Structural effects of C3 oxygenated fuels on soot formation in ethylene coflow diffusion flames

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Abstract

This paper investigates how the structure of three C3 oxygenated fuels: dimethyl carbonate (DMC), dimethoxymethane (DMM) and isopropanol (IPA) influences soot formation when the fuels are blended with ethylene in laminar coflow diffusion flames. Up to 20% of the total carbon was substituted with oxygenated fuel. Colour-ratio pyrometry was used to measure the soot volume fraction ($f_v$). IPA caused a strong increase in $f_v$, whereas DMM and DMC both caused an initial increase followed by a progressive decrease in $f_v$ as the proportion of oxygenated fuel was increased. Differential mobility spectrometry and thermocouple probes were used to measure the particle size distribution and gas temperature in the flames at 5% blend strength. The hottest region of the 5% flames was consistently about 100 K cooler than the corresponding region of the ethylene flame, indicating a thermal effect of the doping. The 5% flames showed an increase in the maximum centre-line average particle size and $f_v$ versus the ethylene flame, with the IPA showing the largest increase. The evolution of the centre-line particle size distributions showed that the 5% flames experienced earlier particle growth compared to the ethylene flame. Consideration of the role of the chemical pathways towards benzene formation suggests that methyl radicals from the decomposition of the oxygenated fuels are responsible for the increase in $f_v$ at 5% doping. The difference in $f_v$ between the IPA versus DMM and DMC flames is thought to be due to the additional presence of C3 species originating from the carbon-carbon bonded backbone of IPA. Meanwhile, the differences between the DMC versus DMM flames are thought to arise from CO$_2$ produced during the decomposition of DMC, and a corresponding thermal effect where the pyrolysis region of the 5% DMC flame was observed to be about 50 K cooler than the other flames.

Keywords: isopropanol (IPA), dimethoxymethane (DMM, OME1), dimethyl carbonate (DMC), soot formation, particle size distribution, laminar coflow diffusion flame

1. Introduction

The transport sector currently accounts for more than 60% of global oil consumption, corresponding to approximately 24% of global carbon dioxide emissions [1]. Passenger travel is expected to continue to rise in years to come, and hence the demand for energy from the transportation sector will follow suit [1]. Light-duty transportation can be quite straightforward to decarbonise by electrification. Nevertheless, aviation, long-distance transportation and shipping remain a challenge to achieve decarbonisation [2]. Hence, carbon-neutral, sustainable, and energy-dense alternative liquid fuels may still play a critical role in keeping carbon dioxide emissions from these sectors in check [2, 3].

One of the most common and cost-effective sources of alternative liquid fuels is from the conversion of renewable resources [4, 5]. The use of non-fossil carbon in the production of these fuels means that they have a much lower carbon footprint than traditional fossil fuels [6], such that they are often referred to as carbon-neutral fuels, although it would be more accurate to refer to them as low-carbon fuels. Some emerging low-carbon fuels such as dimethyl carbonate (DMC) [7, 8], dimethoxymethane (DMM) [9], isopropanol (IPA) [10]
and poly(oxyethylene) dimethyl ether (also known as OME$_3$ and PODE$_3$) [11] can be sourced sustainably.

Blending low-carbon fuels with fossil-based fuels is a quick and simple strategy to start utilising alternative fuels that are sustainably-sourced [12, 13]. For example, the European Parliament proposed to increase the blending requirement to a minimum of 14% for road and rail transport by 2030 [14, 15].

Even though alternative fuels can be sustainably-sourced, the combustion of most fuels has the side effect of releasing particulate matter (commonly known as soot) into the atmosphere and causes harm to our health [16, 17] and environment [18–21]. Therefore, it is essential to understand how alternative fuels affect the generation of such particulate matter. In general, low-carbon fuels correspond to oxygenated fuels with different functional groups in their molecular structure, which are distinctively different from fossil-based fuels. Thus, this influences their capacity to reduce soot emissions [22–26]. Engine research reported in the literature has found that DMC [7, 27–31], IPA [32–36] and DMM [27, 37–39] are promising oxygenated fuels that could reduce soot emissions. However, the emissions from engines are often governed by a combination of effects relating to the engine operating conditions and the chemical behaviour of the fuel. The influence of the fuel can be decoupled from the engine operating conditions by studying the fuel and the formation of soot precursors in a well-controlled fundamental combustion system such as a laminar coflow diffusion flame [40–43].

A synergistic effect on soot formation is sometimes observed during the combustion of fuel blends (i.e. fuels composed of a mixture of other fuels). This is defined as occurring when there is an increase in soot formation during the combustion of the fuel blend compared to the combustion of the individual fuels in the blend. Some of the early works on the synergistic effect in the binary blends of small hydrocarbons were reported in the literature [44–48]. Recently, synergistic effect from blends of conventional hydrocarbons was also shown in the literature experimentally [49] and confirmed numerically [50].

The synergistic effect has also been observed in fuel blends of containing oxygenated fuels [51–54]. The effect is understood to be influenced by the introduction of methyl (‘CH$_3$’) radicals from the fuel blend into a base-fuel environment that is rich in C2 species (ethylene). This consequently leads to an enhancement of propargyl radical (C$_2$H$_3$) formation and eventually benzene production via C$_2$H$_4$ self-combination [42, 47]. This synergistic effect is reported in several other investigations with dimethyl ether [52–54] and is attributed to the significant amount of methyl radicals formed when it decomposes during combustion. Recently, the synergistic effect on soot formation was investigated in a laminar coflow diffusion flame when 5% PODE$_3$ (CH$_3$ → OCH$_2$ → OCH$_3$) was blended with ethylene [55]. Similar to the case with dimethyl ether, PODE$_3$ does not contain any carbon-carbon bonds and the synergistic effect was attributed to the introduction of methyl radicals from the decomposition of the PODE$_3$ into a rich C2 ethylene flame system. The impact of the molecular structure of the fuel on the synergistic effect in soot formation is therefore pivotal in the understanding of the changes induced by fuel blending. Moreover, it is important to take into account that in the combustion of alternative fuels, the oxygen-containing functional groups also play an essential role in determining the sooting tendencies [56]. There is a lack in the understanding of the effect of oxygen-containing functional groups on the synergistic effect in soot formation. In particular, insights on the soot formation of the oxygen-containing functional groups present in some of the emerging carbon-neutral fuels (DMC, DMM and IPA) is valuable when these fuels are considered as practical fuels in the near future.

The purpose of this paper is to understand the structural effects of different oxygenated fuels on soot formation. Three C3 oxygenated fuels were chosen in this investigation to represent three different oxygen-containing functional groups: carbonate ester (DMC), ether (DMM) and hydroxyl (IPA). The combustion of different strength blends of the oxygenated fuels with ethylene are investigated in a laminar coflow diffusion flame. Their effect on the soot formation process is investigated via soot volume fraction, thermocouple and particle size distribution (PSD) measurements. The impact of the different oxygen-containing functional groups and molecular structure in soot formation is critically assessed.

2. Materials and methods

This section provides a concise overview of the experimental setup and methods which were fully described in previous work [55].

2.1. Laminar coflow diffusion flame

Atmospheric-pressure laminar coflow diffusion flames were generated using a Yale Steady Flame Burner [57]. In this study, thirteen flames were investigated. The first flame was a nitrogen diluted ethylene flame (60% C$_2$H$_4$·40% N$_2$). The C$_2$H$_4$ flame corresponds to the ISF-targeted ISF-4 coflow 3 (Condition
C) laminar diffusion flame [58]. The oxygenated fuels were blended with the C2H4 at 5%, 10%, 15% and 20% while maintaining a constant carbon flow rate (9.49 g/h) and a constant cold gas coflow velocity (35 cm/s) for all flames. The ethylene and nitrogen were supplied from 99.99+ purity cylinders, and the air from an in-house compressor. The following naming convention has been adopted for this investigation: The oxygenated fuels are specified as ‘DMC’ (dimethyl carbonate), ‘DMM’ (dimethoxymethane) and ‘IPA’ (isopropanol); followed by the percentage of total carbon contributed to the fuel mixture. Table 1 shows the fuel flow rates for the flames studied in this work for each fuel blends.

Table 1: Fuel molecular structures and flow rates for the flames investigated.

<table>
<thead>
<tr>
<th>Fuel blend flow rate (L/min)</th>
<th>DMC flow rate (g/h)</th>
<th>DMM flow rate (g/h)</th>
<th>IPA flow rate (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.147</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5%</td>
<td>0.140</td>
<td>1.19</td>
<td>0.79</td>
</tr>
<tr>
<td>10%</td>
<td>0.123</td>
<td>2.37</td>
<td>1.58</td>
</tr>
<tr>
<td>15%</td>
<td>0.125</td>
<td>3.56</td>
<td>2.37</td>
</tr>
<tr>
<td>20%</td>
<td>0.118</td>
<td>4.74</td>
<td>3.16</td>
</tr>
</tbody>
</table>

DMC, DMM and IPA were procured from Tokyo Chemical Industry UK Ltd with a purity of at least 95% and used without further purification. The fuel mixtures were evaporated and fed to the burner via heated lines at 373 K. The flames were given 30 minutes to reach stability before performing any measurements. The equipment and measurement procedures are described in detail in previous work [55], and are summarised below.

2.2. Soot volume fraction

The soot volume fraction, \( f_v \), was measured using colour-ratio pyrometry [59, 60]. The measurement system has been described in detail previously [60].

2.3. Flame temperature

The flame temperature was measured using a rapid insertion method with an uncoated 125 µm Type-R thermocouple (Pt/Pt-13%R) [55, 61]. The setup and measurement procedure were described previously [55, 62]. The uncertainty of the measurement is estimated to be ±100K.

2.4. Soot particle size distribution

The particle size distribution (PSD) of the electrical mobility diameter of the soot was measured using a DMS500 Differential Mobility Spectrometer from Cambustion Ltd. The setup and measurement procedure were described previously [55]. In the current study, a room-probe pressure difference of \( \Delta P = 28.0–33.0 \) mbar was used to sample the flame. The total dilution ratio (including the secondary dilution in the DMS500) was at least 600,000, which is comfortably within the range suggested in the literature [63].

2.5. Kinetic modelling

Three kinetic models were established by combining different sub-mechanisms from the literature. The kinetic models were used to support the interpretation of the experimental results. It should be noted that the current work does not attempt to propose a new comprehensive model for each oxygenated fuel. Rather, the intention is to use three kinetic models sharing the same core mechanism to analyse the combustion of the mixtures of the oxygenated fuels with ethylene.

The core mechanism is the USC-Mech II [64]. The USC-Mech II was chosen because it has been extensively calibrated to experimental measurements. The sub-mechanisms for DMM, DMC and IPA [65–67] were combined with the USC-Mech II model, ensuring that all three kinetic models use the same core mechanism. The rate constants, thermodynamic and transport properties from the original mechanisms were used without any alterations. The kinetic models are available in CHEMKIN format in the Supplementary Material, accompanied by their corresponding thermodynamic and transport properties.

The combined kinetic models were tested against experimental and modeling results of ignition delay [68] and laminar flame speed [69–71]. It was confirmed that the inclusion of the DMM, DMC and IPA sub-mechanisms does not compromise the ability of the mechanisms to describe the ethylene chemistry. The pyrolysis of each fuel mixture was simulated using the corresponding kinetic model with an imposed temperature profile from the corresponding flame experiment. The kinetic modelling of pyrolysis is used in this study because pyrolysis is prevalent in the coflow diffusion flame, especially in the fuel-rich part of the coflow flame [72]. Furthermore, it was shown experimentally that the products of pyrolysis are vital in understanding sooting tendencies [72]. Hence, the simulation results were used to help understand the effect of DMM, DMC and IPA on the chemistry leading to the formation of benzene. Details of the simulation methods and results can
be found in Section SM2 of the Supplementary Material.

3. Results and discussion

In this section, the experimental results are presented and discussed. The observed synergistic effect of the selected oxygenated fuels on soot formation is explained in terms of the decomposition mechanisms of the different oxygenated fuels under fuel-rich conditions, supplemented with kinetic modelling.

3.1. Visible flame length

The flame lengths are reported in Table 2, and the corresponding flame images are shown in Figure SM1.1. The flame lengths were averaged over five frames.

The C$_2$H$_4$ flame was observed to have a length of 48.4 mm, which agrees well with the reported flame length for the ISF standard flame [58]. The flame length increased compared to the C$_2$H$_4$ flame for all the cases with 5% oxygenated fuel. The IPA5 flame showed the largest increase and was observed to have a length of 52.1 mm, whilst the DMC5 flame showed the smallest increase and was observed to have a length of 49.4 mm. Two distinct behaviours were observed as the doping level was increased to 10%, 15% and 20%. DMC and DMM showed a progressive decrease in the flame length, whereas IPA flame increased in length to 53.8 mm at 10% blend strength, and then decreased slightly reaching a flame length of about 52.7 mm at 20% blend strength. The different flame lengths can be correlated to the soot volume fraction for each flame, see Section 3.2 for details.

3.2. Soot volume fraction

Figure 1 shows the soot volume fraction distributions measured using colour-ratio pyrometry. At the wings of the C$_2$H$_4$ flame, the maximum soot volume fraction was measured as 2.0 ppm at the wings, amounting to about 11% higher than that of the flame centre-line. This is consistent with the value of 1.8 ppm measured using laser-induced incandescence [73]. For the IPA flames, the peak soot volume fraction of the flame wings are about 4% higher than that of the flame centre-line. As for the DMC and DMM flames, the peak soot volume fraction at the flame centre-line measurements are higher than that of the flame wings by about 16% and 18% respectively. This shift from the flame wings to the centre-line can be attributed to the flames doped with oxygenated fuels could cause partial oxidation on the fuel rich side of the stoichiometric surface of the flame [74, 75]. Hence, the soot formation is concentrated at the centre-line of the flame rather than at the wings of the DMM and DMC flames; and the IPA flames have much decreased differences between the centre-line and wing peak soot volume fraction than that of the C$_2$H$_4$ flame. The maximum centre-line soot volume fraction of the C$_2$H$_4$ flame was measured as 1.8 ppm. In the literature, the value is reported as 1.2 ppm, which was measured using laser-induced incandescence [76]. Given that the uncertainty bounds along the centre-line of the flame are ±10% when using the FLiPPID method to process colour-ratio pyrometry data [60] and that the difference between colour-ratio pyrometry and laser-induced incandescence measurements is typically ±15% [59, 73, 77], the current measurement is considered to be reasonable.

In the interest of providing organised and valuable discussion on the experimental results, the remaining discussion of the work when comparing the peak soot volume fraction with the particle size distribution (PSD) and flame temperature measurements will be limited to the flame centre-line only as the PSD and flame temperature measurements were only performed at the flame centre-line.

The maximum centre-line soot volume fractions are shown in Figure 2. In all cases, the presence of 5% oxygenated fuel causes an increase in the maximum centre-line soot volume fraction compared to the C$_2$H$_4$ flame. The IPA5 and DMM5 flames show almost double the increase observed in the DMC5 flame (28% and 24% versus 11% respectively). As the proportion of oxygenated fuel in the blend is increased, the maximum soot volume fraction continues to increase in the IPA flames, reaching approximately 2.6 ppm in the IPA20 flame, corresponding to a 47% increase compared to the C$_2$H$_4$ flame. In contrast, the DMM and DMC flames show a progressive decrease in the maximum centre-line soot volume fraction. The larger maximum soot volume fraction observed in the DMM compared to the DMC

### Table 2: Visible flame lengths (mm) for the flames investigated with the associated standard error

<table>
<thead>
<tr>
<th>Fuel blends</th>
<th>DMC</th>
<th>DMM</th>
<th>IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>48.8 ±0.1</td>
<td>48.8 ±0.1</td>
<td>48.8 ±0.1</td>
</tr>
<tr>
<td>5%</td>
<td>49.4 ±0.2</td>
<td>50.3 ±0.1</td>
<td>52.1 ±0.2</td>
</tr>
<tr>
<td>10%</td>
<td>49.2 ±0.1</td>
<td>48.6 ±0.2</td>
<td>53.8 ±0.2</td>
</tr>
<tr>
<td>15%</td>
<td>46.7 ±0.1</td>
<td>48.1 ±0.6</td>
<td>53.0 ±0.1</td>
</tr>
<tr>
<td>20%</td>
<td>45.2 ±0.2</td>
<td>46.2 ±0.2</td>
<td>52.7 ±0.2</td>
</tr>
</tbody>
</table>
flame persists in the 10% blend, but is no longer apparent by the time the blend reaches 15% and 20%. These observations are in good agreement with the trends observed in the flame length.

The data are presented in terms of a non-dimensional axial position (NDAP) to enable comparison of the effect of the oxygenated fuels across all the flames with varying flame lengths. The figure is divided into four regions, labelled A–D and demarcated by vertical dashed lines, to facilitate discussion.

The experimental temperature profile and maximum temperature measured in the current study were consistent with measurements reported in the literature for the C$_2$H$_4$ flame [73, 78]. The centre-line flame temperature profiles are quite similar across all the flames and increase with NDAP in Region A (NDAP = 0.1–0.5). The temperature of the DMC5 flame is approximately 50 K lower than for the other flames. The decomposition of DMC in the pyrolysis region of the flame have carbon dioxide as a decomposition product which can result in a thermal change to the flame in the region [79]. This suggests that the soot formation in the DMC5 flame could have a combination of temperature and chemical effects. Detailed discussion on the thermal effect and chemical effect in the soot formation of DMC5 flame will be presented in Section 3.5. The similarity of the centre-line temperatures in the C$_2$H$_4$, DMM5 and IPA5 suggests that the chemistry will play a more significant role in determining the differences in the sooting behaviour of these flames.

The measured centre-line flame temperatures of all the flames show a slight dip followed by a region of approximately constant temperature in Region B (NDAP = 0.50–0.78). This is not uncommon and has been observed in the literature [75, 80–86], and is attributed to the radiative heat loss from the flame due to the soot [87]. At the boundary with Region C (NDAP = 0.78–
1.0), the measured temperature of all of the flames increases rapidly, with the temperature increasing to a maximum that defines the boundary with Region D at NDAP = 1.0.

In Region C, the measured temperature profiles of the 5% blended flames are very similar and are consistently about 100 K lower than that of C$_2$H$_4$ flame. The difference from the C$_2$H$_4$ flame is not reflected in the heating values of the fuels nor in the equilibrium temperature of stoichiometric mixtures of the fuels and air (see Section SM2.3 of the Supplementary Material). The similarity in the temperature profiles of blended flames is also not reflected in the soot volume fraction profiles, which are quite distinct, both from the C$_2$H$_4$ flame and from each other.

3.4. Particle size distribution

The average particle size along the centre-line (top panel of Figure 3) increases slowly in Region A, with the 5% blended flames showing slightly larger average particle size than the C$_2$H$_4$ flame. No signal is observed for the soot volume fraction (bottom panel of Figure 3) as it is below the lower limit of detection of the pyrometry technique. A rapid increase in the average particle size and soot volume fraction is observed in Region B in all flames. The average particle size and centre-line soot volume fraction of the 5% blended flames remain larger than those in the C$_2$H$_4$ flame.

The maximum centre-line average particle size and soot volume fraction are observed in the early part of in Region C, after which they decrease rapidly throughout the remainder of Region C and D. The 5% blended flames have a larger maximum average particle size than the C$_2$H$_4$ flame, with the maximum average particle sizes and percentage differences following in the order 118 nm (IPA5, 13% larger), 116 nm (DMM5, 11% larger), 114 nm (DMC5, 9% larger) versus 103 nm in the C$_2$H$_4$ flame. This is consistent with the trends in the visible flame length (Table 2) and the maximum centre-line soot volume fraction (Figure 2). However, the locations where the maxima are observed do not follow such a direct trend. The IPA5 and DMM5 flames both show the maximum centre-line average particle size at NDAP = 0.85 (the middle of Region C), similar to the C$_2$H$_4$ flame, whereas the DMC5 flame shows the maximum at NDAP = 0.82, slightly earlier than the other flames. Likewise, the C$_2$H$_4$, IPA5, and DMM5 flames show the maximum centre-line soot volume fraction at NDAP = 0.8, whereas the DMC5 flame shows the maximum slightly earlier at NDAP = 0.76. The reasons for this are explored in Section 3.5.1.

Figure 4 shows the full particle size distributions (PSDs) of the C$_2$H$_4$, DMC5, DMM5 and IPA5 flames at different non-dimensional axial positions (NDAP). The evolution of the peak number density of the PSDs provides a deeper insight into the changes in the soot formation process due to the addition of the oxygenated fuels to the 5% blended flames.

Figures 4(a) and (b) show that all the flames have unimodal distributions characteristic of nucleation with particles sizes less than 30 nm for NDAP ≤ 0.40. The 5% blended flames show larger peak number densities and broader size distributions occurring earlier than for the C$_2$H$_4$ flame, indicating earlier nucleation and growth, with the maximum number density and therefore the nucleation occurring earliest in the DMC5 flame.
Figure 4(c) shows that the particles are starting to transition to bimodal size distributions by NDAP = 0.5. For example, the PSD for the C₂H₄ flame has a peak number density at a size of about 15 nm, whilst also showing a shoulder at about 70 nm. The shoulders are more pronounced in the 5% blended flames, consistent with the particles experiencing earlier growth and an earlier transition to bimodal PSDs than in the C₂H₄ flame.

Figures 4(d)–(f) show that the bimodal PSDs are well-established for NDAP ≥ 0.70, with the PSDs showing a weak mode below 30 nm and a strong accumulation mode in the range 40–300 nm. In all cases, the peak number density is achieved before NDAP = 0.70 and continues to decrease with NDAP. The number densities of the 5% blended flames are consistently lower than that of the C₂H₄ flame.

3.5. Effect of C₃ oxygenated fuels on soot formation

The formation of benzene is generally believed to be the rate-limiting step in the formation of the polycyclic aromatic hydrocarbons that ultimately leads to the formation of soot [88–92]. Resonance-stabilised radicals (RSRs) are known to be important in the production of the first aromatic ring [40, 92], in particular ‘C₅H₅, i-C₅H₅, i-C₅H₅ and ‘C₆H₆ [89, 93–98].

Figure 5 shows the major reaction pathways involving ethylene, DMM, DMC and IPA leading to the formation of benzene [65, 66, 89, 93, 99–102]. The species in the figure are numbered to facilitate the ensuing discussion. The pathways can be categorised into odd (C₃+C₃ and C₅+C₁) and even (C₄+C₂) pathways [92]. Hydrogen abstraction from ethylene (111 kcal/mol bond energy) is more energetically favourable than carbon–carbon double bond cleavage (174 kcal/mol) [103]. The hydrogen abstraction produces species including vinyl radicals (·C₂H₃), acetylene (C₂H₂) and ethynyl radicals (·C₂H) [99, 100] that can combine to form C₄ species [99, 100, 104] including i-C₄H₅ and i-C₅H₅. In the presence of C₂ species, these C₄ RSRs can provide a major route for the formation of benzene via the C₂+C₄ pathway [94, 105]. In the C₂H₄ flame, the concentration of C₂ and C₄ species dominates compared to C₁ species [106, 107]. This is reflected in the pyrolysis simulation results (see Section SM2.2 of the Supplementary Material). Figures SM2.4(g) and (h) show that the C₁ species mole fractions are lower than that of all the mixtures containing oxygenated fuels. Meanwhile, Figures SM2.4(k) and (l) show that the C₄ species mole fractions are higher for pyrolysis of ethylene than for all the mixtures containing oxygenated fuels.

The following sections describe how doping ethylene...
flames with DMM, DMC and IPA affects the pathways leading to the formation of benzene. Figure SM3 shows the structure of DMM, DMC and IPA, along with annotations and bond dissociation energies to facilitate with the following discussion.

3.5.1. Effect of DMM and DMC on soot formation

DMM and DMC have several similarities in terms of their molecular structure and how they decompose, both providing a source of methyl radicals.

DMM can decompose through hydrogen abstraction and carbon-oxygen scission reactions [65]. Hydrogen abstraction can occur at the α and β carbon-hydrogen bonds, both of which have similar bond dissociation energies, as shown in Figure SM3 [108]. Consideration of the number of α and β carbon-hydrogen bonds suggests that hydrogen abstraction at the α bond may occur more frequently. The resultant dimethoxymethyl (1) and methoxymethoxymethyl (2) radicals can decompose to form methyl (\(·\text{CH}_3\)) radicals and formaldehyde (\(\text{CH}_2\text{O}\)) [65]. Similarly, two consecutive carbon-oxygen bond scissions can produce methyl radicals and formaldehyde [65] via methoxymethyl (3).

DMC can decompose via three pathways: decarboxylation, carbon-oxygen bond dissociation and hydrogen abstraction [66], with significant formation of carbon dioxide [109]. The decarboxylation produces carbon dioxide and dimethyl ether (4), which subsequently undergoes hydrogen abstraction and carbon-oxygen bond scission to form methyl radicals and formaldehyde [66]. The carbon-oxygen bond dissociation can happen at either the α or the β carbon-oxygen bond from the carbonyl group, with the bond dissociation energies suggesting that the dissociation may favour the β more than the α carbon-oxygen bond. The hydrogen abstraction produces \(\text{CH}_3\text{OCOOCCH}_2\text{·}\) (6) radicals which can decompose into methyl radicals and carbon dioxide.

The soot volume fraction and maximum average particle size (Figures 2 and 3) are observed to increase in the DMM5 and DMC5 flames compared to the \(\text{C}_2\text{H}_4\) flame. The dopants provide a source of methyl radicals, which can react with ethynyl radicals (\(·\text{C}_2\text{H}_2\)) to form methylacetylene (\(\text{C}_3\text{H}_4\)) and subsequently propargyl (\(·\text{C}_3\text{H}_3\)) RSRs via a hydrogen abstraction. The presence of C3 species also enables benzene formation via the C5+C1 pathway (involving the RSR \(·\text{C}_3\text{H}_2\)) [93, 110, 111]. It is thought that the availability of methyl radicals and the consequent formation of ben-
zene via the odd pathways, in addition to the even pathways that dominate in the \( \text{C}_2\text{H}_4 \) flame, that is responsible for the synergistic increase in soot production in the DMM5 and DMC5 flames. This is reflected in the pyrolysis simulation results (see Section SM2.2 of the Supplementary Material), where Figures SM2.4(g)-(j) and (m) show that the species that contribute to the odd pathways have species mole fractions that are consistently higher than in the \( \text{C}_2\text{H}_4 \) flame.

The soot volume fraction and maximum average particle size (Figures 2 and 3) are observed to decrease as the doping level of DMM and DMC is increased from 5% to 10%, 15% and 20%. This is interpreted as an indication that there is a decrease in the rate of formation of benzene, despite the increase in the concentration of methyl radicals as a result of increased doping with DMM and DMC. It is apparent that the additional methyl radicals originating from the DMC and DMM are less important at higher blend strengths. What makes this situation distinct from the 5% flames is that the odd pathways are already open. Given that the total carbon mass flow remains constant, the additional DMM and DMC results in a decrease in the mass flow of \( \text{C}_2 \) species supplied via the ethylene part of the fuel mixture. This is unfavourable for benzene formation because not all of the carbon provided by the oxygenated fuel participates in soot production, but instead forms carbon monoxide (via formaldehyde, \( \text{CH}_2\text{O} \)) [109, 112] and carbon dioxide (in the case of DMC) as the oxygenated fuel decomposes. These observations are consistent with the literature, where \( \text{C}_2\text{H}_4 \) flames have been doped with dimethyl ether [52], PODE \( ^+ \) \( \text{CH}_3 + \text{OCH}_2 + \text{HCH}_3 \) [55], methane [46] and ethanol [113].

A further observation is that the DMC flames are less sooting than the DMM flames. For example, the DMC flames show lower maximum centre-line soot volume fractions and the DMC5 flame shows a smaller maximum centre-line average particle size than the corresponding DMM flames. The observed differences between the synergistic effect in soot formation of DMC5 flame and DMM5 flame can be attributed to the coupled effect of thermal effect and chemical effect [114–116]. For the temperature effect, it is evident from the Region A in Figure 3. The flame temperature of DMC5 flame is lower than that of DMM5 flame by 50 K. As higher temperature in pyrolysis is often linked to a promotion in soot formation [117], the DMC5 flame being lower in flame temperature is therefore having reduced soot formation. The chemical effect that resulted in the differences between the DMC5 and DMM5 flames is via a reduction in the H-abstraction-\( \text{C}_2\text{H}_4 \)-addition (HACA) growth of polycyclic aromatic hydrocarbons [88, 118, 119]. This may occur through increased consumption of hydrogen radicals by carbon dioxide from DMC decomposition in \( \text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH} \) reactions [115, 116].

3.5.2. Effect of IPA on soot formation

IPA can decompose via dehydration, hydrogen abstraction + \( \beta \)-scission, carbon-oxygen bond dissociation and carbon-carbon bond dissociation [101, 120]. The main decomposition species are methyl radicals, water and C3 species; markedly different from DMM and DMC. In particular, the dehydration of IPA leading to the formation of \( \text{C}_3\text{H}_6 \) and water may be more significant than other decomposition pathways [101]. This is reflected in the pyrolysis simulation results (see Section SM2.2 of the Supplementary Material), where Figures SM2.4(d) and (i) show that water and \( \text{C}_3\text{H}_6 \) are produced in higher amounts by the IPA fuel blend compared to the DMM and DMC blends. The water is not thought to have a significant chemical effect on the growth of soot [115]. There are three possible sites for hydrogen abstraction: the carbon-hydrogen bond \( \alpha \) to the hydroxyl group, the carbon-hydrogen bond \( \beta \) to the hydroxyl group and the oxygen-hydrogen bond in the hydroxyl group, where consideration of the bond dissociation energies suggests that hydrogen abstraction at the carbon-hydrogen bond \( \alpha \) to the hydroxyl group (95.0 kcal/mol) is most favourable [101, 120]. The bond dissociation energies of the carbon-carbon (85.9 kcal/mol) and carbon-oxygen (94.2 kcal/mol) bonds [121] suggest that cleavage of both these bonds is more favorable than hydrogen abstraction.

The soot volume fraction and maximum average particle size (Figures 2 and 3) are observed to be larger in the IPA flames compared to all the other flames. In contrast to DMM and DMC, the carbon-carbon bonded backbone of IPA is such that the decomposition of IPA produces C3 in addition to C1 species, enabling the direct formation of benzene via the C3+C3 pathway [99]. The C3 species can also easily react with C2 species from ethylene to form C5 species, promoting the C5+C1 pathway [122, 123]. The C5+C1 pathway involving cyclopentadienyl (\( \text{C}_5\text{H}_5 \)) RSRs and methyl radicals has been shown to have a significant role in the formation of benzene [96–98, 123]. The radicals can react to form to fulvene, followed by ring-enlargement reactions to provide a fast route to benzene [97, 98, 102]. In addition, the recombination of \( \text{C}_5\text{H}_5 \) RSRs can directly form naphthalene [124, 125], which may also be an important reaction that increases the rate of formation of larger polycyclic aromatic hydrocarbons in IPA.
flames [124, 125].

The increase in the soot volume fraction observed up to 15% IPA blending in Figure 2 suggests a continued increase in the rate of benzene formation. It is postulated that the reason for the difference in behaviour from the DMM and DMC flames is the direct access to C3 species that arises as a consequence of the C-C bonded backbone of IPA. When the proportion of IPA is increased, the increased abundance of C3 species (more than) compensates for the reduction in C2 species due to displacement of ethylene. This is in marked contrast to DMM and DMC, where the displacement of C2 species from the ethylene eventually leads to a decrease in soot formation. The slight decrease in soot volume fraction as the IPA blend strength is increased from 15% to 20% is potentially due to the action of hydroxyl (·OH) radicals resulting from the dissociation of the carbon-oxygen bond in the IPA. The presence of low concentrations of ·OH radicals will promote hydrogen abstraction reactions, leading to the formation of water and an increase in the H-abstraction-C2H2-addition (HACA) growth of polycyclic aromatic hydrocarbons [88, 118, 119] and a consequent increase in soot production. However, if the blend strength is increased high enough, the presence of high concentrations of ·OH radicals is expected to promote oxidation, leading to a net decrease in the rate of production of soot [40, 120].

4. Conclusions

In this work, the effect of the molecular structure of different C3 oxygenated fuels on soot formation was investigated in laminar coflow diffusion flames. Three C3 oxygenated fuels were chosen to represent different oxygen-containing functional groups: carbonate ester (dimethyl carbonate, DMC), ether (dimethoxymethane, DMM) and hydroxyl (isopropanol, IPA). The oxygenated fuels were blended with ethylene at 5%, 10%, 15% and 20% of the total carbon flow rate to enable oxygenated fuel-blended flames with constant carbon flow rate. Colour-ratio pyrometry was used to measure the soot volume fraction. Differential mobility spectrometry and thermocouple measurements were used to measure the particle size distribution of the soot and temperature of the flame in the 5% blends.

At 5% blending, the maximum centre-line soot volume fraction and maximum centre-line average particle increased compared to the pure ethylene flame. The percentage increases were 13%, 11% and 9% in the maximum centre-line soot volume fraction, and 28%, 24% and 11% in the the maximum centre-line average particle size for the IPA, DMM and DMC blends respectively. The maximum centre-line soot volume fraction showed two distinct trends with increasing blend strength (up to 20%). IPA caused a strong increase in the maximum centre-line soot volume fraction up to 15% blend strength followed by a small decrease between 15% and 20% blend strength, while DMM and DMC both caused a progressive decrease in the maximum centre-line soot volume fraction as the blend strength increased from 5% to 10%, 15% and 20%.

The effect of the fuel blend on the soot production can be explained in terms of the molecular structure of the oxygenated fuels. The decomposition pathways suggest that the oxygenated fuels provide a source of methyl radicals. In the case of the 5% blends, it is believed that the introduction of methyl radicals (from the oxygenated fuels) into an environment that is rich in C2 species (from the ethylene) promotes soot growth by enabling the formation of benzene via C3+C3 and C5+C1 pathways in addition to C2+C4 pathways. In the case of DMM and DMC, it is believed that the reduction in soot at higher blend strengths is due to carbon from the oxygenated fuels displacing carbon from the ethylene. This results in a decrease in the carbon available for the C2+C4 pathways and an increase in the proportion of carbon that does not participate in soot production, but that forms carbon monoxide and carbon dioxide (in the case of DMC) during the decomposition of the oxygenated fuels. In the case of IPA, it is believed that the increase in soot production with blend strength is due to the presence of the C3 carbon-carbon bonded backbone, which results in a number of C3 decomposition products. This enables direct access to benzene formation via the C3+C3 pathways (as opposed to DMM and DMC, which access the C3 pathways via C1 species). This more than compensates for the decrease in the carbon available for the C2+C4 pathways, such that the IPA-doped flames produce more soot than any of the other flames.

Research data

Research data supporting this publication is available in the University of Cambridge data repository (doi:10.17863/CAM.59634).

Acknowledgements

This research was supported by the National Research Foundation, Prime Minister’s Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme. Y. R. Tan
acknowledges financial support provided by Fitzwilliam College Cambridge, Trinity College Cambridge and the Cambridge Trust. J. Bai acknowledges financial support provided by CSC Cambridge International Scholarship from Cambridge Trust and China Scholarship Council. M. Kraft gratefully acknowledges the support of the Alexander von Humboldt Foundation.

The authors would like to thank Wenyu Sun from the Institut de Combustion Aéothermique Réactivité et Environnement (ICARE), CNRS Orleans Campus; Bing Yang from the Center for Combustion Energy and the Department of Energy and Power Engineering, Tsinghua University; Lorena Marrodán from Universidad de Zaragoza for providing the data that assisted in the simulation; Chiara Saggese from Lawrence Livermore National Laboratory and Scott S. Goldsborough from Argonne National Laboratory for providing the isopropanol submechanism.

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