

Two-Stage Aerosol Formation in Low-Temperature Combustion

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Abstract

Low-temperature combustion is a promising strategy for reducing pollutant formation in internal combustion engines. However, there is a lack of understanding of how the chemistry governing the differences in ignition between low-temperature and conventional combustion affects the emission rates and physicochemical properties of particulate matter (aerosols). Here, we conducted combustion experiments in an atmospheric-pressure reactor controlled at constant equivalence ratio ($\phi = 2.3$) and $O_2/N_2 = 0.06$, and at temperatures varied between 200 °C and 1035 °C. We used two fuels: toluene, which has high sooting propensity, and *n*-heptane, which has a comparatively lower sooting propensity but exhibits two-stage ignition that is not present in toluene combustion. We performed real-time measurements of aerosol size distributions, volatility, and light-absorption properties. We also performed offline molecular-size characterization. Aerosols emitted from both fuels were comprised of light-absorbing organics that are categorized as brown carbon. At the highest combustion temperature (1035 °C), the aerosol emissions from toluene combustion were a factor of 20 larger than *n*-heptane. The aerosol emissions from toluene combustion had more abundance of large molecular-size species, were less volatile, and were more light-absorbing than *n*-heptane. For both fuels, aerosol emission factors exhibited a steep drop with decreasing temperatures. However, there was a resurgence in aerosol emissions at lower temperatures with a peak at 290 °C for *n*-heptane combustion that was not observed for toluene. This is consistent with chemical kinetics simulations that show prominent two-stage ignition behavior for *n*-heptane, but not for toluene.

1. Introduction

Advanced compression-ignition (ACI) is a next-generation strategy in internal combustion engines that aims to achieve high efficiency while maintaining low levels of pollution emissions [1-3]. Several ACI technologies have been proposed, including homogeneous charge compression-ignition (HCCI), premixed charge compression ignition (PCCI) [4-7], and reactivity controlled compression-ignition (RCCI) [8, 9], as well as hybrid concepts that combine different ACI strategies [10, 11]. All these approaches rely on low-temperature combustion (LTC) to reduce pollutant emissions by avoiding the NO_x-soot tradeoff that occurs at the combustion conditions typical for conventional diesel combustion (CDC) [12, 13]. The widely accepted model [14] is that NO_x forms at high temperatures ($T > 1900$ °C) and fuel-lean conditions (equivalence ratio, $\phi < 1$) while soot forms at relatively lower temperatures ($T \approx 1100$ °C – 1700 °C) and fuel-rich conditions ($\phi > 2$). CDC systems involve inhomogeneous combustion conditions with respect to fuel/air mixing and temperature. As a result, conditions in those systems span both the soot- and NO_x-formation regions. Any alterations to engine operation within the CDC environment would push the conditions further into one of these two regions, hence the NO_x-soot tradeoff [3]. On the other hand, the premixing and ignition delay employed in LTC engines allow for a more homogeneous fuel-lean combustion at temperatures substantially lower than CDC, thus avoiding both soot and NO_x formation regions. Given the strong dependence of NO_x formation on combustion temperature, its near-elimination in LTC is certain. However, the elimination of soot formation in LTC is not as straightforward.

The terminology concerning aerosols, or particulate matter, in combustion emissions can be confusing. Therefore, it is important to explain the terminology that we adopt in this paper. In combustion engines literature, and to a certain extent in atmospheric science literature, the term “soot” is used to represent aerosol combustion emissions that are comprised of solid aggregates of elemental carbon (EC). EC is also often used synonymously with black carbon (BC) in the atmospheric science literature due to its black appearance (strong light absorption in the visible spectrum) [15]. However, depending on the combustion conditions, a significant fraction of aerosol combustion emissions can be organic and is referred to as organic aerosol (OA) or organic carbon (OC) (i.e. when only accounting

for the carbon content of the organic molecules). In fact, OA can form through the same soot-formation route as EC, which involves growth and aggregation of polycyclic aromatic hydrocarbons (PAHs) [16, 17] but under conditions that are not conducive for the completion of the soot-formation process. To emphasize this connection, Michelsen [17] refers to this OA as “incipient soot” and the solid aggregates, mostly EC aerosols as “mature soot.” In this paper, we adopt the Michelsen terminology, and hereafter, we add (mature) before “soot” when referencing previous studies to emphasize that what those studies refer to as “soot” is indeed “mature soot.” We have shown that incipient soot comprises a major fraction of atmospheric brown carbon (BrC) [18]. BrC, or light-absorbing OA, is less absorptive than BC in the visible spectrum and exhibits absorption more skewed toward the short wavelengths, which gives it its brown color [19, 20]. BC, mostly comprised of elemental carbon, has relatively constrained light-absorption properties while BrC is comprised of a multitude of organic species with light-absorption efficiencies that vary over several orders of magnitude [21, 22]. BrC plays an important role alongside BC in absorbing solar radiation and climate forcing [21, 22]. For completeness, we note that OA in combustion-engine emissions also includes organic species other than incipient soot (e.g. from lubricating oil [23]), and altogether, OA emissions from combustion are referred to as primary organic aerosol (POA). For readers not familiar with aerosol terminology, we summarize the key definitions discussed in this paragraph in Table 1.

Table 1. Summary of definitions of key terms related to combustion aerosols

Term	Definition
Mature soot [17]	<ul style="list-style-type: none"> - Solid aggregates of mostly elemental carbon emitted from incomplete combustion. - Often referred to as just “soot” in both combustion and atmospheric science literature.
Incipient soot [17]	<ul style="list-style-type: none"> - Organic aerosol emitted from incomplete combustion that form through the same soot-formation route as mature soot but under conditions (e.g. low temperature) not conducive for the completion of the soot-formation process. - Is categorized as POA. - Can be light-absorbing and thus categorized as brown carbon (BrC)

Black carbon (BC) [15]	<ul style="list-style-type: none"> - Comprised mostly of elemental carbon, it is defined operationally based on its black appearance (strong light absorption in the visible spectrum). - Its definition largely overlaps with that of mature soot.
Brown carbon (BrC) [20]	<ul style="list-style-type: none"> - Light-absorbing organic aerosol (OA). - Defined operationally based on its light-absorption properties that exhibit strong wavelength dependence in the visible spectrum (increased absorption toward short wavelengths), thus giving it a brown appearance.

72

73 Previous studies have reported substantial decrease of (mature) soot production in engines [9, 24-
74 29] and constant-volume combustion chambers [30, 31] operated in LTC mode versus CDC mode.
75 However, these reports are based on optical techniques that are tailored for measuring CDC aerosol
76 emissions, which are dominated by mature soot. The most common method is the filter smoke number
77 (FSN) obtained from reflectance measurements of particles collected on a filter [28, 29, 32, 33]. Other
78 techniques include the commercially available Opacimeter [24] and Micro Soot Sensor [25, 34], as well
79 as other light-extinction techniques (e.g. forward illumination light extinction) [30]. All these
80 techniques exploit the strong light-absorptive nature of mature soot and convert the observed light
81 absorption into particle mass based on either calibration against or assumed light-absorption properties
82 of mature soot (or BC). Because LTC emissions are dominated by OC , which is significantly less
83 absorptive than EC [2], these techniques would severely underestimate the mass loadings of aerosols
84 emitted under LTC conditions [32].

85 Realizing that the aerosol emissions in LTC are dominated by OA, several studies have applied
86 aerosol characterization techniques that do not rely on light absorption and are therefore not specific
87 for mature soot. Northrop et al. [35] showed that even though the production of EC (i.e. mature soot)
88 was largely reduced in LTC of biodiesel, the emissions contained considerable amounts of OA that
89 were characterized using electrical mobility measurements. Lucachick et al. [36] reported that the
90 aerosol emissions in LTC (PCCI and RCCI) contained substantially less (mature) soot than CDC and
91 were dominated by semi-volatile OA, as shown by volatility tandem differential mobility analysis.
92 Storey et al. [32] reported that while the FSN method predicted negligible aerosol emissions from an

engine operated in RCCI mode compared to CDC mode, gravimetric analysis showed that the mass loadings of aerosol emissions from the two modes were of the same order of magnitude. Moses-DeBusk et al. [2] reported that the aerosol emissions from an engine operated at HCCI conditions were dominated by OA, as obtained using an OC-EC analyzer. Consequently, the aerosol mass emission rate measured using a Micro Soot Sensor was an order of magnitude smaller than that measured using the OC-EC analyzer, emphasizing the inadequacy of instruments tailored to detect mature soot at quantifying LTC aerosol emissions.

The studies summarized above demonstrate that LTC suppresses (mature) soot production but it can potentially lead to significant OA production. However, while the framework for the chemistry governing autoignition at LTC conditions is well understood as a degenerate chain-branching mechanism [37], the dependence of aerosol emission rates and their physicochemical properties on combustion temperature within LTC conditions is not. In this study, we performed controlled-combustion experiments at temperatures relevant for LTC conditions (≤ 1035 °C) and quantified the aerosol emissions and characterized their molecular sizes, volatility, and light-absorption properties. The experiments involved two structurally different fuels (toluene and *n*-heptane) in order to investigate the effect of differences in fuel reactivity on the emitted aerosols.

2. Materials and Methods

2.1. Approach

The suppression of mature soot (EC) and elevated levels OA in LTC compared to CDC can be understood within the context of the soot-formation process in combustion. The initial steps of the process involve the formation of small aromatic species, which then aggregate to form polycyclic aromatic hydrocarbons (PAHs) [16]. Aided by radical chain reactions, PAHs and other available hydrocarbons cluster to form condensable organic particles [38], or incipient soot [17]. These organic particles then undergo progressive dehydrogenation and aggregation to eventually form the EC aggregates that comprise mature soot [17]. While the combustion conditions in CDC promote the generation of mature soot, it is plausible that the low temperatures in LTC are not conducive for the

completion of the soot-formation process (i.e. complete soot maturation), thus leading to the production of organic incipient soot. We have previously shown that incipient soot (or BrC) exhibits wide variability in physicochemical properties (molecular sizes, volatility, and light-absorption properties) [18, 39-41] depending on combustion conditions. Here, we isolate the effect of temperature.

We performed controlled-combustion experiments at constant pressure (1 atm), equivalence ratio ($\phi = 2.3$), and oxygen-to-nitrogen ratio ($O_2/N_2 = 0.06$), and varied the temperature between 250 °C and 1035 °C. This temperature range covers the lower end of in-cylinder temperatures encountered in LTC conditions, which are typically between 700 °C and 1700 °C [3]. It also encompasses exhaust temperatures, which range from 120 °C to 400 °C [42, 43], where unburned fuel can continue to react. These low temperatures are also representative of “cold start” conditions in conventional engines, during which the majority of aerosol emissions take place over a typical driving cycle [44]. We investigated the effect of molecular structure by performing the experiments with two structurally different fuels that have been previously utilized in LTC studies: *n*-heptane [45, 46] and toluene [45, 47-52].

In each experiment, we performed online measurements to characterize the emission factors, size distributions, volatility, and light-absorption properties of the emitted aerosols. We also collected filters for offline chemical characterization using laser desorption ionization mass spectrometry (LDI-MS). The experimental setup is shown in Figure 1 and the associated measurements are described in detail in the subsequent subsections. To complement the experiments, species profiles of *n*-heptane, toluene, and several intermediates were simulated using the chemical kinetics mechanism of Mehl et al. [53].

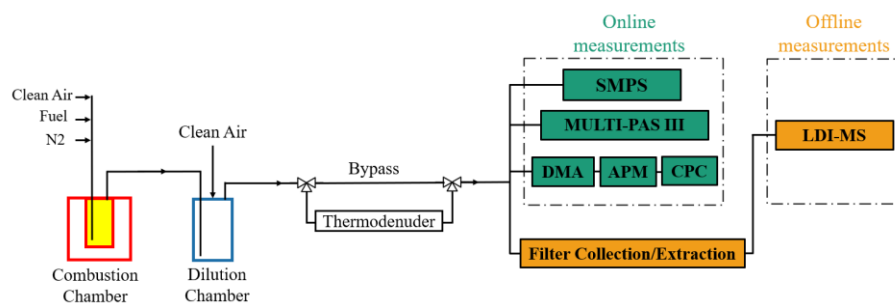


Figure 1. Schematic of the experimental setup

2.2. Combustion system

The combustion experiments were performed using a custom-built controlled-combustion system [18, 39, 40, 54]. It consists of a custom-made cylindrical quartz chamber (~0.24 L) enclosed in a heater (Thermcraft). The combustion reaction is temperature-initiated. A PID controller (OMEGA, CNi3244) controls the wattage of the heater to achieve a set combustion temperature measured at the center of the combustion chamber using a high-temperature K-type thermocouple. In this study, we controlled the temperature in the combustion chamber to set values between 250 °C and 1035 °C. Fuel is introduced into the combustion chamber in vapor form by flowing a stream of clean dried air, controlled using a mass flow controller (DAKOTA, 6AGC1AL55-09AB), into a bubbler containing the fuel. We have previously performed mass transfer calculations and confirmed that the residence time of a bubble rising in the bubbler is greater than the time required to saturate it with fuel [39]. Therefore, the flowrate of the fuel exiting the bubbler can be calculated from knowledge of the fuel saturation pressure and the air flowrate. We controlled the equivalence ratio ($\phi = 2.3$) and $O_2/N_2 = 0.06$ by mixing the fuel-saturated air stream with a controlled stream of clean air and a controlled stream of N_2 . The values of the flowrates are given in Table S1 in the Supplementary Material (SM).

2.3. Online measurements

We measured the electrical-mobility size distributions of the emitted aerosols at each combustion temperature using a scanning mobility particle sizer (SMPS, TSI 3882) in the range of 10-500 nm. The SMPS uses an electrostatic classifier (TSI, Model 3082), a long differential mobility analyzer (DMA, TSI, Model 3081A00), and an advanced aerosol neutralizer (TSI, Model 3088) along with a condensation particle counter (CPC, TSI, Model 3772). We also integrated the SMPS size distributions in conjunction with particle effective densities to obtain total aerosol mass concentrations (C_{aerosol}). The particle effective densities were obtained using the tandem differential mobility analyzer – aerosol particle sizer (tandem DMA-APM) technique [55]. Particles were classified based on their electrical-mobility diameter (d_m) using the DMA (TSI, Model 3081A00) and their mass (m_p) was measured using the APM (Kanomax, Model 3601). The effective density was then calculated as:

$$\rho_{\text{eff}} = m_p / v_p ; v_p = \pi d_m^3 / 6 \quad (1)$$

The uncertainties in d_m and m_p are $< 1.5\%$ [56] and $< 5\%$ [57], respectively. This leads to a propagated uncertainty of $< 7\%$ in ρ_{eff} . We obtained $\rho_{\text{eff}} = 1.3 \pm 0.09 \text{ g/cm}^3$ for emissions from both fuels, which is consistent with values typically reported for OA [39, 58, 59].

We calculated the aerosol emission factors per unit mass fuel as:

$$\text{EF} = C_{\text{aerosol}} / C_{\text{fuel}} \quad (2)$$

Where C_{fuel} is the mass concentration of the fuel entering the combustion chamber, calculated as:

$$C_{\text{fuel}} = M_{\text{fuel}} * Q_{\text{fuel}} / Q_{\text{total}} \quad (3)$$

Where Q_{fuel} is the fuel flowrate into the combustion chamber, Q_{total} is the total flowrate (fuel + air + N_2) (Figure 1), and M_{fuel} is the molar mass of the fuel.

We measured the absorption coefficients (b_{abs} , Mm^{-1}) at three wavelengths ($\lambda = 422, 532, \text{ and } 782 \text{ nm}$) using a photoacoustic spectrophotometer (MULTI-PAS III) [60]. For aerosols, b_{abs} is an extensive property that represents the total light absorption cross-section of the particles per unit volume of air, and should not be confused with the absorption coefficient used in UV-vis spectroscopy, which has the same inverse length dimensions but represents absorbance per unit path length and is an intensive property. Normalizing b_{abs} by the total mass concentration of the particles (C_{aerosol}) yields the mass absorption cross-section (MAC, m^2/g):

$$\text{MAC}(\lambda) = \frac{b_{\text{abs}}(\lambda)}{C_{\text{aerosol}}} \quad (4)$$

MAC exhibits an inverse power-law dependence on λ with the exponent of the power-law known as the absorption Ångström exponent (AAE). MAC and AAE, are not true intensive properties as they depend on particle size and morphology, but they can be conveniently calculated from light-absorption and particle concentration measurements and are thus often used as effective light-absorption properties.

We also retrieved the fundamental light-absorption property of the aerosols, namely the imaginary part of the refractive index (k) using optical closure [18, 40, 61]. We performed optical calculations based on Mie theory [62] with the aerosol size distributions obtained from SMPS measurements as model inputs and $k(\lambda)$ as a free parameter. We have previously shown that particles emitted at similar conditions were liquid near-spherical particles based on scanning electron microscopy (SEM) imaging [18], thus justifying the application of Mie theory. Therefore, the mobility equivalent We retrieved k values from matching the calculated absorption coefficients ($b_{\text{abs,Mie}}(\lambda)$) to $b_{\text{abs}}(\lambda)$ measured using the MULTI-PAS III. Similar to MAC, k also exhibits an inverse power-law dependence on λ with an exponent w [22]. In the small particle limit ($d \ll \lambda$), $\text{AAE} \approx w + 1$ [22].

For select combustion-chamber temperatures, we sampled the emitted aerosols through a thermodenuder to characterize their volatility. The thermodenuder is a stainless-steel tube ($L = 100$ cm, $\text{ID} = 2.5$ cm) wrapped with heating wire that is controlled using a PID controller (OMEGA, CNi3244) to maintain a set temperature measured at the centerline of the flow using a K-type thermocouple. In this study, we applied 3 thermodenuder temperatures (50 °C, 100 °C, and 150 °C) and obtained the aerosol mass fraction remaining (MFR) at each temperature as:

$$\text{MFR} = C_{\text{aerosol,TD}} / C_{\text{aerosol,bypass}} \quad (5)$$

Where $C_{\text{aerosol,bypass}}$ is the original aerosol mass concentration and $C_{\text{aerosol,TD}}$ is the mass concentration after heating in the TD (see Figure 1). Plots of MFR versus TD temperature, or thermograms, can be used to compare the volatility of different aerosol samples, where a steeper thermogram indicates higher volatility. We note that MFR is not a fundamental property as it depends on the initial aerosol mass concentration (i.e. $C_{\text{aerosol,bypass}}$) [63]. Therefore, using thermograms to compare the volatility of different aerosol population requires that $C_{\text{aerosol,bypass}}$ is the same. In this study, we ensured that $C_{\text{aerosol,bypass}}$ was consistent (350 $\mu\text{g}/\text{m}^3$) across different experiments by applying controlled dilution to the emissions downstream of the combustion chamber (Figure 1).

2.4. Offline chemical analysis

For select combustion-chamber temperatures, we collected aerosol samples for offline analysis using laser desorption ionization mass spectrometry (LDI-MS). Aerosol samples were collected on 47 mm Teflon filters (0.2 μm pore size, Whatman) at a flowrate of 10 LPM. The targeted mass loading on the filters was typically 300 μg in order to avoid filter clogging which occurs at ~ 350 μg . The filters were then immersed in 10 ml dichloromethane (DCM) and sonicated for 40 minutes to extract the aerosol samples. We spotted 10 μl of the extracted solution on an LDI-MS plate and let the DCM evaporate leaving the sample for analysis using a Bruker Autoflex TOF mass spectrometer operated in reflectron mode. The instrument uses a 337 nm Nitrogen laser in positive mode. The ion source was set to 19 kV and the reflector voltage to 20 kV. The spectrum for each sample was obtained as an average from 200 laser shots.

The advantage of LDI-MS is that it is soft-ionizing and thus allows for the detection of the large molecules, including polycyclic aromatic hydrocarbons (PAHS) and their derivatives, that make up the organic incipient soot particles [18, 61, 64-66]. We note that LDI-MS measurements are semi-quantitative due to differences in desorption and ionization efficiencies between different molecules that largely depend on the operating conditions [67]. However, one can make qualitative comparisons between mass spectra of samples obtained under the same LDI-MS operating conditions.

3. Results

3.1. Emission factors and size distributions

Figure 2a depicts emission factors (EFs) of the aerosol emitted from the combustion of toluene and *n*-heptane as a function of combustion-chamber temperature. At the highest temperature (1035 $^{\circ}\text{C}$), the EFs of toluene were approximately 800 mg/kg-fuel, a factor of 20 larger than that of *n*-heptane (approximately 40 mg/kg-fuel), demonstrating a strong dependence of aerosol formation on fuel molecular structure. These findings indicate that, as expected, above 800 $^{\circ}\text{C}$ toluene has a larger propensity for forming large organic molecules (including PAHs and their derivatives) that have low enough volatilities to condense and form incipient soot particles, as further discussed in Section 3.3.

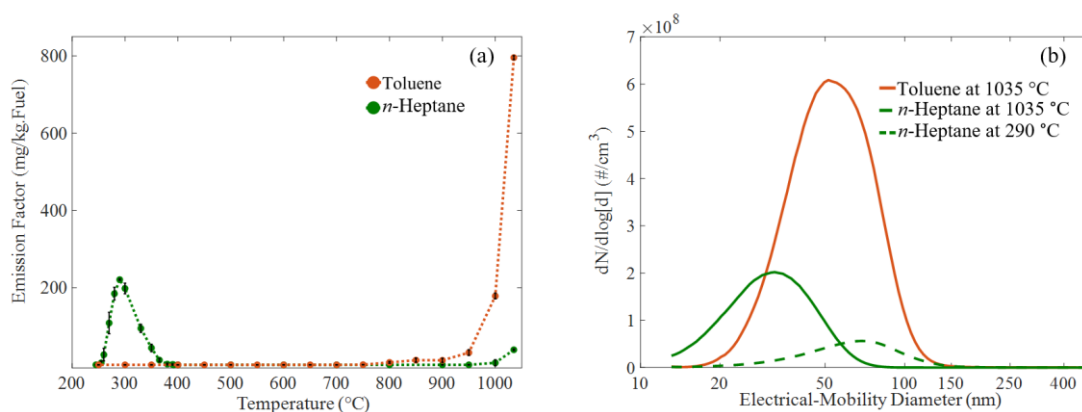


Figure 2. (a) Emission Factors of aerosols from toluene and *n*-heptane combustion as a function of combustion-chamber temperature. The error bars represent standard deviations from three separate experiments, with five measurements within each experiment. (b) Number distributions of aerosols from the combustion of toluene at 1035 °C, *n*-heptane at 1035 °C, and *n*-heptane at 290 °C, the peak temperature in the NTC region where aerosols were observed.

For both fuels, EFs exhibited a strong temperature dependence. Toluene EFs dropped by a factor of 25 as the combustion-chamber temperature decreased from 1035 °C to 950 °C, and the aerosol emissions completely disappeared at temperatures below 750 °C. Similarly, aerosol emissions from *n*-heptane combustion disappeared at temperatures below 950 °C. However, at low temperatures (< 350 °C), *n*-heptane combustion exhibited a sharp resurgence in aerosol emissions that was not observed with toluene, with EF peak of approximately 200 mg/kg-fuel at 290 °C. This rather striking two-stage aerosol formation directly reflects low-temperature ignition behavior, which is a trait of *n*-alkanes and is driven by the formation and reaction of peroxy radicals (ROO) that lead to several classes of intermediates, including cyclic ether isomers and alkene isomers, as further discussed in Section 3.2. Such reactions are not relevant in the oxidation of toluene largely due to the inability to form ROO because of the stability of the aromatic structure that creates high C–H bond energy (~112 kcal/mol) on phenylic sites, which resist H-abstraction at lower temperatures.

The strong dependence of aerosol EFs on fuel molecular structure and combustion temperature highlights the potential importance of combustion conditions and types of fuel blends in dictating aerosol formation in engines. The results in Figure 2a suggest that relatively small differences in in-

cylinder temperature profiles can lead to large differences in aerosol emissions. Furthermore, our results suggest that different fuel blends might have significantly different aerosol EF profiles.

Figure 2b shows number size distributions of the aerosol particles emitted from toluene combustion at combustion-chamber temperature of 1035 °C and from *n*-heptane combustion at combustion-chamber temperatures of 1035 °C and 290 °C. We note the emissions were diluted by clean air prior to measurement (Figure 1). Therefore, the size distributions in Figure 2b were obtained by scaling the SMPS measurements by the dilution factor in each experiment (66 for toluene and 16 for *n*-heptane). The aerosol particles in all experiments were mostly ultrafine (< 100 nm), which is consistent with aerosol size distributions measured in LTC engine emissions [2, 36] and indicates that the particles are dominated by OA (incipient soot) with negligible contribution from BC (mature soot) [18].

3.2. Chemical kinetics modeling of species profiles

Species profiles of *n*-heptane and toluene were simulated at the conditions of the experiments using the perfectly stirred reactor module in the ChemKin-Pro 19.2 program with the reaction mechanism of Mehl et al. [53]. Table 2 shows the initial conditions used in the simulations. It is important to note that this mechanism was developed to predict ignition delay times, not soot formation, the chemical mechanisms for which differ substantially. Additional work is required to produce mechanisms capable of describing ignition chemistry simultaneously with soot formation [68-72]. As shown in Figure 3a, the depletion profile for *n*-heptane exhibits clear NTC (negative temperature coefficient) behavior starting near ~ 325 °C, which is due to a shift in the balance of reactions derived from ROO from chain-branching to chain-propagating and chain-inhibiting. The simulations also show the depletion of *n*-heptane beginning at the lower end of the temperature range. In contrast, toluene mole fractions remain unchanged until ~ 600 °C, above which significant depletion is evident in the mole fraction predictions over a relatively narrow temperature range. Moreover, no NTC behavior is observed, which is consistent with the diminished importance of ROO chemistry in toluene combustion.

Table 2. Initial mole fractions for reactants of each species and reactor conditions used in chemical kinetics simulations.

	toluene combustion	<i>n</i>-heptane combustion
Mole Fraction (fuel)	0.014	0.012
Mole Fraction (O ₂)	0.056	0.053
Mole Fraction (N ₂)	0.930	0.935
Residence Time (min.)	0.310	0.300
Temperature (°C)	200 – 1100	

Intermediates produced from peroxy radicals are major species in the NTC region. To examine the temperature dependence of partially oxidized species, mole fractions were also simulated for two classes of intermediates: cyclic ethers and isomers of heptene. The latter class includes 1-heptene, 2-heptene, 3-heptene, and 4-heptene, while the former comprises a total of ten cyclic ether isomers, including 2-methyl-5-ethyl tetrahydrofuran and 2-pentyloxirane. Based on the mole fraction results, percent yield calculations were conducted (Figure 3b) to quantify the extent to which the formation of the ROO-derived intermediates overlap with the temperature region where aerosol formation is observed (cf. Figure 2a). In the present context, the percent yield is a measure of the total amount of intermediates produced from ROO-mediated pathways, such as in Figure 3c, relative to the initial concentration of *n*-heptane (12000 ppm). As noted previously, the chemical kinetics mechanism used for the simulations excludes soot formation chemistry, which is a likely reason for the temperature dependence of the simulations differing from the experiments. However, as evident in Figure 3b, the two classes of intermediates are formed in abundance in the region where aerosols are produced in the experiments, which could explain the difference between the emissions trends in *n*-heptane versus toluene. More specifically, considering that ROO chemistry occurs in the combustion of *n*-heptane, and not toluene, it is plausible that the species produced in the NTC region where aerosols are observed experimentally are involved in the formation pathways of the aerosols.

Notably, the 13 species included in the mole fraction profiles in Figure 3b (10 cyclic ethers and 3 heptene isomers) comprise only ~1% of the total number of reactions in the mechanism of Mehl et al. [53] (1389 species), yet account for ~20% of the gas-phase product formation in the NTC region of *n*-

308 heptane. Moreover, cyclic ethers may provide what effectively serves as the first ring required for
309 particle formation in low-temperature combustion, similar to that required for the HACA mechanism
310 [16] for high-temperature combustion, which is initiated via propargyl + propargyl, propargyl + allyl,
311 among other reactions to provide the first ring. The pathways that may unfold after the initial (cyclic
312 ether) ring are unclear. However, as cyclic ethers become oxidized and increasingly unsaturated, low-
313 temperature particle formation may follow a HACA-type mechanism with one or more oxygen atoms
314 embedded in polycyclic structures, the presence which may alter aerosol reactivity, physical properties,
315 and optical properties.

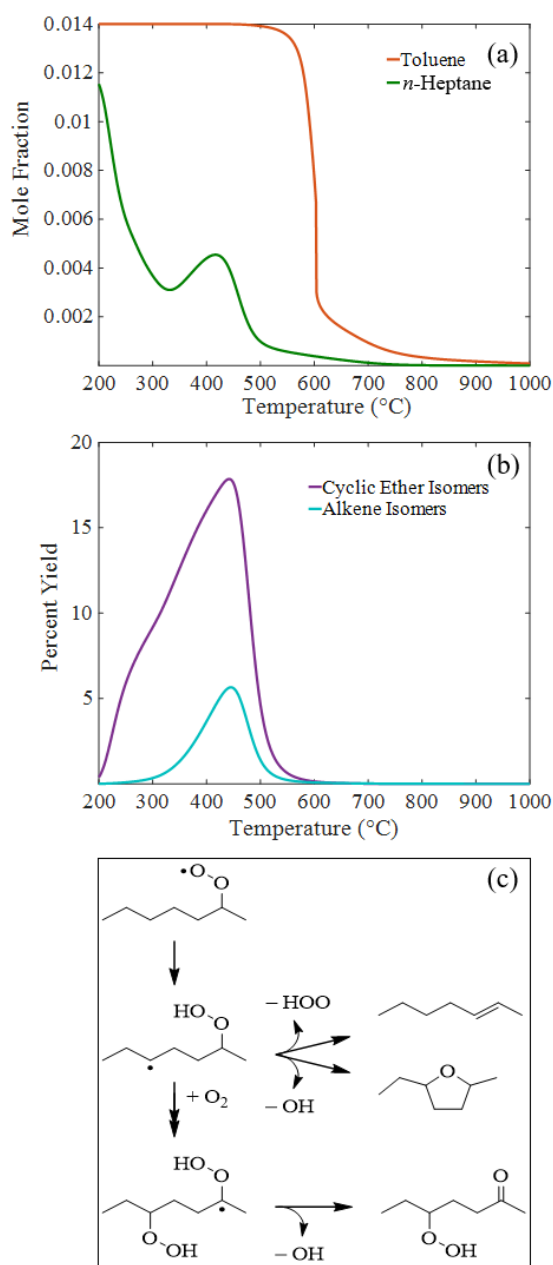


Figure 3. (a) ChemKin simulations of mole fractions of toluene and *n*-heptane conducted at 1 atm as a function of temperature. (b) Percent yields of cyclic ethers and conjugate alkenes derived from reactions of *n*-heptane-derived ROO radicals. (c) Reaction scheme of 2-heptylperoxy forming 2-heptene and 2-methyl-5-ethyltetrahydrofuran via QOOH decomposition and hept-2-one-5-hydroperoxy via second-O₂-addition. Combined, the yield through cyclic ether and alkene channels accounts for significant consumption of *n*-heptane in the region where organic aerosol is observed (cf. Figure 2a).

3.3. Volatility and molecular sizes

Figure 4 shows the aerosol mass fraction remaining (MFR) at different thermodenuder temperatures, or thermograms. At a combustion-chamber temperature of 1035 °C, the thermogram of *n*-heptane-combustion aerosol is steeper than that of toluene-combustion aerosol, indicating that the *n*-heptane-combustion aerosol is more volatile. At the largest thermodenuder temperature (150 °C), MFR of toluene-combustion aerosol was 0.17 compared to 0.06 for *n*-heptane-combustion aerosol. The aerosol produced in the low-temperature region from *n*-heptane-combustion (290 °C; Figure 2a) evaporated completely (i.e. MFR = 0) at thermodenuder temperature of 100 °C, indicating that it was significantly more volatile than the aerosol produced by the same fuel at 1035 °C. These results suggest a strong dependence of aerosol volatility on fuel type and combustion temperature.

Differences in aerosol volatility have implications to the atmospheric concentrations and lifecycle of the aerosol species. Specifically, even for the same emission rate, a relatively low-volatility aerosol would have higher atmospheric particle concentrations than a relatively high-volatility aerosol because it is more resistant to evaporation upon dilution in the atmosphere [73]. On the other hand, the amounts of semi-volatile organic compounds (SVOCs) that partition into the gas phase upon dilution in the atmosphere would be higher for the high-volatility aerosol. SVOCs are efficient secondary organic aerosol (SOA) precursors [74]. Thus, the high-volatility aerosol emissions can potentially lead to higher levels of SOA than the low-volatility aerosol emissions.

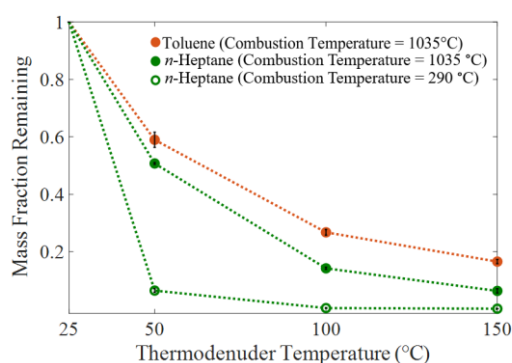


Figure 4. Thermograms showing mass fraction remaining (MFR) of toluene and *n*-heptane combustion aerosols at different thermodenuder temperatures.

Mass spectra obtained from LDI-MS measurements for the aerosol emitted from toluene and *n*-heptane combustion at combustion-chamber temperature of 1035 °C are shown in Figure 5a for $m/z < 700$ and Figure 5b for $1500 < m/z < 2100$. The mass spectra of molecules emitted from the two fuels had similar signatures with sequences of major and minor peaks, each exhibiting spacings of 24 atomic mass units with 12 atomic mass units separating the peaks of the two sequences. These signatures have been previously observed in LDI-MS measurements of soot emissions [18, 61, 65] and are characteristic of organic molecules in incipient soot undergoing growth by the hydrogen-abstraction acetylene-addition (HACA) mechanism [16]. The similarity in mass spectra indicates that despite the difference in molecular structure of the two fuels, the incipient soot emitted from their combustion is comprised of species with similar molecular structure, likely dominated by polycyclic aromatic hydrocarbons (PAHs) [16]. The peak intensities for $m/z < 700$ are of similar magnitude for the emissions from both fuels. However, toluene-combustion aerosols had higher intensities in the large-molecular-size range (Figure 5b), indicating that toluene-combustion aerosols had more abundance of large-molecular-size species than aerosols emitted from *n*-heptane combustion. This is in-line with the finding that toluene-combustion aerosols were less volatile than the *n*-heptane-combustion aerosols (Figure 4) because for species with similar general molecular structure (e.g. the incipient soot produced in these experiments), volatility decreases with increasing molecular size [75]. We note that due to differences in ionization and desorption efficiencies of different molecules, the comparison shown in Figure 5 is qualitative. Specifically, we expect the ionization and desorption, thus signal intensity [76], to decrease with increasing molecular size. Therefore, we expect that in reality, the difference in abundance of molecules on the large-end of the spectra to be more prominent than depicted in Figure 5b.

The aerosol emissions from *n*-heptane combustion in the low-temperature region did not exhibit any discernible LDI-MS mass spectra. The LDI-MS technique requires that the sample absorbs the 337 nm laser significantly enough in order for it to desorb. As discussed in Section 3.4, the aerosol emissions from *n*-heptane combustion at low temperatures exhibited weak absorption in the visible spectrum, thus it is likely they were not absorptive enough to be detected by LDI-MS. Based on their high volatility

(Figure 4), we expect these aerosols to be comprised of species with smaller molecular size than those emitted in the high-temperature region.

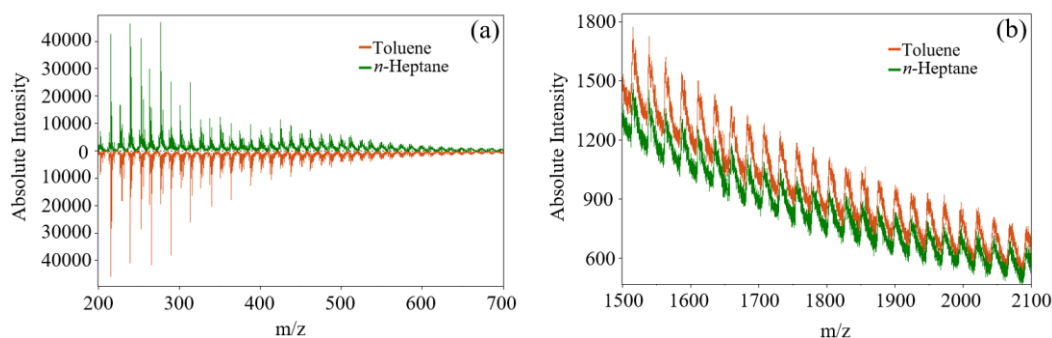


Figure 5. LDI-MS spectra of aerosol emitted from toluene and *n*-heptane combustion at 1035 °C.

3.4. Light-absorption properties

The light-absorption properties of the aerosol emitted from the combustion of toluene (at combustion-chamber temperature of 1035 °C) and *n*-heptane (at combustion-chamber temperature of 1035 °C and 290 °C) are depicted in Figure 6. Figure 6a shows the imaginary part of the refractive indices at 422 nm, 532 nm, and 782 nm (k_{422} , k_{532} , and k_{782} , respectively) retrieved from optical closure and Figure 6b shows the mass absorption cross-sections (MAC_{422} , MAC_{532} , and MAC_{782}) obtained from normalizing the measured absorption coefficients by the mass concentration (Section 2.3). At combustion-chamber temperature of 1035 °C, aerosols from both toluene and *n*-heptane combustion exhibit significant absorption in the visible spectrum and are categorized as brown carbon (BrC). The toluene-combustion aerosol is more absorptive (has larger k and MAC) than the *n*-heptane-combustion aerosol, which is visually manifested as darker samples when collected on Teflon filters (Figure 6c). However, k and MAC of *n*-heptane-combustion aerosol have a stronger wavelength dependence ($w = 7.6$ and $\text{AAE} = 8.7$) than toluene-combustion aerosol ($w = 4.1$ and $\text{AAE} = 5.6$). This inverse relation between k and w (MAC and AAE) is consistent with previous reports showing that more absorptive BrC is characterized with flatter absorption spectra [18, 22, 39, 77, 78].

We note that these findings, in conjunction with the differences in molecular sizes (Figure 5) and volatility (Figure 4), are consistent with the brown-black continuum hypothesis that we have previously

introduced to describe the light-absorbing carbonaceous aerosols, including BrC and BC, generated via the soot-formation route in combustion [18]. As the soot-formation process progresses toward full maturation (BC formation), it produces incipient soot (or BrC) comprised of increasingly larger organic molecules that are less volatile and more light-absorbing (larger k and smaller w). Our results indicate that toluene-combustion BrC is further ahead in the soot-formation process than *n*-heptane-combustion BrC (closer to the BC-formation threshold) and is therefore darker, less volatile, and exhibits molecular size distributions skewed toward larger sizes than *n*-heptane-combustion BrC.

For *n*-heptane combustion at 290 °C, the emitted aerosol exhibited measurable absorption only at 422 nm (Figure 6a and 6b) and was thus barely visible when collected on a Teflon filter (Figure 6c). This indicates that unlike at the higher combustion temperature of 1035 °C, the low combustion temperature of 290 °C was not conducive for the formation of large-molecular-size PAHs that exhibit absorption spectra extending into the visible wavelengths. Based on the chemical kinetics modeling results (Section 3.2), the aerosols emitted at 290 °C are possibly comprised of cyclic ethers, which do not contain chromophores that are significantly absorptive at mid- and long-visible wavelengths.

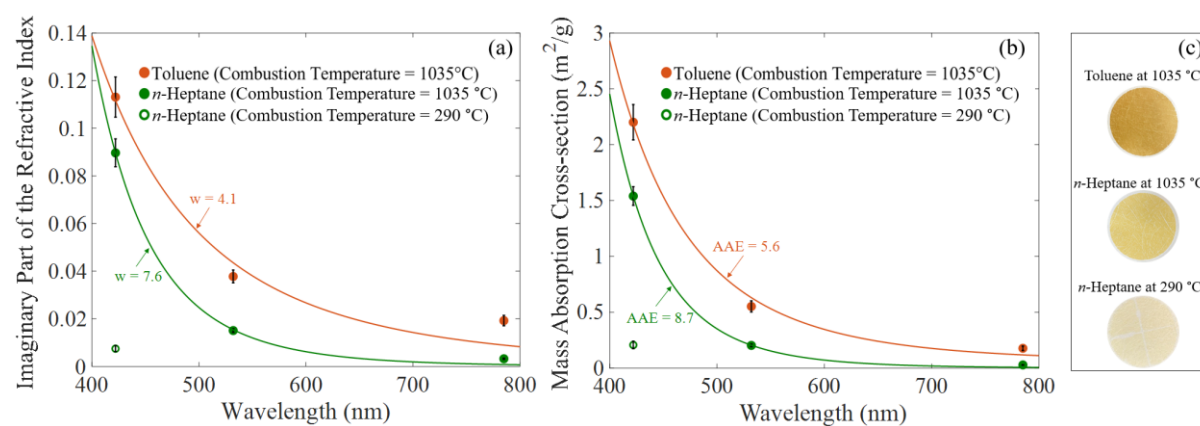


Figure 6. Light-absorption properties of aerosols emitted from toluene and *n*-heptane combustion. (a) Imaginary part of the refractive index (k) at different wavelengths. (b) Mass absorption cross section (MAC) at different wavelengths. Solid lines are power-law fits and the exponents are w and AAE, which represent the wavelength depends of k and MAC, respectively. The aerosol emitted from *n*-heptane combustion at 290 °C did not exhibit measurable absorption at 532 nm and 782 nm, thus light-absorption

properties are only reported at 422 nm (open green circles in panels (a) and (b)). (c) Pictures of filter samples that visually illustrate the differences in optical properties of the aerosol emissions.

The BrC (incipient soot) emissions at the low-temperature combustion conditions in this study are significantly less absorptive than the BC (mature soot) emitted at typical CDC or laboratory flame conditions. Mature soot has $MAC_{532} \approx 8 \text{ g/m}^2$ and relatively flat wavelength dependence with $AAE \approx 1$ [15]. An important implication of this difference in light-absorption properties is that incipient soot produced at low-temperature combustion conditions would not be accurately quantified using techniques that rely on optical measurements tailored for mature soot, e.g. filter smoke number (FSN) or microsoot sensor (MSS) [28, 29, 32, 33]. The MSS is a photoacoustic instrument that converts absorption measurements at 880 nm to soot mass concentrations based on calibration against combustion soot with high EC content (i.e. mature soot) [79]. Therefore, embedded in the reported MSS mass concentrations is an assumption that the measured aerosol has the same MAC_{880} as mature soot ($\approx 5 \text{ g/m}^2$). The aerosol emitted from toluene and *n*-heptane combustion at 1035 °C had MAC_{880} of 0.03 g/m^2 and 0.0025 g/m^2 , respectively, a factor of 152 and 1963 smaller than MAC_{880} of EC. Therefore, their mass concentrations would be underestimated by the same factors if measured using a MSS. Such large underestimation in mass concentrations of aerosol emissions from engines operated at LTC conditions has been previously reported for FSN [32] and MSS [2]. Our findings provide support for these reports and further indicate that optical absorption instruments are not suitable for quantifying LTC aerosol emissions even if they are calibrated with aerosol emissions at LTC conditions. Unlike mature soot which has relatively uniform light-absorption properties [21] regardless of emission source (conventional diesel combustion, laboratory diffusion flames, etc.), the light-absorption properties of incipient soot produced at LTC conditions can vary over several orders of magnitude depending on combustion conditions (Figure 6), making it impossible to produce a calibration standard.

4. Conclusions

Using an atmospheric-pressure reactor controlled at a constant equivalence ratio and O_2/N_2 , we investigated the effect of combustion temperature on the formation and physicochemical properties of aerosols emitted from the combustion of toluene at *n*-heptane at temperatures between 200 °C and 1035

°C. Consistent with fuel reactivity versus temperature profiles predicted by ignition chemistry simulations, aerosol emission factors from toluene combustion exhibited steep decrease with decreasing combustion temperature, while the emission rates from *n*-heptane combustion exhibited steep decrease with decreasing temperatures followed by resurgence that peaked at 290 °C. The physicochemical properties of the aerosols varied with both fuel type and combustion temperature. At 1035 °C, toluene combustion produced aerosols with molecular size distributions skewed to larger sizes compared to aerosols emitted from *n*-heptane. The toluene-combustion aerosols were also less volatile and more light-absorbing (darker), though both toluene-combustion and *n*-heptane-combustion aerosols are categorized as brown carbon (BrC). For *n*-heptane combustion, the aerosols emitted at 290 °C were significantly less light-absorbing and more volatile than those emitted at 1035 °C. The findings reported here provide the first evidence for the strong dependence of aerosol formation at low-temperature combustion conditions on ignition chemistry, particularly the two-stage aerosol formation in *n*-heptane combustion that reflects its two-stage ignition chemistry behavior. They also highlight the importance of further investigating the parameter space (fuel type and combustion conditions) associated with aerosol emissions at LTC conditions in order to identify regions within this space that can potentially minimize the emissions.

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