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Formation of Soot in Laminar Premixed *n*-Butanol and *i*-Butanol Flames

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Butanol isomers are important candidates for the next generation of biofuels. At present, the fuel-rich and sooting chemistry of these alcohol fuels is largely unknown. In the present study, we examine the evolution of the particle size distribution function (PSDF) of nascent soot produced in atmospheric-pressure burner-stabilized stagnation (BSS) flames of premixed *n*-butanol and *i*-butanol. To better understand the influence of the alcohol groups on soot formation, we also carried out similar experiments on *n*-butane and *i*-butane. The similar features of the PSDF in *i*-butanol and *i*-butane flames indicate that the fuel bound oxygen in the branched isomer may not affect the processes of soot formation. On the other hand, the critical C/O ratio for sooting in *n*-butanol flames was shown to be lower than the aliphatic counterpart. The complex competition of kinetic soot processes is observed in the contrasting sooting behavior between butanol isomers. In terms of soot formation, the dominance of the branching functional group over the effect of fuel bound oxygen is kinetic process that is observed.

1. Introduction

Concerns over CO₂ emissions and limited fossil fuel resources have sparked interests in biofuels such as *i*-butanol and *n*-butanol. Candidates for the next generation of transportation biofuels must be commercially viable and butanol fuels are made more attractive by processes such as efficient fermentation and dehydration of *i*-butanol [1-3]. Understanding the processes of soot formation in butanols, and how these processes vary with isomeric structure will be important to rational utilization of these fuels. Also, the examination of oxygenated fuels may reveal insights into mechanisms of soot nucleation and growth for all fuels in general.

Basic understanding of the competition between kinetic processes such as PAH formation and fragmentation is required in order to understand effects of fuel structure on sooting behaviors [4]. Fundamental properties such as laminar flame speeds, ignition delay times and counter-flow measurements have been carried out to describe the combustion behavior of *i*-butanol and *n*-butanol [5-8]. In addition, the flame chemistry of the butanol isomers has been compared to the aliphatic counterparts in a number of experimental and computational studies [9-12]. The development of soot chemistry requires more direct observations of sooting behavior because competing processes other than small hydrocarbon chemistry are present [4]. The sooting behavior of butane isomers has been studied [13-15] but a cross comparison to the behavior of the alcohol counterparts is only recently being examined.

In the present study, the role of branching and oxygenation on soot formation is investigated for laminar premixed flames of *n*-butane, *i*-butane, *n*-butanol and *i*-butanol with an emphasis on the detailed particle size distribution function (PSDF). A comparison is made to the aliphatic analogs of the butanol isomers in order to observe the role of branching and oxygenation separately. In terms of soot formation, a systematic approach must be applied such that the effect of local flame temperature and carbon to oxygen ratio are isolated. The burner

stabilized stagnation flame method (BSS); described in detail elsewhere [16, 17]; was employed to investigate the evolution of size distribution in nascent soot from particle nucleation to mass growth. The method allows for intrusive soot sampling while directly accounting for probe obstruction to the flame. A conventional burner stabilized flame is subjected to flow stagnation and probe sampling simultaneously such that the temperature at the top of the flame can be rigorously defined as a boundary condition in reacting flow simulations. With the flow field defined, the flame temperature and species concentrations up to lower PAHs can be directly modeled using a quasi one dimensional opposed jet code without imposing a measured temperature profile or correcting for artificial probe perturbation [16].

2. Experiment

The BSS flame approach [16, 17] has been extended to the aforementioned butane and butanol isomers. The BSS flame configuration can be simulated directly as a reacting flow because the sampling probe simultaneously acts as stagnation surface with a well defined boundary temperature. Four lightly sooting flames were stabilized at atmospheric pressure with comparable maximum flame temperature and flow conditions summarized in Table 1.

Table 1. Summary of flame conditions. The butanol flame temperatures were not corrected for radiation thus the reported temperature is an estimate based on comparisons to the aliphatic counterparts.

Mole fractions			C/O ratio	Equivalence ratio, f	Velocity, v_o (cm/s) ^a	Flame temperature, $T_{f,max}$ (K) ^b
n -C ₄ H ₉ OH	O ₂	Ar				
0.1177	0.2823	0.6000	0.69	2.50	4.64	1740
iso -C ₄ H ₉ OH	O ₂	Ar	0.63	2.25	4.64	1790
0.1089	0.2901	0.6001				
n -C ₄ H ₁₀	O ₂	Ar	0.63	2.05	3.58	~1750
0.0958	0.3042	0.6000				
iso -C ₄ H ₁₀	O ₂	Ar	0.63	2.05	3.58	~1750
0.0958	0.3042	0.6000				

A chemical kinetic model for *i*-butanol and *n*-butanol combustion is yet to be incorporated into the calculations, thus the flames were chosen with uncorrected flame temperatures similar to the alkane counterparts. The gas temperature profiles were measured with a coated Type-S thermocouple. Radiation correction was carried out numerically in a procedure discussed earlier [16]. The test flames were chosen with overlapping temperature profiles before radiation correction. Based on the numerical radiation correction for *i*-butane and *n*-butane, the maximum flame temperature of the *i*-butanol and *n*-butanol flames is assumed to be within 1740K and 1800K.

The liquid fuels were vaporized and injected into the fuel line in a manner similar to previous studies [16]. The flat flame burner is 5 cm in diameter and is uncooled because of potential condensation of the fuel in the porous material. Without water cooling, however, the pores tend to close the pores in its center, thus modifying the local unburned velocity. For this reason, fresh porous material was always used to keep the flame roughly one dimensional. The

mass flow rates of oxygen, argon and nitrogen are measured by critical orifices and the flow of argon driving the fuel nebulizer was calibrated by bubble displacement. Particle size distributions were determined with a standard TSI 3090 SMPS[16]. The flame gas entered the probe through the orifice and was immediately diluted with a cold nitrogen flow to prevent particle losses. The dilution range and calibration has been used before and care was taken to avoid diffusion losses, condensation of higher PAHs, and probe-induced coagulation during dilution [18]. Limitations of the Cunningham slip correction cause particles below 10 nm to be overestimated by mobility measurements and thus a nano-particle transport theory was used for small particles to obtain more accurate particles sizes [19-21].

The experimentally measured temperature profiles for the *i*-butane and *n*-butane are radiation corrected by using transport and flow properties that are calculated by a modified version of OPPDIF [16]. The probe separation to plate diameter ratio is much less than unity so the quasi 1-D assumption applies. The flame chemistry is calculated with JetSurF (version 2.0) [22]. By energy conservation, the modified OPPIF code allows for the calculation of the temperature and species profile without the need for a measured temperature profile as an input. The radiation corrected temperature profiles are compared to the calculated OPPDIF profile to test the validity of the experimental and numerical procedures. The inlet fuel temperature was extrapolated from the measured temperature profile and the probe temperature was measured with a type K thermocouple embedded on the stagnation surface.

3. Results and Discussion

A comparison of typical measured/radiation corrected and simulated temperature profiles is shown in Figure 1. The degree to which the stagnation probe causes flow divergence and heat loss is shown. In both fuels, the agreement between radiation corrected measurements and simulated temperatures is within thermocouple positioning uncertainty of ± 0.03 cm and ± 70 K for temperature. The position of the thermocouple is affected by the tension of the wire and other factors and the emissivity of the thermocouple during measurements is assumed to be between 0.3 and 0.6 [23].

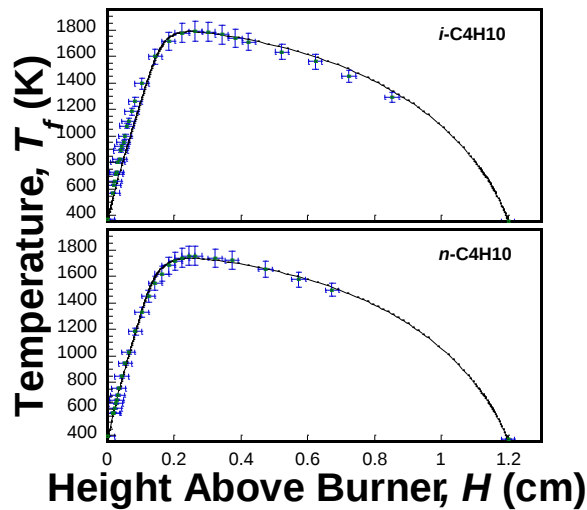


Figure 1: Comparison of temperature profiles for measurements (symbols, radiation corrected) and simulation (lines) of the *i*-butane flame (top) and the *n*-butane flame (bottom). The profiles were simulated with a modified version of OPPDIF which utilized JetSurF 2.0 flame chemistry [22].

The model solves the energy equation without the measured temperature profiles as an input. Thus, agreement between radiation corrected measurements and the simulation addresses uncertainty within the JetSurF mechanism itself by yielding information on local heat release and loss rates [16]. Such information allows for the uncertainty within the simulated local temperature to be defined along with the resulting Arrhenius reaction kinetics and species transport. Furthermore, the agreement in measured temperatures and the model confirms that the flame conditions are comparable in the *i*-butane and *n*-butane flames.

Radiation correction was only carried out on the *n*-butane and *i*-butane because the flame chemistry model for the butanol isomers has not yet been incorporated. The uncorrected temperature profiles for the C₄ fuels are shown in Figure 2. The over-lapping features of the measured temperature profile indicate that the flames studied contain comparable local temperature conditions. The numerically calculated radiation correction *n*-butane and *i*-butane is assumed to be similar for the butanol counterparts. Therefore, the maximum flame temperature for *n*-butanol and *i*-butanol are estimated to be comparable to the butane flames.

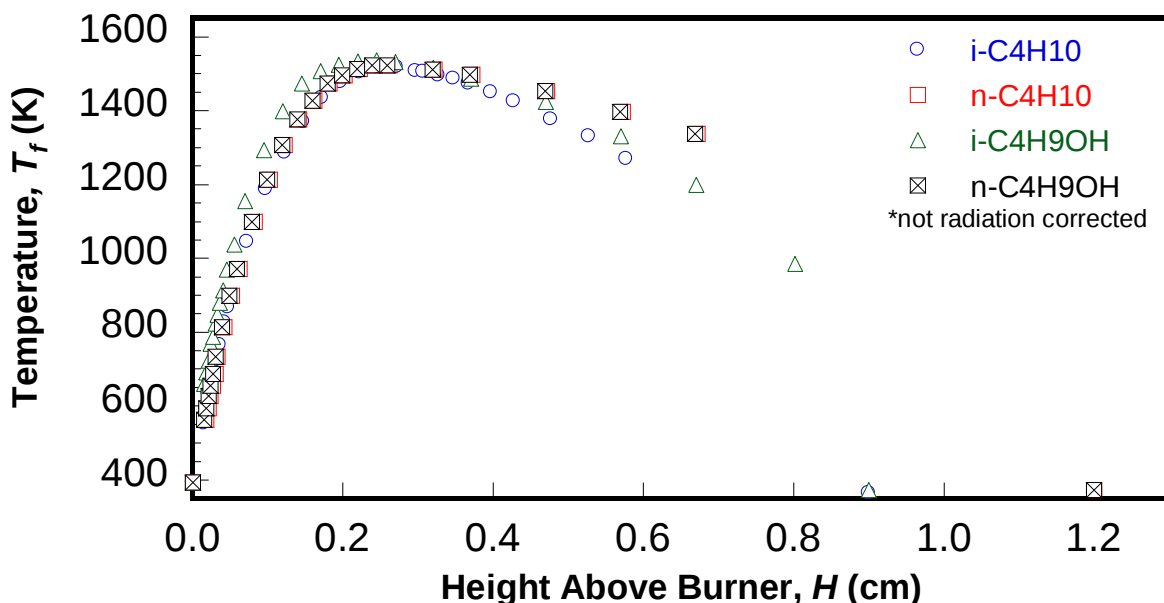


Figure 2: Measured temperature profiles for BSS flames of the C₄ isomers without radiation correction.

The PSDF for sooting flames was measured in the BSS configuration for the butane and butanol isomers. The evolution of the PSDF from nucleation of soot to its growth is summarized in Figure 3. The detailed distributions provide insight into the competitive processes such as nucleation, coagulation and surface growth. Such processes are heavily dependent upon temperature therefore the comparable local temperature conditions allow for the isolated study of branching and oxygenation within the fuel structure.

The lack of fragmentation of soot precursors allowed for steady nucleation and the PSDFs assumed a bimodal distribution containing a prominent nucleation tail existing well into the post-flame region. The details of the PSDF for the C₄ fuels are similar to previous measurements of ethylene and dodecane at comparable flame conditions [16, 17]. Overall, the competition between nucleation and growth appears to be similar across the flames despite the presence of the fuel bound oxygen. However, fuel bound oxygen affects the sooting behavior of *n*-butanol flames by increasing

the observed critical sooting C/O ratio in comparison to the other flames. Unlike the other flames, the carbon to oxygen ratio for *n*-butanol was increased from 0.63 to 0.69 in Figure 3 in order to observe a bimodal distribution within the PSDF. The alcohol group on the straight chain fuel hinders particle nucleation. The observation is expected but not currently fully understood kinetically. In contrast, Figure 3 shows the PSDF does not seem to be affected by the alcohol group in the branched fuels. The dissimilar PSDF responses to the molecular structures of the two alcohols indicates that fuel structures may greatly impact the chemistry of precursor formation, especially for oxygenated fuels. Observations of the detailed PSDFs suggest that the effect of branching within the fuel structure overrides the effect of the alcohol group in terms of soot formation.

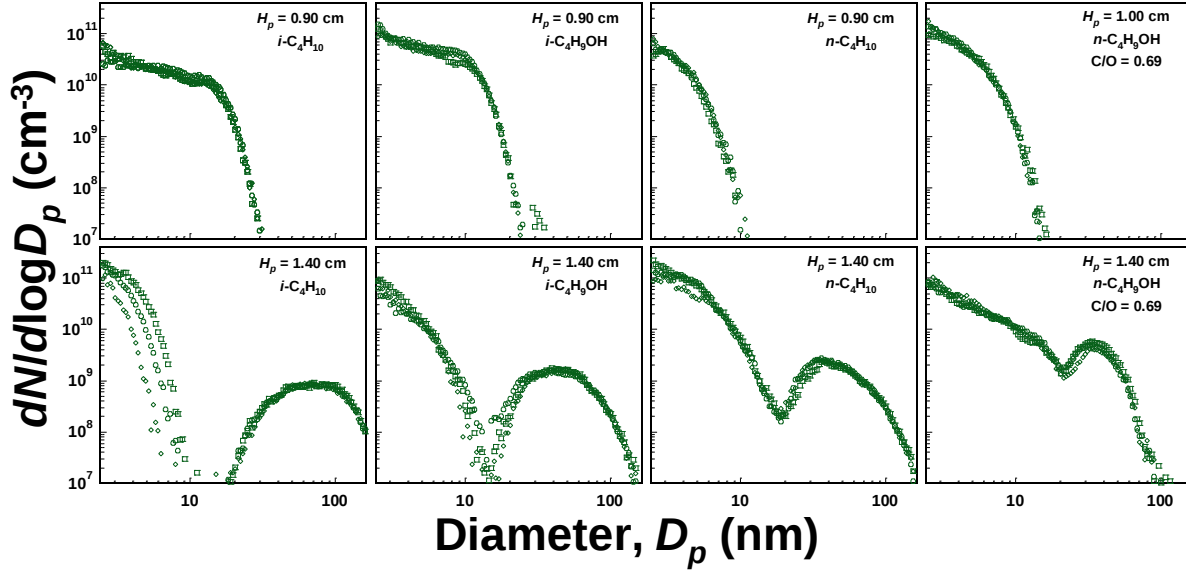


Figure 3: Summary of the development of the PSDF for BSS flames of the C₄ fuels. The *n*-butanol flame carbon to oxygen ratio was increased from 0.63 to 0.69 in order to observe the bi-modal distribution.

The global sooting behavior for each flame can be determined in terms of the total soot volume fraction by integrating the PSDF. The volume fraction as a function of burner to probe separation, H_p , is shown in Figure 4. The volume fraction in the *i*-butane and *i*-butanol flames at each H_p is nearly identical indicating that (1) alcohols do not always yield less soot than their alkane counterparts, and (2) the extent of soot suppression in alcohols is strongly dependent on the fuel structure. The total volume fraction in the *n*-butanol flame is consistently lower than the other C₄ flames even though the carbon to oxygen ratio was higher.

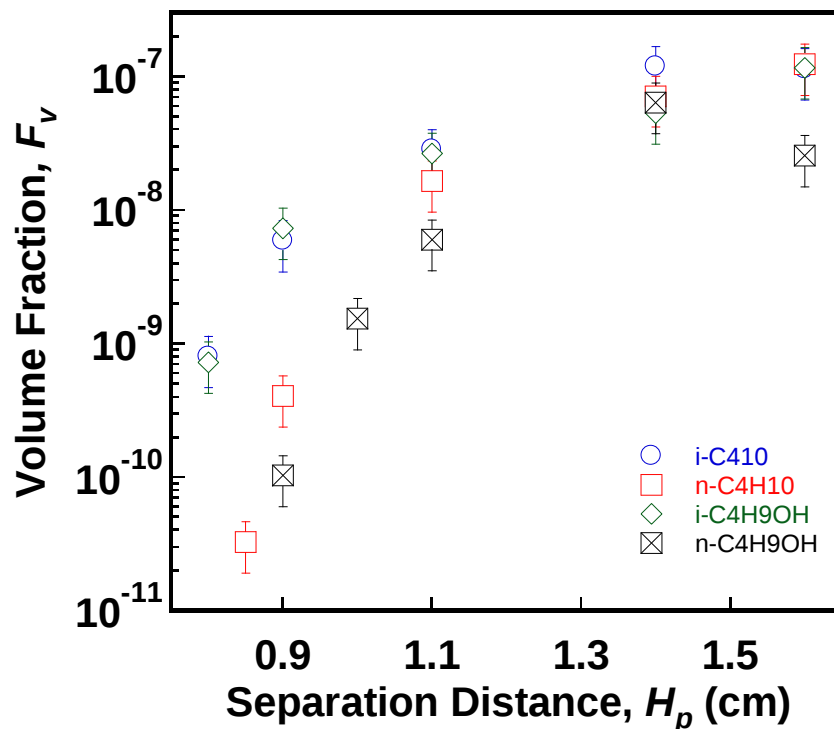


Figure 4. Total volume fraction measured at several H_p for the C_4 fuels. The n -butanol flame carbon to oxygen ratio was increased from 0.63 to 0.69 in order to observe a comparable volume fraction.

4. Conclusions

The PSDF measurements of butane and butanol isomers under comparable flame conditions show that the presence of branching within the fuel structure dominates over the effect of oxygenation in terms of soot formation. A deeper fundamental understanding of competitive soot processes and the impact of fuel structure on these processes is required to explain such phenomena.

5. Acknowledgements

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