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Laser-Driven Calorimetry of Single-Component Liquid Hydrocarbons

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Abstract

A novel laser-heating technique, referred to as the laser-driven thermal reactor (LDTR), was used to determine sample thermal (exothermic/endothermic) behavior, specific heat release rate, and total specific heat release of three volatile single-component liquid hydrocarbons, i.e., *n*-decane, *n*-butylcyclohexane and *n*-butylbenzene. The objective was to demonstrate measurement repeatability and extend the LDTR model from earlier investigations. The experimental apparatus consists of a copper sphere-shaped reactor mounted within a vacuum chamber, with sample and substrate supported on a thermocouple near the center of the reactor. The reactor is heated from opposing sides by a near-infrared laser to achieve nearly uniform sample temperature. The change in temperature with time (i.e., thermogram) is compared to a previously recorded baseline (no liquid sample) thermogram. A model, based on thermal energy conservation, is used to evaluate the thermograms for the thermochemical characteristics of interest. This study represents a step toward applying this technique to more complex volatile multi-component fuels of unspecified composition. Results for the LDTR were compared with a differential scanning calorimetry/thermal gravimetric analysis (DSC/TGA) instrument. The model analysis was extended to include an estimation of the hydrocarbon mass change with increasing temperature, based on the temporal change in the specific heat release rate. An estimate of the total specific heat release was obtained for these three liquid hydrocarbons and found to be consistent with the literature values when the measurements were carried out under suitable operating conditions.

Keywords

calorimetry; heating value; laser-driven thermal reactor; *n*-butylbenzene; *n*-butylcyclohexane; *n*-decane; single-component liquid hydrocarbons; total specific heat release

INTRODUCTION

Single-Component Hydrocarbons

Transportation (gasoline, diesel, and jet) fuels are chemically complex mixtures of organic compounds. Simpler mixtures, containing alkanes, naphthenes (i.e., cycloalkanes and

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alkylcycloalkanes), aromatics, or olefins, have been considered as surrogates that mimic the physical and chemical characteristics of more complex mixtures.^{1–3} Examples of studies discussing the suitability of these mixtures as surrogates are described with some pertinent findings. Oxidation and pyrolysis chemistry for decane (alkane),^{4–6} butylcyclohexane (alkylcycloalkane),^{7–9} and butylbenzene (aromatic)^{10–12} have been studied extensively under a variety of reaction conditions to provide chemical mechanisms for combustion models. Several studies have been carried out to confirm the suitability of these surrogate mixtures to mimic the combustion behavior of conventional fuels. In one study,¹³ a simple surrogate mixture (aviation fuel surrogate) of three single-component liquid hydrocarbons; i.e., 2:1:1 *n*-decane/*n*-butylcyclohexane/*n*-butylbenzene was suggested for evaluation among a palette of many other compounds. Netalson et al.^{14,15} also studied a similar surrogate mixture in a pressurized flow reactor and single-cylinder engine with comparison to JP-8. The operating conditions were carried out in the 600 K to 1000 K temperature range (classified as low-temperature oxidation, producing key temperature-dependent radicals from reactions occurring in this temperature regime). Results indicated that the surrogate was more reactive than the conventional aviation fuel. In a separate study for low-temperature oxidation of *n*-butylcyclohexane, Netalson et al.¹⁶ found that there was more pre-ignition reactivity (i.e., CO production) than for conventional fuels, over a temperature range of 600 K to 780 K (peaking at about 670 K) – a range of temperatures substantially smaller than that defined for low-temperature oxidation. The study found that reactivity was dependent on the interaction between the *n*-butyl chain and the cyclohexane ring. It was demonstrated that compounds similar to *n*-butylcyclohexane, but without the *n*-butyl/cyclohexane relationship (e.g., methylcyclohexane or *n*-butylbenzene), did not exhibit the same reactivity. Because of these research efforts, it was deemed reasonable to employ such single-component hydrocarbons for thermochemical studies and analysis before investigating more complex real-fuel mixtures.

Related Calorimetry Techniques

Thermochemical analysis techniques of liquid fuels, such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermal gravimetric analysis (TGA), bomb calorimetry (BC), and micro-scale combustion calorimetry (MCC), are commonly used tools for determining material thermal behavior and decomposition (i.e., pyrolysis and devolatilization). In general, these techniques are constant heating approaches and sample sizes are smaller than a few milligrams. A review of the use of several techniques with fossil fuels is given in Kk.¹⁷ For DSC,^{18–21} the material thermal behavior is characterized by comparing the power needed to heat a sample to a temperature similar to that of a reference cell. The difference in energy input with time is used to identify thermal degradation processes and the change in enthalpy. Similarly, for DTA,²² the substance under study and reference cell are made to undergo identical thermal cycles, while recording any temperature difference between the sample and reference. For the TGA instrument,^{23–25} chemical decomposition processes are analyzed by detecting sample mass change with time. A pan with sample is placed on a precision balance inside a programmable furnace with a thermocouple to monitor the temperature. The furnace can be programmed either for a constant heating rate or a constant mass loss with time. The BC, also referred to micro-bomb combustion calorimetry,^{26–29} not to be confused with micro-scale combustion calorimetry

(MCC), is a constant-volume calorimeter that is typically used to measure the heat of combustion of a material. The sample is electrically ignited to release thermal energy to the surrounding containment vessel. The vessel has an isothermal surface with no thermal losses to the surrounding environment. Sample calorific content is detected through the change in the temperature of a surrounding water jacket or by means of heat flux meters. The MCC, also referred to as pyrolysis-combustion flow calorimetry,^{30–33} measures the specific heat release rate and enthalpy of combustion, typically of solids. Sample gases are released by controlled pyrolysis in an inert gas stream, which is followed by high-temperature oxidation of the volatile pyrolysis byproducts. The transient oxygen consumption and combustion gas generation are monitored to enable calculation of the sample mass loss rate³⁴ and enthalpy of combustion of the flowing byproducts. Note that other techniques such as cone calorimetry^{35,36} and thin-skin calorimetry³⁷ measure the heat release rate, heat flux, and other combustion/fire-related parameters of solids (typically of polymers), but off large-scale material surfaces.

In general, the above-mentioned calorimetry techniques are appropriate for temperature levels up to 1000 K and heating rates of less than 1 K/s (limited by instrument design and intended application). For volatile liquids, the relatively low heating rate (longer time scale) can cause thermochemical phenomena to remain undetected before completion of chemical reactions. Preferential vaporization of the volatile components may also be consumed before reaching the operating steady-state temperature,³⁸ resulting in the potential loss of important process information. Higher heating rates or larger sample mass can enable one to monitor the thermal behavior before and during the occurrence of chemical reactions. However, larger sample mass is an issue regarding sample containment within the pan and sample temperature uniformity. The rapid attainment of high temperatures is achievable with laser-heating techniques. More recently, rapid-heating, micro (or flash) differential scanning calorimetry^{39–41} has been used to heat energetic materials, using a silicon based micro-DSC device (with a heating rate of up to 1×10^7 K/s). However, these devices are limited in liquid sample mass (i.e., to less than a microgram) and temperature range (less than 800 K), and therefore the sample may be consumed before completion of the thermal cycle (or the measurement completed before termination of the sample reactions), resulting in the loss of important thermogram details.

Investigation Objectives

The focus of this investigation was to evaluate the suitability of using a novel laser-heating technique, referred to as the laser-driven thermal reactor (LDTR), to determine the endothermic/exothermic behavior and total specific heat release of three volatile single-component liquids, representing three different classes of hydrocarbons, i.e., *n*-decane (alkane), *n*-butylcyclohexane (alkylcycloalkane), and *n*-butylbenzene (aromatic). This work builds upon an earlier work⁴² with biofuel standard reference materials from the National Institute of Standards and Technology. In the earlier investigation, the fuels were mixtures composed of known fatty-acid-methyl-ester constituents with the results showing well-defined exothermic behavior at specific temperature regimes near the boiling point of each liquid.

EXPERIMENTAL ARRANGEMENT

Apparatus

The experimental methodology used in this investigation focuses on the temporal change in temperature of a substance that results from the heat exchanged with the surroundings by both its thermal and chemical behavior. The technique has been applied for a variety of applications.⁴³ Details regarding the methodology and apparatus are provided elsewhere in earlier investigations.^{38,42,44} Although the basic features of the apparatus have been described before in previous articles, each new study (in which different materials are applied for the first time) extends the application of the technique to new situations, requiring modification to the basic arrangement. The motivation for the current arrangement and operating conditions was based on determining the feasibility of the apparatus to measure the thermochemical characteristics of liquids that evaporate and react. Specific changes to the facility are discussed, along with procedural modifications implemented for these experiments. Figures 1 and 2 show the experimental arrangement along with the optical components, gas-supply, and computer-controlled data-acquisition. Within a vacuum chamber, sample is mounted on a thermocouple, that is centered inside a copper sphere (referred to as the 'reactor'). A relatively simple procedure was established to fabricate the sphere reactor in the laboratory beforehand. This was accomplished by preheating a piece of copper shim stock ($\approx 50 \text{ mm}^2$ with a thickness of $\approx 0.02 \text{ mm}$) and casting it into a hemisphere by placing the malleable copper inside a premade copper hemispherical-shaped form with a stainless-steel sphere insert. Tightening in a vise and periodically turning the form resulted in shaping of the hemisphere. Two hemispheres were matched to form a sphere that had an outer diameter of $18.20 \pm 0.03 \text{ mm}$ (expanded uncertainty), which was then installed within the vacuum chamber. [The measurement uncertainty is estimated from replicated measurements (referred to as Type A evaluation of uncertainty), and other sources of specified uncertainty (referred to as Type B evaluation of uncertainty).⁴⁵ Type A expanded uncertainty is determined from ku_c , where k is the coverage factor and u_c is the combined standard uncertainty (estimated by $sn^{-1/2}$, where s is the sample standard deviation and n is the number of samples. The level of confidence is 95 % for the chosen values of n and k .] The sample (i.e., liquid hydrocarbon) was placed inside a substrate (copper pan) that rests on a thermocouple (insert in Fig. 1) that defines the 'sample temperature' (see Terminology section). The thermocouple bead was in contact with the pan bottom outer surface. The customized K-type fine-wire thermocouple had a 0.25 mm bead diameter, unsheathed wires, and a $0.200 \text{ s} \pm 0.002 \text{ s}$ response time. The pan mass was $(49.0 \pm 0.1) \text{ mg}$ with the following dimensions: inner diameter of $(4.950 \pm 0.001) \text{ mm}$, height of $(2.340 \pm 0.001) \text{ mm}$, and thickness of $(0.1250 \pm 0.0006) \text{ mm}$. A second thermocouple (same type as the pan thermocouple) was flush with the inner surface of the reactor sphere ('reactor temperature'). A near-infrared continuous-wave Nd:YAG laser beam (wavelength of $1.064 \text{ }\mu\text{m}$) was used to heat the reactor sphere from two sides to achieve a nearly uniform sample temperature (on the order of 1 K)³⁸ near the center of the sphere (within a volume of about 10 mm diameter by 5 mm height). For these experiments, the laser beams were not expanded to impinge over the entire sphere surface in order to maximize the laser intensity (lenses normally used to expand the beams reflect a percentage of the incident light and thus were removed from the experimental setup) and achieve higher heating rates and operating

temperatures. The effect of laser-beam multimode intensity distribution was considered non-influential to the measurements. The gas pressure and composition around the sample were controlled by placing the reactor assembly inside the vacuum chamber. Conduction heat transfer within the sample was evaluated by the lumped-capacitance approximation⁴⁶, which specifies that the sample temperature remains spatially uniform during the transient process for a Biot number less than 0.1. This condition was satisfied for this investigation. A data acquisition system (sampling rate at 100 Hz) was used to record and process the sample and reactor temperatures with respect to time. The limited thermocouple response time required that the data be averaged and reported every 0.25 s.

The 'heating-rate approach' was used in which the reactor is heated to a steady-state temperature.³⁸ Initially, two 'baseline thermogram' measurements are carried out with respect to time (including the pan substrate and no liquid sample) for both the sample and reactor temperatures. The measurements are then carried out with sample (providing a 'sample thermogram' and 'reactor thermogram'). With the four thermograms, two 'sample-baseline temperature difference' profiles are obtained by subtracting the sample thermogram or reactor thermogram from that of the respective baseline thermogram. Two profiles are also defined as the 'sample derivative' and 'reactor derivative', which represents the dependence of the sample or reactor temperature-time derivative on time (or sample/reactor temperature) for measurements with sample. An additional two 'baseline derivative' profiles are defined for the sample and reactor temperature-time derivative cases without sample. The difference between two adjacent data points per time interval defines the derivative. Again, see the Terminology section for definition of these terms.

Hydrocarbon Characteristics

Following Presser et al.,⁴² three single-component volatile liquids, representing three different classes of hydrocarbons, were used in this investigation, i.e., *n*-decane (*n-DEC*), *n*-butylcyclohexane (*n-BCH*), and *n*-butylbenzene (*n-BBZ*). They were commercially acquired, each with a purity > 99 %. The physical/chemical properties, as estimated from several sources in the literature, are summarized in Table 1.

Experimental Uncertainties and Measurement Repeatability

Expanded uncertainties associated with the apparatus components are described elsewhere in Nazarian and Presser,^{38,44} and Presser et al.⁴² For these experiments, the copper pan was pre-positioned near the center of the reactor sphere and the liquid sample added to the pan to eliminate the uncertainty of placing the pan on the sample thermocouple from one run to the next, and to enable initiation of experiments within 30 s. A Hamilton 10 μ L cemented-needle syringe with an imprinted scale was chosen because the desired liquid mass (about 2 mg droplets) could be delivered directly into the pan. [Certain commercial equipment or materials are identified in this publication to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for this purpose.] A procedure was established to release droplets of approximately the same mass in a consistent manner. The liquid mass extruded from the syringe was determined by ejecting individual droplets onto a copper pan and

placing the pan inside a precision digital electronic balance. The balance measurement uncertainty was ± 0.1 mg. Different syringe settings were used to determine the repeatability of extruding one droplet with a particular mass. A setting of 4 μL appeared to provide the smallest variation in ejected droplet mass with an uncertainty of less than 0.01 %.

Regarding sample mass change (due to evaporation) with time during the preparation of an experiment in the laboratory (i.e., from sample preparation/weighing until initiation of laser heating in the vacuum chamber), the three hydrocarbons were considered to have negligible change in initial mass. The percent change in sample mass from its initial value was less than 1.3 % over a period of a minute for each hydrocarbon. As mentioned above, the experiment preparation time was generally carried out within 30 s.

The expanded uncertainty for the baseline (sample temperature) and sample thermograms were evaluated from two replicate runs. For these experiments, *n*-decane was chosen arbitrarily as the liquid for demonstrating the measurement repeatability. An example of the *n*-decane baseline and sample thermograms is presented in Fig. 3, in air at ambient (laboratory) pressure with a 2.5 mg sample mass (laser power output of 134 W). The heating rate was between 65 K/s and 70 K/s, defined by the maximum value in the baseline (sample temperature) derivative profile, see Fig. 3B. The variation in the derivative profiles near the peak in Figs. 3B and 3D is attributed to the data acquisition rate of 0.25 s; longer sampling times would average out the variations but might affect detection of other important profile features. The expanded uncertainty with respect to each mean temperature was within 1.0 % for the baseline sample temperature, 1.5 % for the baseline reactor temperature, 1.5 % for the *n*-decane sample temperature and 2.5 % for the *n*-decane reactor temperature. Note the dip in the *n*-decane sample derivative profile, being initiated near the *n*-decane boiling-point temperature (447 K) with a minimum near the auto-ignition temperature (AI) of 483 K. This feature, which will be discussed further, is indicative of liquid evaporation.

Measurement Protocol

Preparation for an experimental run entailed dripping with the syringe one to two liquid droplets (ranging between 2 mg and 5 mg) into the copper pan, closing the vacuum chamber to isolate the liquid from the surrounding environment (with the chamber pressure remaining at that of the laboratory). It was determined from an earlier investigation⁴² that operating under reduced pressure inhibits liquid reactivity with air. However, operating at atmospheric pressure reduces the lifetime of the reactor sphere to about 10 runs before replacement. The chosen condition was to operate at atmospheric pressure and replace the reactor sphere when required.

Prior to a measurement, the outer face of the copper sphere was pre-oxidized by using the laser to heat momentarily the surface to 773 K (ambient pressure), which formed a CuO layer (having a dark grey appearance). Measurements were then carried out by operating the laser at a chosen power level, which resulted in heating the sample from ambient temperature to a steady-state temperature. Measurements were carried out for different operating conditions (i.e., different laser power settings, chamber gases, and liquid masses). The laser power level (controlling the heating rate and maximum temperature) and sample mass were changed to determine which conditions adequately revealed the features of the

thermogram. Before carrying out an experiment with sample, a baseline measurement was obtained with an empty oxidized copper pan. The baseline measurement is expected to remain unchanged after a run with sample if there are no changes in the experimental and operating conditions. However, this is true only if the Cu_2O layer (with a reddish appearance) that forms on the sphere surface at higher temperatures (above 973 K) during an experiment is re-oxidized back to CuO ; namely, as existed before the run.⁴² This is accomplished before the next run by reheating the sphere surface with the laser beam to 773 K, as described earlier. Following this procedure reverts the apparatus back to its original condition, and thus prepares the reactor for the next run, eliminates repeatability issues, and reduces measurement uncertainty. If the CuO layer is not reformed prior to an experiment, then the sphere thermal behavior will be altered and will perform as if one had reduced the laser power.

Experiments were carried out at 101.3 kPa in air with the laser heating rate between 60 K/s and 90 K/s (with the maximum steady-state temperature reaching between 900 K and 1200 K), and sample mass between 2 mg and 5 mg (a smaller mass helps increase the lifetime of the reactor sphere). During a run (for each hydrocarbon), the two thermocouple temperatures were recorded by the data acquisition software. The resulting thermograms from each experiment were used to evaluate the hydrocarbon thermal behavior. Expressions representing the thermochemical behavior of a sample material are derived from an equation for thermal energy conservation and evaluated using Microsoft Excel.

THEORETICAL MODEL

Thermal Energy Conservation

The thermal energy balance that governs the heating process is represented by:

$$m(t)c_p(T)dT/dt = I_l A \beta(T, \lambda) - F(T, T_o) + \Delta m(t)q(T) \quad (1)$$

where the term on the left side of Eq. 1 represents the rate of change of sample internal thermal energy. The parameter T is the sample temperature, $c_p(T)$ is the sample specific heat capacity at the sample temperature, and $m(t)$ is the sample total mass (i.e., substrate and liquid hydrocarbon combined) at time t . The thermal energy absorbed by the sample is represented by the first term on the right side of the Eq. 1. The parameter I_l is the laser beam incident radiation intensity that heats the sample, A is the sample geometric cross-sectional area, and $\beta(T, \lambda)$ is the sample spectral hemispherical absorptivity at temperature T and laser wavelength λ . The second term, $F(T, T_o)$, represents the sample thermal losses due to conduction, convection, and radiation. The parameter T_o is a reference temperature. The transfer of thermal energy due to chemical reaction (combustion, decomposition, vaporization, etc.) is considered if the sample mass decreases from its initial value, $m(t)$, with respect to time (i.e., after an experiment and rechecking the mass). The term $q(T)$ is the specific heat release rate due to chemical reactions (i.e., the rate of released/absorbed thermal energy by a substance to/from the surrounding environment per unit mass during a chemical reaction).

For the heating-rate approach (i.e., heating the reactor to the steady-state temperature), the heat transfer term is given by: $F(T, T_o) = m(t) c_p(T) (T - T_o)/\tau$, where τ is the temperature-dependent relaxation time (or heat transfer parameter).³⁸ To evaluate τ , the baseline sample and reactor temperatures are recorded at two or more different laser fluences (see Fig. 4). From two sets of baseline thermograms, one can derive the following relationship:

$$\tau = \frac{T_2 - T_1}{\left(\frac{dT}{dt}\right)_1 - \left(\frac{dT}{dt}\right)_2} \quad (2)$$

where T_1 and T_2 are the baseline sample temperatures for the two different laser fluences at times t_1 and t_2 , respectively, corresponding to the same reactor temperature, T_r (see Fig. 4). The reactor temperature is chosen so that one can adequately calculate the baseline (sample temperature) derivatives, $(dT/dt)_1$ and $(dT/dt)_2$, at T_1 and T_2 , respectively.

After determining the relaxation time, a set of experiments (for the baseline and then with sample) is carried out for a selected laser fluence (defining the sample heating rate and steady-state temperature). A 'pan-based analysis' is then carried out using the baseline (sample temperature) and sample thermograms. The equations representing the heat transfer processes are:

sample thermal energy balance

$$m_{sas}(t) c_p(T_{sas}) dT_{sas}/dt = I_l A \beta(T_{sas}, \lambda) - F(T_{sas}, T_o) + \Delta m_{sas}(t) q(T_{sas}) \quad (3)$$

baseline thermal energy balance

$$m_{so}(t) c_p(T_{so}) dT_{so}/dt = I_l A \beta(T_{so}, \lambda) - F(T_{so}, T_o) \quad (4)$$

where 'sas' refers to the measurement with substrate and liquid hydrocarbon combined (for Eq. 3), and 'so' refers to the substrate-only baseline measurement (for Eq. 4). We assume that $m_{sas} \approx m_{so} \equiv m$, $c_{p,sas} \approx c_{p,so} \equiv c_p$ and $\beta_{sas} \approx \beta_{so} \equiv \beta$ because the sample mass is small compared to that of the substrate. Subtracting Eq. 4 from Eq. 3, substituting in Eq. 2, and rearranging terms results in an expression for the specific heat release rate, $q(T)$:

$$q(T_{sas}) = \frac{m(t) c_p(T_{sas})}{\Delta m(t)} \left[\frac{T_{sas} - T_{so}}{\tau} + \frac{dT}{dt} \Big|_{sas} - \frac{dT}{dt} \Big|_{so} \right] \quad (5)$$

Note that the thermal behavior is endothermic when $q(T) < 0$, and exothermic when $q(T) > 0$. Integrating Eq. 5 with respect to time for the various endotherms and exotherms results in the total specific heat absorbed or released for that part of the process. The total specific heat release during the exothermic process is the gross heating value and given by: $Q = \int q(T) dt = -H$, where H is the change in enthalpy for the chemical reaction.³⁸

Since the liquid hydrocarbon sample in the pan partially evaporates prior to the onset of chemical reactions, the possibility exists for these unburnt hydrocarbon vapors to chemically react on the reactor inner surface. Thus, another approach, referred to as the ‘reactor-based analysis’, was also used to determine the total specific heat release Q . This approach characterizes the specific heat release rate from the reactor surface, $q(T_r)$, by considering the absorption and release of thermal energy from the reactor outer surface to the surroundings. In this case, reactions occurring within the reactor volume are considered to influence heat transfer to and from the reactor surface. It is assumed that the temperature measurement on the reactor surface (carried out at whatever location) is representative of the heat transfer processes of the reactor, with the sphere temporal response (having a relatively larger mass) being slower than that of the pan. The heat transfer from the reactor outer surface is then expressed by Eqs. 3 and 4, with the temperature equated to that of the reactor, T_r . The total mass $m(t)$ is that of the sphere, pan, and liquid hydrocarbon (which is approximated by the sphere mass). Since τ is referenced to the reactor temperature, it is only applicable to the pan-based analysis (as defined in Eq. 5). Thus, evaluation of Eqs. 3 and 4 at the reactor sphere surface requires that $R(T, T_o)$ be evaluated by Eq. 13b in Nazarian and Presser.³⁸ Combining Eqs. 3 and 4, and substituting in for $R(T, T_o)$, results in:

$$q(T_{r,sas}) = \frac{m(t)c_p(T_{r,sas})}{\Delta m(t)} \left[\left. \frac{dT_r}{dt} \right|_{sas} - \left. \frac{dT_r}{dt} \right|_{so} \right] + \frac{\pi d^2}{\Delta m(t)} \left[\frac{Nu \kappa_g(T_g)(T_{r,sas} - T_{r,so})}{d} + \varepsilon(T_r, \lambda) \sigma (T_{r,sas}^4 - T_{r,so}^4) \right] \quad (6)$$

where d is the reactor diameter, Nu is the Nusselt number, T_g is the gas (i.e., air) temperature, $\kappa_g(T_g)$ is the gas thermal conductivity, $\varepsilon(T_r, \lambda)$ is the spectral hemispherical emissivity of the sphere (assuming that $\varepsilon(T_{r,sas}, \lambda) \approx \varepsilon(T_{r,so}, \lambda) \approx \varepsilon(T_r, \lambda)$ over the temperature range of the experiment),³⁸ and σ is the Stefan–Boltzmann constant ($5.670373 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$). The thermal energy released from the upper opening of the hemisphere (for placing the sample in the copper pan) is assumed to be negligible, since it is covered with a small piece of oxidized copper during experiments. Note that both approaches, using either Eq. 5 or Eq. 6, should result in equivalent values for Q for chemical reactions reaching completion.

Sample Mass Temporal Change

As discussed earlier, the liquid mass does not change significantly from preparation to initiation of an experiment (at the ambient temperature). Since the measurement capability to monitor $m(t)$ during an experiment is not currently available, the following analysis was formulated to estimate the sample mass change with time. The mass loss rate is negatively proportional to the heat release rate (units of watts), as given by the following relationship:^{32,33}

$$\frac{d\Delta m(t)}{dt} = - \frac{\Delta m(t)q(T)}{Q^*}, \quad (7)$$

where Q^* is a proportionality constant that is set initially to the value of Q available in the literature (see Table 1). Using a downward-differencing representation, $[d\Delta m(t)/dt]_i = [\Delta m(t)_{i+1} - \Delta m(t)_i] / \Delta t_{i+1}$, then Eq. 7 can be rewritten as:

$$\Delta m(t)_i = \Delta m(t)_{i-1} \left[1 - \frac{\Delta t_i}{Q^*} q(T)_{i-1} \right] = \Delta m(t)_{i-1} e^{-\Delta t_i q(T)_{i-1} / Q^*} \quad (8)$$

and

$$\left[\frac{d\Delta m(t)}{dt} \right]_i = \frac{\Delta m(t)_{i+1} - \Delta m(t)_i}{\Delta t_{i+1}} = - \frac{\Delta m(t)_i q(T)_i}{Q^*} \quad (9)$$

where $\Delta t_i = t_i - t_{i-1}$ for $i = 1, 2, 3, \dots, n$ and is constant (i.e., the data acquisition system acquires data at a fixed time interval). Required is an initial value for $\Delta m(0)$, which is defined in units of mass and estimated by $(t_{max} - t_0)/n$ where t_{max} is the time to reach the maximum value of the sample-baseline (sample temperature) temperature difference or when the sample mass becomes negligible (generally occurring at about the same time) for exothermic behavior. If the process is entirely endothermic, then t_{max} is set to the time when the calculated sample mass becomes negligible. The term n is the recorded number of data samples from t_0 to t_{max} . The sample mass changes from one time step to the next using: $m_i = m_{i-1} - m(t)_i / m(0)$. Note that these equations hold true for substance exothermic behavior; however, when the sample behavior is endothermic, the minus sign in Eqs. 8 and 9 is changed to a plus sign to ensure that the mass of the vaporizing liquid continues to decrease with time.

Baseline (Sample Temperature)/Sample Thermogram Alignment

As described above, the variation of the sample and reactor temperatures with time is obtained for the baseline and sample runs. Since the baseline (sample temperature) and sample thermograms are obtained sequentially, criteria for aligning the two thermograms are required in order to evaluate $q(T)$ in Eqs. 5 and 6. These equations are dependent on determining the sample-baseline temperature difference (for the respective sample or reactor temperatures), and difference in the sample or reactor derivative profiles, whose values are dependent on alignment of the baseline (sample temperature) and sample thermograms. There are several reasonable approaches that could be used for this alignment, for example, matching the 1) time when the two profiles separate, i.e., matching the point for each run when laser heating is initiated (leading to no initial endothermic behavior), or 2) curves so that the liquid boiling point occurs at approximately the same time (resulting in a large endotherm and little exotherm). A third approach was adopted in which the energy associated with the initial endotherm (assuming that the hydrocarbons evaporate before the

onset of combustion) was calculated using $E_{endo} = -m(t)[c_p(T_{bp})T + h_{vap}]$, which accounts for the change in enthalpy due to the increasing temperature and liquid evaporation. This value was then compared to the energy absorbed with the change in the specific heat release rate during evaporation, as estimated by $E_{endo} = \sum[q(T) - t m]_i$ for $i = 1, 2, 3, \dots$ and $q < 0$ (from initiation of the run until q became positive - exothermic), and m_i is changing due to evaporation. It is assumed that evaporation occurs up to the liquid boiling-point temperature, T_{bp} , and thus $T = T_{bp} - T_{air}$. Values for h_{vap} were taken from a fit to data in the literature⁴⁷ with the following exponential relationship: $h_{vap} = h_{vap}^0 + ae^{bT}$ where the values for h_{vap}^0 , a , and b are respectively, 19.65494, 55.282, and -0.00186 for *n-DEC*; 37.8543, 39.237, and -0.0046 for *n-BCH*; and 85.18921, -20.68368 , and 0.00171 for *n-BBZ*. The specific heat capacity for these liquid hydrocarbons (between T_{air} and T_{bp}) was estimated to be:^{48,49} $c_p = a + bT$ where the values for a and b are respectively, 0.9582 and 0.00413 for *n-DEC*, 0.57097 and 0.00454 for *n-BCH*, and 0.68624 and 0.00374 for *n-BBZ*. Since evaporation of the liquid hydrocarbons is relevant only with regard to the liquid sample in the pan, the comparison of the calculated value for E_{endo} to the estimation is only relevant for the pan-based analysis. Thus, once Eq. 5 is evaluated for $q(T)$, and initial values for E_{endo} determined, one may then adjust the thermograms so that the calculated and estimated values for E_{endo} are similar. The adjustment of the thermograms is carried out by increasing or decreasing the time associated with the baseline thermograms for both the sample and reactor temperatures together, so as to form an endotherm with the sample thermogram. Since the adjustment is made at the discrete time intervals (as recorded by the data acquisition), the adjustment is fixed when the estimated value for E_{endo} is best approximated to the calculated value. Once this is accomplished, $q(T)$ and E_{endo} are updated automatically in Microsoft Excel.

As discussed in Presser et al.,⁴² a change in the reactor sphere oxide layer during a run with sample can reduce the maximum temperatures achieved for subsequent baseline measurements, requiring re-oxidation of the sphere back to the initial CuO state before running the next experiment. Also, other systemic changes in the operating conditions (e.g., replacement of the reactor sphere) may have a similar effect. A procedure was developed to occasionally modify the baseline thermogram in a fashion that results in matching of the higher steady-state temperatures with that of the sample thermogram (as if there was no systemic effects). This procedure enables analysis of more runs during the sphere lifetime. Note that at the higher temperatures, sample has already been consumed and reactions completed, thus the sample thermogram should transition back to matching that of the baseline. Essentially, the baseline temperatures (starting from the thermogram inflection point) are shifted to higher temperatures in parallel to the maximum baseline derivative (i.e., peak value of the baseline derivative profile, which also corresponds to that at the thermogram inflection point). This procedure preserves the baseline thermogram curvature until the baseline steady-state temperature matches that of the sample thermogram. The procedure entails modification of the baseline thermogram (for both the sample and reactor temperatures) past the inflection point. For each subsequent time step, the baseline time, t_b , is updated by maintaining the same maximum slope and using the unchanged sample thermogram temperatures to update the baseline temperatures, as illustrated in Fig. 5. The equations used are:

$$t_j^* = t_i + \frac{(T_{\text{sas}} - T_{\text{so}})_i}{\left(\frac{dT_{\text{sas}}}{dt}\right)_{\text{max}}} \quad (10)$$

for $t_i > t_i[(dT/dt)_{\text{so,max}}]$, and

$$T_i = T_{j-1,\text{sas}} + (t_i - t_{j-1}^*) \frac{(T_j - T_{j-1})_{\text{sas}}}{(t_j^* - t_{j-1}^*)} \quad (11)$$

where $t_{j-1}^* \leq t_i \leq t_j^*$. Once the updated values of time, t_j^* , are determined using Eq. 10, one can interpolate to obtain new baseline temperatures, T_b , as given in Eq. 11, and corresponding to the fixed times, t_i (obtained from the data acquisition system). The corrected curve is illustrated by the dashed line in Fig. 5.

Analysis Protocol

The experimental results provide four thermograms from a set of runs with and without sample. The four respective temperature-time derivative profiles are calculated from the temperature difference between adjacent data points and divided by the time interval. The temperature difference is obtained by taking the difference between the sample or reactor temperature and the respective baseline (sample or reactor temperature). The difference in the sample or reactor derivatives is also obtained in a similar fashion. The analysis now takes two tracks, i.e., one related to evaluating the term $q(T)$ in Eq. 5 (pan-based analysis) and the second regarding the solution of Eq. 6 (reactor-based analysis). Both analyses are used to obtain values for Q .

Pan-Based Analysis

Equation 5 is evaluated by determining the initial mass of the liquid hydrocarbon and pan prior to an experiment. The above-mentioned analysis for the mass change with time is used to estimate the sample total mass, $m(t)$, during heating of the sample. The total mass is approximated by that of the pan, being much larger than the liquid mass. The change of the liquid mass with time while reacting is also accounted for, although its effect on the total mass is small. The time corresponding to complete consumption of reactants and termination of chemical reactions occurs typically near the peak in the sample-baseline (sample temperature) temperature difference profile; this point also matches the return in the sample derivative profile to that of the respective baseline at higher temperatures⁴²- see Fig. 6. Figure 6 also identifies the initiation of chemical reactions (i.e., when the sample-baseline temperature difference becomes positive in Fig. 6B) and the boiling-point temperature (as denoted by the feature formed at approximately 7 s in Figs. 6B and 6C). For the pan and sphere, the specific heat capacity⁵⁰ for copper is $c_{p,\text{Cu}} = 0.4234 - 0.18548 e^{-T/193.695}$, which was evaluated at the sample and reactor temperatures, respectively. The estimated specific heat capacity for each liquid hydrocarbon is reported earlier. The overall specific heat capacity was set to the mass-based weighted sum (while accounting for the change in fuel mass with temperature). The value for τ was 1.15; several baseline (sample temperature)

thermograms, obtained at different laser fluences, were used to evaluate Eq. 2 and the results averaged afterward.

Once the values of $q(T)_i - t_i$ are calculated per time interval, one can define the regions where there is an endotherm (negative values) and exotherm. The range of values considered for the exotherm (and being positive) are assumed for this study to be from the hydrocarbon boiling point to the end of reactions when there remains negligible sample mass. The trapezoidal rule is used to obtain the total specific heat release $Q = \int q(T) dt$ from the experimental results, which is then compared with the previously assumed literature value, Q^* . If different, the value of Q^* is then adjusted (which will affect $m(t)_i$ in Eq. 8, and thus Q) until it matches Q (to ensure that the integrated thermal energy per time step released during the reaction of the sample matches the overall release of energy), to obtain the final measurement value.

Reactor-Based Analysis

For Eq. 6, m is the total mass under consideration including that of the reactor sphere (noting that the sample and substrate masses are small relative to that of the sphere), $c_p(T_{r,sas})$ is for copper (the copper oxide layer is considered negligible compared to the remaining copper) and is defined by the relationship given in the previous section (but at the reactor temperature), $\kappa_g(T_g)$ was $0.024 \text{ Wm}^{-1}\text{K}^{-1}$ (in air),⁴⁶ and $\varepsilon(T_r, \lambda)$ was estimated to be 0.45 for CuO (recognizing that the oxide layer changes at higher temperatures during an experiment).³⁸ Since this analysis represents all the mass within the sphere (whether vapor or liquid), the value of $m(t)$ is set to the total hydrocarbon mass.

Normally, thermal convective heat transfer is negligible under reduced pressure, however, it must be considered when operating at atmospheric pressure (as mentioned earlier for these experiments). Thus, the Nusselt number (Nu) must be determined and substituted into Eq. 6. The expression used for this investigation is for an external free convection flow over a sphere, and given by:⁴⁶ $Nu = 2 + 0.589 Ra^{1/4} / (1 + (0.469/Pr)^{9/16})^{4/9}$. This correlation is dependent only on the air properties surrounding the reactor sphere. The above-mentioned relationship for Nusselt number is a function of the Rayleigh number, $Ra = g(T_r - T_{air})d^3 / T_f(\nu\alpha)_{air}$, and Prandtl number, $Pr = (\nu/\alpha)_{air}$. The film temperature is $T_f \equiv (T_r + T_{air})/2$, g is the gravitational constant (9.8 m s^{-2}), T_{air} is the ambient temperature (294 K), and values for ν_{air} (air kinematic viscosity) and α_{air} (air thermal diffusivity) were determined from polynomial fits to the data listed in Incropera and DeWitt⁴⁶ ($\nu_{air} \times 10^6 = -3.84567 + 0.03354 T_f + 1.14564 \times 10^{-4} T_f^2 - 2.23249 \times 10^{-8} T_f^3$; $\alpha_{air} \times 10^6 = -18.54664 + 0.11592 T_f + 6.9914 \times 10^{-5} T_f^2 + 1.26139 \times 10^{-9} T_f^3$). Note that for no thermal convection (e.g., under reduced pressure), $Nu = 2$, corresponding to conduction heat transfer from a spherical surface to a stationary, infinite medium around the surface.⁴⁶ Other variables in Eqs. 6 are discussed earlier or provided in Table 1.

Like the pan-based analysis, the thermograms at the reactor surface indicate an initial endotherm followed by exothermic behavior. The range of values considered for the exotherm at the reactor surface are assumed to include all reactor temperatures with positive values of $q(T)_i - t_i$. The reason is that at the reactor surface, unburnt hydrocarbon vapors release thermal energy during the entire experiment, and are not limited by the hydrocarbon

boiling point or complete evaporation of sample mass, as with the pan-based approach. Also, since the internal thermal energy terms in Eq. 6 (first two terms, right-hand side) must be positive if the thermal behavior is exothermic, it is excluded in determining $q(T_r)_i$ if negative. The total specific heat release again is determined using the trapezoidal rule to determine $Q = \int q(T) dt = \sum q(T_r)_i t_i - 0.5[q(T_r)_0 t_0 + q(T_r)_n t_n]$.

RESULTS AND DISCUSSION

Evaluating the Operating Conditions

To determine the appropriate experimental operating conditions (i.e., the conditions enabling detection of the liquid hydrocarbon thermal behavior while limiting the degradation of the reactor sphere), the heating rate (which specifies the maximum steady-state temperature), sample mass, and surrounding environment (nitrogen and air) were varied for a 2.5 mg *n*-decane sample. Regarding the surrounding environment, the results indicated that *n*-decane was endothermic in inert nitrogen, while the thermal behavior was exothermic with air. This behavior is exemplified in Fig. 7A and 7B, which presents the sample and reactor derivative profiles, respectively, for both nitrogen and air ($m(l) = 2.5$ mg and $P = 134$ W). The nitrogen profile (Fig. 7A) was similar to that of the baseline, and the air profile showed a significant decrease in the derivative near the boiling-point temperature. The decrease in the derivative is attributed to fuel evaporation (near the boiling-point temperature), while the rapid increase is attributed to reaction of the fuel vapors (near the auto-ignition temperature). The reactor derivative profiles (Fig. 7B) indicated an asymmetric shift for increasing values of the derivative to lower temperatures, as compared to the nitrogen case. These results appear to indicate hydrocarbon evaporation in the pan while the hydrocarbon vapor reacts on reactor sphere surface to about 600 K. As will be discussed further in the next section, the *n*-decane endothermic/exothermic behavior is also dependent on the sample-baseline (sample temperature) temperature difference, which was determined to be the dominant term, as compared to the difference in derivative terms in Eq. 5. For nitrogen, the sample-baseline temperature difference (for both the sample and reactor temperatures) was negative (not shown), indicating endothermic behavior (i.e., *n*-decane evaporation). For air, the sample-baseline temperature difference (for both the sample and reactor temperatures) indicated an exothermic behavior. The specific heat release rate calculated from both sample and reactor thermograms also indicated an exothermic (reactive) behavior for *n*-decane in air.

The effect of increasing the heating rate essentially causes a rise in the steady-state temperature. The sample derivative profile for different laser power settings is presented in Fig. 7C for a 2.5 mg *n*-decane sample in air. The figure again indicates a significant decrease in the derivative near the *n*-decane boiling-point temperature with the thermal behavior being detected when the laser power (i.e., laser output power) reached 85 W. Note that the laser power is reported as measured with a power meter at the sphere outer surface. The actual power reaching the pan and sample will be smaller. One can estimate the incident laser power ($P = I_r A$) at the pan by substituting into Eqs. 3 or 4, but the analysis is more complicated than it appears and will be discussed further in a future article.

The effect of initial mass on the sample derivative profiles in air ($P = 134$ W), is given in Fig. 7D. The results indicate that when the mass was too small, the decrease in the sample

derivative profile (indicative of hydrocarbon evaporation) was between 400 K and 500 K (at a lower temperature than the *n*-decane boiling point), whereas at a mass of 2.5 mg the dip was present near the boiling-point temperature. (The different maximum temperatures were a result of systemic changes, i.e., new sphere, different pan to hold the larger 5 mg mass). This result is consistent with the fact that the rate of evaporation increases with exposure to a larger surface area (i.e., of the pan), requiring less thermal energy to break the intermolecular bonds (i.e., lower temperatures).⁵¹ One would expect that a sample of relatively small mass would coat and expose much of its volume to the bottom of the hot pan, allowing the liquid to evaporate more readily (below the liquid boiling point), as compared to a larger-mass sample.

Estimated Total Specific Heat Release

Table 2 presents the estimated total specific heat release as determined by the LDTR for the three liquid hydrocarbons at a laser power of 134 W and an estimated sample mass between (2.0 and 3.0) mg. These operating conditions were found generally (through several preliminary trial runs) to be the most suitable for expressing the sample exothermic behavior in the thermogram. Values are given for both the pan- (Q_p) and reactor-based (Q_r) analyses. At the appropriate operating conditions, the estimated LDTR total specific heat release was similar to the literature values (see Table 1) for all three hydrocarbons regardless of the analysis approach. To demonstrate how the results change when the experiments are not carried out at the appropriate operating conditions, the laser power and sample mass were changed for *n*-butylcyclohexane. For example, the behavior for *n*-butylcyclohexane was endothermic when the laser power was at a lower setting (i.e., 102 W) than the optimum setting (134 W). This behavior is indicative of just liquid evaporation from the pan. The value for Q_p was -14.8 kJ g^{-1} , while Q_r indicated some endothermic (-1.4 kJ g^{-1}) and exothermic (12.1 kJ g^{-1}) behavior. The detection of some apparent exothermic behavior with the reactor-based analysis was attributed to reaction of vapors on the hot reactor sphere surface. This value may have been larger if the oxygen content within the vacuum chamber (this capability is currently unavailable) was increased significantly from that of air.

Figure 8 presents the A) thermograms, B) sample-baseline temperature difference profiles, and C) temperature-time derivatives profiles, respectively, for the laser power setting of 102 W. The thermograms in Fig. 8A indicate that the processes were endothermic. The fuel should evaporate completely when the temperature reaches the boiling point, causing the sample thermogram to return gradually to the baseline (the change is not immediate because of the thermal inertia of the larger pan or reactor sphere mass). The temperature difference profiles in Fig. 8B are indicative of endothermic behavior (negative values) for both the sample and reactor temperatures. The double dip in the thicker-solid reactor profile is attributed to some reactivity of liquid vapors on the hot reactor surface (but not having enough energy to make the profile exothermic), as opposed to only liquid evaporation from the pan (sample profile). The dip in the sample derivative profile (Fig. 8C) (between 420 K and 520 K) is indicative of endothermic behavior (also see *n*-decane results in Fig. 7). This case is interesting because the reactor profile in Fig. 8C is indicative of exothermic release of energy (i.e., the thick-solid reactor-derivative profile is above the baseline between 460 K and 620 K). The indication from Eq. 6 for the reactor specific heat release rate is that the

internal energy term (dependent on the difference in the sample derivatives) is significantly larger than the convection/radiation terms (dependent on the sample-baseline (sample temperature) temperature difference profile). Thus, one must base the substance thermal behavior on determination of $q(T)$, which is a function of both the sample-baseline temperature difference and the temperature-time derivatives.

When the laser power setting was higher (i.e., 198 W) than 134 W, the findings were similar to those at the optimum setting ($Q_p = 41.2 \text{ kJ g}^{-1}$ and $Q_r = 46.5 \text{ kJ g}^{-1}$). The value for Q_p was somewhat lower, perhaps due to matching of the sample and baseline thermograms. Considering the sample mass, when the mass was higher (i.e., 5.0 mg and 7.5 mg) than the optimum value, again the liquid behavior was endothermic for the pan-based analysis ($Q_p = -32.9 \text{ kJ g}^{-1}$ and -46.7 kJ g^{-1} , respectively), which was attributed to the need for more thermal energy to combust instead of evaporate the liquid from the pan. For the reactor-based analysis, there was in addition to the endotherm, some exothermic behavior ($Q_r = -0.7 \text{ kJ g}^{-1}$ and 16.6 kJ g^{-1} for $m(0) = 5.0 \text{ mg}$, and -4.7 kJ g^{-1} and 3.0 kJ g^{-1} for $m(0) = 7.5 \text{ mg}$) again attributed to reaction of liquid vapors on the hotter reactor sphere surface. When the sample mass was lower (i.e., 1.4 mg) than the optimum value, the behavior was exothermic but the value was low for the pan-based analysis ($Q_p = 19.8 \text{ kJ g}^{-1}$), while the reactor-based analysis resulted in the expected value ($Q_r = 46.6 \text{ kJ g}^{-1}$).

Calorimetry Measurements

Measurements using a DSC/TGA instrument were carried out for the three liquid hydrocarbons and results compared with those obtained with the LDTR. The instrument model was a NETZSCH STA 449 F1 Jupiter that integrates a high-performance heat-flux DSC with a nanogram-resolution thermobalance TGA.⁵² Both temperature (relationship between the measured and actual sample temperature) and sensitivity (conversion between the voltage difference generated by the sample and reference thermocouples, and the sample heat flow⁵³) calibrations were completed to check the precision of the actual sample temperature. Measurements were carried out in nitrogen (Fig. 9A) and air (Fig. 9B) at a heating rate of 50 K/min (maximum heating rate available with the instrument) to about 623 K. The initial mass (in nitrogen/in air, respectively) was different for each run: 11.8 mg/24.6 mg for *n-DEC*, 41.6 mg/24.9 mg for *n-BCH*, and 46.2 mg/27.7 mg for *n-BBZ*. The Al_2O_3 crucible mass was 159.8 mg/162.0 mg, 161.2 mg/161.9 mg, and 165.7 mg/164.0 mg, respectively, and the reference crucible mass was 155.7 mg for all runs. The measurements were assumed to be unaffected by the different initial masses, as long as the initial mass was above 5 mg (the samples were generally larger than that required for the LDTR). As indicated in Fig. 9, the general trend for the mass change and thermal behavior of the three hydrocarbons was similar whether carried out in nitrogen or air. The hydrocarbon mass decreased exponentially with increasing temperature and was completely evaporated by 460 K in nitrogen and 450 K in air (the boiling-point temperature for each hydrocarbon is given in Table 1). The change in specific heat release rate with temperature indicates endothermic behavior up to about 400 K, after which the hydrocarbon thermal behavior is exothermic, reaching a maximum value of about 6 W/g between 420 K and 460 K in nitrogen and between 430 K and 450 K in air (corresponding to the point of negligible liquid mass and termination of the liquid thermal decomposition). The specific heat release rate then begins

to decay back to the baseline at temperatures above 460 K. The *n*-decane results were somewhat different than the other two hydrocarbons when the measurements were carried out in nitrogen (the reason for this result is unclear). For the air case, the behavior for the three hydrocarbons was similar, being displaced to higher temperatures with increased hydrocarbon boiling point. Note that the DSC values of the specific heat release rate are on the order of watts per gram and not the expected kilowatts per gram (as with the LDTR), which is attributed to the slow heating rates (see Fig. 10 in Ref. 44).

As an example of the LDTR measurement, a set of results for 2.23 mg *n*-butylcyclohexane at a laser power of 134 W is presented in Fig. 10. The thermograms and sample-baseline temperature difference (Figs. 10A and 10B) indicate the presence of endothermic behavior (i.e., liquid evaporation) followed by exothermic behavior. Figure 10C presents the temperature-time derivative profiles with temperature indicating a significant exothermic behavior with the sample curves being above the baselines. Based on the maximum value for the baseline (sample temperature) derivative profile, the defined heating rate was about 72.5 K/s and the maximum temperature reached about 1100 K. Note that reactions tend to be completed when the sample derivative profile returns to the baseline (see Fig. 6), which corresponds to the peak in the sample-baseline (sample temperature) temperature difference profile at around 940 K. This feature is highlighted by the vertical dashed line in Fig. 10D, which presents the difference in the derivative profiles between that for the sample/reactor and the respective baseline. Figure 10E presents the sample normalized mass change and specific heat release rate with sample temperature for *n*-butylcyclohexane. The specific heat release rate for the LDTR reached a value of about 11 kW g⁻¹ between 940 K and 1000 K (at a heating rate of about 70 K s⁻¹) and $Q_p = 47.3$ kJ g⁻¹ over a time period of about 16 s, see Table 2). The DSC system (for *n*-butylcyclohexane) reached a value of $q \approx 5$ W g⁻¹ at 440 K (see Fig. 9B), and the total specific heat release was estimated to be 41.7 kJ g⁻¹; over a time period of 178 s – an order of magnitude longer than for the LDTR). The total specific heat release for the LDTR provided comparable results to that of the DSC instrument. For this investigation with single-component fuels, the time factor is not expected to affect the results, however, this may be untrue for multi-component fuels for which the fuel constituents may vaporize preferentially, and affect detection of detailed features related to the sample thermal behavior and decomposition.⁴²

Also presented in Fig. 10E is the corresponding TGA result taken from Fig. 9B. The TGA mass appears to be depleted between 450 K and 600 K, while the mass for the LDTR is exhausted between 700 K and 900 K. One would expect that the liquid mass would become gaseous through evaporation when reaching its boiling-point temperature, which is the case for the TGA but not for the LDTR result. With the LDTR, liquid evaporation is associated with rapid heating rates to temperatures well above the liquid boiling point, which should result in shorter liquid evaporation times, as compared to what is achieved with the TGA instrument. One possible explanation for this apparent discrepancy in temperature may be attributed to the Leidenfrost effect, in which liquid evaporation forms an insulating vapor layer between the pan surface and liquid. This results in slower evaporation of the levitated liquid over a longer period of time, while the pan heats up beyond the liquid boiling-point temperature. Similar phenomena have also been observed in the literature for droplets placed in contact with hot surfaces.⁵⁴ The resulting separation affects the heat transfer between the

liquid and pan, causing the thermocouple to sense the pan temperature and not that of the liquid directly (with the liquid evaporating at its boiling-point temperature); thus, this a subject for further investigation.

One can estimate the liquid temperature by assuming that the liquid evaporates by the time it reaches the liquid boiling-point temperature, and comparing the estimated specific heat release ($q(T)_i \Delta t$) for each time step (i) to the total specific heat release (Q). Note that the specific heat release rate (q) is a measure of the liquid reactivity. The estimated liquid temperature (T^*) is then given by:

$$T^* = T_{\text{air}} + \frac{(T_{\text{bp}} - T_{\text{air}})}{Q^*} \sum_{i=1}^n q(T)_i \Delta t \quad (12)$$

The change in mass with regard to the estimated liquid temperature is presented in Fig. 10E by the dashed curve. The result indicates that the liquid evaporates at a lower temperature than that of the DSC/TGA system, which is expected, since the LDTR heating rate is an order of magnitude higher than that for DSC/TGA.

SUMMARY

A laser-heating technique was used to determine sample exothermic/endothermic behavior, specific heat release rate, and total specific heat release of three volatile single-component liquid hydrocarbons, i.e., *n*-decane, *n*-butylcyclohexane and *n*-butylbenzene. Experiments were carried out at a liquid mass of about 2.5 mg and laser power of 134 W (heating rate between 70 K/s and 80 K/s, and steady-state temperatures of about 1100 K) in air. The technique consists of sample placed in a pan substrate, which rests upon a thermocouple positioned near the center of a spherical copper reactor. The reactor is heated from two sides with a high-power laser to the steady-state temperature. Recorded thermograms (temperature vs time) are used to evaluate an equation for conservation of thermal energy. The study successfully demonstrated the overall repeatability of the thermograms. The analysis was expanded to estimation of the mass change with time, based on the temporal change of the specific heat release rate. A scheme was also presented to estimate the liquid temperature during evaporation of the hydrocarbon mass. The effect of changing the liquid mass and laser power indicated that there were optimum operating conditions for efficacious evaluation of substance thermochemical behavior. The liquid hydrocarbon mass had to be sufficient to detect adequately the thermogram features, remain contained within the pan during an experiment, and maintain sample temperature uniformity. Similarly, the required laser power enabled detection of the thermogram features, while higher values did not result in any additional detail. The LDTR evaluated the thermochemical behavior of single-component liquid hydrocarbons with the total specific heat release found to be similar to values available in the literature.

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NOMENCLATURE Greek symbols Subscripts Superscripts

a, b	coefficients to regressive fit
A	sample geometric cross-sectional area [m ²]
$c_p(T)$	specific heat capacity [J g ⁻¹ K ⁻¹]
d	reactor sphere diameter [m]
(dT/dt)	sample temperature-time derivative [K s ⁻¹]
(dT_r/dt)	reactor temperature-time derivative [K s ⁻¹]
E	energy [J]
$F(T, T_o)$	heat transfer term [W]
g	gravitational constant (9.8 m s ⁻²)
I_I	intensity of the laser beam that heats the sample [W m ⁻²]
k	coverage factor
$m(t)$	sample total mass [mg]
n	number of samples
Nu	Nusselt number
P	laser output power [W]
Pr	Prandtl number
$q(T)$	specific heat release rate due to chemical reaction [kW g ⁻¹]
Q	total specific heat release [kJ g ⁻¹]
Ra	Rayleigh number
s	standard deviation
t	time [s]
T	sample temperature [K]
T_{air}	ambient air temperature [K]

T_{bp}	boiling-point temperature [K]
T_f	film temperature, = $(T_r + T_{air})/2$ [K]
T_o	reference temperature [K]
T_r	reactor temperature [K]
T_1, T_2	baseline sample temperatures at two different laser fluences [K]
u_c	combined uncertainty
α	thermal diffusivity [$\text{m}^2 \text{s}^{-1}$]
$\beta(T, \lambda)$	spectral hemispherical absorptivity
H	change in enthalpy [kJ g^{-1}]
h_{vap}	enthalpy of evaporation [kJ g^{-1}]
h^o_{vap}	enthalpy of evaporation at the standard state [kJ g^{-1}]
$m(t)$	mass of the reactive portion of the sample, mass loss [mg]
t	time interval [s]
T	change in temperature, = $T_{bp} - T_{air}$ [K]
$\epsilon(T, \lambda)$	spectral hemispherical emissivity of copper oxide
$\kappa_g(T_g)$	gas thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]
λ	laser wavelength [m]
ν	kinematic viscosity [$\text{m}^2 \text{s}^{-1}$]
σ	Stefan–Boltzmann constant ($5.670373 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4}$)
τ	temperature-dependent relaxation time [s]
<i>air</i>	ambient (laboratory) air
<i>Cu</i>	copper
<i>endo</i>	endotherm
<i>g</i>	gas
<i>i, j</i>	index
<i>max</i>	maximum
<i>n</i>	final value of indexed series
<i>p</i>	pan-based analysis
<i>r</i>	reactor-based analysis

<i>sas</i>	substrate and liquid hydrocarbon combined
<i>so</i>	substrate only (baseline)
<i>vap</i>	evaporation
<i>0</i>	initial indexed value
<i>1,2</i>	corresponding to two different laser fluences
<i>*</i>	modified value

Appendix

TERMINOLOGY

Sample temperature [T]

- pan thermocouple reading

Reactor temperature [T_r]

- sphere thermocouple reading

Sample thermogram [$(T)_{sas}$ vs. t]

- sample temperature vs. time (with sample)

Reactor thermogram [$(T_r)_{sas}$ vs. t]

- reactor temperature vs. time (with sample)

Baseline (sample temperature) thermogram [$(T)_{so}$ vs. t]

- sample temperature vs. time (without sample)

Baseline (reactor temperature) thermogram [$(T_r)_{so}$ vs. t]

- reactor temperature vs. time (without sample)

Sample-baseline (sample temperature) temperature difference [$(T)_{sas} - (T)_{so}$]

- sample thermogram minus the baseline thermogram (sample temperature)

Sample-baseline (reactor temperature) temperature difference [$(T_r)_{sas} - (T_r)_{so}$]

- reactor thermogram minus the baseline thermogram (reactor temperature)

Sample derivative [$(dT/dt)_{sas}$]

- differential change in sample temperature with time (with sample)

Reactor derivative [$(dT_r/dt)_{sas}$]

- differential change in reactor temperature with time (with sample)

Baseline (sample temperature) derivative [$(dT/dt)_{so}$]

- differential change in sample temperature with time (without sample)

Baseline (reactor temperature) derivative [$(dT_r/dt)_{so}$]

- differential change in reactor temperature with time (without sample)

Difference in the sample derivatives [$(dT/dt)_{sas} - (dT/dt)_{so}$]

- between the sample derivative and baseline (sample temperature) derivative

Difference in the reactor derivatives [$(dT_r/dt)_{sas} - (dT_r/dt)_{so}$]

- between the reactor derivative and baseline (reactor temperature) derivative

Figure 1.
Schematic of the LDTR copper reactor sphere.

Figure 2.
Schematic of the LDTR vacuum chamber and subsystems.

Figure 3. Repeatability experiments for four LDTR baseline and sample runs with 2.5 mg *n*-decane (laser power output of 134 W); i.e., variation of A, C) sample temperature with time, and B, D) sample temperature-time derivative with sample temperature, for the baseline and sample runs, respectively. The terms BP and AI are the indicated *n*-decane boiling point and auto-ignition temperatures from the literature, respectively.

Figure 4.

The LDTR thermal analysis protocol using the heating-rate approach. Two or more baseline runs (no liquid hydrocarbon) are carried out at different laser powers (P). For each run, the sample and reactor temperatures are recorded with respect to time.

Figure 5. Schematic illustrating modification of LDTR baseline thermogram and resulting profile (dashed curve). Dashed arrow indicates location of the inflection point.

Figure 6.

Example of the relationship between the A) measured LDTR sample/baseline (sample temperature) thermograms and both the B) sample-baseline (sample temperature) temperature difference and C) sample/baseline (sample temperature) derivatives for *n*-decane, $m(l) = 2.5$ mg and $P = 134$ W. The vertical dashed lines indicate the approximate 1) initiation of chemical reactions, 2) boiling-point temperature, T_{bp} (as indicated by the horizontal dashed line in frame A), 3) inflection point, and 4) termination of chemical reactions (approximate time of complete fuel mass consumption).

Figure 7.

Variation of the LDTR temperature-time derivative with A) sample temperature and B) reactor temperature for different environments (*n*-decane in nitrogen and air) - $m(0) = 2.5$ mg and $P = 134$ W, and C, D) sample temperature for different laser power settings ($m(0) = 2.5$ mg) and sample masses ($P = 134$ W), respectively - *n*-decane in air. The terms BP and AI are the indicated *n*-decane boiling point and auto-ignition temperatures from the literature, respectively.

Figure 8. Results using the LDTR for *n*-butylcyclohexane at a laser power of 102 W: A) thermograms, B) sample-baseline temperature difference profiles, and C) temperature-time derivative profiles.

Figure 9. Variation of the sample normalized mass and specific heat release rate with temperature for the three single-component fuels from the DSC/TGA apparatus in A) nitrogen and B) air.

Figure 10.

Results using the LDTR for 2.23 mg *n*-butylcyclohexane and a laser power of 134 W: A) sample and baseline thermograms, B) sample-baseline temperature difference for the sample and reactor temperature profiles, C) sample and reactor derivative profiles, D) difference in the derivative profiles between that for the sample/reactor and the respective baseline, and E) variation of the sample normalized mass and specific heat release rate with sample temperature. The corresponding TGA mass change profile from Fig. 8B (curve labeled

TGA) is also presented for comparison with the LDTR result (solid curve). The LDTR mass change profile using the estimated liquid temperature is represented by the dashed curve.

Table 1

Relevant physical and thermochemical properties for the three liquid hydrocarbons, as acquired from the literature.

Compound	Chemical formula ^a	Molecular weight ^a [g mol ⁻¹]	Boiling point ^a [K]	Auto-ignition [K]	Enthalpy of combustion [kJ g ⁻¹]	Enthalpy of evaporation ^{a,g} [J g ⁻¹] @ 298/T _{bp}	Vapor pressure ^h [kPa]	Specific heat capacity ^j [J g ⁻¹ K ⁻¹] @ 298 K	Liquid thermal conductivity ^a [W m ⁻¹ K ⁻¹] @ 298	Density ^a [g cm ⁻³] @ 293 K	Dynamic viscosity ^j [mPa s] @ 293 K	Surface tension ^m [mN m ⁻¹] @ 293 K
<i>n</i> -decane	C ₁₀ H ₂₂	142.28	447.1	480.9 ^b	47.64 ^d	361.4/278.2	0.182 ⁱ @ 298 K	2.210	0.130	0.7300/ [0.7266@ 298 K]	0.925 [0.838 ^a @ 298 K]	23.83
<i>n</i> -butylcyclohexane	C ₁₀ H ₂₀	140.27	453.9	519 ^c	46.56 ^e	351.9/277.0	1.333 @ 332.7 K	1.932 ^k	-	0.7902	1.309	27.03
<i>n</i> -butylbenzene	C ₁₀ H ₁₄	134.22	456.3	685.4 ^b	43.76 ^f	378.5/289.6	0.133 @ 295.9 K	1.813	0.126	0.8601	0.950 ^a @ 298 K	29.23

^aRef 50,^bRef 49,^cRef 55,^dRef 56,^eRef 57,^fRef 58,^gRef 59,^hRef 60,ⁱRef 61,^jRef 48,

$k_{\text{Ref } 62},$
 $f_{\text{Ref } 63},$
 $m_{\text{Ref } 64}.$

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Table 2

Estimated LDTR total specific heat release for the optimum condition, as obtained by the pan-based (Q_p) and reactor-based (Q_r) analyses. See Table 1 for the literature values (i.e., enthalpy of combustion).

sample	condition	Q_p [kJ g ⁻¹]	Q_r [kJ g ⁻¹]
<i>n</i> -decane	$P = 134$ W, $m(t) = 2.88$ mg	47.7 ± 1.6	47.9 ± 1.6
<i>n</i> -butylcyclohexane	$P = 134$ W, $m(t) = 2.23$ mg	47.3 ± 1.6	46.5 ± 1.6
<i>n</i> -butylbenzene	$P = 134$ W, $m(t) = 2.52$ mg	43.9 ± 1.6	43.8 ± 1.6