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Laser-Driven Calorimetry Measurements of Petroleum and Biodiesel Fuels

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Abstract

Thermochemical characteristics were determined for several National Institute of Standards and Technology standard-reference-material petroleum and biodiesel fuels, using a novel laser-heating calorimetry technique. Measurements focused on the sample thermal behavior, specific heat release rate, and total specific heat release. The experimental apparatus consists of a copper sphere-shaped reactor mounted within a chamber, along with laser-beam-steering optical components, gas-supply manifold, and a computer-controlled data-acquisition system. At the center of the reactor, liquid sample is injected onto a copper pan substrate that rests and is in contact with a fine-wire thermocouple. A second thermocouple is in contact with the inner reactor sphere surface. The reactor is heated from opposing sides by a continuous-wave, near-infrared laser to achieve nearly uniform sample temperature. The change in temperature with time (thermogram) is recorded for both thermocouples, and compared to a baseline thermogram (without liquid in the pan). The thermograms are then processed (using an equation for thermal energy conservation) for the thermochemical information of interest. The results indicated that the energy reaching the pan is dominated by radiative heat transfer processes, while the dominant thermal process for the reactor sphere is the stored (internal) thermal energy within the sphere material. Sufficient laser power is necessary to detect the fuel thermal-related characteristics, and the required power can differ from one fuel to another. With sufficient laser power, one can detect the preferential vaporization of the lighter and heavier fuel fractions. The total specific heat release obtained for the different conventional and biodiesel fuels used in this investigation were similar to the expected values available in the literature.

Keywords

biodiesel fuels; calorimetry; heating value; standard reference materials; petroleum fuels; total specific heat release

1. Introduction

Biofuels have generated significant interest to complement (i.e., mixture blends), and eventually replace, petroleum-based fuels. Drop-in biofuel replacements are substitutes for conventional fuels for which engine performance, equipment, or other infrastructure changes

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are not required to initiate their use [1]. New drop-in biofuels are being developed with diverse chemical composition and performance characteristics due to the use of different manufacturing processes and feedstock types [2]. Most efforts by industry are currently devoted to development of biofuel production processes, system-level evaluation for various transportation and propulsion platforms, and establishment of specifications based on physical properties testing. In addition, statistical models [3] are being developed to define fuel selection criteria and screening methodologies, based on the chemical identity of the biofuel constituents and impurities. A screening methodology would assist industry in rationally reducing the number of biofuel candidates in which to invest resources for further testing and selection as suitable drop-in replacements.

Among the various candidates, biodiesel fuel blends are being considered as possible drop-in fuels [4,5]. Biodiesel fuel is manufactured from a variety of feedstocks, including vegetable/plant oils (e.g., soybean, cottonseed, canola, corn, coconut), recycled cooking greases or waste oils (e.g., yellow grease), or animal fats (beef tallow, pork lard), as well as various combinations of these feedstocks [6]. Biodiesel fuel is produced through transesterification of fatty acids (within the feedstock composition) with a short-chain alcohol (usually methanol) in the presence of a catalyst (usually sodium hydroxide or potassium hydroxide) to form fatty acid methyl esters (FAMEs) and glycerin [7,8]. Biodiesel fuel is usually more viscous and has a higher boiling-point temperature than conventional hydrocarbon diesel fuels, which require further processing to ensure compatibility. In general, the more abundant FAMEs in biodiesel are methyl palmitate ($C_{17}H_{34}O_2$), methyl stearate ($C_{19}H_{38}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), and methyl linolenate ($C_{19}H_{32}O_2$) [4,9,10]. Each type of feedstock is characterized by a unique FAME profile [4,9], and thus screening methodologies can use this chemical information to classify each biodiesel fuel. With neat biodiesel (B100) fuel, the refining and blending processes from different feedstocks have no significant effect on energy content because the energy content is similar for the fats and oils used in biodiesel production [6]. Of further interest, is the need to evaluate to what extent thermal behavior is influenced by the unique FAME signature of a specific biodiesel fuel, and whether this information can contribute to the screening of biofuel candidates.

Thermochemical characteristics of conventional and biodiesel fuel compositions in air were investigated using a laser-heating calorimetry methodology, referred to as the laser-driven thermal reactor (LDTR). In an earlier study, this methodology was applied to different National Institute of Standards and Technology Standard (NIST) standard reference material (SRM) fuels, which included an ultra-low-sulfur diesel fuel (SRM 2771), soybean-based biodiesel fuel (SRM 2772), and a prototype unblended B100 biodiesel fuel. For this study, three NIST SRM conventional fuels were used, namely, high-sulfur kerosene (SRM 1617b), reformulated 10 % ethanol/gasoline (SRM 2297), and 10 mg/kg sulfur in diesel fuel oil (SRM 2723b). Also included was an animal-fat biodiesel (SRM 2773) and five manufactured biodiesel fuels derived from a variety of sources (viz., waste grease, soybean, beef tallow, animal fat, and canola). Reported is the endothermic/exothermic behavior of each fuel, as well as their specific heat release rate and total heat release (i.e., enthalpy of combustion; gross heating value). The importance of such thermochemical characteristics is to provide a better understanding of the influence of temperature on the energy (heat)

transfer and reactive nature of a substance, upon which so many industrial processes are dependent for ensuring product development and quality. The results are compared with information available in the literature.

2. Experimental arrangement

2.1. Fuel properties

For this investigation, three NIST SRM conventional fuels were used, i.e., high-sulfur kerosene (SRM 1617b) used to simulate aviation/turbine jet fuel, reformulated 10 % ethanol/gasoline (SRM 2297), and 10 mg/kg sulfur in diesel fuel oil (SRM 2723b). Estimated values for various fuel properties from the material data sheets are given in Table 1. Five manufactured biodiesel fuels were also included in this study, which were derived from a variety of feedstocks, including vegetable oils (soybean and canola), animal fats (beef tallow), and waste grease. The manufacturers of each biodiesel fuels were [9]: soybean from Minnesota Soybean Processors (MSP)*, canola oil from Archer-Daniels-Midland (ADM) Company, beef tallow from Texas Green Manufacturing (TGM), LLC., animal fat from Iowa Renewable Energy (IRE), LLC., and waste grease from TMT Biofuels, LLC. Also, evaluated was NIST SRM animal-fat biodiesel (SRM 2773), which was composed of 85 % animal fat (70 % choice white grease and 15 % edible pork lard) and 15 % soy oil. The animal fat sources are approximately 50 % to 60 % pork, 20 % beef, and 10 % to 20 % poultry, and was obtained from Smithfield BioEnergy, LLC. In an earlier investigation [11], a NIST standard reference material, SRM 2772, was evaluated and is compared with the results from this study. The manufacturer of this SRM was Ag Processing, Inc. Since the physical properties were unknown for each non-SRM biodiesel fuel, values were estimated from other referenced sources and used for each fuel. The relevant parameters are: boiling-point temperature (620 K) [12], specific heat capacity ($2.13 \text{ kJ kg}^{-1} \text{ K}^{-1}$) [11], enthalpy of evaporation (0.245 kJ g^{-1}) [13], and heating value (37.5 kJ g^{-1} [12] to 39.6 kJ g^{-1} for SRM 2771 soy biodiesel [11]). Expressions for a polynomial fit of the specific heat capacity is also given as a function of temperature in [14] for an animal fat and soybean oil-derived biodiesel. For SRM 2773, the gross heating value given in the NIST Certificate of Analysis [15] is $39.66 \text{ kJ g}^{-1} \pm 0.017 \text{ kJ g}^{-1}$. The mass spectrometry analysis for the five manufactured biodiesel fuels are provided in Ref. [9]. The mass spectral information for the four SRM materials (three conventional fuels and the animal-fat biodiesel) are provided in the individual certificates of analysis [15–18].

2.2. Apparatus

The LDTR approach measures the temporal temperature response of a substance due to the heat exchanged with the surroundings by both its thermal, chemical, and physical behavior. The technique has been applied for a variety of applications [19]. Details from earlier studies of the LDTR experimental facility and analysis procedure are provided elsewhere [11, 20,21]. Additional information describing the experimental apparatus and procedure is provided in the online Supplemental Information (*SI*) section. Although the basic features of

*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.

the apparatus have been described before in previous articles, each new study (in which different materials are employed for the first time) extends the application of the technique to new situations, requiring modification to the basic arrangement. The motivation for the arrangement and operating conditions of this study is based on the capability of the apparatus to measure the thermochemical characteristics of liquids that evaporate and react. Some pertinent information is summarized for clarity, along with procedural modifications implemented for these experiments.

The experimental apparatus consists of a copper spherical reactor (diameter of 18.20 mm $\pm$ 0.03 mm expanded uncertainty^{**}) mounted within a chamber, with sample and substrate (copper pan) supported on a ‘pan thermocouple’ near the center of the reactor. The chamber is used to isolate the measurements from the surrounding laboratory environment (experiments were carried out at laboratory ambient pressure). The copper pan substrate is used simply to contain the liquid fuel sample. The reactor is heated from opposing sides by a continuous-wave, high-power (250 W), near-infrared Nd:YAG laser (at a wavelength of 1064 nm) to achieve nearly uniform sample temperature. The sphere temperature (inner surface) is monitored with a second ‘sphere thermocouple’. Normally, the laser beams are expanded with lenses to cover most of the sphere’s surface. For these experiments, the unexpanded beams (lenses were removed; the beam diameter was approximately 5 mm in diameter) were used to maximize intensity, heating rates, and operating temperatures.

Measurements are based on heating the reactor to a steady-state temperature (referred to as the ‘heating-rate approach’ [21]). The change in sample temperature with time is referred to as a ‘thermogram’. Experiments are initially carried out for the two ‘baseline thermograms’ (including the pan substrate and no liquid sample), i.e., for the sample temperature and reactor temperature with respect to time. Then the measurements are repeated with sample (‘sample thermogram’ and ‘reactor thermogram’). From these four thermograms, all other terms are defined, as listed in the SI and *Terminology sections*.

2.3. Measurement uncertainties

The expanded uncertainties for the various experimental components are described in Refs. [11, 20,21]. 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 used to deliver sample directly into the pan (2 mg to 4 mg per droplets). A procedure was formulated to release droplets of approximately the same mass in a consistent manner. The liquid mass extruded from the syringe was determined by ejecting a droplet onto a copper pan and then placing the pan inside a precision digital electronic balance. The balance measurement uncertainty was $\pm$ 0.1 mg. A setting of 4 μ L was found to provide the

^{**} Measurement uncertainty for this study is determined from a series of replicated measurements (referred to as Type A evaluation of uncertainty), and from means other than statistical analysis (referred to as Type B evaluation of uncertainty) [22]. The Type A expanded uncertainty is calculated as kuc , where k is the coverage factor and uc is the combined standard uncertainty. The value for uc is estimated statistically by $\sigma n^{-1/2}$, where σ is the sample standard deviation and n is the number of samples. For $n=2, 3$, and 50, $k=4.30, 3.18$, and 2.01, respectively, representing a level of confidence of 95 % (2σ).

smallest variation in ejected droplet mass with an expanded uncertainty of less than 0.01 % in mass.

The sample mass change due to evaporation for the kerosene, diesel fuel oil, and all five biofuels was negligible during the time required to initiate an experiment. Sample initial mass was estimated from these experiments and used for the post analysis of results. The only fuel mass to change significantly with time was the SRM 2297 reformulated gasoline (see Fig. 1). This was attributed to its comparatively higher vapor pressure (see Table 1). To work with the reformulated gasoline, a droplet was introduced directly onto the pan and then the experiment was initiated immediately (within 10 s; after placing the fuel on the pan, closing the chamber lid, starting the data acquisition, and pushing the button to open the laser aperture, which involved using two people) to minimize the change in fuel mass before heating. Note that sample heating is initiated upon opening the laser aperture, so the only thermal effects on the environment surrounding the reactor sphere (within the chamber) are during the laser heating process.

2.4. Measurement conditions

Experiments were carried out for each investigated fuel on two different days (i.e., resulting in two sets of replicated thermograms for each fuel under similar operating conditions). The pan and reactor sphere were replaced for the repeated runs because of degradation of the copper (due to repeated re-oxidation of the sphere surface before each run [11]) from the first set of runs. Respectively, the pan masses were $(50.9 \text{ and } 57.2) \text{ mg} \pm 0.1 \text{ mg}$ with dimensions of $4.950 \text{ mm} \pm 0.001 \text{ mm}$ (inner diameter), $2.340 \text{ mm} \pm 0.001 \text{ mm}$ (height), and $0.1250 \text{ mm} \pm 0.0006 \text{ mm}$ (thickness). The sphere masses were $(2.50 \text{ and } 2.33) \text{ g} \pm 0.01 \text{ g}$, respectively. Measurements were then carried out by operating the laser at a chosen power level (at $P = 134 \text{ W}$ or $P = 162 \text{ W}$, respectively), which resulted in heating the sample from ambient temperature to different steady-state temperatures.

The chosen experimental conditions were fixed at 101.3 kPa in air with a laser heating rate between 60 K/s and 100 K/s (with maximum steady-state temperatures reaching between 900 K and 1200 K), and sample initial mass between 2.0 mg and 4.0 mg per droplet from the syringe (3.0 mg to 3.8 mg for biodiesel, 3.0 mg to 3.4 mg for kerosene and diesel, and 2.0 mg to 2.1 mg for gasoline). Note that the fuel initial mass per droplet from the syringe correlates to the fuel density and viscosity (see Table 1), i.e., biodiesel mass > diesel mass > kerosene mass > gasoline mass.

3. Model description

3.1. Thermal energy balance

The theoretical model is based on a representation of the heating process associated with the above-mentioned experimental arrangement. The following thermal energy conservation equation governs the heating process:

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

where the term on the left side is the rate of change of sample internal thermal energy. The first term on the right side is the thermal energy absorbed by the sample (assuming laser heating), followed the term for the sample thermal energy losses due to conduction, convection, and radiation throughout the experimental arrangement, and the last term is the transfer of thermal energy due to sample chemical reaction and vaporization. All parameters are defined in the *Nomenclature* section, as well as in the online SI section, which also provides additional information on the model development.

3.2. Total thermal power sensed by the sample

It is of interest to estimate the broadband thermal energy incident on the opaque fuel/pan surface (i.e., transferred to the fuel/pan from the reactor sphere), as given by the thermal energy balance in Eq. 1. It is also of relevance to determine the dominant modes of energy transfer at the pan and sphere. Addressing these two issues is accomplished by independently looking at the individual terms in the thermal energy balance for either the sample run (Eq. S3, *SI section*) or for the baseline (Eq. S4). Since the incident laser power, $P \equiv (I_r A)_{sph}$, impinging on the reactor sphere surface is measured with a power meter (obtained in separate measurements), one can solve the energy balance equation at the sphere surface for the copper absorptivity, $\beta(T, \lambda)$, as well as evaluate the individual terms for the change in internal energy ($E_{int} \equiv m c_p dT/dt$), heat-transfer-related thermal energy loss ($E_{heat} \equiv F(T, T_o) \equiv F_{cond/comv} + F_{rad}$), and chemistry-related thermal loss/gain of all fuel liquid or vapor within the sphere ($E_{chem} \equiv m q$). It is assumed that the absorption behavior of the sphere with temperature is the same as that of the pan since they are both copper (viz., $\beta(T, \lambda)_{sph} = \beta(T, \lambda)_{pan}$) and that $\beta_{sas} \approx \beta_{so}$. After a polynomial is fit to $\beta(T, \lambda)_{sph}$, one can then evaluate the energy balance equation at the pan and solve for the total (broadband) incident power, $(I_r A)_{pan}$ emitted from the sphere to the pan. Since the reference temperature T_o is unknown (it cancels out when deriving Eq. S5), the total heat loss term is evaluated in a similar fashion as that for the sphere, but the Nusselt number is approximately equal to 1 for a pan [23] (see SI section).

3.3. Analysis protocol

In the SI section, expressions are presented for the specific heat release rate, $q(T)$, based on the heat transfer processes occurring at the pan substrate ('pan-based analysis', Eq. S5) and at the reactor sphere surface (sphere-based analysis', Eq. S65). Also, presented is an expression for the sample mass change with time to estimate sample evaporation and reaction (Eq. S7). The experimental measurements result in four thermograms from each set of runs with and without sample. The thermograms are then used in evaluating each equation, for which $q(T)$ should result in the same value regardless of the approach.

For the conventional hydrocarbon samples, the dependency of the heat capacity with temperature [24] appeared to be linear in the liquid phase. Carrying out a regression fit to their data results in the following expressions: $c_{p, gasoline} = 1.0119 + 0.0037 * T$, $c_{p, jet fuel} = 0.911758 + 0.00382 * T$, $c_{p, diesel} = 0.75 + 0.00393 * T$, having units of $J g^{-1} K^{-1}$. For the biodiesel fuels, the dependence of the specific heat capacity on temperature was unavailable in the literature, and thus was assumed that the change with temperature was small, i.e., each fuel was assumed to have a value of $2.12 J g^{-1} K^{-1}$ (see Table 1).

4. Results and discussion

A typical set of results representing the conventional fuels is presented in Fig. 2 for SRM 2297 (reformulated gasoline) at a laser power of 134 W (incident on the sphere surface). The figure includes the A) sample and baseline thermograms, B) sample-baseline temperature difference for the sample and reactor temperature profiles, C) sample and reactor derivative profiles, and D) variation of the sample mass and specific heat release rate with sample temperature. For this run, the sample and reactor thermograms reached a steady-state temperature of approximately 1000 K and 1040 K, respectively (see Figs. 2A and 2B) in less than 30 s. Chemical reactions tend to terminate near the peak of the temperature difference (within about 15 s) at which point the difference decrease to return to the baseline (see Fig. 6 in Ref. [25]). The thermogram expanded uncertainty with respect to each mean temperature was assumed to be similar to the repeatability measurements reported in Ref. [25] (i.e., 1.0 % for the baseline sample temperature, 1.5 % for the baseline reactor temperature, 1.5 % for the sample temperature, and 2.5 % for the reactor temperature) since the experiments were carried out using the same protocol and experimental conditions. The error bars were not included in the histograms (Fig. 2A) to ensure clarity. The heating rate was about 60 K/s (peak of the dashed baseline profile near 600 K in Fig. 2C). The thermal behavior was essentially exothermic (positive values for the specific heat release rate at the pan in Fig. 2D). The specific heat release rate increases typically with temperature exponentially, assumed to be represented by an Arrhenius-type expression [21]. The estimated mass change during evaporation of the liquid (the dash curve accounts for all the liquid fuel evaporating before the boiling-point temperature in about 8.5 s (derived by matching the sample temperature when the mass becomes negligible with the time in Fig. 2A), see discussion in SI section) is also presented in Fig. 2D.

4.1. Baseline (st)/sample thermogram alignment

Since the baseline (*st*) and sample thermograms are obtained sequentially, criteria for aligning the two thermograms are required to evaluate $q(T)$ (see Eqs. S5 and S6). These equations are dependent on determining the sample-baseline temperature difference (for the respective sample or reactor temperatures), and difference between the sample or reactor derivative profiles, whose values are dependent on alignment of the baseline (*st*) and sample thermograms. The approach used for alignment is based on calculating the energy associated with the initial endotherm (assuming the liquid fuel evaporates before the onset of reactions) and comparing it with the measured value. The calculation entails summing terms for the change in enthalpy during the initial increase in temperature and liquid evaporation; i.e., $E_{endo} = m(t)[c_p(T_{bp} - T) + h_{vap}]$. It is assumed that evaporation occurs up to the liquid boiling point, T_{bp} , and thus $T = T_{bp} - T_{amb}$. Estimated values for h_{vap} for the fuels are given in Table 1. Note that evaporation of the liquid fuels is relevant only to the pan-based analysis. Thus, once initial values for $q(T)$ (using Eq. S5) and E_{endo} are determined, then one may adjust the thermograms until the calculated and experimentally derived 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 (at the discrete time intervals recorded by the data acquisition) for both the sample and reactor temperatures together.

This approach is effective when the sample derivative increases rapidly (above the baseline indicating exothermic release of energy and the occurrence of chemical reaction), followed by termination of reactions and return to match the baseline (*st*) thermogram at the end of the run (at the steady-state temperature); similar to that for the reformulated gasoline (e.g., Fig. 2). However, for the biodiesel fuels, the thermogram slope decreases at the boiling-point temperature for both the sample and reactor profiles, as exemplified in Fig. 3A (see circles) for canola-oil biodiesel fuel at a laser power of 162 W. This feature was also observed in the earlier investigation [11] with soy-bean biodiesel (SRM 2772) and conventional diesel (SRM 2771) fuel. Thus, the sample temperature may fall below the baseline (*st*) temperature profile (indicating endothermic behavior) at temperatures above the fuel boiling point. In addition, the calculated mass change profile (see Fig. 3B) indicates that the fuel mass was depleted in about 8.5 s (through evaporation and possibly reaction) before reaching the boiling point (*bp* in the figure denotes the biodiesel boiling-point temperature range), unlike the conventional fuels. Therefore, the change in slope of the sample thermogram occurs after completion of reactions, with its gradual return to the baseline profile. All the investigated fuels, except reformulated gasoline (which, as noted earlier, evaporates more readily than the other conventional and biodiesel fuels), exhibited this decrease in the slope of the sample and reactor thermograms. This feature is also highlighted by the arrows in the sample-baseline temperature difference profiles for both the sample and reactor temperatures (Fig. 3D), and sample and reactor derivative profiles (Figs. 3E and 3F), respectively. Pairing of the sample and baseline thermograms at higher temperatures (after completion of reactions) was thus used as another criterion for aligning the two thermograms.

4.2. Effect of laser power

Results for $P = 162$ W are compared with those at a lower laser power of $P = 134$ W. Comparing Figs. 3C and 3D, a peak forms near 610 K for the sample temperature (at the pan) for the higher laser power (than two smaller peaks at the lower laser power in Fig. 3C), and one near 860 K for the reactor temperature, indicating greater reactivity at the higher laser power. A similar behavior is indicated in Figs. 3E and 3F at the higher laser power. For the sample derivative at higher laser power in Fig. 3E, the rapid (sudden) rise in the sample derivative above the baseline (*st*) derivative profile (indicative of sample chemical reaction), followed a decay below the baseline and another rise above the baseline, is indicative of preferential vaporization of the fuel fractions [11]. The lower-temperature peak of about 120 K s^{-1} at around 590 K is attributed to the exothermic release of energy by the lighter biodiesel fuel fractions. The drop in the curve below the baseline profile (minimum value of about 65 K s^{-1} at about 650 K), as opposed to returning gradually to the baseline, is attributed to endothermic behavior of the heavier fuel fractions. This is then followed by another rise above the baseline profile (peak of 83 K s^{-1}) at about 850 K. For the lower laser power in Fig. 3E, the profile is similar to the baseline except for some endothermic behavior (between 520 K and 650 K, Fig. 3E) that is followed by an exotherm, indicative of fuel evaporation. For the reactor derivative profiles in Fig. 3F, there is a peak at around 860 K for the higher laser power (as noted for the temperature difference profile in Fig. 3D), while the lower laser power case was similar to the baseline.

4.3. Estimation of the sample thermal losses and total thermal power

Variation of the terms in the thermal energy balance equation for both the pan- and reactor-based analyses, is presented in Fig. 4. Each term of the thermal energy balance equation (for the change in internal energy, E_{int} , heat-transfer-related thermal energy loss, E_{heat} , and chemistry-related thermal energy loss/gain, E_{chem}) is presented in terms of the variation of power with sample temperature (pan-based analysis) and reactor temperature (reactor-based analysis), Figs. 4A and 4B, respectively. The variation of power with respect to sample and reactor temperature for the heat-transfer-related thermal loss (radiation, and conduction/convection) is presented in Figs. 4C and 4D), respectively. The results indicate that the heat-transfer-related ‘thermal energy’ loss for liquid sample in the pan (pan-based analysis) is the dominant process and grows nonlinearly with increasing sample temperature, which is expected since this term is a monotonic function of the temperature (Fig. 4A). The nonlinear increase in this term is attributed mainly to the T^4 dependence of the radiation term (see Fig. 4C), whereas the convection/conduction is dependent on T , and to a lesser extent the sample-baseline (s/t) temperature difference (see Fig. 2B). The boxed insert (Fig. 4A) is a magnified scale of the chemistry-related thermal loss/gain term. On the reactor sphere surface (reactor-based analysis), the internal energy is the dominant term, reaching a peak at around 550 K in Fig. 4B. The profile is similar to that of the reactor derivative profiles in Fig. 2C, which is expected since the internal energy term in the thermal energy balance equation is a function of the temperature-time derivative. One can speculate that the internal energy term is relatively large for the reactor-based analysis (Fig. 4B) because all the fuel (evaporated and liquid) within the sphere is considered in this analysis. In contrast, the liquid fuel for the pan-based analysis is not contained within the pan while evaporating or reacting, causing in the internal energy term for this analysis to remain relatively small. The chemistry-related thermal energy loss/gain term (see also boxed insert for Fig. 4B) is small relative to the other terms, because $m(t)$ is small. It is also smaller for the pan than the sphere surface by an order of magnitude, which may indicate more reactivity of the fuel on the reactor sphere. Again, the nonlinear nature of the thermal energy term is attributed to the T^4 dependence of the radiation term (Fig. 4D).

Figure 5A presents the variation of the spectral hemispherical absorptivity, $\beta(T, \lambda)$, with reactor temperature (reactor-based analysis) at the laser power ($P = 134$ W) and wavelength ($\lambda = 1064$ nm) incident on the sphere surface. The value of $\beta(T, \lambda)$ reaches a maximum value of about 0.6 at a temperature between 550 K and 650 K. The shape of the dependency is similar to that of the dominant internal energy term at the sphere surface (Fig. 4B). Variation of the broadband thermal energy reaching the pan from the sphere surface with sample temperature is presented in Fig. 5B. The power increases exponentially with increasing temperature, reaching about 80 W at 1000 K (noting again that the incident laser power on the sphere surface was 134 W).

4.4. Estimation of the biodiesel fuel thermal behavior

The estimated values for the LDTR total specific heat release (i.e., enthalpy of combustion) is provided in Table 2, as obtained by the pan-based (Q_p) and reactor-based (Q_r) analyses. The expanded uncertainty for the values of Q was estimated to be about 1.6 kJ g^{-1} . In general, the value for biodiesel is lower than that of the conventional hydrocarbon fuels, as is

well documented in the literature (e.g., Refs. [8,26]). In this investigation, the values of Q_p under estimated the literature values (see Table 1), while the values obtained from the reactor-based analysis were more in line with those found in the literature. The reason for this underestimation by Q_p is attributed to evaporation of the liquid fuel in the pan as discussed above, while the reactor-based analysis senses all evaporated fuel reacting on the sphere inner surface. However, the results for two biodiesel diesel fuels (MSP soy bean and TMT waste grease) exhibited the opposite result, i.e., the values for Q_p were closer to the literature values and the values for Q_r were underestimated. When the laser power was increased to 162 W in subsequent measurements, the results returned to the original trend. This result emphasizes the need for adequate laser heating to properly sense the thermal behavior of the liquid in the pan or on the sphere surface.

To explain the effect of the laser power on the results (using the pan-based analysis, i.e., evaluating Eq. S5), the dominant term is the temperature difference term, as compared to the difference between the sample and baseline derivatives. As discussed before, this means that the radiative heat transfer is the dominant process at the pan, as opposed to the change in internal energy and chemistry-related thermal loss/gain terms. The opposite occurs when using the reactor-based analysis (i.e., evaluating Eq. S6), in that the difference between the derivatives (based on the change in internal energy) terms is dominant as compared to the temperature difference (heat-transfer-related thermal energy loss) terms. This explains why the heat transfer processes at the pan are sufficient to detect the total fuel heat release when the laser power is lower, while on the sphere the power is insufficient. At a higher laser power, fuel evaporation and reactions are too rapid to be fully detected at the pan, while the sphere surface is hot enough to detect the full fuel total fuel heat release.

To emphasize this point further, Fig. 6 presents the A, B) sample-baseline temperature difference for the sample and reactor temperature profiles, and C, D) sample and reactor derivative profiles for soy-bean biodiesel at the two laser power settings of 134 W and 162 W. At the lower laser power setting, the reactor temperature difference (solid curve in Fig. 6A) is lower than that for the sample temperature difference. However, at the higher laser power setting (Figs. 6B), the reactor temperature different increases threefold, while the sample temperature difference decreases. The sample and reactor temperature derivatives (Figs. 6C and 6D, respectively) indicate that for the lower laser power, reactions occur at higher temperatures (i.e., where the soy-bean biodiesel profile separates from the baseline). For the higher laser heating setting, reactions occur at the onset of the run. The dip in the soy-bean biodiesel profile (see arrow in Fig. 6C) at a sample temperature of around 650 K is typical of many results for which there is a preferential vaporization of fuel fractions (as discussed earlier regarding Fig. 3E). Also, note the similarity in results obtained for soy-bean biodiesel (SRM 2772) fuel in Ref. [11].

5. Summary

Laser-driven calorimetry measurements were carried out on several NIST SRM petroleum and biodiesel fuels to determine sample thermal (exothermic/endothermic) behavior, specific heat release rate, and total specific heat release. Experiments were carried out at a liquid mass between 2.0 mg to 4.0 mg per droplet place in a copper pan substrate. Two laser power

settings were used at 134 W and 162 W (heating rate up to about 100 K/s, and steady-state temperatures up to about 1100 K) in air. The technique consists of sample placed in a pan substrate, which rests upon a thermocouple positioned near the center a spherical copper reactor. The reactor is heated from two sides with a high-power laser to the steady-state temperature. Recorded thermograms (temperature versus time) were used to evaluate an equation for conservation of thermal energy. The results indicated that the energy at the pan is dominated by radiative heat transfer processes, while the change in the internal energy is the dominant thermal process at the reactor sphere. Also, the laser power required for detecting thermal-related characteristics in a thermogram can differ from one fuel to another. With sufficient laser power, the results can detect the preferential vaporization of the lighter and heavier fuel fractions. Both the sample-baseline temperature difference and temperature-time derivatives profiles can serve as useful signatures in identifying a fuel thermal characteristics and sensitivity to the operating conditions. The total specific heat release obtained for the different conventional and biodiesel fuels used in this investigation were similar to the expected values available in the literature. Note that comparison of results with a differential scanning calorimeter was carried out in another investigation with single-component liquids [25].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Nomenclature

A	sample geometric cross-sectional area [m^2]
$c_p(T)$	specific heat capacity [$\text{J g}^{-1} \text{K}^{-1}$]
(dT/dt)	sample temperature-time derivative [K s^{-1}]
E	energy [J]
$F(T, T_o)$	heat transfer term [W]
I_I	intensity of the laser beam that heats the sample [W m^{-2}]
k	coverage factor
$m(t)$	total mass [mg]
n	number of samples, final value of indexed series
P	laser output power [W]
$q(T)$	specific heat release rate due to chemical reaction [kW g^{-1}]

Q	total specific heat release [kJ g^{-1}]
t	time [s]
T	sample temperature [K]
T_{bp}	boiling-point temperature [K]
T_o	reference temperature [K]
u_c	combined uncertainty
$\beta(T\lambda)$	spectral hemispherical absorptivity
h_{vap}	enthalpy of evaporation [kJ g^{-1}]
$m(t)$	mass of the reactive portion of the sample, mass loss [mg]
T	change in temperature, = $T_{bp} - T_{amb}$ [K]
λ	laser wavelength [m]
σ	standard deviation
amb	ambient (laboratory) air
$chem$	chemistry-related thermal loss/gain term
$cond$	conduction
$conv$	convection
$endo$	endothermic
$heat$	heat-transfer-related thermal loss term
int	change in internal energy term
p	pan-based analysis
pan	pan
r	reactor-based analysis
rad	radiation term
sas	substrate and liquid hydrocarbon combined
so	substrate only (baseline)
sph	sphere
0	initial indexed value

Sample temperature [T]

pan thermocouple reading

Reactor temperature $[T_r]$

sphere thermocouple reading

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

sample temperature vs. time (with sample)

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

reactor temperature vs. time (with sample)

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

sample temperature vs. time (without sample)

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

reactor temperature vs. time (without sample)

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

sample thermogram minus the baseline thermogram (sample temperature)

Sample-baseline (rt 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 (st sample temperature) derivative $[(dT/dt)_{so}]$

differential change in sample temperature with time (without sample)

Baseline (rt 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 (st) derivative

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

between the reactor derivative and baseline (rt) derivative

References

1. Karatzos, S., McMillan, JD., Saddler, JN. The potential and challenges of drop-in biofuels; Task 39, IEA Bioenergy. 2014. p. 24<http://task39.org/files/2014/01/Task-39-Drop-in-Biofuels-Report-FINAL-17-July-2014-ecopy.pdf>
2. Xu Y, Keresztes I, Condo AM Jr, Phillips D, Pepiot P, Avedisian CT. Droplet combustion characteristics of algae-derived renewable diesel, conventional #2 diesel, and their mixtures. Fuel. 2016; 167:295–305.
3. Fortunato de Carvalho Rocha W, Schantz MM, Sheen DA, Chu PM, Lippa KA. Unsupervised classification of petroleum certified reference materials and other fuels by chemometric analysis of gas chromatography-mass spectrometry data. Fuel. 2017; 197:248–258. [PubMed: 28603295]

4. Blakey, S., Rye, L., Wilson, CW. Proc. Vol. 33. Combustion Institute; 2011. Aviation gas turbine alternative fuels: A review; p. 2863-2885.
5. Kotrba, R. Hard work has made biodiesel a 'drop-in' fuel. Biodiesel magazine, BBI Int. 2010. <http://www.biodieselmagazine.com/articles/4252/>
6. Alleman, TL., McCormick, RL., Christensen, ED., Fioroni, G., Moriarty, K., Yanowitz, J. Biodiesel handling and use guidelines. 5th. National Renewable Energy Laboratory, Office of Energy Efficiency & Renewable Energy, U.S. Department of Energy; 2016. DOE/GO-102016-4875
7. American Society for Testing and Materials (ASTM). Designation: D6751-15c^{e1}. ASTM International; PA: 2016. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.
8. Demirbas, A. Biodiesel: A realistic fuel alternative for diesel engines. Springer; London: 2008. Chapter 5
9. Goding JC, Ragon DY, O'Connor JB, Boehm SJ, Hupp AM. Comparison of GC stationary phases for the separation of fatty acid methyl esters in biodiesel fuels. Anal Bioanal Chem. 2013; 405(18): 6087–6094. <http://irebiodiesel.com/>. [PubMed: 23728727]
10. Castellanos Díaz O, Schoeggl F, Yarranton HW, Satyro MA, Lovestead TM, Bruno TJ. Modeling the Vapor Pressure of Biodiesel Fuels. Int J Chem Mol Nucl Mater Metall Eng. 2012; 6(5):460–470.
11. Presser C, Nazarian A, Bruno TJ, Murray JA, Molloy JL. Thermochemical characterization of bio- and petro-diesel fuels using a novel laser-heating technique. Energy Fuels. 2015; 29(9):5761–5772.
12. Starkey Ott L, Bruno TJ. Variability of biodiesel fuel and comparison to petroleum-derived diesel fuel: Application of a composition and enthalpy explicit distillation curve method. Energy Fuels. 2008; 22(4):2861–2868.
13. Sundarapandian S. Performance and emission analysis of bio diesel operated CI engine. J Eng, Comp Archit. 2007; 1(2):1–22. www.scientificjournals.org/journals2007/articles/1174.pdf.
14. Da Silva NL, Batistella CB, Maciel Filho R, Wolf Maciel MR. Investigation of biofuels properties. Chem Eng Trans. 2011; 25:851–856. DOI: 10.3303/CET1125142
15. National Institute of Standards and Technology(NIST). Certificate of analysis, standard reference material 2773, B100 biodiesel (animal-based). 2011. <https://www-s.nist.gov/srmors/certificates/2773.pdf>
16. National Institute of Standards and Technology(NIST). Certificate of analysis, standard reference material 2297, reformulated gasoline (10 % Ethanol). 2012. Safety data sheet, CAS Registry No. 8006-61-9 <https://www-s.nist.gov/srmors/certificates/2297.pdf> <https://www-s.nist.gov/srmors/msds/2297-MSDS.pdf>
17. National Institute of Standards and Technology(NIST). Certificate of analysis, standard reference material 1617b, sulfur in kerosene (high level). 2014. Safety data sheet, CAS Registry No. 8008-26-6 <https://www-s.nist.gov/srmors/certificates/1617B.pdf> <https://www-s.nist.gov/srmors/msds/1617B-MSDS.pdf>
18. National Institute of Standards and Technology(NIST). Certificate of analysis, standard reference material 2723b, sulfur in diesel fuel oil (nominal mass fraction 10 mg/kg). 2015. Safety data sheet, CAS Registry No. 68476-30-2 <https://www-s.nist.gov/srmors/certificates/2723B.pdf> <https://www-s.nist.gov/srmors/msds/2723B-MSDS.pdf>
19. Presser C, Nazarian A, Conny JM. Thermochemical characterization of materials using a novel laser-heating technique. Proc 52nd AIAA Aerospace Sciences Meeting, AIAA. 2014:2014–1071.
20. Nazarian A, Presser C. Forensic analysis methodology for thermal and chemical characterization of homemade explosives. Thermochim Acta. 2014; 576(1):60–70.
21. Nazarian A, Presser C. Thermal and chemical kinetic characterization of multiphase and multicomponent substances by laser heating. Int J Heat Mass Transf. 2008; 51(5-6):1365–1378.
22. Taylor, BN., Kuyatt, CE. NIST Technical Note 1297. National Institute of Standards and Technology; Gaithersburg, MD: 1994. Guidelines for evaluating and expressing the uncertainty of NIST measurement results.
23. Sucec, J. Heat Transfer. W.C. Brown Publishers; Dubuque, IA: 1985. p. 648-650.

24. Zanier A, Jäckle HW. Heat capacity measurements of petroleum fuels by modulated DSC. *Thermochim Acta*. 1996; 287(2):203–212.
25. Presser C, Nazarian A. Laser-driven calorimetry of single-component liquid hydrocarbons. *Energy Fuels*. 2017; 31(7):6732–6747. [PubMed: 28894348]
26. Sivaramakrishnan K, Ravikumar P. Determination of higher heating value of biodiesels. *Int J Eng Sci Technol*. 2011; 3(11):7981–7987.
27. Faires, VM. *Thermodynamics*. 5th. MacMillan; New York: 1971.
28. Department of Energy. Alternative Fuels Data Center – Fuel Properties Comparison. 2014. http://www.afdc.energy.gov/fuels/fuel_comparison_chart.pdf
29. Chemwatch safety data sheet. Ethanol. CAS Registry No. 64-17-5; 2016.
30. Chemwatch safety data sheet. No. 2 fuel oil. CAS Registry No. 68476-30-2; 2016a
31. National Institute of Standards and Technology (NIST) Chemistry WebBook. NIST standard reference database number 69, standard reference data program. <http://webbook.nist.gov/chemistry/.2016>
32. Balabin RM, Syunyaev RZ, Karpov SA. Molar enthalpy of vaporization of ethanol–gasoline mixtures and their colloid state. *Fuel*. 2007; 86:323–327.
33. PubChem. Methyl linoleate. U.S. National Library of Medicine, National Center for Biotechnology Information. 2005. <http://pubchem.ncbi.nlm.nih.gov/compound/5284421>
34. PubChem. Methyl linolenate. U.S. National Library of Medicine, National Center for Biotechnology Information. 2005a. http://pubchem.ncbi.nlm.nih.gov/compound/methyl_linolenate
35. PubChem. Methyl oleate. U.S. National Library of Medicine, National Center for Biotechnology Information. 2005b. http://pubchem.ncbi.nlm.nih.gov/compound/methyl_oleate
36. PubChem. Methyl palmitate. U.S. National Library of Medicine, National Center for Biotechnology Information. 2005c. http://pubchem.ncbi.nlm.nih.gov/compound/methyl_palmitate
37. PubChem. Methyl stearate. U.S. National Library of Medicine, National Center for Biotechnology Information. 2005d. http://pubchem.ncbi.nlm.nih.gov/compound/methyl_stearate
38. Rose A, Supina WR. Vapor pressure and vapor-liquid equilibrium data for methyl esters of the common saturated normal fatty acids. *J Chem Eng Data*. 1961; 6(2):173–179.
39. Haynes, WM., editor. *Handbook of chemistry and physics*. 96th. CRC, Taylor and Francis Group; Boca Raton, FL: 2015–2016. p. 7-9.

Figure 1.

Variation of the non-dimensional mass with time at the ambient temperature and pressure for gasoline, kerosene, and diesel fuel oil. The initial mass was 2.0 mg, 3.1 mg, and 3.3 mg for each fuel, respectively. The regression fit (dashed line) through the gasoline data given by $m(t)/m(0) = 0.06587 + 0.92943 e^{-0.01754 t}$.

Figure 2.

The SRM 2297 (reformulated gasoline) at a laser power of 134 W (incident on the sphere surface): variation of the A) sample and reactor temperatures (for the gasoline and baseline runs) with time (thermograms), B) sample-baseline temperature difference for the sample and reactor temperature profiles with respective temperature, C) sample and reactor derivative profiles (for the gasoline and baseline runs) with respective temperature, and D) sample mass and specific heat release rate with sample temperature. The estimated mass (considering T_{bp} , see Eq. S8 in the SI section) is represented by the dashed curve. The error bars are not included in the histograms to ensure clarity.

Figure 3.

Canola-oil biodiesel at different laser power (134 W and 162 W) incident on the sphere surface: variation of the A) sample and reactor temperatures (for the biodiesel and baseline runs) with time (thermograms), B) normalized mass with sample temperature (*bp* indicates the boiling-point temperature range), C, D) sample-baseline temperature difference for the sample and reactor temperature profiles with respective temperature, E, F) sample and reactor derivative profiles (for the biodiesel and baseline runs) with respective temperature. The error bars are not included in the histograms to ensure clarity.

Figure 4.

The SRM 2297 (reformulated gasoline) at a laser power of 134 W (incident on the sphere surface): variation of power for each term of the thermal energy balance equation (change in the internal energy, heat-transfer-related thermal loss, and chemistry-related thermal loss/gain) with A) sample temperature, and B) reactor temperature. The variation of power for the heat-transfer thermal loss terms (radiation, and conduction/convection) with C) sample temperature and D) reactor temperature. The boxed inserts are expanded views of the chemical energy curves.

Figure 5.

The SRM 2297 (reformulated gasoline) at a laser power of 134 W (incident on the sphere surface): variation of the A) hemispherical absorptivity and B) incident total hemispherical power on the pan.

Figure 6.

Soy-bean biodiesel at different laser power (134 W and 162 W) incident on the sphere surface: variation of the A, B) sample-baseline temperature difference for the sample and reactor temperature profiles, and C, D) sample and reactor derivative profiles, respectively.

Table 1

Estimated physical and thermochemical properties for the SRM hydrocarbon and biodiesel fuels, as available from the literature. LHV - lower heating value, HHV - higher heat.

property	High sulfur in kerosene (aviation/turbine jet fuel) (SRM 1617b) ^a	Reformulated gasoline with 10 % ethanol (SRM 2297) ^a	10 mg/kg sulfur in diesel fuel oil (SRM 2723b) ^a	B100 biodiesel (animal-based) (SRM 2773) ^a	FAME biodiesel fuel/
Compound and chemical formula	aviation kerosene (C ₈ - C ₁₆) ^b	gasoline (C ₄ - C ₁₂) ^e ethanol (C ₂ H ₆ O)	diesel fuel oil (C ₈ - C ₂₅) ^e	methyl palmitate (C ₁₇ H ₃₄ O ₂) methyl stearate (C ₁₉ H ₃₈ O ₂) methyl oleate (C ₁₉ H ₃₆ O ₂) methyl linoleate (C ₁₉ H ₃₄ O ₂) methyl linolenate (C ₁₉ H ₃₂ O ₂)	
Molecular weight [g mol ⁻¹]	≈ 170	144.5 [g] ^c 46.07 [e]	170 ^f - 200 ^e	184 [g/kg] 87.8 343 226 25	270.45 ^k 298.50 ^k 296.49 ^k 294.47 ^k 292.46 ^k
Boiling-point temperature range [K]	424 - 574	311 - 477 [g] 351.3 - 351.5 [e]	423 - 643	-	604.9 633.9 616.9 619.0 620.0
Autoignition temperature [K]	483	553 - 729 [g] 636, 638 ^f [e]	> 519, 530 ^f	-	- - - -
Enthalpy of combustion (LHV - HHV) [kJ g ⁻¹]	43.2 - 46.3 ^c	43.7 - 47.0 ^c [g] 27.7 - 30.6 ^c (29.7 ^b) [e]	43.2 - 45.8 ^c	39.66	37.1 37.4 37.5 37.3 37.2
Enthalpy of vaporization [kJ g ⁻¹]	0.251 ^d	0.272 [g] 0.846 ^d [e]	0.250 ⁱ	-	< 0.245 ⁱ
Vapor pressure [kPa]	0.667 @ 311 K	≈ 30 [g] ^b 5.332 @ 292 K [e]	0.347 @ 293 K	-	1.91 @ 467 K ^j 1.27 @ 477 K ^j - - -
Specific heat capacity [J g ⁻¹ K ⁻¹] @ 298 K	2.03 ^d	2.11 ^d [g] 2.44 ^e [e]	1.87 - 1.92 ^d 1.85 ^f	-	2.11 ^m 2.12 ^m - - -

property	High sulfur in kerosene (aviation/turbine jet fuel) (SRM 1617b) ^a	Reformulated gasoline with 10 % ethanol (SRM 2297) ^a	10 mg/kg sulfur in diesel fuel oil (SRM 2723b) ^a	B100 biodiesel (animal-based) (SRM 2773) ^a	FAME biodiesel fuel/ ⁱ
Density [kg m ⁻³] @ 293 K	805.57	694.1 @ 288 K [g] 790 ^f [e]	870 – 900	876.28	878 ⁿ
Dynamic viscosity [mPa s] @298 K	1.58 @ 293 K	1.22 – 1.41 @293 K [e]	2.44 @ 313 K	6.26 @ 293 K	3.8 ^m 5.0 ^m 5.6 ^m 4.4 ^m 3.9 ^m
Sulfur content [mg kg ⁻¹]	7.3	–	9.06	7.39	negligible ⁿ

^aRefs. [15–18],

^bRef. [4],

^cRef. [27],

^dRef. [24],

^eRef. [28],

^fRefs. [29,30],

^gRef. [31],

^hRef. [32],

ⁱRef. [13],

^jRef. [11],

^kRefs. [33–37],

^lRef. [38],

^mRef. [39],

ⁿRef. [6].

[g] - for gasoline, [e] - for ethanol, [ge] - for gasoline/10 % ethanol

Table 2

Estimated LDTR total specific heat release, as obtained by the pan-based (Q_p) and reactor-based (Q_r) analyses. See Table 1 for the estimated literature values (i.e., enthalpy of combustion). The expanded uncertainty for the values of Q was estimated to be about 1.6 kJ g^{-1} (assumed to be similar to the repeatability experiments reported in Ref. [25]).

sample	condition	Q_p [kJ g ⁻¹]	Q_r [kJ g ⁻¹]
SRM 1617b (kerosene)	$P = 134 \text{ W}$, $m(\dot{O}) = 3.1 \text{ mg}$	31.9	44.8
SRM 2297 (reformulated gasoline)	$P = 134 \text{ W}$, $m(\dot{O}) = 2.1 \text{ mg}$	33.8	45.8
SRM 2723b (diesel fuel oil)	$P = 134 \text{ W}$, $m(\dot{O}) = 3.3 \text{ mg}$	38.3	45.2
SRM 2773 (animal-based biodiesel)	$P = 134 \text{ W}$, $m(\dot{O}) = 3.1 \text{ mg}$	30.8	37.0
IRE animal-fat biodiesel	$P = 134 \text{ W}$, $m(\dot{O}) = 3.8 \text{ mg}$	36.2	41.3
TGM beef-tallow biodiesel	$P = 134 \text{ W}$, $m(\dot{O}) = 3.6 \text{ mg}$	36.6	42.1
ADM canola-oil biodiesel	$P = 134 \text{ W}$, $m(\dot{O}) = 3.0 \text{ mg}$	39.0	42.8
MSP soy-bean biodiesel	$P = 134 \text{ W}$, $m(\dot{O}) = 3.3 \text{ mg}$	41.5	27.3
	$P = 162 \text{ W}$, $m(\dot{O}) = 3.5 \text{ mg}$	28.6	42.3
TMT waste-grease biodiesel	$P = 134 \text{ W}$, $m(\dot{O}) = 3.6 \text{ mg}$	35.5	16.3
	$P = 162 \text{ W}$, $m(\dot{O}) = 3.7 \text{ mg}$	19.0	37.2