deliberately short. The purpose of limiting the length of the tip is to minimise the residence time of the sample before mixing with the diluent to quickly cool the soot and combustion gases extracted from the flame, to quench post-sampling chemical reactions, to avoid water condensation and to limit particle aggregation. The main body of the probe has an outer diameter of 12 mm and an inner diameter of 8 mm. Full details of the probe are reported in the existing literature [42].



Figure 2: Quartz probe design and sampling setup for particle size measurements.

A nitrogen dilution flow of 7.8 L_n /min from the DMS500 mass flow controller was supplied to the side port of the quartz probe. The design of the probe is such that the dilution gas flows towards the tip of the probe through the annulus between the inside of the quartz probe and the outside of a stainless steel tube contained within the probe (see Figure 2). At the tip of the probe, the nitrogen flow draws in a sample from the flame and, together with the sample, flows inside of the stainless steel tube to the DMS500. Inside the DMS500, the sample is further diluted by a factor of 500 using a rotating disc diluter before it is analysed. The volume of the sample drawn into the probe can be controlled by adjusting a Swagelok needle valve located between the probe and the DMS500.

The dilution ratio as a function of the pressure drop for the sampling system was measured using a Cambridge Sensotec Rapidox 7100 multigas analyser, fitted with an electrochemical oxygen sensor capable of measuring oxygen concentrations from 0.1% to 30%. The calibration was performed by heating the quartz probe to flame temperature and adjusting the needle valve to vary the room-probe pressure difference from 25.0 mbar to 50.0 mbar to draw in different volumes of air. The oxygen concentration of the diluted sample was monitored using the oxygen sensor. Using this method, it was possible to calculate the dilution of the sample drawn into the probe as a function of ΔP at a certain dilution flow, which in this case was 7.8 L_n/min. This procedure for determining the dilution ratio is similar to procedures reported in the literature [50, 51].

In the current study, a room-probe pressure difference of $\Delta P = 30.0-35.0$ mbar was used to sample the flame. The pressure difference was measured using an Omega DPG 4000-15 digital pressure gauge. The pressure drop was chosen to minimise the flame perturbation while maintaining a first dilution ratio of at least 1200, and was sufficient to give reliable signal strength in the DMS500. The total dilution ratio (including the secondary dilution in the DMS500) in the current study was therefore at least 600,000, which is comfortably within the range suggested in the literature [47, 50, 51]. The PSD was measured and recorded for about 10 s at each height above the burner (HAB) at a rate of 10 Hz, averaged and corrected by the dilution ratio. Each flame measurement was repeated four times and error bars showing the standard error are reported to exemplify the reproducibility of the experiments.

3 Results and discussion

In this section, the experimental results from thermocouple measurements, colour ratio pyrometry and differential mobility spectrometry of the E100, P5, P10 and P20 flames are presented and discussed. The effect of $PODE_3$ on the soot formation observed in the experimental work is then explained through mechanisms for the decomposition of ethylene and PODE₃ under fuel rich conditions.

3.1 Visible flame lengths

The E100 base flame and the PODE₃-blended flames (P5, P10 and P20) were all slightly lifted, with the base of the flame located about 1.0 mm from the fuel tube. This minimises the impact of heat transfer from the flame to the fuel tube on the flame temperature profile [52]. **Figure 3** shows an image of each flame. The visible flame lengths were measured as the length from the fuel tube to the point where the soot incandescence from the flame ends, as viewed by the ImageJ software. The flame lengths averaged over five frames are reported in **Table 1**.



Figure 3: Visible flame lengths. The images were taken with the same exposure time (498 μ s), aperture opening (full opening) and colour balance ratio (red:blue = 1.0:2.6). The white line indicates the length of flame E100. The two red lines indicate the region in which the temperature measurements show a dip in the flame temperature. This dip will be explained in Section 3.2.

The E100 flame has a length of 48.4 mm, which agrees well with the reported flame length for the ISF standard [38]. Upon doping 5% of PODE₃, there was a slight increase in the visible flame height by about 1 mm and an elongated yellow luminescence zone compared to flame E100. This may be attributed to two factors: an increase in the fuel stream momentum, stemming from the larger mass of PODE₃ per unit mass of carbon (2.23 g/g_c) compared to ethylene (1.17 g/g_c) and an enhanced soot volume fraction (see Section 3.3) which resulted in longer survival time of the particles in the flame before being fully oxidised [29, 30].

At 10% and 20% PODE₃, the flame lengths were progressively shorter than that of flame E100. Notably, flame P20 was 6 mm shorter than flame E100. With increasing amounts of PODE₃ in the blends, there was a decrease in the soot loading (see Section 3.3), which translates to a decrease in the soot produced. Although the addition of PODE₃ increases the fuel stream momentum, above 5% fuel-carbon, the corresponding decrease in soot loading has a more prominent effect and thus the overall flame length is lowered.

3.2 Flame temperatures

Figure 4 shows the measured flame temperature in each flame. The data are presented in terms of a non-dimensional axial position (NDAP) to enable comparison of the effect of $PODE_3$ across all the flames. NDAP has been used in the literature to establish chemical species and temperature correlations between flames of different lengths [53, 54].



Figure 4: Radiation-corrected thermocouple temperatures measured along the centreline of the E100, P5, P10 and P20 flames as a function of non-dimensional axial position (NDAP). The error bars show the standard error over four measurements at each position. The coloured dotted lines at NDAP = 0.51–0.58 show the start of the dip in the temperature for each flame. The grey dotted line at NDAP = 0.78 shows the end of the dip, which is common across all flames.

The location of the maximum temperature was used to define NDAP = 1.0. Figure 4 shows that the maximum flame temperature is about 1900 K for each flames, within the experimental error of \pm 100 K and aligned at NDAP = 1.0. For flame E100, the experimental temperature profile and maximum temperature measured in the current study were consistent with measurements reported in the literature [55, 56]. Notably, there is a dip at in the range NDAP = 0.50–0.78 which is attributed to radiative heat loss due to soot deposition on the thermocouple in regions with high concentrations of soot. This dip has been observed in the literature [54, 57, 58].

The flame temperature profiles are similar across all flames, with the exception of a slightly higher temperature in the upper region of flame P20. This difference can be attributed to the significant reduction of soot generated in the flame P20, which results in a decrease in radiative heat loss. Overall, the addition of the PODE₃ has minimal effect on the flame temperature profiles. This suggests that the soot formation in the different flames is more likely due to a chemical effect of the fuel than a temperature effect.

3.3 Soot volume fraction and soot temperature

As the colour ratio pyrometry technique relies on the radiative emission from the flameheated soot particles, the soot temperature, T_{soot} , and soot volume fraction, f_v , measurements were only available at flame locations with detectable soot luminosity [59]. Figure 5 shows the spatial distribution of the measured soot volume fraction.



Figure 5: Soot volume fraction, f_v , distributions of the E100, P5, P10 and P20 flames measured using colour-ratio pyrometry. The grey dotted lines indicate the region of the flame with a dip in the flame temperature measurements observed in Figure 4.

The peak soot volume fraction of the E100 flame, located in the wings of the flame, was measured as 2.0 ppm, which is consistent with the value of 1.8 ppm measured by Smooke et al. [55] using laser-induced incandescence (LII). The maximum centre-line soot volume fraction was measured as 1.8 ppm, which is consistent with the value of 1.2 ppm measured by LII [60]. Qualitatively, the regions with the highest soot volume fraction are located along the centre-line and in the wings for all the flames investigated.

A non-monotonic trend in the soot volume fraction is observed with increasing PODE₃ content. Relative to the E100 flame, the maximum soot volume fraction increased by 10% to 2.2 ppm in the P5 flame, whereas it decreased by 5% to 1.9 ppm in the P10 flame and by 40% to 1.2 ppm in the P20 flame. This non-monotonic change of the soot volume fraction has also been observed with non-premixed DME/ethylene flames [24, 27–29] and is commonly known as the *synergistic effect*, which will be discussed further in Section 3.5. The current results show that the synergistic effect is also observed when using PODE₃ in place of DME. This observation is important because it shows that PODE₃, which is of active interest as a potential soot-reducing alternative fuel for use in diesel blends [32–34], will increase the concentration of soot if blended at low concentrations under non-premixed conditions.

Figure 6 shows the spatial distribution of the measured soot temperature. A non-monotonic trend is again observed with increasing PODE₃ content. Relative to the E100 flame, there is a 5% decrease in the maximum centre-line soot temperature of the P5 flame, as opposed to a progressive increase in the maximum centre-line soot temperature in the P10 and P20 flames. Notably, the P20 flame has the highest soot temperature profile amongst all the flames, approaching 2100 K at the flame wings. The lower soot temperatures in the P5 flame can be linked to an increase in the soot volume fraction (*i.e.* larger soot particles).



Figure 6: Soot temperatures of the E100, P5, P10 and P20 flames measured using colourratio pyrometry. The grey dotted lines indicate the region of the flame with a dip in the flame temperature measurements observed in Figure 4.

A direct comparison of the flame temperature measurements (see Section 3.2) and the soot temperature profile measurements should not be made because they represent different types of temperature. In brief, the flame temperature was measured from the heat released from exothermic reactions in the gas phase, whereas the soot temperature was determined from the radiative emission of the soot particles in the flame. The flame temperature measurement has strong discontinuity due to the dip in the region of NDAP = 0.50-0.78 which has been reported in the literature [54, 57, 58]. This dip is not seen in the pyrometry measurements on the centre-line in Figure 6 (grey dotted lines region). Nevertheless, it is worth pointing out that Figure 4 shows that the dip in flame temperature starts at about NDAP 0.50-0.58, an effect attributed to the soot deposition [54] and corresponds to the lower grey dotted lines in Figure 6. Meanwhile, the pyrometry measurements of the soot temperature first detect soot temperature on the centre-line at about HAB 25 mm in Figure 6, which is broadly consistent with the location of the lower grey dotted line in Figure 6 for each flame.

3.4 Particle size distribution

Figure 7 shows the average particle size along the centre-line of all the flames as function of non-dimensional axial position (NDAP). It is clear that amongst all the flames studied, the average particle size along the centre-line is largest in the P5 flame and smallest in the P20 flame. This once again clearly illustrates the synergistic effect of the PODE₃ in the P5 flame. For example, at NDAP = 0.61, the addition of PODE₃ results in approximately 6% increase in the average particle size in the P5 flame, but a 73% decrease in the average particle size at the same NDAP in the P20 flame. The raw PSDs are provided in **Appendix A**.



Figure 7: Average particle size for the E100, P5, P10 and P20 flames as a function of non-dimensional axial position (NDAP). The error bars show the standard error of the measurements over three repeats. The grey dotted lines indicate average particle sizes (and the corresponding values of NDAP) selected for further analysis.

To the best of the authors' knowledge, this is the first time that PSDs and average particle sizes have been reported for the ISF-4 coflow 3 (Condition C) laminar diffusion flame [38]. Hence, there are no comparable data for the current E100 flame.

The maximum average particle size follows the same trend. For flame P5, the maximum average particle size along the centre-line reaches 113 nm, 3 nm larger than for the E100 flame and the largest amongst the flames investigated. The maximum average particle size along the centre-line was 107 nm in the P10 flame and 92 nm in the P20 flame, indicating a progressive inhibition of the growth of the particles. Further discussion of this observed behaviour is provided in Section 3.5.

Figure 8 shows the PSD of each flame at non-dimensional axial positions (NDAP) corresponding to different given values of the average particle size. This is The largest size considered in the figure is 90 nm, which was chosen because the P20 flame has a maximum average particle size of about 92 nm at NDAP 0.95. At an average particle size of 15 nm, Figure 8(a), the PSDs were unimodal and the maximum detected particle size was



Figure 8: Particle size distribution (PSD) measured using DMS500 along the centre-line of the E100, P5, P10 and P20 flames. The error bars show the standard error of the measurements at each position over three repeats. The data are grouped by average particle size (a) 15 nm, (b) 30 nm, (c) 80 nm and (d) 90 nm. The non-dimensional axial position (NDAP) of the PSD data for each flame is reported in the legend.

less than 50 nm for all flames. As the average particle size increases, Figure 8(b)–(d), the PSDs progressively become bimodal. The first mode (nucleation mode) corresponds to measured particle sizes below 30 nm, while the second mode (accumulation mode) corresponds to measured particle sizes in the range 40–300 nm, with the maximum number density increasing in step with the average particle size used to group the data. At larger average particles sizes, only the accumulation mode is seen (see Figures SM1.1–SM1.3).

The PSDs in Figure 8 are remarkably similar at each given average particle size. Even with the addition of PODE₃, the shape of the PSDs and the particle number concentrations remained unaffected. These observations suggest that the nucleation and accumulation processes are unaffected by the difference in the fuel blends (at least when comparing particles on the basis of average size). On the other hand, the maximum average particle size attained in the flames changes non-monotonically with PODE₃ addition, implying an impact on the growth of the soot. A further discussion of this is presented in Section 3.5.

Figure 9 shows the PSD data grouped by NDAP. The point at which the PSD transitions from unimodal to bimodal differs for each flame. The P5 flame shows the earliest transition, as shown in Figure 9(a), where the start of the transition can just be observed at NDAP = 0.41. The start of the transition of the P10 flame can just be observed in Figure 9(b) at NDAP = 0.50 the P10 flame, by which time both the P5 and E100 flames show bimodal distributions, whilst the distribution in the P20 flame is still unimodal. Figure 9(c) shows that the PSDs for all the flames were bimodal By NDAP = 0.75. These observations suggest that soot formation progress differs between all the flames and again highlights the non-monotonic effect of the PODE₃ addition.



Figure 9: The particle size distributions (PSDs) for flame E100, P5, P10 and P20 at selected non-dimensional axial positions (NDAP). The error bars show the standard error of the measurements at each position over three repeats. The data are grouped by (a) NDAP = 0.41, (b) NDAP = 0.50 and (c) NDAP = 0.75.

Comparison of the PSD for the P20 flame in Figure 9(a) and (b) shows that the number concentration of particles in the first mode increases up to NDAP = 0.5. This increase suggests active nucleation in this region of the flame. Comparison of Figure 9(b) and (c), shows that the particle number concentration subsequently exhibits a characteristic decrease with further increase in NDAP. This is typically due to agglomeration of the smaller particles [61], where it has been shown experimentally by Sirignano and D'Anna [62] that these particles have a high effective coagulation efficiency. The data in Figure 9

for the E100, P10 and P20 flames all show this behaviour, whereas the number concentration for flame P5 has already reached a maximum by NDAP = 0.41 and the characteristic decrease already started by NDAP = 0.5. Figure 9(c) shows that the number concentration of the P5 flame is lower than for all of the other flames by NDAP = 0.75. This suggests that the 5% blend of PODE₃ induced earlier agglomeration and coagulation of the soot.

3.5 Effect of PODE₃ on soot formation

The importance of the fuel structure and the mechanisms that lead to benzene formation, and consequently the formation of soot, have been highlighted in the literature [63]. It is generally accepted that the formation of the first aromatic ring is the rate limiting step for the formation of polycyclic aromatic hydrocarbons (PAHs) and ultimately soot [17, 64–67]. For aliphatic fuels, a number of reactions involving C_3H_3 , C_4H_3 , C_4H_5 and C_5H_5 isomers have been considered as possible precursors to form the first aromatic ring [66–69]. Some important species that contributed to the pathways for benzene formation are resonance-stabilised radicals (RSRs), which include C_3H_3 , $i-C_4H_3$ and $i-C_4H_5$ [65, 70, 71]. These are key-species because radical-radical reactions can proceed quickly in flames [70]. In reality, not all reactions contribute equally to the formation of benzene and pathways involving RSRs are often deemed to be crucial pathways in understanding soot formation for different fuels [67]. The current discussion focuses on the C3 and C4 + C2 pathways.



Additional pathways that are available from PODE₃

Figure 10: Proposed decomposition mechanisms of ethylene and $PODE_3$ under fuel rich conditions. Ethylene combustion normally follow the C4 + C2 pathway. $PODE_3$ (and $PODE_n$) decompose to form CH_3 species, that react with the ethylene to activate the C3 pathway.

Figure 10 shows the proposed major reaction pathways leading to the formation of the first aromatic ring [40, 65, 70, 72, 73]. PODE₃ decomposes mainly into methyl radicals ($^{\circ}CH_3$) and formaldehyde (CH_2O) [40] at temperatures below 1000 K [39]. This corresponds to NDAP ≤ 0.2 on basis of the flame temperature profiles in Figure 4. Formaldehyde is then converted into formyl radicals ($^{\circ}CHO$) and finally to carbon monoxide (CO) via H-atom abstraction [74].

Large hydrocarbons such as those present in fossil-based fuels (diesel and kerosene) or surrogate fuels (*n*-heptane, *n*-decane, iso-octane, *n*-decane, methylcyclohexane, and toluene) decompose at flame temperatures into small species such as CH₄, C₂H₄ and C₃H₆ due to the low energy barrier of carbon-carbon β -scission of alkyl radicals [75–78]. For example, H₂, CH₄, C₂H₄, and C₃H₆ were found to form in abundance during the pyrolysis of n-dodecane, with ethylene (C₂H₄) being the dominant species [79]. These small species play an important role in the flame chemistry [77, 78]. In particular, ethylene is known to play a key role in soot formation. The C–H bond in ethylene can break leading to the formation of other C2 species [72, 73], whereas the scission of the ethylene C=C bond to form C1 species is unlikely because the bond energy of the C=C bond is much higher than that of the C–H bond (174 kcal/mol *vs* 111 kcal/mol) [80].

In order for benzene formation to occur via the C3 pathway in Figure 10, both C1 and C2 species must be present. In the E100 flame, the concentration of C1 species is insignificant compared to C2 and C4 species, both of which are abundant [69, 81]. The benzene formation in the E100 flame is therefore likely follow the C4 + C2 pathway. The pathway is proposed to involve four C4 species that are important in reactions with C2 species to form benzene [82]: n- \cdot C₄H₃ and i- \cdot C₄H₅, and n- \cdot C₄H₅. The *i*-isomers are RSRs which it is thought may contribute significantly to the pathways for benzene formation [65, 70]. Given that the *n*-isomers can easily convert to the *i*-isomers via H-atom-assisted isomerisation in the fuel rich regions of the current system [70, 81], benzene formation via the *i*-isomers may play a more significant role than via the *n*-isomers in the C4 + C2 pathway [83]. Nevertheless, there are still considerable uncertainties regarding the relative importance of the pathways involving these C4 radicals, specifically in an ethylene coflow diffusion flame [71].

The PODE₃ provides a source of C1 species in the P5, P10 and P20 flames, enabling concurrent benezene formation via the C3 pathway in Figure 10. The C_3H_3 RSR is the key species in this pathway [40, 65, 70]. We hypothesise that for aliphatic fuels, the C3 pathway has a high rate [72] and provides a crucial contribution to benzene formation in flames [70, 84, 85]. It is proposed that is this availability of C1 species and the consequent benzene formation via the C3 pathway, over and above that in the E100 flame, that is thought to be responsible for the synergistic increase in soot production in the P5 flame.

Another factor contributing to the synergistic effect in the P5 flame may be the oxygen introduced into the fuel stream by the PODE₃. The presence of O[•] radicals resulting from the decomposition of PODE₃ could induce the cleavage of the ethylene C=C bond to form C1 species including methyl radicals and species with C=O bonds [17, 86–88]. This could provide another route for the activation of the C3 pathway. However, consideration of the decomposition mechanism of PODE₃ [39] suggests that this is unlikely to make a significant contribution to the observed synergistic effect.

The soot volume fraction (Figure 5) and maximum average particle size (Figure 7) are observed to decrease as the level of PODE₃ is increased from the P5 to the P10 and P20 flames. This is interpreted as indicating a decrease in the rate of formation of benzene, despite the increase in the concentration of C1 species likely to result from the increased concentration of PODE₃. What makes this situation distinct from that described in relation to the P5 flame is that the C3 pathway is already open. It is apparent that the additional PODE₃ does not open this pathway further, or at least not to an observable extent. Further, given that the total carbon mass flow remains constant, the additional PODE₃ results in a decrease in the mass flow of C2 species supplied via the ethylene part of the fuel mixture. This is unfavourable in terms of benzene formation because both the C3 and C4 + C2 pathways are dependent on C2 species. It is additionally noted that most of the carbon content provided by the PODE₃ would be converted to carbon monoxide, which does not contribute to benzene formation [74]. The combination of these factors results in the lower soot loading observed in the P10 and P20 flames.

Despite the fact that the maximum average particle size (Figure 7) showed a significant decrease between the P5 and P10 flames and between the P10 and P20 flames, the PSDs at a given average particle size were observed to be independent of the fuel blend (Figure 8). This suggests that the PODE₃ affects the rate of *growth* of the soot particles, but not the nucleation and accumulation processes. The transition from unimodal to bimodal distributions was also observed to occur later in the P10 and P20 flames (Figure 9), again consistent with a reduction in the rate of growth as the PODE₃ loading was increased. The reduction in the rate of growth can be explained in terms of the decrease in the mass flow of C2 species in the P10 and P20 flames and is consistent with current models of soot growth. Such models are typically based on the H-abstraction-C₂H₂-addition (HACA) mechanism [64, 89, 90] and identify C2 species as crucial building blocks for aromatic species growth.

4 Conclusions

The effect of PODE₃ on the formation of soot has been investigated in an ethylene laminar coflow diffusion flame. Colour ratio pyrometry and differential mobility spectrometry were used to measure the soot volume fraction and particle size distribution of the soot in the flames. An increase in the soot volume fraction and average particle size was observed when PODE₃ was blended with ethylene at 5% (by carbon content). An increase in the proportion of PODE₃ (and corresponding oxygen addition) to 10% and 20% showed the opposite trend, with a decrease in soot volume fraction and average particle size. The maximum average particle size progressively decreased and shifted to larger non-dimensional axial positions (*i.e.* normalised height above burner) with PODE₃ addition above 10%. However, each flame showed the same particle size distribution and number concentration at axial positions corresponding to a given average particle size.

The increase in the soot volume fraction and average particle size at 5% PODE₃ can be explained mechanistically in terms of the pathways leading to the formation of the first aromatic ring. When PODE₃ is blended at 5%, it can lead to significantly higher concentrations of methyl radicals whilst resulting in only a small reduction in the amount

of carbon originating from the ethylene. This enables benzene formation via a C3 pathway, which typically has higher rates than the C2+C4 pathway with pure ethylene. When $PODE_3$ is blended at 10% or more, there is a reduction in soot formation due to a significant reduction in the proportion of carbon-carbon bonded species originating from the ethylene in the fuel blend.

From this work, we are able to establish that $PODE_3$ does not always reduce the formation of soot under non-premixed conditions, despite the absence of carbon-carbon bonds and high oxygen content. More importantly, the experimental data reported with this paper provides information about the sooting behaviour of $PODE_3$ and its interactions with C_2H_4 , a prominent real-fuel small species. The data highlights the importance of considering the fuel decomposition pathways and species interactions in the evaluation of soot reduction when considering $PODE_3$ as a potential alternative fuel.

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A Appendix



Figure SM1.1: Raw particle size distributions (PSDs) for flame E100.



Figure SM1.2: Raw particle size distributions (PSDs) for flame P5.



Figure SM1.3: Raw particle size distributions (PSDs) for flame P10.



Figure SM1.4: Raw particle size distributions (PSDs) for flame P20.

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