



Full Length Article

Laser-driven calorimetry measurements of petroleum and biodiesel fuels

Cary Presser*, Ashot Nazarian, Amit Millo

National Institute of Standards and Technology, Gaithersburg, MD 20899, United States



ARTICLE INFO

Keywords:

Biodiesel fuels
Calorimetry
Heating value
Standard reference materials
Petroleum fuels
Total specific heat release

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 beam 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.

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 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)

* Corresponding author at: National Institute of Standards and Technology, Bldg. 221, Rm. B310, 100 Bureau Dr., Stop 8320, Gaithersburg, MD 20899-8320, United States.
E-mail address: cpresser@nist.gov (C. Presser).

Nomenclature			
A	sample geometric cross-sectional area [m^2]	Δh_{vap}	enthalpy of evaporation [kJ g^{-1}]
$c_p(T)$	specific heat capacity [$\text{J g}^{-1} \text{K}^{-1}$]	$\Delta m(t)$	mass of the reactive portion of the sample, mass loss [mg]
(dT/dt)	sample temperature–time derivative [K s^{-1}]	ΔT	change in temperature, = $T_{\text{bp}} - T_{\text{amb}}$ [K]
E	energy [J]	λ	laser wavelength [m]
$F(T, T_o)$	heat transfer term [W]	σ	standard deviation
I_l	intensity of the laser beam that heats the sample [W m^{-2}]	<i>Subscripts</i>	
k	coverage factor	<i>amb</i>	ambient (laboratory) air
$m(t)$	total mass [mg]	<i>chem</i>	chemistry-related thermal loss/gain term
n	number of samples, final value of indexed series	<i>cond</i>	conduction
P	laser output power [W]	<i>conv</i>	convection
$q(T)$	specific heat release rate due to chemical reaction [kW g^{-1}]	<i>endo</i>	endothermic
Q	total specific heat release [kJ g^{-1}]	<i>heat</i>	heat-transfer-related thermal loss term
t	time [s]	<i>int</i>	change in internal energy term
T	sample temperature [K]	<i>p</i>	pan-based analysis
T_{bp}	boiling-point temperature [K]	<i>pan</i>	pan
T_o	reference temperature [K]	<i>r</i>	reactor-based analysis
u_c	combined uncertainty	<i>rad</i>	radiation term
<i>Greek symbols</i>		<i>sas</i>	substrate and liquid hydrocarbon combined
$\beta(T, \lambda)$	spectral hemispherical absorptivity	<i>so</i>	substrate only (baseline)
		<i>sph</i>	sphere
		<i>0</i>	initial indexed value

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 (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),¹ 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 50–60% pork, 20% beef, and 10–20% 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 Ref. [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

¹ 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.

Download English Version:

<https://daneshyari.com/en/article/6632494>

Download Persian Version:

<https://daneshyari.com/article/6632494>

[Daneshyari.com](https://daneshyari.com)