Variability of Biodiesel Fuel and Comparison to Petroleum-Derived Diesel Fuel: Application of a Composition and Enthalpy Explicit Distillation Curve Method†

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We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. This new method is a significant improvement over current approaches, featuring, for two examples, a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis) and an assessment of the energy content of each distillate fraction. Herein, we compare the distillation curves of four different biodiesel fuel samples to assess possible variations in the distillation curves based on the source of the fuel. Next, we utilize the composition-explicit data channel to characterize distillate cuts of each of the four biodiesel fuels in terms of available energy content. The measure we use for the fluid energy content of each distillate fraction is the composite enthalpy of combustion. On a molar basis, the enthalpy of combustion of the four biodiesel fuels increased slightly with increasing distillation temperature. The biodiesel fuel sample with the highest methyl oleate content had a somewhat different distillation curve and distillate fraction enthalpies of combustion that were higher than those for the other three biodiesel fuels. Then, we compare both the distillation curves and enthalpies of combustion as a function of distillate fraction of the four biodiesel fuels with those for one petroleum-derived diesel fuel. The petroleum-derived diesel fuel is much more volatile than the biodiesel fuels, complete with a difference in initial boiling point of approximately 120 °C. Importantly, on a molar basis, the enthalpies of combustion of biodiesel fuels were greater in every distillate fraction compared to those of petroleum-derived diesel fuel; however, on a mass or volume basis, the petroleum-derived diesel fuel sample was more energetic.

Introduction

Biodiesel Fuel. Biodiesel fuel has been the focus of a great deal of media attention and scientific research in the last several years as a potential replacement for petroleum-derived diesel fuel. As a replacement fuel, biodiesel fuel has several advantages, which include its renewability (biodiesel can be prepared from sources such as vegetable oil, animal fats, used cooking oil, and microalgae[1,2]), the ability to produce it domestically, biodiesel having increased lubricity compared to low-sulfur petroleum-derived diesel fuel fuels, being noncarcinogenic, nonmutagenic, and biodegradable, and decreasing certain emissions (including carbon monoxide, unburned hydrocarbon, and particulate matter).[1] There are also some disadvantages to biodiesel fuel, including increased NO_x emissions,[3] oxidative instability,[4] moisture absorption during storage,[5] and higher freezing point.

For biodiesel fuel to replace petroleum-derived diesel fuel, it is necessary to be able to substitute the two fuels in a fairly straightforward manner (that is, biodiesel fuel must be a drop-in). In terms of transportation, storage, and distribution to the consumer, substitution of biodiesel fuel for petroleum-derived diesel fuel is in most cases possible. Yet, some chemical properties of the two fluids make biodiesel fuel and petroleum-derived diesel fuel quite different. For example, unblended biodiesel fuel (referred to as B100, where the number indicates the volume percent biodiesel fuel) and petroleum-derived diesel fuel have different chemical compositions, densities, viscosities, and cold flow properties.

Another fluid property that is vital for fuel replacement purposes and proper engine performance is fuel volatility. To compare the volatility differences between petroleum-derived diesel fuel and biodiesel fuel, one must accurately measure the distillation curves of the two fluids.

Advanced Distillation Curve Measurement. Simply stated, the distillation curve is a graphical depiction of the boiling temperature of a fluid or fluid mixture plotted against the volume fraction distilled.[6–8] The most common presentation of the distillation curve is a plot of the boiling temperature (at ambient pressure) against volume fraction. The standard test method,

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(1) http://www.nrel.gov/docs/fy06osti/40555.pdf (accessed September 10, 2007).

(2) Chisti, Y. *Biotechnol. Adv.* **2007**, *25*, 294–306.

(3) http://www.biodiesel.org/resources/fuelfactsheets/default.shtm (accessed June 2007).

(4) Ribeiro, N. M.; Pinto, A. C.; Quintella, C. M.; da Rocha, G. O.; Teixeira, L. S. G.; Guarieiro, L. L. N.; Rangel, M. D.; Veloso, M. C. C.; Rezende, M. J. C.; da Cruz, R. S.; de Oliveira, A. M.; Torres, E. A.; de Andrade, J. B. *Energy Fuels* **2007**, *21*, 2433–2445.

(5) He, B. B.; Thompson, J. C.; Routt, D. W.; Van Gerpen, J. H. *Appl. Eng. Agric.* **2007**, *23*, 71–76.

(6) Leffler, W. L. *Petroleum Refining in Nontechnical Language*; PennWell: Tulsa, OK, 2000.

(7) Kister, H. Z. *Distillation Operation*; McGraw-Hill: New York, 1988.

(8) Kister, H. Z. *Distillation Design*; McGraw-Hill: New York, 1991.

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ASTM D-86, provides the usual approach to measurement.[9] The data obtained with ASTM D-86 are the initial boiling point, the temperature at predetermined distillate volume fractions, and the final boiling point. The ASTM D-86 test suffers from several drawbacks, including large uncertainties in temperature measurements and little theoretical significance.[10]

In an effort to remedy the shortcomings of the standard distillation method described above, we have recently reported in detail an improved distillation method and apparatus.[10–12] Improvements to the traditional distillation apparatus include (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) a corrosivity assessment of each distillate fraction. This improved distillation method also provides important advantages over other methods such as the simulated distillation method embodied in procedures such as ASTM D-2887. In that method, for example, one uses the gas chromatographic behavior of a suite of compounds as a frame of comparison with a fuel. A significant advantage offered by the metrology discussed in this paper is the ability to develop a thermodynamic model of the distillation curve with an equation of state.[13,14]

Perhaps the most important advantage presented by the advanced distillation curve metrology is the ability to sample the fluid during the course of the distillation. Sampling very small volumes of the distillate (5−25 μL) yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows for some understanding of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids.

Chemical Analysis. The composition-explicit data channel of the advanced distillation curve metrology allows for a detailed fraction-by-fraction chemical analysis of the composition of the fluid under study. Some suitable analytical techniques include gas chromatography with either flame ionization detection (GC-FID) or mass spectral detection (GC-MS), element specific detection (such as gas chromatography with sulfur chemiluminescence detection, GC-SCD), Fourier transform infrared spectrophotometry (FTIR), or nuclear magnetic resonance spectroscopy (NMR).

The composition-explicit data channel also allows us to add thermochemical data to the distillation curve.[15–17] In the case of fuels, it is clear that knowledge of the enthalpy of combustion of each fraction of the distillation curve would be invaluable. Fortunately, the enthalpy of combustion is a well-known thermochemical quantity for a large number of compounds, tabulated in several reliable databases.[18–20] Thus, for a mixture, knowledge of the identities of the chemical components and their relative concentrations allows access to the composite enthalpy of combustion of the mixture. In this way, the composition-explicit data channel of the advanced distillation curve approach allows determination of the composite enthalpy of combustion of each distillate fraction.

Theory—Enthalpy of Combustion. The enthalpy of combustion is the heat released when a given amount of a combustible pure substance is burned (in oxygen) to form incombustible products (e.g., water and carbon dioxide). For example, the combustion reaction of *n*-octane is

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O \quad (1)$$

which results in an enthalpy of combustion of −5074 kJ/mol.[19] This thermochemical quantity is a characteristic of the substance. Enthalpies of combustion are routinely used as a basis for comparing the heating value of fuels, since the fuel that produces the greater amount of heat for a given cost is often the more economical. Enthalpies of combustion of pure substances are also used in comparing the stabilities of chemical compounds. One must be explicit in terms of the definition of the enthalpy of combustion, since it is possible to define the water produced in terms of vapor or liquid[15] (also called the higher and lower heats of combustion). If the enthalpy is specified in terms of $H_2O_{(g)}$, then the enthalpy is called the net heat or net enthalpy of combustion. If the enthalpy is specified in terms of $H_2O_{(l)}$, then the result is called the gross heat or gross enthalpy of combustion. The difference between the two values is the enthalpy of vaporization of water. Throughout this paper, we will use the net enthalpy of combustion, in which the product specification is for $H_2O_{(g)}$.

In the case of mixtures, the situation is complicated slightly by the enthalpy of mixing, although in most practical situations this is not a concern.[15] The enthalpy of combustion is much larger than the enthalpy of mixing for hydrocarbon species. For example, a typical enthalpy of mixing of two hydrocarbons, that of *n*-hexane + toluene, is 0.8−0.9 kJ/mol.[15] Since this is in the range of 0.02% of the enthalpy of combustion and most tabulated enthalpies of combustion (for hydrocarbons, such as those found in petroleum-derived diesel fuel) report uncertainties between 0.2 and 3%, we will neglect this effect. Ignoring the enthalpy of mixing, the composite enthalpy of combustion, which we will represent as $-\Delta H_c$, can be found by multiplying the enthalpy of combustion of each of the pure (or individual) components by the mole fraction of that component, and then adding the individual components to obtain the composite result:

$$-\Delta H_c = \sum x_i(-\Delta H_i) \quad (2)$$

where *i* refers to the individual components that have been identified or selected.

Experimental Section

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography

(9) Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, ASTM Standard D 86-04b. *Book of Standards*; American Society for Testing and Materials: West Conshohocken, PA, 2004.

(10) Bruno, T. J. *Ind. Eng. Chem. Res.* **2006**, *45*, 4371–4380.

(11) Bruno, T. J.; Smith, B. L. *Ind. Eng. Chem. Res.* **2006**, *45*, 4381–4388.

(12) Smith, B. L.; Bruno, T. J. *Int. J. Thermophys.* **2006**, *27*, 1419–1434.

(13) Huber, M. L.; Lemmon, E. W.; Diky, V.; Smith, B. L.; Bruno, T. J. *Energy Fuels* **2008**,

(14) Huber, M. L.; Smith, B. L.; Ott, L. S.; Bruno, T. J. *Energy Fuels* **2008**, *22*, 1104–1114.

(15) Bruno, T. J.; Smith, B. L. *Energy Fuels* **2006**, *20*, 2109–2116.

(16) Smith, B. L.; Bruno, T. J. *Energy Fuels* **2007**, *21*, 2853–2862.

(17) Smith, B. L.; Bruno, T. J. *Ind. Eng. Chem. Res.* **2007**, *46*, 310–320.

(18) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Yang, Y.; Daubert, T. E.; Danner, R. P. *DIPPR® Data Compilation of Pure Chemical Properties*; Design Institute for Physical Properties, AIChE: New York, NY, 2006.

(19) NIST Chemistry Web Book, NIST Standard Reference Database 69, March 2006 release.

(20) Kazakov, A. F.; Muzny, C. D.; Chirico, R. D.; Diky, V.; Stevenson, R. A.; Frenkel, M. *NIST/TRC Web Thermo Tables (WTT) - Professional Edition, NIST Standard Reference Subscription Database 3*, NIST Standard Reference Data Program: Gaithersburg, MD, 2007.

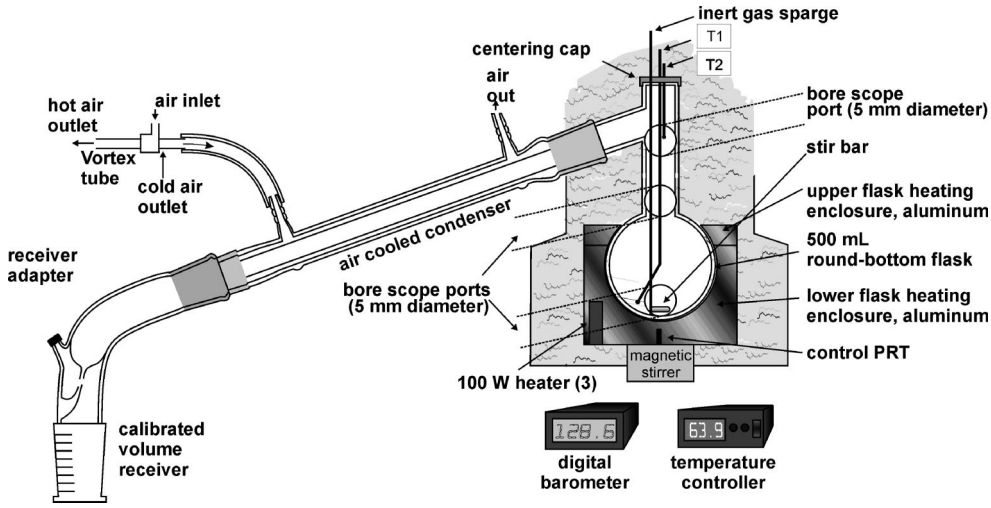

Figure 1. Distillation curve apparatus with inert gas sparge.

(30 m capillary column of 5% phenyl−95% dimethyl polysiloxane having a thickness of 1 μm and a temperature program from 50 to 170 °C at a heating rate of 5 °C/min) with flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99%, and the fluid was used without further purification.

Four biodiesel fuel samples were examined. Three were obtained from commercial sources: they were labeled C1, C2, and C3. Each of the commercial samples was prepared from soybean oil feedstocks, and the crude biodiesel fuels were washed with water to remove the alcohol and catalyst impurities remaining from the biodiesel fuel preparation before the biodiesel fuel was distributed. The fourth biodiesel fuel was prepared in-house following the "World Famous Dr. Pepper Technique" (WFDPT).[21] For this fluid, commercially available olive oil was used as the feedstock, and KOH was used as the catalyst in HPLC-grade methanol. The cloudy yellow crude biodiesel fuel product was decanted from the dark brown glycerin byproduct. The crude biodiesel fuel was washed according to the WFDPT;[21] it was labeled IHP for in-house prepared.

The four biodiesel fuel samples were stored tightly sealed in plastic jugs to avoid absorption of water. No other precautions were taken, nor were the samples physically or chemically dried. Each biodiesel fuel sample was clear, but there was significant variation in color. For example, one commercial sample made from a virgin soybean oil feedstock was light yellow in color, while the IHP biodiesel fuel was green.

The petroleum-derived diesel fuel sample used for comparison with the biodiesel fuel samples was a winter grade, low wax, ultralow sulfur diesel fuel that incorporated a red dye (specifying off-road use) and was refined locally from petroleum of the Denver−Julesburg field. It was stored tightly sealed in a plastic jug to minimize evaporation and/or uptake of water.

Analysis of the Biodiesel Fuels and Petroleum-Derived Diesel Fuels. Each of the four biodiesel fuel samples and the petroleum-derived diesel fuel sample was analyzed to qualitatively determine its chemical composition. These analyses were performed by diluting approximately 7 μL of each fuel in 1 mL *n*-hexane and subjecting the samples to GC-MS in scanning mode. Each chromatographic peak was identified with the assistance of the NIST Mass Spectral Database.[22]

The biodiesel fuel samples were analyzed on a 30 m capillary column with a 0.1 mm coating of 50% cyanopropyl−50% dimethylpolysiloxane as the stationary phase. This phase provides separations based upon polarity and is specifically intended for the analysis of the fatty acid methyl esters (FAMEs) that compose biodiesel fuel. Samples were injected via syringe into a split/splitless injector set with a 100 to 1 split ratio. The injector was operated at a temperature of 325 °C and a constant head pressure of 10 psig. The sample residence time in the injector was very short, thus the effect of sample exposure to this high temperature is expected to be minimal. The column was temperature programmed to provide complete and rapid elution with minimal loss of peak shape. Initially, the temperature was maintained isothermally at 80 °C for 2 min, followed by a 8 °C/min ramp to 285 °C, and finally maintained at 285 °C for 5 min. Although the analysis was allowed to run for more than 33 min, all peaks were eluted after approximately 19 min.

The petroleum diesel samples were analyzed on a 30 m capillary column of 5% phenyl−95% dimethyl polysiloxane having a thickness of 1 μm. Initially, the temperature was maintained isothermally at 70 °C for 2 min, followed by a 7 °C/min ramp to 260 °C, followed by a 60 °C/min ramp to 300 °C. Although the analysis was allowed to run for 30 min, all peaks were eluted after approximately 26 min.

Advanced Distillation Curves. For each experiment, 200 mL of petroleum-derived diesel fuel or biodiesel fuel was placed into the boiling flask of the distillation curve apparatus.[10] The thermocouples were then inserted into the proper locations to monitor T_k, the temperature in the fluid, and T_h, the temperature at the bottom of the takeoff position in the distillation head. The uncertainty in the thermocouple measurements was 0.05 °C. Enclosure heating was then commenced with a four-step program based upon a previously measured distillation curve.[23] Volume measurements were made in a level-stabilized receiver.[10]

The distillation curves for the petroleum-derived diesel fuel samples were measured as described earlier.[24] The distillation curve measurements on the biodiesel fuel samples required a modification of the apparatus. Initial measurements on a sample of biodiesel fuel from one commercial supplier showed a variance of 5−7 °C at each distillate volume fraction recorded. This large variance is unexpected, since the advanced distillation curve metrology generally yields temperature measurements that are within 0.5 °C between separate experiments. Since oxidative degradation is a well-known difficulty with biodiesel fuel,[4] we placed an argon sparge tube into the distillation kettle and bubbled the fluid for 10 min with stirring (see Figure 1). Before applying heat to the kettle, the argon sparge tube was removed from the fluid and positioned directly above the fluid; an argon purge of the atmosphere above kettle was maintained throughout the distillation. Keeping the argon sparge above the fluid instead of in it was necessary to avoid affecting the fluid temperature during the distillation. Using the sparge tube procedure for the

(21) http://www.biodieselcommunity.org/makingasmallbatch/ (accessed July 17, 2007).

(22) NIST/EPA/NIH Mass Spectral Database, S. R. D., SRD Program 2005.

(23) Smith, B. L.; Bruno, T. J. *Int. J. Thermophys.* **2006**, *27*, 1419–1434.

(24) Smith, B. L.; Ott, L. S.; Bruno, T. J. *Environ. Sci. Technol.* **2008**,

Table 1. Vapor Rising Temperatures for the Four Biodiesel Fuel Samples

	C1	C2	C3	IHP
vapor rising, °C	350.2	352.2	351.6	352.9

biodiesel fuel decreased the variance in the temperature measurements to approximately 0.5 °C.

Each of the distillation curves was measured at ambient atmospheric pressure. The pressure was measured with an electronic barometer; the expanded total uncertainty ($k = 2$) in the pressure measurements was 0.003 kPa. Distillation temperature readings were corrected to what should be obtained at standard atmospheric pressure. This was done with the modified Sidney Young equation, in which the constant term was assigned a value of 0.000 109.[25–27] The magnitude of the correction depends on the extent of departure from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level, resulting in a typical temperature correction of 7 °C.

To provide the composition channel to accompany the temperature information on the distillation curves, sample aliquots were withdrawn for 10 selected distillate volume fractions. To accomplish this, aliquots of ~7 μL of emergent fluid were withdrawn from the sampling hammock in the receiver adapter with a blunt-tipped chromatographic syringe and added to a sealed autosampler vial containing a known mass of *n*-hexane solvent. A sample was withdrawn at the first drop of fluid from the condenser and then at each of 9 additional predetermined volume fractions of distillate, for 10 total sample aliquots.

The biodiesel fuel distillate samples were evaluated in mass spectral scanning mode on the same column and with the same temperature program described earlier for the analysis of the starting fluid. Mass spectra were collected for each peak from 15 to 550 RMM units. The area under each peak was integrated with a commercial algorithm optimized to identify peaks that were at least an order of magnitude larger than the noise level.

After qualitative identification, each peak was quantitated by standardization of the GC with external standards. Standardization was done on the basis of extracted ions (sometimes called single ion monitoring or selected ion monitoring, SIM).[28] The compounds used for standardization were purchased from a commercial supplier. Four concentrations of each standard solution were prepared by diluting the compound of interest in *n*-hexane; each standard solution was subjected to seven replicate analyses. Each fatty acid methyl ester (FAME) compound present in the biodiesel fuel samples was used to standardize the biodiesel fuel samples. The *m*/*z* ratios of 41, 54, 67, 81, and 95 are common to all FAME compounds and were dwelled on during SIM. In the majority of the biodiesel fuel distillate fractions, there were six or fewer FAME peaks present on the raw total ion chromatogram (TIC) and no other identifiable peaks. Greater than 97% of the TIC was integrated for each biodiesel fuel sample; we expect that neglecting the minor components, present in a sum of less than 3% of the total uncalibrated response, will not affect the uncertainty of the composite enthalpy in a significant way.[15]

The petroleum-derived diesel fuel distillate fractions were evaluated in scanning mode on the same column and with the same temperature program described earlier for the analysis of the starting fluid. These distillate samples were more complex than the biodiesel fuel samples, with the petroleum-derived diesel fuel distillate samples containing substituted aromatics, straight chain hydrocarbons, and branched chain hydrocarbons. The aromatic hydrocarbons were standardized with benzene (with the $m/z = 77$ ion dwelled on during SIM). Each straight chain hydrocarbon was standardized separately with the actual compound, and branched chain hydrocarbons were standardized with the straight chain backbone of the branched chain hydrocarbon and SIM dwelling on the most abundant shared *m*/*z* peak. For the petroleum-derived diesel fuel samples, which contain far more components than the biodiesel fuel samples, the eight peaks with the highest total area count from each raw TIC were identified and integrated for enthalpy calculations; small peaks with uncalibrated area counts accounting for no more than 4% of the total uncalibrated area were omitted. In past work, we determined that neglecting peaks with total uncalibrated area percentages of up to 4% increased the uncertainty of the enthalpy calculation by only 1.5%.[15] We therefore expect the neglect of minor components in petroleum-derived diesel fuel distillate fractions to be a minor source of uncertainty that will not affect the uncertainty of the composite enthalpy in a significant way.

After standardization, the enthalpy of combustion analysis was performed for the four biodiesel fuel samples and the petroleum-derived diesel fuel on distillate fractions corresponding to 0.025, 10, 50, and 80 vol. % of the distillate. Calculation of the composite enthalpies of combustion and their associated uncertainties will be discussed further in the following sections.

Results and Discussion

1. Chemical Composition of Four Biodiesel Fuel Samples. The chemical composition of each of the four biodiesel fuel samples was examined with GC-MS. The main components of each biodiesel fuel were five FAMEs: methyl palmitate (hexadecanoic acid, methyl ester; CAS No. 112-39-0), methyl stearate (octadecanoic acid, methyl ester; CAS No. 112-61-8), methyl oleate (octadecenoic acid, methyl ester; CAS No. 112-62-9), methyl linoleate (octadecadienoic acid, methyl ester; CAS No. 112-63-0), and methyl linolenate (octadecatrienoic acid, methyl ester; CAS No. 301-00-8). These five FAMEs constitute the "average" composition found in biodiesel fuel derived from soybean oil.[3] Three other FAMEs were present in minor amounts: methyl myristate (tetradecanoic acid, methyl ester; CAS No. 124-10-7), methyl arachidate (eicosanoic acid, methyl ester; CAS No. 1120-28-1), and methyl behenate (docosanoic acid, methyl ester; CAS No. 929-77-1). Each FAME was present in different proportions in the four samples. The influence of these proportions on the distillation curves and enthalpies of combustion will be discussed in the sections that follow.

2. Advanced Distillation Curves of Four Biodiesel Fuel Samples. *a. Initial Boiling Behavior.* During the initial heating of each sample in the distillation flask, the behavior of the fluid was observed. In our previous work, three temperature measurements were collected: at the onset of bubbling, when the fluid displays sustained bubbling, and when vapor is observed rising into the distillation head.[10] In the present study, the dark color of some of the biodiesel fuel samples prevented an accurate measurement of the onset of bubbling and the sustained bubbling temperatures. Despite the difficulties with these two measurements, the temperature at which vapor is first observed to rise into the distillation head can still be observed. This temperature measurement is actually the most valuable of the three measurements, since the vapor rising temperature is essentially the initial boiling temperature that can be modeled theoretically with an equation of state. The vapor rising temperatures, presented as averages of two to three separate determinations, are provided in Table 1. The uncertainty in the vapor rise temperature measurement was approximately 0.5 °C.

Table 1 shows that all four biodiesel fuel samples have vapor rising temperatures within 2.7 °C of one another. This similarity is required for the commercially obtained samples, which have been tested for and adhere to the ASTM standards for, among

(25) Young, S. *Proc. Chem. Soc.* **1902**, *81*, 777.
(26) Young, S. *Fractional distillation*; Macmillan and Co., Ltd.: London, 1903.
(27) Young, S. *Distillation principles and processes*; Macmillan and Co., Ltd.: London, 1922.
(28) Karasek, F. W.; Clement, R. E. *Basic Gas Chromatography-Mass Spectrometry: Principles and Techniques*; Elsevier: Amsterdam, 1988.

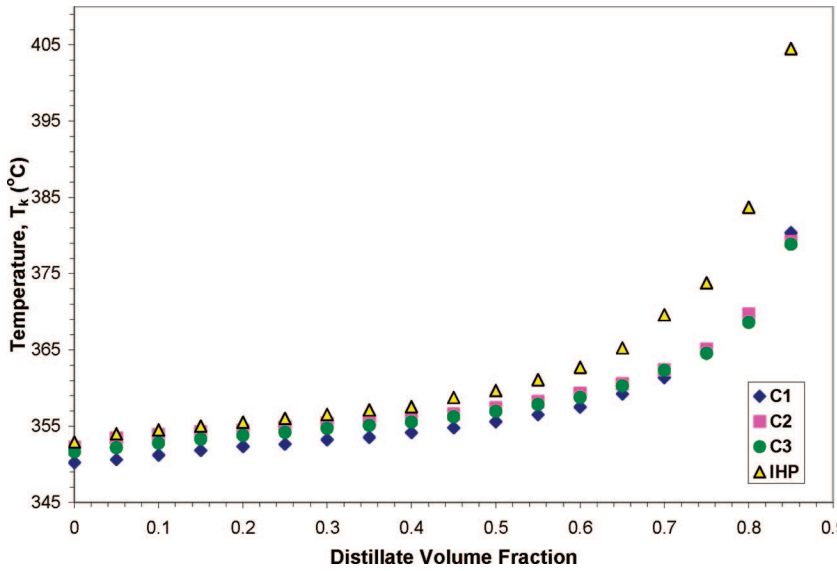

Figure 2. Distillation curves for each of the four biodiesel fuel samples. Each single curve shown for a given sample is representative of data collected for 3−6 distillation curves. The error bars on the temperature measurement are smaller than the symbols used.

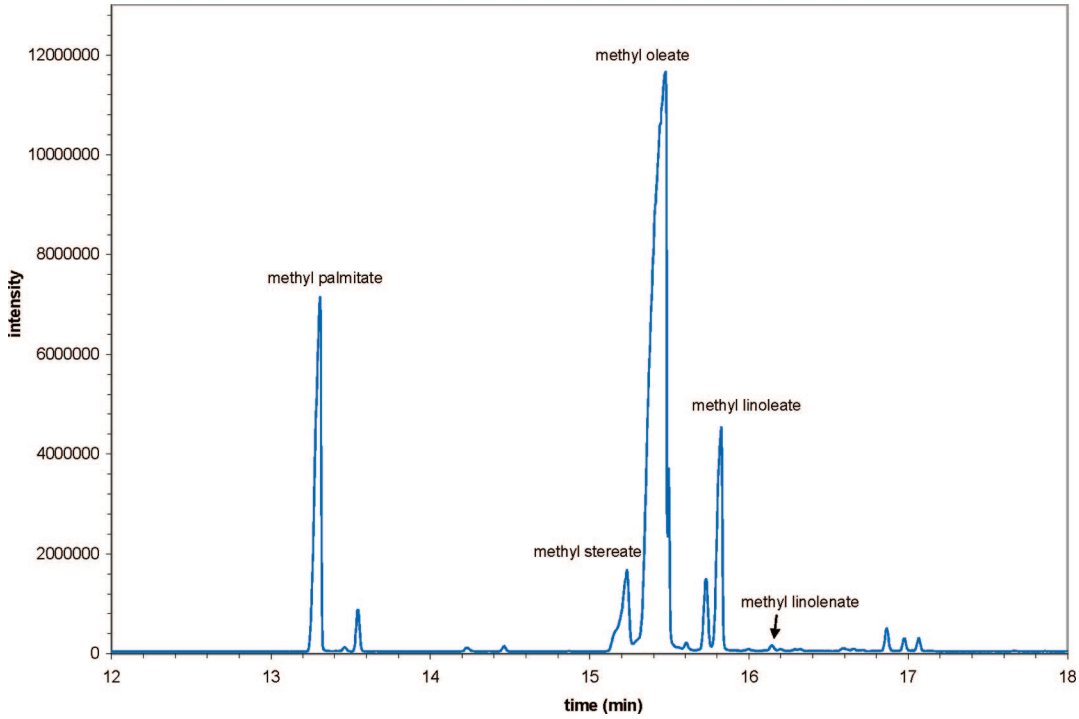

Figure 3. Uncalibrated total ion chromatogram of the 50% distillate volume fraction for the IHP biodiesel fuel. The five main FAMEs present in biodiesel are labeled; the predominant peak at 15.4 min is methyl oleate.

other things, composition and boiling point.[29] The similarity of the vapor rise temperature of the IHP sample indicates that this sample would also meet ASTM standards for boiling point, although the IHP sample was not tested for its compliance. Even though the four vapor rising temperatures are similar, it is useful to note that the C1 sample had the lowest temperature, while the IHP biodiesel fuel had the highest. The distillation curves presented below will show that the highest and lowest values for vapor rising temperatures were consistent with the behavior of the distillation curves of these two fuels.

b. Distillation Curves. Representative distillation curves for the four biodiesel fuel samples are shown in Figure 2; the use of the advanced distillation metrology to measure the distillation curves of biodiesel fuels with low uncertainties in pressure, temperature, and volume measurements is very important for the development of thermodynamic models.[13,14] Each of the four distillation curves shows the same general shape, a very subtle sigmoid proceeding from approximately 350 °C to approximately 385 °C. The major advantage of the composition-explicit distillation curve metrology is that the slight differences in these four curves can be probed and understood by use of the composition-explicit data channel. The C1 biodiesel fuel, consistent with its initial boiling behavior, has distillation temperatures that are 2 to 3 °C less than those of the other two commercial samples throughout the first 70% of the distillation. GC-MS data shows that, at early points during the distillation, these lower distillation temperatures are likely due to the

(29) Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels; ASTM Standard D 6751. In *Book of Standards*; ASTM: West Conshocken, PA, 2002.

Table 2. Experimental Enthalpies of Combustion of the Pure FAME Compounds[18]

compound	enthalpy of combustion (−kJ/mol)
methyl palmitate	9950
methyl stearate	11160
methyl oleate	11100
methyl linoleate	10980[a]
methyl linolenate	10850[a]

[a] This value was calculated with the standard state enthalpy of formation.[18]

presence of shorter-chain alkanes and alkenes (C_8-C_{10}) plus some light aromatic compounds in addition to the expected FAME compounds. Other effects of these shorter chain and aromatic compounds will be addressed in more detail when the enthalpies of combustion of the biodiesel fuel samples are discussed. The two remaining commercial biodiesel fuels, C2 and C3, have distillation curves that are always within 1 °C of one another, and for the majority of the distillation, the difference between these two biodiesel fuels is less than 0.5 °C.

The distillation curve of the IHP sample was somewhat different from those of the three commercially obtained samples. For the first 25% of the distillation, the IHP biodiesel fuel is comparable to the C2 and C3 samples. After this point, however, the IHP distillation curve begins to diverge from the others with increasingly higher temperatures. The GC-MS data shows that the IHP biodiesel fuel above 25 distillate vol. % has a significantly greater mole fraction of methyl oleate in comparison with the other three biodiesel fuel samples (see Figure 3 for a chromatogram of the 50 vol. % distillate fraction of the IHP sample). The greater mole fraction of methyl oleate raises the distillation temperatures of these distillate fractions, due to the 25 to 35 °C higher boiling point of methyl oleate compared to the four other major FAME compounds present in the biodiesel fuels. (Additionally, the lower level of unsaturation of methyl oleate compared to either methyl linoleate or methyl linolenate implies that the IHP sample will be less susceptible to oxidative degradation and have a higher cetane number.[4])

3. Enthalpy of Combustion of Four Biodiesel Fuel Samples. The composite enthalpy of combustion of each of the four biodiesel fuel samples was calculated at four distillate volume fractions: 0.025, 10, 50, and 80 vol. %. The enthalpies of combustion of the pure components for the five main FAMEs are presented in Table 2; the composite enthalpies of combustion for the four biodiesel fuel samples are presented in Table 3. We have discussed the contributions to the overall uncertainty of the composite enthalpy of combustion at great length.[16,17] The contributions included (1) the neglect of the enthalpy of mixing, (2) the uncertainty in the individual enthalpy of combustion as tabulated in the databases, (3) the uncertainty in the measured mole fraction, (4) the uncertainty posed by very closely related isomers that cannot be resolved by the analytical protocol, (5) the uncertainty introduced by neglecting components present at very low concentrations (that is, uncertainty associated with the chosen area cutoff), (6) the uncertainty introduced by a complete misidentification of a component, (7) the uncertainty attributable to unresolvable overlapping peaks in the chromatogram, and (8) the uncertainty arising from the absence of experimental enthalpy of combustion values for some components and the subsequent substitution of calculated enthalpies determined with the Cardozo method.[17] In view of these sources of uncertainty, the overall combined uncertainty in our earlier composite enthalpy of combustion calculations (with a coverage factor $k = 2$) was 4 to 5%. For the biodiesel fuel samples, which contain a small number of easily identified and resolvable peaks, the uncertainty posed by sources 4−7 above is negligible. The enthalpy of mixing of FAMEs in *n*-hexane solvent is estimated to be 0.3−0.4 kJ/mol,[30] which is less than 0.01% of the enthalpy of combustion of the FAMEs compounds. Additionally, the uncertainty in 8 was investigated more thoroughly by comparing each experimental FAME value present in the database[18] with the value calculated by the Cardozo method for the same compound; the expanded total uncertainty ($k = 2$) was 1.4%. With these uncertainties, the overall combined uncertainty for the biodiesel distillate fractions is 3.3%. The uncertainty is dominated by the analytical measurement and determination of the component mole fraction.

The data point that immediately stands out is the 0.025% volume fraction of the C1 sample (this distillate volume fraction corresponds to the first drop of distillate to travel down the condenser). The C1 sample is approximately half a s energetic as the first drop of the other three samples. GC-MS data indicate that this is due to a large mole fraction of light aromatic compounds (such as toluene and *p*-xylene) in the first drop of the C1 sample. Since the pure component enthalpy of combustion of aromatic compounds such as *p*-xylene is approximately half that of any of the five main FAME compounds, the enthalpy of combustion of the first drop of the C1 sample is dramatically reduced compared to that for the other three biodiesel fuel samples. Aromatic compounds such as *p*-xylene are found in petroleum-derived diesel fuel, so it is possible that this commercial biodiesel fuel sample was contaminated with petroleum-derived diesel fuel during its transportation and/or storage.

Save this outlying point, the enthalpies of combustion are all within the uncertainty of the calculation at each volume fraction measured. This indicates that any compositional variability in the four biodiesel fuel samples studied herein does not significantly affect the molar enthalpy of combustion of the distillate fractions.

4. Chemical Composition of Petroleum-Derived Diesel Fuel in Comparison with Biodiesel Fuels. In contrast to the relatively simple FAME-dominated chemical composition of the biodiesel fuel samples, petroleum-derived diesel fuel had many more components. Petroleum-derived diesel fuel is composed primarily of hydrocarbon chains ranging in length from C_8 to C_{20} and also commonly has aromatic compounds present. In general, petroleum-derived diesel fuel contains 65−85 vol. % aliphatic hydrocarbons, 5−30 vol. % aromatic hydrocarbons, and 0 to 5% olefins.[31] There are no FAME compounds present in petroleum-derived diesel fuel.

5. Comparison of the Distillation Curves of Biodiesel Fuel and Petroleum-Derived Diesel Fuel. *a. Initial Boiling Behavior.* While the vapor rising temperatures of all four biodiesel fuel samples are within 2.7 °C of one another, the vapor rising temperature of the petroleum-derived diesel fuel, at 233.4 °C,[24] is approximately 120 °C lower than each of the biodiesel fuel samples. This striking difference in vapor rising temperature has many implications, including for the ease of starting a diesel engine (especially in cold weather).[15] The much lower vapor rising temperature also suggests that the distillation curves of the petroleum-derived diesel fuel and biodiesel fuel will be very different.

b. Distillation Curves. Representative distillation curves for each the four biodiesel fuel samples as well as a petroleum-derived diesel fuel sample are shown in Figure 4. The difference in the distillation curves between the petroleum-derived diesel

(30) Gonzalez, C.; Resa, J. M.; Concha, R. G.; Goenaga, J. M. *J. Am. Oil Chem. Soc.* **2004**, *81*, 817–822.

(31) Liang, F.; Lu, M.; Keener, T. C.; Liua, Z.; Khangb, S.-J. *J. Environ. Monit.* **2005**, *7*, 938–988.

Table 3. Enthalpies of Combustion (−kJ/mol) of Four Distillate Fractions for the Four Biodiesel Fuel Samples[a]

volume fraction (%)	C1	C2	C3	IHP
0.025	5104 (168)	10478 (346)	10403 (343)	10610 (350)
10	10477 (346)	10470 (346)	10468 (345)	10650 (351)
50	10562 (349)	10568 (349)	10579 (349)	10742 (355)
80	10680 (352)	10679 (352)	10689 (353)	10910 (360)

[a] The uncertainties (−kJ/mol) are provided in parentheses.

Table 4. Enthalpies of Combustion of the C3 Biodiesel Fuel and the Petroleum-Derived Diesel Fuel (PDDF)

vol frac (%)	C3 (−kJ/mol)	PDDF (−kJ/mol)	C3 (−kJ/L)	PDDF (−kJ/L)	C3 (−kJ/g)	PDDF (−kJ/g)
0.025	10403 (343)	5090 (168)	31517 (1040)	34161 (1708)	35.9 (1.2)	42.1 (2.1)
10	10468 (345)	6258 (207)	31502 (1040)	34518 (1725)	36.2 (1.2)	42.4 (2.1)
50	10579 (349)	9847 (325)	31663 (1045)	33212 (1660)	36.3 (1.2)	44.0 (2.2)
80	10689 (353)	10572 (349)	31772 (1049)	32953 (1648)	36.5 (1.2)	43.9 (2.2)

fuel and the biodiesel fuels is remarkable. The distillation of petroleum-derived diesel fuel begins approximately 120 °C lower than biodiesel fuel. Additionally, the distillation of petroleum-derived diesel fuel is complete by the time the fluid temperature reaches 328 °C, while none of the four samples of biodiesel fuel have begun distilling at this same temperature. At no point do the biodiesel fuel and petroleum-derived diesel fuel curves overlap. The difference in the distillation curves echoes the difference in the vapor rising temperatures, with the petroleum-derived diesel fuel being far more volatile than the biodiesel fuels.

6. Comparison of the Enthalpy of Combustion of Biodiesel Fuel and Petroleum-Derived Diesel Fuel. The composite enthalpies of combustion (−kJ/mol) of the petroleum-derived diesel fuel distillate fractions was calculated for the same four distillate volume fractions as the biodiesel fuel samples and are shown graphically in Figure 5. The uncertainty in the enthalpies of combustion for the petroleum-derived diesel fuel includes all eight sources of uncertainty discussed earlier. The complexity of the petroleum-derived diesel fuel and the treatment of the chromatograms were similar to those in our previous work with gasoline;[15,32] therefore, we have assigned a similar expanded total uncertainty of 5% to the petroleum-derived diesel fuel distillate fractions.

It is interesting to note that the first drop of the petroleum-derived diesel fuel and C1 biodiesel fuel have the same enthalpy of combustion within the uncertainty of the measurement. This measurement reflects the shorter-chain hydrocarbon and aromatic compounds present in the first drop of the C1 biodiesel fuel and indicates that it is these compounds that are the primary contributors to the enthalpy of combustion (conversely, the similar vapor rising temperature of the C1 sample with the other three biodiesel fuels indicates that the FAME compounds present in the first drop are the primary contributors to the initial boiling behavior). On a per-mole basis, the 0.025, 10, and 50% distillate fractions of the remaining three samples of biodiesel fuel have higher enthalpies of combustion than the petroleum-derived diesel fuel sample. At the 80% distillate fractions, the petroleum-derived diesel fuel sample and all four biodiesel fuel samples have equivalent enthalpies within the uncertainty of the measurement.

While the presentation of the data on a molar basis is useful for design and modeling studies, presentation of the data on a volume basis is also valuable (since consumers are more accustomed to thinking about fuel values on a per-volume basis instead of a per-mole basis). The conversion to a volume basis is simple, requiring only the molecular weights and densities of the constituents of each sample at each distillation temperature.[18] One additional, useful presentation of the data is in a mass basis. For simplicity, we compare the petroleum-derived diesel fuel with just one representative biodiesel fuel (C3). The data in molar, volume, and mass bases are compiled in Table 4 and are presented graphically for the mass basis in Figure 6.

In contrast to the molar enthalpies shown in Figure 5, the enthalpies of combustion of petroleum-derived diesel fuel on a mass basis are higher for every distillate fraction than that of

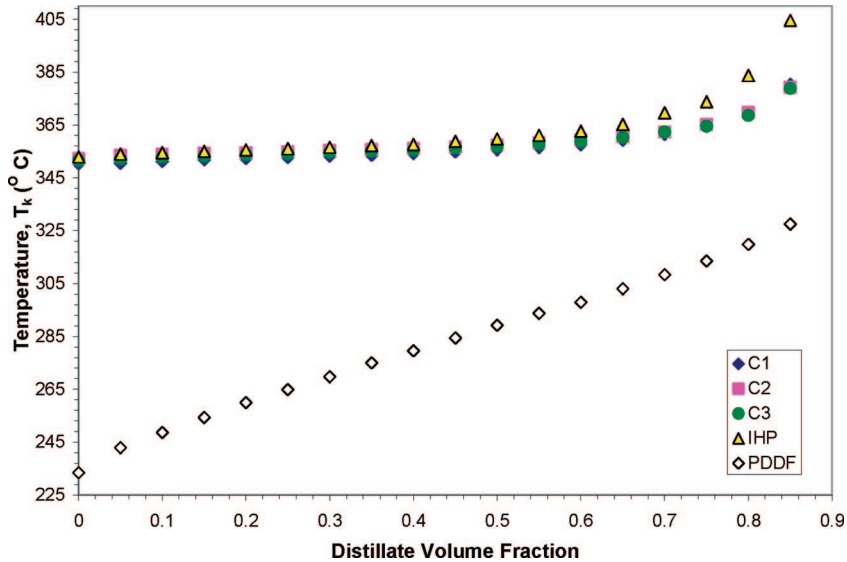

Figure 4. Distillation curves of the four biodiesel fuel samples and the petroleum-derived diesel fuel (PDDF) sample. The uncertainty on the temperature measurements is smaller than the symbols used.

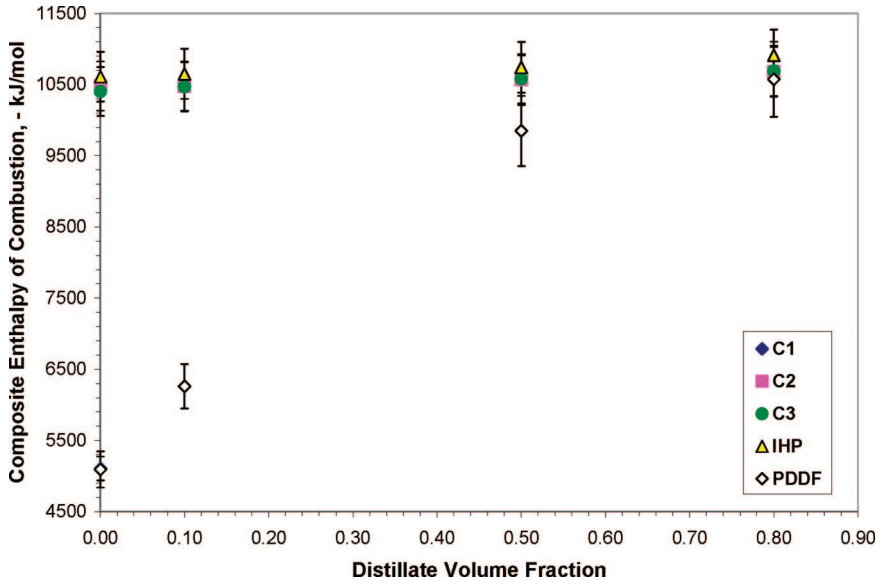

Figure 5. Enthalpy of combustion (−kJ/mol) of the petroleum-derived diesel fuel and four biodiesel fuel samples. For the first drop of the petroleum-derived diesel fuel and C1 biodiesel fuel, the symbols overlap.

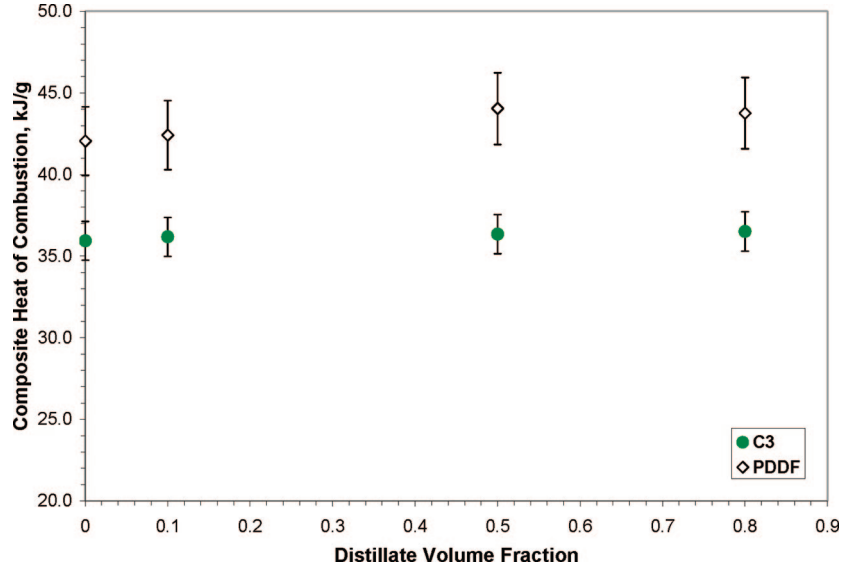

Figure 6. Enthalpies of combustion (−kJ/g) of one representative biodiesel fuel sample (C3) and the distillate fractions of the petroleum-derived diesel fuel (PDDF).

biodiesel fuel. On average, the enthalpy of combustion of each distillate fraction of petroleum-derived diesel fuel is 16% higher than that of biodiesel fuel. This difference can be attributed to the oxygen moieties in biodiesel fuel constituent molecules, which lower the energy content on a mass basis. Additionally, the enthalpies of combustion of petroleum-derived diesel fuel on a volume basis are higher for every distillate fraction than that of biodiesel fuel. On a volume basis, however, the average difference in enthalpy is lowered to 6%, and the enthalpies of combustion of the 80% distillate fraction are equivalent within the uncertainty of the measurement.

Conclusions

We examined the distillation curves and enthalpies of combustion as a function of distillate cut of four biodiesel fuels and one petroleum-derived diesel fuel. The use of the advanced distillation metrology to measure the distillation curve of biodiesel fuels with low uncertainties in pressure, temperature, and volume measurements is very important for the development of thermodynamic models. The differences in the distillation curves of biodiesel fuel and petroleum-derived diesel fuel are striking, beginning with initial boiling points that differ by approximately 120 °C. The composition-explicit data channel of the advanced distillation curve method allowed for a thorough composition and enthalpy comparison of the five fuels. On a molar basis, each of the distillate fractions of biodiesel fuel examined had a higher energy content than the petroleum diesel sample. On a mass and volume basis, however, the petroleum diesel sample has a higher energy content due to lower oxygen content and lower density than the biodiesel fuels. These insights may lead to better understanding of the relationship between fuel makeup and performance.

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(32) Smith, B. L.; Bruno, T. J. *Ind. Eng. Chem. Res.* **2007**, *46*, 297–309.