

# Sooting Limits of Nonpremixed *n*-Heptane, *n*-Butanol, and Methyl Butanoate

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## Abstract

The sooting limits of nonpremixed *n*-heptane, *n*-butanol, and methyl butanoate flames were examined experimentally in a liquid pool stagnation-flow configuration. In addition, complementary simulations with detailed polycyclic aromatic hydrocarbon (PAH) and a detailed soot model, based on the Hybrid Method of Moments (HMOM), are performed and compared with the experimental critical strain rates for sooting flames. *n*-Heptane and *n*-butanol exhibited similar sooting characteristics, and methyl butanoate was found to have the least sooting propensity. Further sensitivity and reaction path analysis demonstrates that the three fuel share similar PAH chemical pathways, and the differences in sooting propensity lie in the fuel breakdown processes. The oxygen bounded in *n*-butanol mainly goes through the intramolecular water elimination reactions and is afterwards bounded in the water molecule. Another product from these reactions is 1-butene ( $\text{P-C}_4\text{H}_8$ ), which is an important soot precursor for both *n*-heptane and *n*-butanol. On the contrary, 1-butene is not formed during methyl butanoate breakdown processes, and the fuel bound oxygen reduces the concentration of soot precursors by truncating the long carbon chain and promoting its oxidization.  $\text{C}_5$  and  $\text{C}_6$  ring formation from the intermediate chain species is found to be the rate limiting step and is responsible for the critical strain rate.

**Keywords:** Soot, Nonpremixed stagnation-flow flame, Hybrid Method of Moments, *n*-Butanol, Methyl butanoate

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## 1. Introduction

The utilization of biofuels, which are potential partial replacements for liquid fuels derived from fossil fuels, is garnering wide attention not only because these fuels are renewable, locally producible, and carbon neutral [1] but also due to their potential positive impacts on particulate matter (PM) emission control. Biofuels, including bioalcohols and biodiesels, mainly consist of oxygenated hydrocarbons, such as ethers, alcohols, and esters. When used as additives in conventional diesel fuels, PM emissions have been found to decrease as oxygenated additive concentrations increase [2].

However, the role of oxygenated additives on soot emission reductions has not yet come to a scientific consensus. For example, Frijters and Baert [3] attributed the PM reduction to the fuel oxygen content, which reduced the local

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equivalence ratio. Westbrook *et al.* [4] performed simulations of premixed *n*-heptane and oxygenates flames and found that, even with the same oxygen content, the oxygenates had distinct efficiencies in soot precursor reduction. Furthermore, Pepiot *et al.* [5] proposed a structural group contribution approach to interpret diesel engine experimental data. This study noted that aromatics contained in the conventional diesel fuel had very strong sooting tendencies and were replaced by clean-burning oxygenated additives. Therefore, this replacement effect should be identified and quantified to reveal the role of the oxygen moieties.

Conversely, McEnally and Pfefferle [6, 7] found that butanol isomer doped co-flow diffusion methane flames produce more soot than the undoped ones and concluded that the fuel carbon number and structure was more important than the fuel bound oxygen. Similar conclusions were reached by Camacho *et al.* [8] by probing the evolution of the detailed particle size distribution function in a set of laminar premixed flames of *n*- and *i*-butane/butanol with fixed C/O ratio and maximum temperature.

Although valuable efforts have been made, well-controlled fundamental experiments and detailed chemical kinetic models are still needed to understand the chemical pathways for soot formation of oxygenated fuels. Moreover, it is also noted that soot formation is a kinetically controlled process [9], thus the residence time of soot precursors also influences the sooting propensities[10]. Therefore, the present experimental and computational study focuses on the sooting limits of three pure liquid diesel/biofuel components, specifically, *n*-heptane, *n*-butanol, and methyl butanoate, in a nonpremixed stagnation-flow system. A combined chemical kinetic model with detailed polycyclic aromatic hydrocarbon (PAH) chemistry is proposed to investigate the important pathways of soot formation with these three fuels. The choice of target fuels is motivated by both practical and scientific concerns. First, butanol has more diverse sources of supply than ethanol, which is obtained primarily from corn. Second, methyl butanoate is chosen not only because it is a typical biodiesel surrogate but also due to the availability of detailed chemical kinetic models. Third and the most important, the boiling points of *n*-butanol and methyl butanoate are 391 K and 375 K, respectively, which are very close to that of *n*-heptane (372 K). This similarity in vaporization characteristics enables similar fuel concentrations in the liquid pool stagnation-flow apparatus and the fuels to be readily mixed for use in practical systems.

## 2. Experimental Methodology

The sooting limits of nonpremixed model diesel/biofuel components, in terms of the critical strain rate (CSR) at which soot inception starts to happen when the residence time, which is the inverse of the strain rate, is further increased, were measured at atmospheric pressure in a liquid pool stagnation-flow configuration described in detail by elsewhere [11]. In the present work, unheated oxidizer stream impinged against the liquid fuel pool, and flames were established by spark ignition. Unlike previous studies, the separation distance between the oxidizer nozzle and liquid pool was increased to 13 mm to enable better measurement of the velocity field by Laser Doppler Velocimetry (LDV).

Table 1: Oxidizer stream composition in mole fractions.

		$O_2$									
		0.1950	0.1975	0.2000	0.2025	0.2050	0.2075	0.2100	0.2150	0.2200	0.2250
$n - C_4H_9OH$	$N_2$	0.7718	0.7679	0.7640	0.7600	0.7560	0.7521				
	$Ar$	0.0332	0.0346	0.0360	0.0375	0.0390	0.0404				
$C_5H_{10}O_2$	$N_2$					0.7119	0.7068	0.7017	0.6915	0.6811	0.6707
	$Ar$					0.0831	0.0857	0.0883	0.0935	0.0989	0.1043

It should be noted that, due to the oxygen content in  $n$ -butanol and methyl butanoate, their flame temperatures are lower than  $n$ -heptane. As soot formation is highly sensitive to temperature [12], this thermal effect has to be eliminated to elucidate the chemical effects. In the present study,  $n$ -butanol and methyl butanoate flame temperatures were kept the same as  $n$ -heptane by replacing a portion of the nitrogen in the oxidizer stream with argon, which is the same approach taken by Law and co-workers [13–15]. The amount of nitrogen replacement was calculated with CHEMKIN’s equilibrium solver EQUIL[16] for stoichiometric fuel/oxidizer mixture, and the diluent concentrations are summarized in Table. 1. Liquid  $n$ -heptane,  $n$ -butanol, and methyl butanoate were fed to the liquid pool by a syringe pump at room temperature.

Soot detection was based on luminosity observations, as Du *et al.* [13] found that such measurements agreed well with light scattering detection and were a convenient indicator of the presence of soot particles. The experimental procedure to identify the sooting limit is briefly summarized here. First, the oxidizer component flow rates were set and a non-sooting blue flame was established. Then, the bypass valve placed upstream of the oxidizer nozzle was slowly adjusted to divert oxidizer out of the system, effectively reducing the velocity of the stream and, consequently, the strain rate. The residence time was further increased until yellow luminosity began to appear on the fuel rich side of the flame. A standard single-component LDV measurement was performed along the axial centerline under this threshold flow condition, and the local strain rate experienced by the reactant was determined as the axial velocity gradient upstream of the flame [13]. Following this procedure, the sooting limits for the three fuels with different oxygen concentrations in the oxidizer streams were identified.

### 3. Computational Methodology

The liquid pool stagnation-flow flames were simulated with the FlameMaster code [17], including detailed PAH chemistry and a detailed soot model. The boundary conditions on the fuel side were specified by Bui-Pham *et al.* [18]. In brief, the Antoine equation [19] was used to close the boundary value problem by relating the liquid pool surface temperature and vapor pressure, yielding a relationship for the fuel mole fraction. As in the experiment, the strain rate was determined as the gradient of the velocity profile ahead of the flame. Furthermore, to mimic the luminosity observations, the computational CSRs were determined based on a global soot volume fraction ( $f_v$ ). The threshold value was determined to match the experimental results of  $n$ -heptane at larger  $X_{O_2}$  cases and was kept fixed for all other cases.

A detailed chemical model including PAH chemistry was combined from three well validated models corresponding to the fuels of interest. A mechanism with PAH chemistry of engine relevant fuels was developed by Blanquart, Pitsch, and co-workers [20, 21]. This mechanism has been validated extensively against experimental measurements at ignition delay times, laminar burning velocities, and species profiles in both premixed and nonpremixed flames over a large range of equivalence ratios and pressures. Of particular interests to this work, the mechanism has been validated in *n*-heptane nonpremixed flames against the measurements of Berta *et al.* [22]. In the present study, this mechanism was adopted as the base mechanism with PAH chemistry. Conversely, although efforts have been made in developing chemical kinetic models for *n*-butanol and methyl butanoate in recent years, less emphasis has been placed on their PAH pathways. Therefore, the oxidation/pyrolysis chemistry of detailed *n*-butanol and methyl butanoate kinetic models, which was originally developed by Sarathy *et al.* [23] and Gail *et al.* [24], respectively, and reduced and validated by Liu *et al.* [1] was combined with the base mechanism. The thermal and transport data of the species appeared only in the *n*-butanol and methyl butanoate mechanism was also included in the base data files. This combined mechanism consists of 220 species and 2259 forward and backward reactions. It was further validated against laminar flame speed measurements [1] and compared with the predictions by the original mechanisms, and the results of this validation are included as Supplemental material.

The detailed soot model is based on the Hybrid Method of Momnet developed by Mueller *et al.* [25–27]. The detailed model considers particle nucleation from PAH dimers [28–30], PAH dimer condensation, particle coagulation [26], surface growth by the HACA mechanism [31], oxidation [32, 33], and oxidation-induced fragmentation [27]. In addition, the model considers thermophoresis but neglects molecular diffusion. In total, four quantities are used to describe the evolution of the soot population.

#### 4. Results and Discussion

The critical strain rates (CSRs) corresponding to the sooting limits from the experiments and computations, are shown in Fig. 1. For each set of data, the region above/left of the data corresponds to non-sooting flames and the region below/right of the data corresponds to sooting flames. For all three fuels, the CSR increases with increasing oxygen concentration in the oxidizer stream, which has been previously characterized as a thermal effect [14]. In addition, both experiment and computation show that methyl butanoate has substantially lower CSRs compared to *n*-heptane and *n*-butanol. The fall-off between experimental and computational results might due to the uncertainty of the yellow luminosity determination. On the other hand, the integrated  $f_V$  under various strain rates are shown in the right part of Fig. 1. For all three fuels, less soot is formed due to reduced residence time, and *n*-butanol is overall as sooty as *n*-heptane, while methyl butanoate is the least sooty. Since the CSR was experimentally measured and accordingly defined in computations based on the absolute value of  $f_V$ , lower CSR indicates a lower sooting propensity. The choice of the the integrated  $f_V$  threshold value does not change the clear trend of sooting propensity between the fuels.

To understand these distinct differences between the three fuels, sensitivity and reaction path analysis was per-

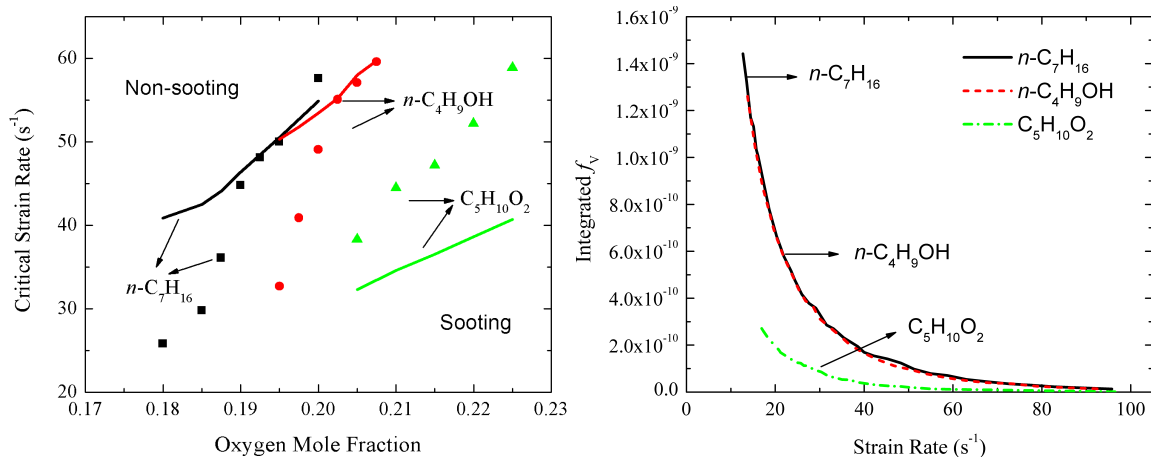


Figure 1: Left: Experimental (symbols) and computational (lines) CSRs. Right: The responses of the integrated  $f_V$  to strain rate at  $X_{O_2} = 0.2$ .

formed on a representative PAH species, naphthalene (C<sub>10</sub>H<sub>8</sub>). As shown in Fig. 2 and Fig. 3, naphthalene shows roughly the same sensitivities to the same reactions for each of the fuels, and the chemical pathways of naphthalene are essentially the same subsequent to the fuel cracking. Initially, fuel cracks to unsaturated C<sub>3</sub> to C<sub>5</sub> chains through H abstraction followed by  $\beta$ -scission reactions. These smaller molecules further decompose into allyl radicals (A-C<sub>3</sub>H<sub>5</sub>, CH<sub>2</sub>=CH-CH<sub>2</sub><sup>\*</sup>) and propene (C<sub>3</sub>H<sub>6</sub>), which contribute to C<sub>5</sub> and C<sub>6</sub> ring formation by either combining with acetylene (C<sub>2</sub>H<sub>2</sub>) or forming propargyl (C<sub>3</sub>H<sub>3</sub>), which further combines with itself to form aromatic rings. Larger rings are formed by the combination of phenyl (C<sub>6</sub>H<sub>5</sub>) and smaller radicals, such as CH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>3</sub>H<sub>3</sub>. Two pathways directly contribute to naphthalene formation, namely, twocyclopentadienyl (C<sub>5</sub>H<sub>5</sub>) radicals recombination and indenyl (C<sub>9</sub>H<sub>7</sub>) methyl addition reactions

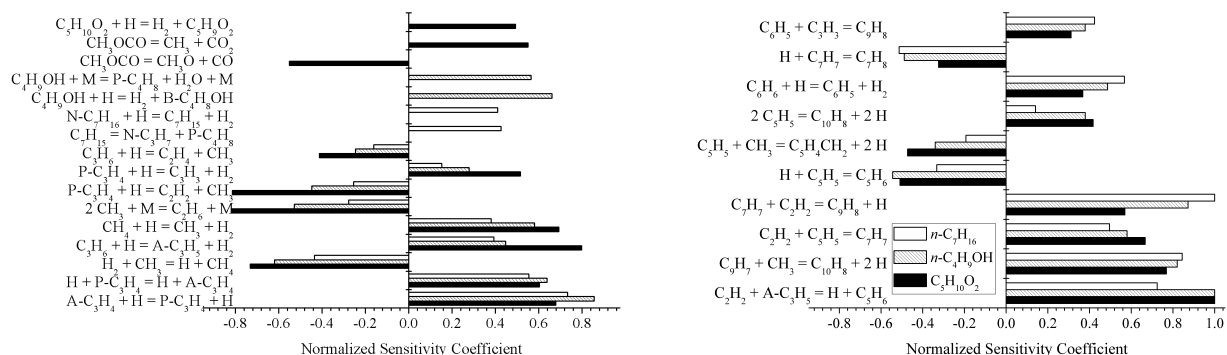
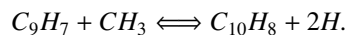
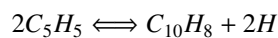


Figure 2: Sensitivity of the maximum naphthalene mass fraction to kinetics at the strain rate of 16 s<sup>-1</sup> and  $X_{O_2} = 0.2$ . Left: Intermediate chain radical reactions. Right: Ring formation reactions.

Although the PAH pathways for the three fuels are similar, the formation of these soot precursors from the fuel

cracking processes and the relative importance of the subsequent chemical pathways of PAH growth are fuel specific. Noting the similarity in the chemical pathways beyond  $A-C_3H_5$  and  $C_3H_6$ , the fuel specific breakdown pathways that lead to the generation of these precursors are depicted in Fig. 4. For both  $n$ -heptane and  $n$ -butanol, 1-butene ( $P-C_4H_8$ ) is formed from the fuel decomposition, which contributes to 25% of  $A-C_3H_5$  production and is strongly promoting naphthalene formation, as indicated by the sensitivity analysis in Fig. 2. Moreover, the fuel bound oxygen in  $n$ -butanol is converted into water during an intramolecular water elimination reaction and does not contribute to carbon reduction [6, 7], which explains the similar sooting behavior as  $n$ -heptane.

Conversely,  $C_3$  species are the largest species formed from methyl butanoate cracking due to the fuel bound oxygen. As pointed out by Westbrook *et al.* [4], the double  $C=O$  bond is very difficult to break, such that the carbon chain length is reduced when  $C-C$  bond is broken due to  $\beta$ -scission. The oxygenated parts are then oxidized to  $CO$  and  $CO_2$ , preventing the carbon from entering the pool for soot formation [34, 35]. In Fig. 2, it further shows that when two oxygen atoms in  $CH_3OCO$  keeps attaching to different carbon atoms, which corresponds to the reaction that forms  $CO$  rather than  $CO_2$ , it is more efficient to demote naphthalene formation, as the concentration of  $CH_3$  is reduced. Due to the reduction in allyl radicals, the concentration in  $C_5H_5$  is also reduced. Since one of the pathways for naphthalene depends quadratically on  $C_5H_5$ , even moderate reductions in the radical concentration will significantly reduce naphthalene. As a result, in methyl butanoate flames, the  $C_5H_5$  recombination pathway is negligible to the  $C_9H_7$  pathway. This reduction in soot precursors from fuel cracking processes distinguishes methyl butanoate from  $n$ -heptane and  $n$ -butanol, in terms of the sooting propensity.

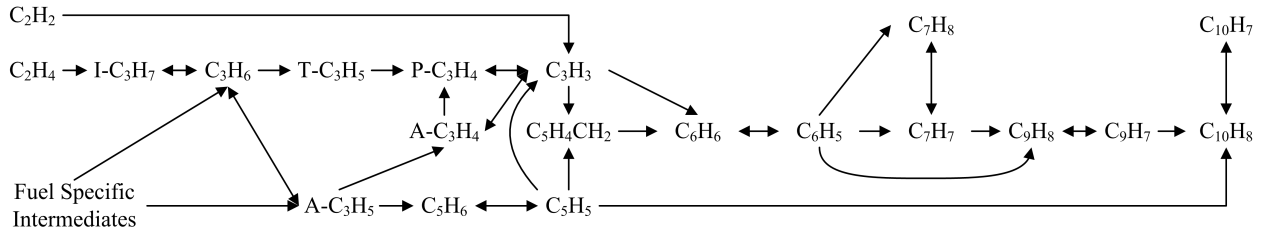


Figure 3: Chemical pathways for naphthalene formation at the strain rate of  $16 \text{ s}^{-1}$  and  $X_{O_2} = 0.2$ .

At this point, we have identified pathways and species that are responsible for soot formation. The next question that naturally arises is how sensitive they are to the increasing strain rate that leads to reduced soot formation. To answer this question, integrated  $f_V$  under various strain rates and  $f_V$  profiles for low and critical strain rate cases were presented in Fig. ???. All profiles shift in the direction of the liquid pool as higher flow rate pushes the stagnation plane further towards the pool. As expected, sooting propensities drop due to reduced residence time, and methyl butanoate is the least sooty, while  $n$ -butanol is overall as sooty as  $n$ -heptane. Although not shown here, sensitivity and reaction path analysis were conducted and no substantial difference was found compared with low strain rate cases. As the CSR was measured and defined based on the absolute value of  $f_V$ , it is reasonable to anticipate a lower CSR for methyl butanoate, since it is the least sooty fuel even at lower strain rates. However, if the CSR is defined based on

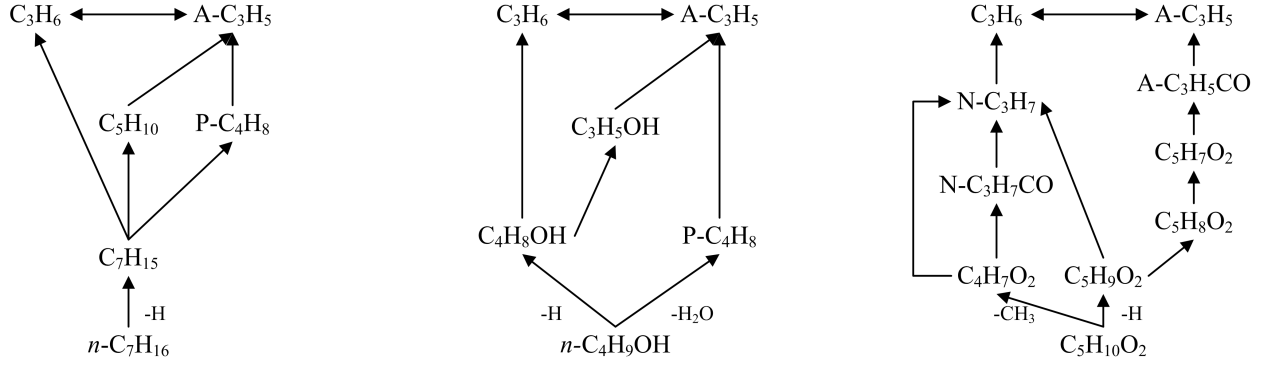
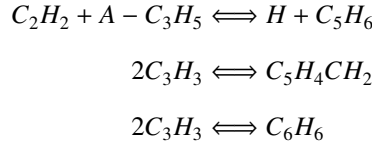


Figure 4: Fuel specific pathways for  $C_3H_6$  and  $A-C_3H_5$  formation at the strain rate of  $16 \text{ s}^{-1}$  and  $X_{O_2} = 0.2$ . From left to right: *n*-heptane, *n*-butanol, and methyl butanoate.

a relative metric, in other words, to be the strain rate at which the  $f_V$  is 10% of the value at a fixed low strain rate ( $16 \text{ s}^{-1}$ ), the three fuels are very close, which indicates the potential similarity in rate limiting steps of the soot formation.

To elucidate the rate limiting step, profiles of soot precursors at low and critical strain rates were computed. As shown in Fig. 5, all profiles shift in the direction of the liquid pool as higher flow rates at increased strain rates push the stagnation plane towards the pool. Species with ring structures, specifically,  $C_5H_6$  and  $C_9H_8$ , both have lower concentrations at CSR, responding to strain similar to  $f_V$ . However, the upstream  $C_3$  precursors,  $A-C_3H_5$  and  $C_3H_3$ , have higher concentrations at CSR. This indicates that these species have insufficient residence times to form rings, resulting in the observed decrease in soot. Therefore, the ring formation reactions



are the rate limiting steps and are sensitive to strain rates.

## 5. Conclusions

In this work, *n*-heptane, *n*-butanol, and methyl butanoate were chosen as diesel/bioalcohol/biodiesel surrogates of interest, due to their similar volatilities and consequent potential applications in diesel fuel blending. Their sooting limits were measured experimentally with the stagnation-flow apparatus. Computations were conducted for the same cases using detailed PAH chemistry and a detailed soot model based on the Hybrid Method of Moments (HMOM). Both experimental and computational results showed the critical strain rates of the three fuels, based on the absolute soot volume fraction, increase with increasing oxygen mole fraction in the oxidizer, due to the thermal effect. Moreover, although *n*-heptane and *n*-butanol show similar sooting propensities, methyl butanoate is distinctly less sooty.

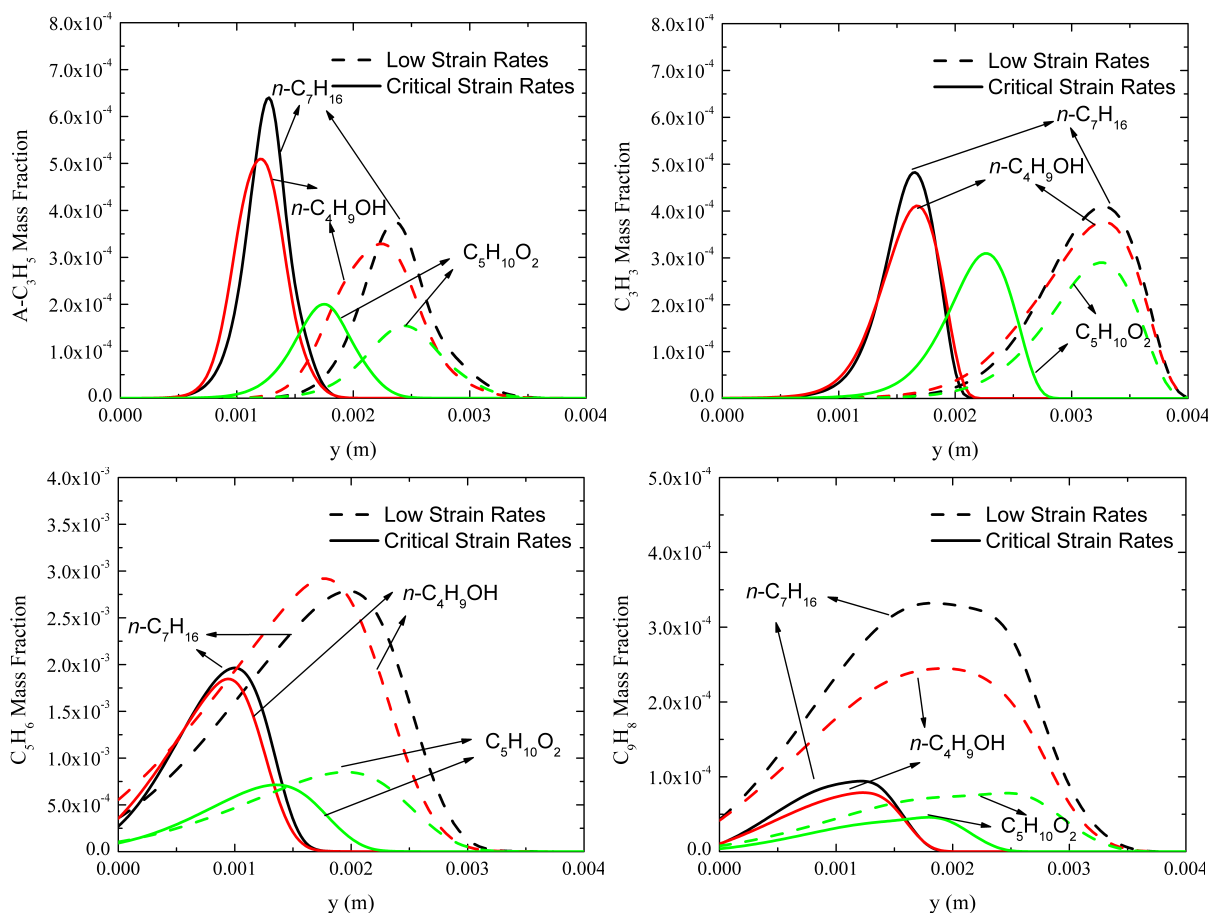


Figure 5: Key intermediate species profiles at low strain rates ( $16 \text{ s}^{-1}$ ) and CSRs.  $X_{O_2} = 0.2$ .

Sensitivity and reaction path analysis was performed for naphthalene, the first PAH species from which soot forms. This analysis revealed that, despite different sooting tendencies, the three fuels shared similar PAH chemical pathways.  $C_5$ ,  $C_6$ ,  $C_7$ ,  $C_9$  rings, and naphthalene are formed sequentially through the combination of  $C_3$  and smaller chain radicals resulting from fuel cracking processes. Due to the fuel bound oxygen in methyl butanoate, less and shorter chain radicals are available for soot formation, compared with the other fuels, such that methyl butanoate has the lowest critical strain rates.

Finally, the strain rate effects on soot formation were examined. For all three fuels,  $C_5$  and  $C_6$  ring formation reactions are the rate limiting steps. Their concentrations drop as the residence time is reduced, such that the downstream PAH chemistry is consequently inhibited, resulting in the sooting limits.

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