Pyrolytic decomposition of methanol, ethanol, and butanol at various temperatures and residence times in a high-temperature flow reactor

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ABSTRACT

The potential use of low-carbon renewable fuel molecules, such as short chain alcohols, as a substitute or extender for fossil fuels, offers an opportunity to address pollutant emissions from transport and the sustainability of energy sources. Moreover, it may help reduce pollutants detrimental to air quality and human health, of which particulate matter (PM) is a significant contributor. To this end, the pyrolysis of three renewable alcohol fuels, methanol, ethanol, and butanol, has been studied in a laminar flow reactor at a sample inlet temperature range of 869 °C to 1120 °C. All the tested fuels were injected into a nitrogen carrier gas stream at a fixed concentration of 10,000 ppm on a carbon atom basis. A range of pyrolysis temperatures and residence times were selected to gain insight into the pyrolytic decomposition of short chain alcohol fuels to intermediate species important to the subsequent formation of benzene rings, larger polycyclic aromatic hydrocarbons (PAH), and particulate matter. In this paper, the presence of ten intermediary species that may aid in the formation of benzene rings and the growth of PAHs were quantified, with an emphasis on probable routes of first ring formation from the alcohols of varying chain length. Gaseous samples were collected from the pyrolyser at different temperatures and residence times using a novel high-temperature air-cooled ceramic sampling probe. The identification and quantification of intermediate gaseous species were undertaken by Gas Chromatography-Flame Ionization Detection (GC-FID). During methanol pyrolysis, only a tenth of the supplied carbon was detected as hydrocarbon gaseous species (mainly methane), with no benzene found, highlighting that methanol pyrolysis does not readily result in polyaromatic hydrocarbons and soot. Ethanol and butanol pyrolysis produced substantial amounts of ethylene and acetylene, suggesting a role in benzene and soot formation. Uniquely, pyrolysis of the long-chain alcohol, butanol, produced appreciable levels of C3 and C4 hydrocarbons, in addition to C1 and C2 hydrocarbons, suggesting additional reaction pathways for benzene formation and growth in comparison with ethanol.

1. Introduction

In today’s world, the pressing issues of energy availability and environmental pollution have become increasingly prominent. These issues have sparked a growing demand for sustainable alternatives, such as biofuels, to address the dual challenges of decarbonising energy and transportation systems. Biofuels have emerged as one of the most efficient solutions to reduce sustainably environmental pollution caused by the use of fossil fuels for transportation and electricity generation. The use of biofuels offers significant potential for decarbonisation and has gained widespread attention in recent years. Increasing global demand for biofuels has reached 170 billion liters worldwide in 2022, indicating the urgent need and relevance of this renewable energy source in help meet both global energy demand and reduction in environmental pollution. The biofuel market has experienced a sharp increase in demand, driven by the need to meet the targets set forth in Net Zero scenarios by 2030 [1,2]. The use of biofuels has drawn increased attention as a result of the ever-increasing fossil fuel prices and the pollutants, including particulate matter (PM), that they emit. Alcohol fuels are seen as viable renewable energy sources, and have also been considered as fossil fuel additives to reduce the formation of polyaromatic hydrocarbons (PAHs) and soot particles [3-6]. Oxygenated biofuels, particularly alcohols, have significant potential since they can be produced from carbon-neutral renewable resources (e.g. macroalgae) and result in net...
reductions in greenhouse gas emissions relative to fossil fuels [7,8]. In several countries, methanol and ethanol are already widely employed as a blend component in fossil fuel additives, as for example E10 in the UK and Europe [9,10]. Butanol has also received significant attention as it has various benefits over lighter alcohols, such as higher energy density, greater miscibility with practical fuels, and typically lower water content following production.

Several previous experimental and modeling studies have examined the combustion and pyrolysis of methanol, ethanol, and butanol and the role of alcohol fuel structure on the formation of soot and PAHs during pyrolysis. Methanol, which has a relatively low carbon-to-oxygen ratio (C/O), mainly formed carbon monoxide and produced little soot. However, larger alcohols with increasing C/O ratios increased the formation of soot. Using a laminar flow reactor and online GC-TCD/FID, Hamidi et al. [27] investigated the effect of high pressure (up to 50 bar) on pyrolysis and oxidation of the gas products of ethanol. They observed a considerable amount of acetalddehyde (CH₃CHO) at lower temperatures, while CO, CH₄, and C₂H₄ were the major pyrolysis products formed. Esarte et al. [13] investigated the gas products during pyrolysis of different proportions of ethanol/1-acetylene mixtures in a plug flow reactor. They observed that increasing the ethanol percentage in acetylene pyrolysis reduced soot production. They suggested that ethanol addition formed CH₄ and CO which could have prevented the formation of PAHs but that C₂H₅ may also have formed, which is an important precursor to PAHs formation.

Khan et al. [17] recently investigated the effect of carbon chain length on the soot and PAH formation during pyrolysis of ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol in a laminar flow reactor. They observed that increasing carbon chain length increased the concentration of PAH and soot mass. Marzio et al. [21] investigated the thermal breakdown of 1-butanol in high-temperature flash pyrolyser equipped with mass spectrometric detection. They observed that butene was an important pyrolysis product under the tested conditions. Stranic et al. [28] investigated the kinetics of 1-butanol pyrolysis by measuring the time history of OH, H₂O, C₂H₆, CO, and CH₄ using shock tube/laser absorption methods (UV and IR) at high temperature. They suggested that the time history of those species were affected by unimolecular decomposition and hydrogen abstraction. Deng et al. [29] investigated experimentally and numerically the propensity of soot formation of non-premixed n-heptane, n-butanol, and methyl butanoate flames in a liquid pool stagnation-flow experimental setup to understand the reaction pathway and crucial control steps that led to the formation of the initial PAHs and soot particles during the combustion process. Both studies showed that n-heptane and n-butanol displayed similar soot formation characteristics and higher propensity than that of methyl butanoate, attributed to the different fuel breakdown processes.

At higher experimental temperatures, particularly above 900 °C it is expected that significant coking and carbon deposition can impact the pyrolysis products. Blekkan et al. studied the characterisation of tar and coke formed during pyrolysis of methane in a tubular reactor with H₂ as diluent gases. They reported that methane hydrogen ratio effected the formation of coke flakes [30]. In the current study, the primary research question centers on exploring the pyrolytic decomposition of short-chain alcohols and investigating the intricate pathways leading to the formation of benzene, and subsequent growth of polycyclic aromatic hydrocarbons (PAHs) to soot. The hypothesis postulates that the pyrolysis of short-chain alcohols yields smaller species, such as methane, ethane, and ethylene, and that the relative abundance of these is influenced by the alcohol structure. It is further postulated that the dominant mechanism for the subsequent synthesis of PAHs from short-chain alcohols is the hydrogen abstraction/acetylene addition (HACA) mechanism. Despite the notable significance of short-chain alcohols as potential renewable fuels, a comprehensive understanding of their pyrolysis reactions at high temperatures in the context of soot and PAH formation is currently lacking.

Experiments were conducted to identify intermediate species during pyrolysis at different residence times by precisely positioning a sampling probe inside the laminar reactor, while rapidly freezing reactions in the sample at the probe’s entry using nitrogen dilution. While the impact of selected alcohol fuels on soot and PAH formation has been previously discussed using the same experimental setup [18], this study represents the first comprehensive examination of the formation of PAH precursors from these small chain alcohol fuels under pyrolytic conditions across a wide range of temperatures and residence times. The research provides a comparative study on the breakdown and formation of PAH precursors for each of the three alcohols under investigation. To collect and freeze the reaction of the samples, a novel high-temperature air-cooled ceramic sampling probe was employed, which had previously been used to sample intermediate gaseous species during the pyrolysis of C1-C4 hydrocarbons [31]. The exploration of combustion experiments for alcohols as alternatives to renewable clean energy can yield valuable insights into the production of environmentally harmful byproducts. However, it is important to emphasize that the study reported here primarily focused on investigating intermediate gaseous species contributing to benzene ring formation. A thorough examination of these species is pivotal for gaining a comprehensive understanding of the complex processes involved in alcohol pyrolysis likely to occur in practical combustion systems utilising stratified air fuel mixtures.

2. Experimental methodology

2.1. Experimental systems and conditions

Methanol, ethanol, and butanol were pyrolysed in the absence of oxygen in a laminar flow reactor at a temperature range of 869 to 1120 °C and varying residence times. Pyrolysis of test fuels took place in nitrogen at a constant concentration of 10,000 ppm on a carbon atom basis. Oxygen-free nitrogen was used as the carrier gas with a fixed flow rate through the pyrolyser tube of 20 l/m and was metered by a mass flow controller. The reactor tube was electrically heated externally and had length of 1440 mm with inner diameter of 104 mm. The reactor radial and axial temperature profiles and operation were described previously in references [17,32–35]. A detailed description of the novel air cooled high temperature ceramic sampling probe and GC-FID methods used for these experiments were previously presented in reference [31]. The novel sampling probe was designed with the consideration of minimizing capillary diameter to prevent carbon build-up and effectively quench reactions within the sample, which is crucial. It is noteworthy that a minimal capillary diameter poses a risk of carbon deposition or coking, potentially disrupting the sample flow. Despite this challenge, the novel sampling probe strategically addresses these concerns by carefully selecting the smallest feasible capillary diameter. This approach aims to prevent carbon build-up while ensuring the efficient quenching of reactions within the sample. In the course of the experiments reported here, no carbon deposition on the sampling probe capillaries was observed during sampling, and therefore, no discernible impact on the dilution level.

The calculation of residence time involves various factors, primarily the dimensions and conditions within the reactor tube. The furnace tube radius, which contributes to the tube’s cross-sectional area, is a key parameter. Additionally, the flow rate of nitrogen (N₂) through the reactor tube and the density of nitrogen at the elevated temperature play crucial roles.

The residence time is influenced by the length of the uniform heating zone within the reactor tube. This length, along with the tube temperature, is integral to the overall calculation. The gas residence time, a
critical parameter in our experimental setup, is determined by the ratio of the tube reactor volume to the gas flow rate at a set temperature, as expressed by the equation \( t = \frac{V}{Q} \), where \( V \) is the volume of the tube reactor (500 mm reaction zone), and \( Q \) is the gas flow rate at the test temperature. This equation allows us to quantify the time the gaseous reactants spend within the reactor. In addition to the factors mentioned, samples were collected at different depths and actual sample gas temperatures (T) ranging from 869 °C to 1213 °C. Specifically, the depths within the reactor tube where samples were taken were 81 cm, 76 cm, 71 cm, 66 cm, and 61 cm from the top of the reactor. To calculate the corresponding residence times at each depth and acknowledging changes in gas density and thus flowrate, for a given reactor temperature (T), the following relationships were utilized: for 81 cm, \( 747/(T + 273) \) (s); for 76 cm, \( 1120/(T + 273) \) (s); for 71 cm, \( 1493/(T + 273) \) (s); for 66 cm, \( 1866/(T + 273) \) (s); and for 61 cm, \( 2240/(T + 273) \) (s).

This particular temperature range was deliberately chosen for this study because preliminary experiments revealed that within this range, the fuel molecules investigated initiated decomposition and produced the final products, including soot. The preliminary experiments showed initial decomposition of the fuel and the formation of intermediate species smaller than benzene and formation of benzene. The measurement of diluted quenched sample gas temperatures was carried out using K-type thermocouples, with an uncertainty of ± 2 °C.

To identify gaseous species using GC-FID, an external standard mixture comprising 11 selected species listed in Fig. 1 was employed. These chosen species were considered potential intermediate compounds that could contribute to the formation of a benzene ring and PAHs, as informed by a review of relevant literature. The species in the external standard mixture were present at a concentration of 1000 ppm, in the balance being nitrogen. Considering the wide range of concentrations exhibited by the gaseous species generated during fuel pyrolysis, the external standard was diluted using high purity nitrogen to create four standards of progressively lower concentration. As an internal standard, a solution of dichloroethane in nitrogen with a concentration of 100 ppm was utilized. To quantify the gaseous species, the internal standard was added to both the samples and calibration standards.

2.2. Test fuels

Three, chemically pure grade 99.9%, alcohol fuels, methanol, ethanol, and 1-butanol were sourced from Fisher Scientific, with the properties of these fuels shown in Table 1.

![Sample chromatogram of external calibration standard mix.](image)

Fig. 1. Sample chromatogram of external calibration standard mix.

The following effects of methanol, ethanol, and butanol fuel molecular structure were investigated by quantifying the abundance of gaseous species sampled at a range of temperatures:

- The initial temperature at which pyrolysis products were detected and the rate at which fuel decomposition proceeded.
- Formation and distribution of potential precursors to first ring formation.
- The conversion pathways of species contributing to benzene production as indicated by relative levels of precursors at varying temperatures and residence times.

3. Results and discussions

The experimental results of gas sample analysis during methanol, ethanol, and butanol pyrolysis at various temperatures and residence times are outlined in this section, while a thorough discussion of these data is provided in Section 6. It is important to note that an attempt was made to represent the results on a single graph with temperature changes, however, this endeavour faced challenges due to the inherent variability in residence times on an absolute basis with changing temperatures. Consequently, the results were portrayed at a constant temperature and different residence times. The main focus of the discussion is the group of 11 intermediate gaseous species that are considered potential precursors for the formation of a benzene ring and the growth of PAHs. These are shown in Fig. 1 and were included in the calibration standard.

3.1. Pyrolysis of methanol, ethanol, and butanol at a constant temperature of 869 °C

The concentrations for gaseous intermediate species detected by GC-FID during pyrolysis of methanol, ethanol, and butanol at a constant temperature of 869 °C and residence times of 0.64 to 1.96 s are shown in Fig. 2. The error bars in Fig. 2 and the following figures show plus and minus one standard deviation from the mean result, which was calculated using three repeats at each residence time. It is interesting to note that at this temperature of 869 °C, acetaldehyde was detected during methanol (at the shortest two residence times) and ethanol pyrolysis, along with C1 and other C2 species, while during butanol pyrolysis C3 and C4 gaseous species were also detected. As mentioned previously, this brief presentation of results will be followed by detailed discussion later, in Section 6.

3.2. Pyrolysis of methanol, ethanol, and butanol at a constant temperature of 1018 °C

Fig. 3 shows the gaseous intermediate species detected during pyrolysis of methanol, ethanol, and butanol at the higher constant temperature of 1018 °C and varying residence times. It is interesting to note that the concentration of benzene during butanol pyrolysis increased with the increase of residence time, while no benzene was detected during methanol and ethanol pyrolysis at any residence times.

3.3. Pyrolysis of methanol, ethanol, and butanol at a constant temperature of 1120 °C

Fig. 4 depicts the concentrations of species observed during pyrolysis of methanol, ethanol, and butanol at the constant temperature of 1120 °C and residence times of 0.54 to 1.61 s. It is apparent from Fig. 4 that butanol pyrolysis produced a relatively higher concentration of C1, C2, C3, and C6 gaseous intermediate species at all residence times.
of the OH group and hydrogenation of the CH atom may be considered. It is interesting to note from Figs. 2, 3, and 4 that the concentration of methane decreases with temperature but does not change with residence time at a constant temperature, which also implies that the abstraction of the OH group and hydrogenation of the CH₂ radical occurs quickly [41]. It can be observed from Figs. 2, 3, and 4 that the distribution of species detected during methanol pyrolysis was affected by the changing temperature, but the apparent effect of residence time is minimal (except its effects on acetaldehyde formation at the lowest temperature of 869 °C). This observation aligns with the findings of Ran et al. (2017), where they observed that the selectivity of methanol decomposition to methane remains relatively unaffected by residence time. The production of methane from methanol pyrolysis is a primary reaction, achieved via a direct path through an unstable methyl radical [42].

As reported previously in the literature [43], methanol pyrolysis includes two decomposition pathways. The first is the breakdown of methanol into hydroxyl and methyl radicals via reaction 6.1 and the other is hydrogen abstraction from methanol via reaction 6.2, producing formaldehyde, which then decomposes to carbon monoxide via reaction 6.3 [43].

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CH}_3 + \text{OH} & \text{6.1} \\
\text{CH}_3\text{OH} & \rightarrow \text{H}_2 + \text{CHO} & \text{6.2} \\
\text{CH}_2\text{O} + \text{H}_2 & \rightarrow \text{H}_2\text{O} & \text{6.3}
\end{align*}
\]

Formaldehyde was not in the selected calibration standards, but during methanol pyrolysis, there were no unidentified peaks during GC-FID analysis, implying an absence of formaldehyde. Fig. 4 shows at residence times longer than 1.31 s at 869 °C that instead of formaldehyde, acetaldehyde was detected, suggesting that formaldehyde may have formed according to reaction 6.2 and subsequently reacted with methyl radicals to form acetaldehyde by the following reaction pathways [44]:

\[
\begin{align*}
\text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{CH}_4 + \text{CHO} \\
\text{CHO} + \text{CH}_3 & \rightarrow \text{CH}_4 + \text{CO} \\
\text{CHO} + \text{CH}_3 & \rightarrow \text{CH}_3\text{CHO}
\end{align*}
\]

It can be seen from Fig. 2 that only 1/10 of the methanol had converted into methane at the lowest temperature of 869 °C and the concentration of methane reduced further as the temperature increased. This observation suggests that for the majority of the methanol supplied the carbon to oxygen bond remained intact [17], likely resulting in CO emission and preventing the formation of methyl radicals or methane. Further evidence that during methanol pyrolysis a majority of methanol is converted to CO is present in the literature [17]. Previous studies state that at temperatures greater than 880 °C, the generation rate of carbon monoxide from methanol pyrolysis increases to approximately 95% [43]. While findings from this experiment suggest that the C-O bond does not break most of the time, the concentration of CO gas was not measured during the study.

In conclusion, among the detected species, methane was the most abundant species at all temperatures and residence times. The concentration of C₂ species was very small and no C6 (benzene) was detected, suggesting that methanol pyrolysis does not readily form polyaromatic hydrocarbons and soot. The same observation was made in a previous study which used the same facilities and conditions [18] and which undertook the analysis of PAHs produced during pyrolysis of C2-C4 alcohols. In preliminary experiments for that study, it was also observed that methanol yielded no soot.

### 4.4. Ethanol fuel

Figs. 2, 3, 4, and 5 show results for ethanol fuel supplied to the reactor at a flow rate of 10,000 ppmC in nitrogen. These figures illustrate the identified species at various temperatures and residence times.

Fig. 2 shows that the concentration of most hydrocarbons examined peaked at the lowest temperature of 869 °C, indicating that ethanol decomposition commenced at this temperature (or lower). At higher temperatures, initial decomposition products had combined to form larger hydrocarbons, as well as PAHs outside the range of species investigated by GC-FID. The same effect of reducing total carbon concentration with increasing temperature and residence times was also observed during the pyrolysis of small chain hydrocarbons fuels using the same conditions and experimental system [31].

Fig. 2 shows that the most abundant intermediate products of ethanol pyrolysis were methane and ethylene, followed by acetaldehyde and acetylene. It can be observed from Fig. 2 that at a temperature of 869 °C methane levels remained constant at all residence times. The concentration of acetylene increased as the residence time increased from 0.64 s to 1.31 s, and then decreased slightly between 1.63 s and 1.94 s. It is apparent from Fig. 2 that at the lowest temperature of 869 °C the concentration of ethylene decreased with residence time. It is interesting to note that acetaldehyde was only detected at 0.64 s and 0.98 s (Fig. 2a and b), while a small concentration of propene was also detected at the shortest residence time.

Fig. 3 shows the species detected at a sample constant inlet temperature of 1018 °C and at varying residence times. It can be seen from Fig. 3 that during ethanol pyrolysis the highest concentrations of the detected C1 and C2 hydrocarbons species were found at the shortest residence times, while concentrations decreased dramatically at longer residence times; these observations imply that at higher residence times the reactions have more time to proceed to PAHs and eventually soot. It should be noted that propene and acetaldehyde were not detected at this temperature (1018 °C).

### Table 1

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Molecular structure</th>
<th>Oxygen to carbon (O/C) ratio</th>
<th>Molar mass (g/mol)</th>
<th>Density (kg/m³) at 25°C</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>1</td>
<td>32.02</td>
<td>792</td>
<td>64.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>0.50</td>
<td>46.06</td>
<td>789</td>
<td>78</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>CH₃(CH₂)₃OH</td>
<td>0.25</td>
<td>74.11</td>
<td>810</td>
<td>118</td>
</tr>
</tbody>
</table>

Z.A. Khan et al.

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Fig. 4 shows that at the highest temperature (1120 °C) and varying residence times, the concentration of detected species dropped significantly relative to the lower temperatures investigated. Ethanol was supplied at 10,000 ppmC but only a very small concentration of carbon was detected in the C1 to C6 species range (Fig. 4), even at the shortest residence time, implying that the decomposition products had already converted to species larger than benzene. It is also noteworthy that no hydrocarbon species were detected at a higher temperature than 1120 °C when preliminary experiments were undertaken at 1213 °C (shown also in Fig. 6 discussed later at the end of section 6.3).

Fig. 2. Concentration of detected species during methanol, ethanol and butanol pyrolysis at a constant temperature of 869 °C and increasing residence time of (a) 0.64 s, (b) 0.98 s (c) 1.31 s, (d) 1.63 s, and (e) 1.96 s. Error bars denote one standard deviation.
The presence of methane seen in Figs. 2, 3 and 4 at all temperatures suggests that the initial pyrolysis of ethanol might occur through unimolecular decomposition. The dominant initiation reaction for ethanol breakdown at lower temperatures has been reported to be via scission of the C-C bond to form methyl radicals, which upon hydrogenation form methane [45]. It is worth noting in Fig. 2 that at the lowest temperature of 869 °C a significant portion of ethanol supplied is transformed to methane (up to 20%). Under the conditions investigated in this work, once formed methane is a relatively unreactive hydrocarbon at this lowest temperature of 869 °C and can be expected to remain as a final reaction product, limiting the formation of common soot precursors such as acetylene. This observation of the stable nature of

Fig. 3. Concentration of detected species during methanol, ethanol, and butanol pyrolysis at constant temperature of 1018 °C and increasing residence time of (a) 0.58 s, (b) 0.87 s, (c) 1.16 s, (d) 1.44 s, and (e) 1.74 s. Error bars denote one standard deviation. Note: the y-axis is significantly magnified for Fig. 3c,d, and e.
methane at a lower temperature is in strong agreement with other results in the literature [14]. In a separate set of experiments performed with ethane in the same experimental system and similar experimental conditions as in this work [31], the pyrolysis of ethanol was observed to produce 3 to 4 times more methane than the pyrolysis of ethane (see Fig. 5). It is likely that this could be attributed to an ethanol decomposing pathway that limits the availability of carbon for the formation of benzene rings, PAHs, and soot. This is illustrated by the following two routes for ethanol decomposition [15], where the second route limits carbon availability and increases methane concentration, as observed in the literature [14].
Fig. 5. Concentration of intermediate species detected during pyrolysis of (a) ethanol at a constant temperature of 869 °C and (b) ethane at a constant temperature of 869 °C [31]. Error bars denote standard deviation.

Fig. 6. GC-FID Chromatogram of gas sample taken during the pyrolysis of (a) methanol, (b) ethanol, and (c) butanol at a temperature of 1213 °C and residence time of 0.50 s.
the work reported here.

\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 + \text{H}_2\text{O} \]

Unlike methanol and ethanol, butanol pyrolysis produced C3 and C4 hydrocarbons in addition to C1 and C2 hydrocarbons. This suggests that additional chemical pathways for benzene formation and growth were available. Propene and propyne are C3 hydrocarbons that may be converted into propargyl radicals, which, together with 1,3 butadiene and vinyl acetylene, are essential precursors for the formation of the first aromatic rings [50, 51].

It is worth noting that the pyrolysis of butanol produced less benzene relative to ethanol. This might be because most butanol carbon continues its chemical routes faster than methanol and ethanol and pass through different intermediates (other than benzene, for example phenyl) on route to production of soot [52]. It is also possible that where butanol is relatively more reactive under pyrolytic conditions the intermediates investigated are present for a shorter duration before converting into larger species and, thus, less easily observed. This observation is further supported by the higher mass of soot produced by 1-butanol as compared to ethanol and propanol [17].

### 4.4. Effect of carbon chain length on the intermediate species formation

In addition to the temperature and residence time effects on the pyrolysis of each alcohol discussed in detail in Sections 6.1, 6.2, and 6.3, it is also apparent that the fuel molecular structure has an effect on initial decomposition, overall distribution, pathways for first ring formation, and equilibrium between different detected species at different temperatures and residence times.

Most readily apparent was that methanol, as the simplest alcohol and with the highest oxygen to carbon ratio of the alcohols, does not produce any potential C2, C3, and C4 intermediate species at or above a pyrolysis temperature of 869 °C. In fact, the only hydrocarbon detected during methanol pyrolysis was methane and at a concentration much less (approximately 1/10th) than the supplied carbon. Furthermore, during ethanol and butanol pyrolysis, the concentration of methane produced at lower temperatures remained constant with increasing residence time, suggestive of its stable nature at lower temperatures. The stability of methane at the lowest tested temperature was also observed during a similar experiment performed with methane, ethane, and butane pyrolysis [31]. Previous studies have reported that during methanol pyrolysis, the concentration of carbon monoxide increases to approximately 95% at temperatures greater than 880 °C [43]. This is in agreement with the low levels of methane observed (Fig. 2) and suggests that at a temperature above 880 °C, the bond between carbon and oxygen remains intact, likely resulting in CO emission and preventing the formation of methyl radicals or methane to form first ring precursors.

During ethanol pyrolysis, it was observed that at lower temperatures a higher concentration of methane was formed (Fig. 2), suggesting that the initial pyrolysis of ethanol might occur through unimolecular decomposition. It has also been reported in the literature that at lower temperature the dominant breakdown pathways of ethanol are via the C-C bond breaking to form methyl radicals, which upon hydrogenation form methane [45]. As methane at the lowest temperature is stable, it would thus not contribute toward the formation of potential intermediate species to form the first ring. Thus, the dominance of this pathway, involving breaking of the C-C bond and hydrogenation to methane reduces the overall formation of PAHs and soot at lower temperatures.

In the case of butanol pyrolysis, a higher concentration of ethylene was observed as compared to methane and acetylene species in a temperature range of 869 to 1018 °C (Figs. 2 and 3), which suggests that the initial decomposition of butanol is via C-C cleavage. The presence of C3 and C4 species, in addition to C1 and C2 ones, during butanol pyrolysis suggested that along with C2 more reaction pathways were available for benzene formation, for example via propargyl radicals or via 1,3 butadiene and vinyl acetylene (see Fig. 2).

The most important chemical processes that occur during the pyrolysis of small chain alcohols are those that lead to the formation of...
acetylene. The dehydrogenation process necessary for formation of acetylene is reversible with the rate of equilibrium controlled by temperature and pressure [49]. According to the literature, dehydrogenation processes are favoured at higher temperatures [48]. From Sections 6.1, 6.2, and 6.3, the equilibrium between the C2 species (especially ethylene and acetylene) at higher temperatures and shorter residence times shifted increasingly toward acetylene formation for all test fuels, but more so in the case of butanol in comparison to ethanol.

Fig. 6 shows a sample chromatogram for methanol, ethanol, and butanol at the highest tested temperature of 1213°C and short residence time of 0.50 s. The numbered peaks shown in Fig. 6 are the detected hydrocarbons, number 1 corresponding to methane, 2 to acetylene and 3 to ethylene, while the single large peak that appeared in the chromatogram, labelled as 'IS' corresponds to the internal standard.

It was observed from Fig. 6 that the supplied 10,000 ppm of carbon is no longer visible among the measured species and the detected species were at very low concentration at the highest tested temperature and low residence time in the case of all test fuels. No other peaks were identified within the chromatograms (Fig. 6), implying that the vast majority of the supplied carbon at this condition had reached stable species (possibly larger PAHs or soot) that do not decompose according to the equilibrium constant.

5. Conclusions

This study investigated the presence and abundance of a variety of intermediate gas-phase species, known to be precursors to the formation of the first aromatic ring, PAH, and soot, during the pyrolysis of methanol, ethanol, and butanol. The test fuels were pyrolysed in a heated nitrogen stream at temperatures ranging from 869°C to 1120°C at a fixed concentration of 10,000 ppm on a C1 carbon basis. A range of temperatures and residence times were employed to generate insight into the pyrolytic decomposition of the three alcohols. The observed distributions of intermediate species suggested variation in the decomposition pathways of each alcohol, relative to one another, with common effects of temperature and residence time also becoming apparent. From the results presented the following specific conclusions can be drawn:

- During methanol pyrolysis, temperature had a significant effect on the initial breakdown of fuel while the effect of residence time was minimal. There were strong indications that in most cases the carbon to oxygen bond within methanol appeared not to break, as the concentration of the most abundant hydrocarbons species detected was 1/10 of the supplied methanol carbon.
- A small concentration of C2 species was detected at the lowest temperatures during methanol pyrolysis, which diminished at higher temperatures. No C6 species were detected, which could be attributed to a higher percentage of carbon monoxide relative to ethanol and thus it is likely that no polyaromatic hydrocarbons or soot were formed during methanol pyrolysis.
- Temperature and residence time both influenced ethanol pyrolysis. Lower temperatures and shorter residence times promoted the formation of methane and ethylene, whereas higher temperatures and longer residence times encouraged faster reactions. Ethanol pyrolysis produced a significant amount of ethylene and acetylene, suggesting a role in the formation of benzene and soot. The abundance of C2 species also suggested dominance of the HACA mechanism for PAHs and soot surface growth.
- Butanol pyrolysis was not rate limited, rather it was temperature limited. In addition to C1 and C2 species, butanol pyrolysis produced C3 and C4 hydrocarbons. The presence of C3 and C4 species indicated that additional chemical routes for benzene or other PAH precursors and growth were opened during butanol pyrolysis compared to ethanol.

CRediT authorship contribution statement

Hellier Paul: Conceptualization, Data curation, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing. Khan Zuhaib Ali: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Validation, Visualization, Writing – original draft. Almaleki Ahmad: Visualization, Writing – review & editing. Ladonmatos Nicos: Conceptualization, Data curation, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

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.

Data availability

No data was used for the research described in the article.

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