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Composition-Explicit Distillation Curves of Commercial Biodiesel Fuels: Comparison of Petroleum-Derived Fuel with B20 and B100[†]

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We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications provide for (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. The composition-explicit channel is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. We have applied the new method to the measurement of rocket propellant, gasolines, jet fuels, diesel fuels, and crude oils. In this paper, we present the application of the technique to representative batches of commercially available biodiesel fuels sold as B20 and B100. The distillation curve data that are presented are of sufficiently low uncertainty that they can be used for thermodynamic modeling of these complex fluids. Moreover, we present not only the distillation curves but also a chemical characterization of the 0.025, 10, 50, and 80% fractions and discuss the contrasts among the various mixtures.

Introduction

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 or extender for petroleum-derived diesel fuel.¹ 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), the potential to produce it domestically, and increased lubricity compared to low-sulfur petroleumderived diesel fuels.²⁻⁴ The fluid is noncarcinogenic, nonmutagenic, and biodegradable, the use of which decreases certain emissions (including carbon monoxide, unburned hydrocarbon, and particulate matter) when compared to petroleum-derived diesel fuel. There are also some serious disadvantages to biodiesel fuel, including increased NO_x emissions, oxidative instability, and moisture absorption during storage.⁵ The major constituents (fatty acid methyl esters, FAMEs) of pure biodiesel are generally relatively few; these are summarized in Table 1, along with some relevant physical properties.

For biodiesel fuel to replace or extend 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.⁶ Despite this, there are some chemical properties of the two fluids that 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 biodiesel fuel.

In diesel engines, it is possible to use the distillation curve in the same way as for gasoline combustion engines to design fuels for operability.^{7,8} Especially important with diesel fuels are the later regions of the distillation curve, which describe the high relative molecular mass components of the fuel.⁹ It is also possible to correlate the distillation curve of fuels with exhaust emissions, a fact that is especially important with diesel engines.^{7,8} The emissions that have been studied include carbon monoxide, particulates, nitrogen oxides, and unburned hydrocarbons.¹⁰ These environmental parameters are typically measured in studies performed on research engines. Among the most useful predictors found for these emissions are the 90% recovery point and the final boiling point of the distillation curve. Beyond the rough prediction of emissions, it has been possible to relate the mutagenic effects of diesel fuel emissions to the distillation curve as well. In this study, the Ames test was applied to the emissions from heavy-duty diesel engines, and it was concluded that mutagenicity negatively correlates with cetane number and the upper distillation curve points.^{11,12} This implies that it is possible to use the distillation curve to aid in the design of fuels that have a decreased genotoxicity.

In earlier work, we described a method and apparatus for an advanced distillation curve measurement that is especially applicable to the characterization of fuels. This method is a significant improvement over current approaches, featuring (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 assess-

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Table 1. Some Representative Properties of the Fatty Acid Methyl Esters Studied in This Work

methyl palmitate

formula = $C_{17}H_{34}O_2$ RMM = 270.4507 CAS no. = 112-39-0 InChI = 1/C17H34O2/ c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17(18)19-2/h3-16H2,1-2H3

 $T_{\text{boil}} = 331.85 \text{ °C}$ (predicted by BYU-NBP method) $T_{\text{fus}} = 29.9 \text{ °C}$

density = 0.858 g/mL (25 $^{\circ}\mathrm{C};$ predicted from the liquid density correlation)

refractive index, $Na^d = 1.437 (30 \ ^\circ C)$

synonyms: palmitic acid, methyl ester; *n*-hexadecanoic acid methyl ester; Metholene 2216; methyl hexadecanoate; methyl *n*-hexadecanoate; methyl palmitate; Uniphat A60; Emery 2216; Radia 7120; acide hexadecanoique methyl ester; hexadcanoic acid, methyl ester

methyl oleate



formula = $C_{19}H_{36}O_2$ RMM = 296.4879 CAS no. = 112-62-9 InChI = 1/C19H36O2/ c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/ h10-11H,3-9,12-18H2,1-2H3/b11-10- T_{boil} = 343.85 °C (predicted from experimental vapor pressure using the vapor pressure correlating equation) T_{fus} = 19.9 °C density = 0.87 g/mL

refractive index, $Na^d = 1.45214 (20 °C)$

synonyms: oleic acid methyl ester; Emery oleic acid ester 2301; methyl *cis*-9-octadecenoate; methyl oleate; (*Z*)-9-octadecenoic acid methyl ester; *cis*-9-octyldecenoic acid, methyl ester; Emery; Emery, oleic acid eseter; methyl 9-octadecenoate; oleic acid methyl ester, *cis*-; Emerest 2301; Emerest 2801; Kemester 105; Kemester 115; Kemester 205; Kemester 213; methyl (*Z*)-9-octadecenoate; Emery 2219; Emery 2301; Kemester 104; methyl ester; Priolube 1400; Witconol 2301; methyl (*Z*)-9-octadecenoate; 9-octadecenoaic acid, methyl ester (*Z*); *cis*-9-octadecenoaic acid, methyl ester; *Cis*-0eate; methyl (*Z*)-9-octadecenoaic acid, methyl ester; *Cis*-0eate; methyl ester (*Z*);

(Z)-9-oleate; *cis*-9-octadecenoic acid, methyl ester; 9-octadecenoic acid (Z)-, methyl ester

methyl linolenate



formula = $C_{19}H_{32}O_2$ RMM = 292.4562CAS no. = 301-00-8 InChI = 1/C19H32O2/c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/ h4-5,7-8,10-11H,3,6,9,12-18H2,1-2H3/b5-4-,8-7-,11-10- $T_{\rm boil} = 347.0$ °C $T_{\rm fus} = -57.0$ °C density = 0.896 g/mL (25 °C; predicted using liquid density correlation) refractive index = 1.4692synonyms: linolenic acid, methyl ester; methyl all-cis-9,12,15-octadecatrienoate; methyl linolenate; methyl (9Z,12Z,15Z)-9,12,15-octadecatrienoate; cis,cis,cis-9,12,15-octadecatrienoic acid, methyl ester; methyl α -linolenate; methyl linolenate, α ; (Z,Z,Z)-9,12,15-octadecatrienoic acid, methyl ester; cis, cis, cis-9, 12, 15-octade catrienoic acid, methyl ester

ment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7)



formula = $C_{19}H_{38}O_2$ RMM = 298.5038 CAS no. = 112-61-8 InChI = 1/C19H38O2/ c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/ h3-18H2,1-2H3 T_{boil} = 360.85 °C (predicted by BYU-NBP method) T_{fus} = 39.0 °C density = 0.85 g/mL (predicted from liquid density correlation equation

at the triple point)

refractive index, Na^d = 1.4383 (35 °C)

synonyms: stearic acid methyl ester; *n*-octadecanoic acid methyl ester; Kemester 9718; methyl *n*-octadecanoate; methyl octadecanoate; methyl stearate; Metholene 2218; Emery 2218; Kemester 9018; methyl ester of octadecanoic acid; Kemester 4516; methyl (*Z*)-9-octadecenoate; octadecanoic acid methyl ester

methyl linoleate



formula = $C_{19}H_{34}O_2$ RMM = 294.4721 CAS no. = 112-63-0 InChI = 1/C19H34O2/ c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/ h7-8,10-11H,3-6,9,12-18H2,1-2H3/b8-7-,11-10- T_{boil} = 346.0 °C

 $T_{\rm fus} = -39.22$ °C (99% purity)

density = 0.886 g/mL (25 °C; predicted using liquid density correlation) refractive index, Na^d = 1.4592

synonyms: linoleic acid methyl ester; methyl

cis,cis-9,12-octadecadienoate; methyl linoleate; methyl octadecadienoate; methyl 9-*cis*,12-*cis*-octadecadienoate; methyl

(9Z,12Z)-9,12-octadecadienoate; natural methyl linoleate;

9,12-octadecadienoic acid, methyl ester, (Z,Z);

cis-9,*cis*-12-octadecadienoic acid, methyl ester; *cis*-linoleic acid methyl ester; methyl linolate; methyl (*Z*,*Z*)-9,12-octadecadienoate; methyl (*Z*,*Z*)-9,12-octadecadienoic acid methyl ester; *cis*-9,*cis*-12-octadecadienoic acid, methyl ester

corrosivity assessment of each distillate fraction.^{13–20} For diesel fuels, as with any fuel, the distillation curve is one of



Figure 1. Schematic diagram of the advanced distillation curve apparatus. Note that the apparatus has been modified by the addition of an inert gas purge line to blanket the sample with argon and, thus, minimize oxidative decomposition.

Table 2. Summary of the Initial Behavior of the Petroleum Diesel Fuel and the Samples of B20 and B100 (Biodiesel Fuel)^{α}

observed	petroleum diesel	B20 biodiesel	B100 biodiesel
temperature (°C)	fuel (83.27 kPa)	fuel (83.39 kPa)	fuel (83.43 kPa)
vapor rising	233.4	237.9	339.1

^{*a*} The vapor rise temperature is that temperature at which vapor is observed to rise into the distillation head, considered to be the initial boiling temperature of the fluid (highlighted in bold print). These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow recovery of the actual measured temperatures. The uncertainties are discussed in the text.

Table 3. Representative Distillation Curve Data for the Samples of Petroleum-Derived Diesel Fuel, B20 and B100 (Biodiesel Fuel)^a

distillate volume fraction	petroleum diesel fuel (83.27 kPa)		B20 biodiesel fuel (83.39 kPa)		B100 biodiesel fuel (83.40 kPa)	
	$T_k, ^{\circ}C$	$T_{\rm h},$ °C	$T_k, ^{\circ}C$	$T_{\rm h},$ °C	^{<i>T</i>_k, °C}	$T_{\rm h},$ °C
0.05	242.9	197.8	248.4	218.4	350.6	342.1
0.10	248.6	212.4	255.0	227.3	351.2	345.4
0.15	254.3	223.4	262.1	235.2	351.8	347.4
0.20	259.9	231.2	268.8	243.2	352.3	348.2
0.25	264.9	234.8	275.2	239.1	352.6	348.1
0.30	269.7	242.6	282.3	251.6	353.2	348.2
0.35	275.0	249.9	289.0	265.1	353.5	348.1
0.40	279.6	254.9	295.2	273.5	354.1	348.8
0.45	284.4	263.1	302.0	283.2	354.8	349.0
0.50	289.2	268.2	308.5	290.1	355.6	349.4
0.55	293.7	274.3	314.8	298.7	356.5	350.0
0.60	297.9	275.0	321.2	305.8	357.5	350.3
0.65	303.0	282.7	327.1	313.5	359.2	350.6
0.70	308.3	286.5	332.7	320.3	361.4	351.8
0.75	313.5	292.4	338.0	326.9	364.5	352.5
0.80	319.8	295.4	342.9	333.4	369.7	353.7
0.85	327.5	299.6	347.6	340.1	380.3	360.5

^{*a*} These data are plotted in the figures. The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided in parentheses to allow recovery of the actual measured temperatures.

the main operational and design parameters used to ensure good engine performance and optimization. Moreover, it was recently cited as one of the properties most needed in the development of diesel fuel surrogates for advanced fuel research.²¹

This approach also provides important advantages over other methods such as the simulated distillation method embodied in



Figure 2. Representative distillation curve for B20 and B100 biodiesel fuel, presented with the distillation curve of a representative petroleum-derived diesel fuel.

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. The very significant advantage offered by the approach discussed in this paper is to provide the user the ability to model the distillation curve resulting from our metrology with an equation of state. Such thermodynamic model development is simply impossible with the classical approach to distillation curve measurement or with any of the other common techniques that are used to assess fuel volatility or vapor—liquid equilibrium.

We have applied this metrology to gasolines, aviation fuels, rocket propellants, diesel fuels, and crude oils. Clearly, it is not always needed or desirable to apply all aspects of the advanced distillation curve metrology in every application. For highly finished fuels such as the low-sulfur petroleum-derived diesel fuels used today, for example, it is usually unnecessary to assess corrosivity as a function of distillate fraction. In the work reported here, we have applied the advanced distillation curve technique to commercially available samples of B20 and B100, currently being marketed as biodiesel fuel.

Experimental Section

The petroleum-derived diesel fuel used in this work was obtained from a commercial source and was stored at 7 °C to



Figure 3. Examples of distillation curves measured for B100 without the use of the inert gas blanket. One can see that the repeatability is very poor, due to oxidative decomposition of the fluid.



Figure 4. Examples of three distillation curves of B100 diesel fuel measured with an inert gas blanket. Note that the curves are essentially overlaid, except for the very late volume fractions in which thermocouple lift-out signals the end of a measurement.

preserve any volatile components. No phase separation was observed as a result of this storage procedure. The fuel 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. This fluid was used without any purification or modification. The composition was studied with a gas chromatographic method (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1 μ m, temperature program from 90 to 275 °C, 9 °C/min) using flame ionization detection and mass spectrometric detection. The samples of B20 and B100 were also obtained from a commercial source, although a different source from which the petroleum-derived diesel fuel was obtained. They were treated and analyzed in the same way as the petroleum-derived diesel fuel.

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane having a thickness of 1 μ m, temperature program from 50 to 170 °C, 5 °C/min) using flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99.9%, and the fluid was used without further purification.

The method and apparatus for the distillation curve measurement has been reviewed in a number of sources, so additional general description will not be provided here.^{13–19,22–25} Rather, we will focus only on the modifications that were required for the study of biodiesel fuel. Early in this work, we found that the oxidative instability of B100 made the distillation curve measurement nearly impossible. As will be discussed below, we were unable to obtain sufficient reproducibility with the original advanced distillation curve apparatus. To decrease oxidative instability, a provision for an inert gas blanket was added to the apparatus. This modification is shown in Figure 1. A length of stainless steel capillary tubing is located in the centering adapter along with the thermocouple leads. This line extends to the bottom of the distillation flask and serves to transport an inert gas purge into the fluid. Nitrogen was used as the inert gas in early experiments, but the higher molecular mass of argon made this gas a more favorable choice for our measurements. Initially, a flow rate of approximately 10 mL/ min is applied through this tube. Flow is begun for approximately 10 min before heat is applied to the distillation flask by the model predictive temperature controller. The purpose of this premeasurement flow is to flush dissolved oxygen from the sample fluid and to clear the measurement head space of oxygen. Once heating was begun, the tube was lifted out of the fluid to blanket the head space, and the flow rate decreased to a few mL/min. This procedure was successful in retarding oxidative decomposition of the biodiesel fuel samples so that a measurement of the distillation curve was possible with our accustomed precision. The other features of the apparatus, including the level-stabilized receiver, the sampling adapter, and the vortex tube chilling of the condenser, are unchanged from previous reports.

The required fluid for the distillation curve measurement (in each case 200 mL) was placed into the boiling flask with a 200



Figure 5. (a) Chromatograms of distillate fractions of B20, presented in arbitrary units of intensity, of the 0.025, 10, 50, and 80% volume fractions. The five main biodiesel FAME peaks are labeled as follows: 1, methyl palmitate; 2, methyl stereate; 3, methyl oleate; 4, methyl linoleate; and 5, methyl linolenate. (b) Chromatograms of distillate fractions of B100, presented in arbitrary units of intensity, of the 0.025, 10, 50, and 80% volume fractions. The five main biodiesel FAME peaks are labeled as follows: 1, methyl palmitate; 2, methyl stereate; 3, methyl oleate; 4, methyl linoleate; and 5, methyl linolenate.



Figure 6. (a)Results of a quantitative determination of FAME mass fractions in the distillate fractions of B20, corresponding to the chromatograms of Figure 5a. (b) The results of a quantitative determination of FAME mass fractions in the distillate fractions of B100, corresponding to the chromatograms of Figure 5b.

mL volumetric pipet. 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 take-off position in the distillation head. Enclosure heating was then commenced with a four-step temperature program based upon a previously measured distillation curve. Volume measurements were made in the level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock. In the course of this work, we performed between four and six complete distillation curve measurements for each of the fluid samples.

Since the measurements of the distillation curves were performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were corrected for what should be obtained at standard atmospheric pressure. This was done with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000109.^{14,26,27} This value corresponds to a carbon chain of 12. In the chemical

analysis of the diesel fuel samples (see above), as well as in previous work on diesel fuel, it was found that *n*-dodecane can indeed represent the fluid as a very rough surrogate. With biodiesel, we observe an increase in the concentration of polar oleates and similar compounds. These can be expected to slightly lower the constant term. Because the oleate group is typically one moiety on a long hydrocarbon chain (that may contain 16-18 carbons), the change that may potentially be introduced into this constant term will be negligible.

The magnitude of the correction is, of course, dependent upon 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. The actual measured temperatures are easily recovered from the Sydney Young equation at each measured atmospheric pressure. This correction causes a negative bias of as much as 2 °C in the results to which it is applied. For this reason, we provide the actual atmospheric pressure at which each measurement was done, so that the raw, uncorrected temperatures may be recovered. The adjusted values are included so that the reader may compare the T_h measurements with historical data, which always incorporate this adjustment. Other aspects of the experimental procedure that are specific to the analysis of the composition-channel results will be presented in the next section.

Results and Discussion

Initial Boiling Temperatures. During the initial heating of each sample in the distillation flask, the behavior of the fluid was observed. Direct observation through the flask window or through the illuminated bore scope typically allows measurement of the onset of boiling for each of the mixtures. During the early stages of a measurement, the first bubbles will appear intermittently, and this action will quell if the stirrer is stopped momentarily. Sustained vapor bubbling is then observed. In the context of the advanced distillation curve measurement, sustained bubbling is also somewhat intermittent, but it is observable even when the stirrer is momentarily stopped. Finally, the temperature at which the vapor is first observed to rise into the distillation head is observed. This is termed the vapor rise temperature. These observations are important because they are the initial boiling temperatures (IBTs) of each fluid. Moreover, these temperatures can be modeled theoretically, for example, with an equation of state.^{28,29}

The dark red dye present in the petroleum diesel fuel sample that we used prevented a measurement of the onset of bubbling and the sustained bubbling temperatures in the mixtures studied in this work. Fortunately, the vapor-rising temperature could still be determined. The measurements, presented as averages of three separate determinations, are provided in Table 2. The uncertainty in the vapor-rise temperature is approximately 1 °C. As we have noted for all other fluids measured with the advanced approach, the IBT values we have presented are very different from those that would be obtained with the classical method, which are systematically in error. We note that the petroleum-derived diesel fuel has the lowest vapor-rise temperature, and as the percentage of bioderived diesel fuel increases, the vapor-rise temperature increases. The initial boiling temperature of B20 is only a few degrees higher than that of a pure petroleum-derived diesel fuel. This is because B20 is dominated by the light constituents of the petroleumderived diesel fuel. The B100 shows a much higher initial boiling temperature, with an increase in excess of 100 °C when compared to petroleum-derived diesel fuel. As we will see below, these initial temperatures are consistent with the behavior seen on the distillation curves.

Distillation Curves. Representative distillation curve data for the samples of petroleum-derived diesel fuel and the samples of commercially sold B20 and B100, presented in both T_k (measured directly in the fluid) and T_h (measured in the distillation head) are provided in Table 3. The T_k data are true thermodynamic state points, while the T_h data allow comparison with earlier measurements. In this table, the estimated uncertainty (with a coverage factor k = 2) in the temperatures is 0.5 °C. We note that the experimental uncertainty of T_k is always somewhat lower than that of T_h , but as a conservative position, we use the higher value for both temperatures. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results, for example, with an equation of state. The data in Table 3 show that T_k leads T_h by several degrees for all distillate volume fractions.

A graphical depiction of the representative distillation curve data for petroleum-derived diesel fuel and B20 and B100 biodiesel fuels is provided in Figure 2. As mentioned in the Experimental Section, oxidative instability of biodiesel fuel is a well-known problem not only with handling of the product in commerce but also in our measurements. Before we modified the apparatus to include an inert gas blanket, the reproducibility of the distillation curve data was unacceptable. As an example, in Figure 3 we present four replicate distillation curves for B100 measured without the blanket. When the inert gas purge was added to the metrology, we were able to measure distillation curves with our accustomed repeatability cited earlier. Three such curves are presented in Figure 4. Note that the three curves are essentially overlaid, except for the very late volume fractions in which thermocouple lift-out signals the end of a measurement.

With reference to Figure 2, we note that the distillation curve for petroleum-derived diesel fuel is a subtle sigmoid or growth curve. This is the same shape we have noted for many complex hydrocarbon mixtures such as aviation fuels and kerosenes. The curve for B20 is displaced to higher temperatures, and it is also more linear, with little discernible sigmoidal features. The displacement to higher temperatures is caused by the addition of the heavier FAME components, which raise the overall boiling point of the fluids across the distillation curve. The linearization of the curve is the result of the mixture becoming less complex in terms of the overall number of components. The FAME fraction only consists of five components.

The curve for B100 is very different from that of B20 or petroleum-derived diesel fuel, originating at a higher temperature and exhibiting a much more gentle slope. The fact that B100 has very few components is reflected in this gentle slope. We also note that the distillation curves extend to higher temperatures than are normally recommended when applying atmospheric pressure metrology. Typically, such measurements do not exceed 310 °C. As we will see below, the composition channel of the advanced approach allows us to explicitly monitor the distillate composition and, therefore, assess any possible thermal decomposition. The major significance of these curves relative to those obtained by the classical method is that the temperature–volume points are thermodynamic state points (related to the fluid composition at each point) that can be modeled with an equation of state.

Composition-Channel Information. The composition channel of the advanced distillation curve metrology allows us to sample distillate cuts on the fly and relate the derived composition information to the thermodynamic information of the temperature volume pairs. This is significant in terms of the phase diagram of a complex fluid, since the distillation curve provides the bubble-point temperatures and the dew-point compositions. This allows the information obtained from the distillation curve to be used in equation-of-state development for these complex fluids. In earlier work, we have demonstrated how this composition channel can be used with hydrocarbon moiety speciation, such as that embodied in the ASTM 2789 test, in which the fractions of paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes are determined, as a function of distillate fraction.³⁰ We have also demonstrated how one can apply universal detection techniques such as infrared spectrophotometry and specific detection

techniques such as sulfur chemiluminescence.³¹ Moreover, we have shown how the sulfur detection can be augmented with corrosivity determination using the copper strip corrosion test.²²

In this paper, we extend these qualitative or semiquantitative approaches to achieve a quantitative determination of the FAME fraction of biodiesel fuel as a function of distillate fraction. This is done by gas chromatography with flame ionization detection. In parts a and b of Figure 5, we present chromatograms of the 0.025, 10, 50, and 80% volume fractions of B20 and B100, respectively. First considering the chromatograms of B20 in Figure 5a, we note that there is a large hydrocarbon cluster (typical for a diesel fuel) in each fraction, but the FAME fraction is present in all the chromatograms, even in the first drop of distillate represented by the 0.025% volume fraction. The FAME fractions can be seen at retention times from 12 to 17 min, and this fraction is clearly seen to increase with later distillate fractions. Examination of the B100 chromatograms in Figure 5b shows the presence of some petroleum diesel fuel in the 0.025% distillate fraction, as well as a large FAME fraction. This petroleum content is not seen beyond this very early distillate fraction and is very likely due to residual petroleum diesel fuel left in the storage tank of the commercial supplier. Later fractions of B100 show only the FAME fraction, summarized in Table 1. For convenience, the identity of each of the FAMEs is labeled in parts a and b of Figure 5.

Since each of the FAMEs are commercially available as analytical standards, it is possible to quantitatively determine the FAME distribution in each distillate fraction. To accomplish this, 7 μ L of each fraction were drawn during a distillation curve measurement and placed in 1 mL of n-hexane as a solvent. These samples were analyzed by GC-FID as discussed above 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 FAMEs that compose biodiesel fuel. Samples were injected via syringe into a split/ splitless injector set with a 100:1 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. External standardization was done with calibration standards prepared from pure FAMEs in *n*-hexane that were analyzed in the same way as the distillate samples.

The results of these analyses are presented in parts a and b of Figure 6 as mass fractions of FAME, plotted as a function of distillate volume fraction. For B20, in which there is always a significant petroleum hydrocarbon content, we note that the mass fraction of each FAME increases with distillate fraction and, thereby, distillation temperature. The increase is especially pronounced between distillate volume fractions of 50 and 80%. We note that the FAME fraction, even at higher temperatures, behaves as a solute in the heavier constituents of petroleum diesel fuel, acting as a solvent. The results for B100 are very different. Here, where the FAME fraction makes up the entirety of the fluid, the mass fractions of the FAMEs are larger. Moreover, we note that the two lightest FAMEs, methyl palmitate and methyl linoleate, actually become depleted at the higher temperatures. The mass fractions of these two FAMEs decrease with distillate volume fraction, after an initial peak in concentration. Similar thermal discrimination can occur in heat exchangers or flash tanks in processing. This composition change, not seen in B20, will have consequences for engine performance and optimization. In addition, this observation will be critical in the development of an equation of state for B100.

Conclusions

In this paper, we have applied the advanced distillation curve method to the analysis of commercial biodiesel fuels, B20 and B100, and have compared the results with those of a typical petroleum-derived diesel fuel. Since the temperature results are thermodynamic state points, these data are amenable to the development of equations of state for biodiesel fuel. The composition channel of the advanced distillation curve provided additional insight, especially highlighting the different behavior between B20 and B100. We found that thermal discrimination occurs with the FAME fraction in B100 but not in B20 where the FAME fraction is present in a background of petroleumderived components. Before a successful distillation curve measurement could be made, we had to modify the apparatus to include an inert gas blanket. This modification will allow future measurements of other fluids that are oxidatively unstable.

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