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Application of the Advanced Distillation Curve Method to the Comparison of Diesel Fuel Oxygenates: 2,5,7,10-Tetraoxaundecane (TOU), 2,4,7,9-Tetraoxadecane (TOD), and Ethanol/Fatty Acid Methyl Ester (FAME) Mixtures*

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Abstract

Although they are amongst the most efficient engine types, compression-ignition engines have difficulties achieving acceptable particulate emission and NO_x formation. Indeed, catalytic after-treatment of diesel exhaust has become common and current efforts to reformulate diesel fuels have concentrated on the incorporation of oxygenates into the fuel. One of the best ways to characterize changes to a fuel upon the addition of oxygenates is to examine the volatility of the fuel mixture. In this paper, we present the volatility, as measured by the advanced distillation curve method, of a prototype diesel fuel with novel diesel fuel oxygenates: 2,5,7,10-tetraoxaundecane (TOU), 2,4,7,9-tetraoxadecane (TOD), and ethanol/fatty acid methyl ester (FAME) mixtures. We present the results for the initial boiling behavior, the distillation curve temperatures, and track the oxygenates throughout the distillations. These diesel fuel blends have several interesting thermodynamic properties that have not been seen in our previous oxygenate studies. Ethanol reduces the temperatures observed early in the distillation (near ethanol's boiling temperature). After these early distillation points (once the ethanol has distilled out), B100 has the greatest impact on the remaining distillation curve and shifts the curve to higher temperatures than what is seen for diesel fuel/ethanol blends. In fact, for the 15% B100 mixture most of the distillation curve reaches temperatures higher than those seen diesel fuel alone. In addition, blends with TOU and TOD also exhibited uncommon characteristics. These additives are unusual because they distill over most the distillation curve (up to 70%). The effects of this can be seen both in histograms of oxygenate concentration in the distillate cuts and in the distillation curves. Our purpose for studying these oxygenate blends is consistent with our vision for replacing fit-for-purpose properties with fundamental properties to enable the development of equations of state that can describe the thermodynamic properties of complex mixtures, with specific attention paid to additives.

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Supporting Information:

Chromatograms of distillate fractions

Hydrocarbon classification of diesel fuel compared to diesel fuel containing 30% TOD

INTRODUCTION

Compression-ignition (CI) engines have been improved incrementally in the last few decades, with attention paid to combustion chambers, the design of fuel systems, and engine control, making CI engines one of the most efficient and common engine types. There have also been major changes in the finished fuels used in CI engines, such as the appearance of ultra-low sulfur diesel (ULSD) fuels. Nevertheless, there is still a need to decrease environmental emissions from diesel engines and fuels.^{1–8} While very efficient, diesel engines have problems reaching acceptably low particulate emission and NO_x formation. Catalytic after-treatment of diesel exhaust has become routine (especially on large power plants) and current efforts to reformulate diesel fuels have concentrated on the incorporation of oxygenates into the fuel.^{9–13}

The addition of oxygenates to diesel fuel has been demonstrated to decrease particulate, SO₂, and NO_x emissions, to decrease catalyst poisoning at the after-treatment devices, to increase the capacity to recirculate exhaust gases, and to decrease in-cylinder radiative heat transfer, which improves engine performance.^{9–12, 14–29} The addition of oxygenates is also applicable to fuels from alternative feed-stocks and could allow more refined after-treatment technologies. Numerous types of compounds have been examined as possible oxygenates for diesel fuel: alcohols, lactones, ethers, glycol esters, ketones, glycol ethers, and carbonates.^{15, 17, 30–37} We have published several extensive studies on some of the most likely candidates from these categories.^{22, 35, 38–43} Several of the additives described in these publications may be appropriate for the reformulation of diesel fuels, however, it remains necessary to identify novel oxygenating compounds with properties appropriate for fuel reformulation.

Potential oxygenating compounds must be miscible with diesel fuel and should not have azeotropic properties with the base diesel fuel.^{44–46} Fuels containing azeotropes may be undesirable due to an increase in vapor pressure that can lead to hot fuel-handling problem.⁴⁶ This can make the selection of oxygenating additives a challenge. In addition to potential oxygenating compounds being miscible and non-azeotropic with the base diesel fuel, they should also be economical and environmentally sustainable, however, these later two qualifiers are not the goal of this work. Ethanol is a readily available and common oxygenate but has some unfavorable properties, particularly its polarity. In the work presented here, we use the addition of fatty acid methyl esters (FAMES) to bridge the polarity gap between ethanol and diesel fuel. The idea of using different types of biodiesel as possible additives to improve the properties of diesel and ethanol fuel mixtures is not new and these mixtures appear to be better candidates for oxygenation than ethanol alone.^{47–49} In addition, we investigate the use of 2,5,7,10-tetraoxaundecane (TOU) and 2,4,7,9-tetraoxadecane (TOD) as oxygenating compounds. These relatively new compounds are being considered as potential oxygenate candidates because their hydrocarbon-like backbones lead to increased miscibility with diesel fuel, and they have the potential to contribute to the energy content of the fuel without adversely affecting the ignition properties.

In order to evaluate a potential oxygenating compound, we have to consider the influence of the additive on the working and thermophysical properties of the subsequent fuel blends. Perhaps the most significant and instructive parameter, which can be measured for all multiple component fluid blend is the distillation curve. Since the working parameters of multi-component fuels relate to the distillation curve, the distillation curve can be used to help design fuels for efficiency,^{50 51-54} and to design fuels with reduced exhaust emissions.⁵⁵ In our previous publications, we have outlined a method and apparatus for the advanced distillation curve (ADC) measurement that is particularly relevant to the determination of the thermophysical properties of complex fuels.⁵⁶⁻⁶² Our goal is to supplant fit-for-purpose measurements with fundamental property measurements and to allow the development of equations of state that can describe the thermodynamic properties of complex fluid mixtures, with particular attention paid to additives.

EXPERIMENTAL

Materials

The diesel fuel used as a base in this work was acquired from a commercial source. Diesel fuel acquired from this source has been used previously and serves as a prototype fluid.³⁸⁻⁴¹ The fuel used was refined locally from petroleum of the Denver-Julesburg field and stored at room temperature. No phase separation was observed as a result of the storage conditions. The fuel was a winter-grade, low-wax, ultra-low-sulfur diesel fuel that incorporated a red dye (signifying off-road use), and this diesel fuel was used without any purification or modification. In addition, soy-based biodiesel fuel (B100) was used as our source of FAMES. As additional information, the chromatograms of the distillate fractions of pure B100 may be seen in Figure S1. The composition of these fuels was examined using a gas chromatographic (GC) method (30 m capillary column of 5 % phenyl-95 %-dimethyl polysiloxane having a thickness of 1 μm , temperature program from 50 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$, 15 $^{\circ}\text{C}$ per minute, and a 100:1 split ratio) with flame ionization detection (FID) and mass spectrometric detection (MS). The injector temperature was set to 325 $^{\circ}\text{C}$ and a constant head pressure of 55.2 kPa (8 psig) was used. Mass spectra were collected for each peak from 15 to 550 relative molecular mass (RMM) units. Peaks were identified as usual “with guidance from the NIST/EPA/NIH Mass Spectral Database, and also on the basis of retention indices.”^{63, 64} These analyses were unremarkable in that the typical patterns of fuels were observed.

The oxygenating compounds (ethanol, TOU, and TOD) and acetone (solvent) used in this work were obtained as pure fluids from a commercial source. Acetone and ethanol were reagent-grade fluids with reported purities of 98 – 99 % (mass/mass). The purities of TOU and TOD were determined by ^1H nuclear magnetic resonance (NMR) spectroscopy. Samples for ^1H NMR spectroscopy were prepared by mixing approximately 15 mg of TOU or TOD in 1 g of CDCl_3 . A commercial NMR spectrometer with a cryoprobe, operated at 600.13 MHz, was used to acquire these spectra. The temperature was set at 25 $^{\circ}\text{C}$ for the NMR measurements. A quantitative ^1H NMR spectra were acquired using a 30 $^{\circ}$ flip angle and a long interpulse delay (5 s acquisition time, 8 s relaxation delay). A sweep width of 12019 Hz (-4 ppm to 16 ppm) was used. After 128 scans the spectra had an average signal-to-noise

ratio of 5×10^5 . The ^1H NMR purity of these samples (98.38 ± 0.02 % for TOU and 98.43 ± 0.02 % for TOD) is based on the mole percent of hydrogen atoms.

Some essential property information about the oxygenates is given in the supplementary information, Table S1. These fluids were analyzed with the same chromatographic method described above for the neat fuels and were not purified further. Mixtures of ethanol and B100 were prepared as stock solutions with the following volume ratios: 5 % ethanol/15 % B100, 10 % ethanol/10 % B100, 15 % ethanol/5 % B100 in commercial prototype diesel fuel. Mixtures of diesel fuel and either TOU or TOD were formulated as stock solutions of 10 %, 20 %, and 30 % (vol/vol) oxygenate in fuel. Making all of our distillation measurements on the same batch of blends ensures uniformity of blend, and thus, repeatability of measurements. Fuels containing 30 % of an oxygenating compound might not be useful for most real-world situations, and the performance of a CI engine using such high oxygenate blends would probably be lower overall.^{19, 20, 65} Occasionally though, high oxygenate fuel blends have been shown to be useful in diesel fuel.³² The oxygenate concentrations of the stock solutions were prepared to encompass a large range of composition in order to be useful for modeling the results with equations of state. Similarly, we used high-purity oxygenate additives instead of the technical-grade fluids that might be used in industry. The examination of a specific oxygenate concentration does not suggest that diesel fuel blends with very high oxygenate concentrations or high purity oxygenates are necessarily useful as formulations for final reformulated diesel fuels. Such philosophy has been previously applied and found to be useful.^{22, 35, 36, 38, 39, 41–43, 66}

Advanced Distillation Curve Measurements and Sampling

The ADC apparatus description and procedure have been provided in previous publications;^{56–62, 67} therefore, only a brief summary is given as follows: “For each measurement, 200 mL of diesel fuel or diesel fuel blend with oxygenate was placed in a boiling flask at atmospheric pressure. The thermocouples were then inserted into the proper locations to monitor (a) the kettle temperature (T_k), the temperature in the fluid, and (b) the head temperature (T_h) the temperature of the vapor at the bottom of the takeoff position in the distillation head. In terms of significance, T_k is a thermodynamically consistent bubble point temperature, while T_h approximates what might be obtained from the classical distillation measurement procedure. Enclosure heating was then commenced with a model-predictive temperature controller. The heating profile was designed to be of similar shape to that of the distillation curve, but it leads the distillation curve by approximately 60 °C. Volume measurements were made in a calibrated level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock.”^{56–62, 67, 68} In previous work,^{69, 70} sparge gas has been used to prevent FAME components from undergoing oxidative-degradation but was not deemed necessary here due to the relatively low concentration of B100, and, indeed, the distillation curve results were highly repeatable.

Because the distillation curves were recorded at ambient atmospheric pressure (measured before and after the distillation with an electronic barometer that had been calibrated with a fixed cistern mercury manometer with an uncertainty of 0.15 Pa)⁷¹, T_k and T_h were modified to what would be expected at standard atmospheric pressure (1 atm = 101.325 kPa). This

adjustment was done by applying the modified Sydney Young equation, where the constant term applied had a value of 0.000109 (consistent with dodecane).^{72–74} It is important to mention here that the Sydney Young constant was intended to be used with hydrocarbon fluids and might not be the most appropriate value with our biodiesel mixtures used herein. Nonetheless, the adjustment serves the purpose of allowing for these data to be compared with historical data from our group, and approximates the temperatures that would be observed at atmospheric pressure.^{72–74} In our earlier publications on diesel fuel, we determined that *n*-dodecane may be used to represent our prototype diesel fuel as a loose surrogate.^{72–74} The amount of the variation between the temperatures is based on the difference between the measured pressure and standard atmospheric pressure.^{61, 62} The laboratory space in which the distillation curves were recorded is located at an elevation of approximately 1650 m above sea level, this results in a characteristic temperature adjustment of approximately 8 °C. The average temperatures can be quickly retrieved from the modified Sydney Young equation at each atmospheric pressure.

The composition channel of ADC can provide further information not available by the examination of the distillation curves alone. In this work, we sampled and examined individual distillate fractions as they flowed out of the condenser. We collected the distillate fractions by extracting approximately 7 µL of the distillate and diluting this distillate sample into a pre-measured mass (~0.8 g) of acetone as a solvent. Acetone was selected as a solvent because it has a short retention time and does not overlap with the GC peaks of the distillate fractions. Each fraction was studied by GC with FID and MS detection using the same column and oven temperature program as described above for the neat fuels. Calibration for the FID was performed using both *n*-octane and the oxygenate being studied in order to quantify the compositional mole fractions in the distillate cuts. In addition, the hydrocarbon classification for 30% TOU and diesel fuel alone may be seen in Figure S2.

RESULTS AND DISCUSSION

Initial Boiling Temperatures

The boiling behavior of the fuel and oxygenate blends was carefully observed during the initial heating of each fuel in the distillation flask. We were able to observe the liquid fuel blend through the flask window, which permitted us to record the temperature of the onset of boiling for the oxygenate/fuel blends (measured with T_k). For each sample, the initial boiling behavior, the onset of bubbling, the temperature at which boiling is continuous, and the temperature at which the vapor rises into the distillation head was recorded. In previous work,⁷⁵ it has been demonstrated that the vapor rise temperature represents the initial boiling temperature (IBT) (which is an approximation of the bubble point temperature at ambient pressure) of the fuel oxygenate blend. This distillation point is noteworthy for any given fluid because this is the singular point when the liquid composition is known (because the initial composition of the fluid is known and none of the chemical compounds have been removed by distillation) and, in addition, it is possible to model the IBT with an equation of state. Due to the significance of this point we have made this symbol a hash mark in distillation curves shown in Figures 1, 2, and 3. Observation of the initial boiling point behavior with the prototype off-road diesel fuel is made slightly challenging by the inclusion

of the red dye mentioned previously. Therefore, we give only the sustained boiling and vapor rise temperatures in Table 1. Vapor-rise also corresponds to a rapid increase in T_h and is thus significantly less subjective to observe. Therefore, this measurement has less uncertainty associated with it than the onset of bubbling or sustained boiling. Past experiments with simple mixtures, including gravimetrically prepared *n*-alkane standard mixtures, allow us to provide an uncertainty in the onset of the bubbling and sustained boiling temperature that is roughly 1 °C. The uncertainty in the vapor rise temperature is 0.5 °C.

The most significant decrease to IBT was seen with blends of the ethanol/B100 and diesel fuel. The IBT was reduced by 135 °C at 15 % ethanol (v/v), this decrease resulted in an IBT of only 83 °C. Changes to the IBT with the addition of TOU and TOD, are smaller but still significant with TOD having a larger effect than TOU due to the lower boiling point of TOD. This is analogous to what we recorded for linear and cyclic oxygenates presented in previous work.^{38–41} We also note that for TOU and TOD the most significant IBT displacement is associated with the addition of the first 10 % (v/v) of the oxygenating blend; the further IBT displacement associated with the 20 % and 30 % blends is not as large as the displacement associated with 10% blends from the base diesel fuel. Similar displacement was also seen with increasing concentrations of ethanol at 5 %, 10 %, and 15 % (v/v). These results are seen because all the oxygenating additives used have boiling temperatures lower than the IBT of the base diesel fuel. Therefore, early distillate volume fractions have higher concentrations of the oxygenate. As the oxygenate concentration in these early fractions increases, the temperature asymptotically merges with the boiling temperature of the oxygenate.

Distillation Curves

Throughout our measurement of the distillation curves, both T_k and T_h were recorded (the kettle and head temperatures, respectively). In addition, we noted the ambient atmospheric pressure in order to adjust the temperatures readings to the value that should be recorded at sea level atmospheric pressure by use of the modified Sydney Young equation, as discussed in detail earlier. The given uncertainty in the recorded temperature, T_k , is approximately 0.5 °C. The uncertainty in the volume measurement of the distillate volume fraction is 0.05 mL for each distillate cut. The average recorded atmospheric pressure as well as both T_k and T_h are given as a function of the distillate volume fraction for each oxygenate blend in Table 2. In addition, Figures 1–3 also represent this data graphically. In the plots, the IBT is shown as a hatch mark on the temperature axis. The magnitude of the difference (temperatures and shape) between the prototype diesel fuel distillation curve and the oxygenate blend can be correlated to the oxygenates' normal boiling temperature. As is the case with all mixtures containing polar or associating components, intermolecular interactions are at the root of perturbations in properties. The differences are the most significant in the blends where with the additive has the lowest boiling temperature (ethanol), and becomes less significant with the oxygenate having a boiling temperature closest to that of the diesel fuel (TOU). These results are also similar to what we have reported for the oxygenates presented in previous work.^{38–41}

As we noted in previous work with ethanol,^{38–41} the addition of 5 % (v/v) ethanol (in the ethanol/B100 blends) to the base diesel fuel gives a distillation curve that is sigmoidal over the whole curve, notwithstanding the large displacement of the onset of boiling to a lower temperature. A rather different shape is observed for the 10 % and 15% (v/v) mixtures, with an initial flattening (also at significantly lower temperatures) of the curves in response to the higher concentration of ethanol. Following this flattening, the curve returns to a sigmoidal shape. (These trends are apparent but less dramatic with the oxygenates TOU and TOD because of their higher boiling temperatures.) The distillation curves of the diesel fuel containing the ethanol/B100 converge after 0.20 distillate volume fraction above the distillation curve for diesel fuel alone. Such displacement of the distillation curves is to be expected because the distillation curve for B100 has been shown to be significantly higher than the distillation curve of diesel fuel alone.^{69, 70} This behavior is interesting and demonstrates the effect on the distillation curve of the addition of two additives with significantly different boiling temperatures. Ethanol off-sets the distillation curve to lower temperatures and B100 off-sets the distillation curve to higher temperatures. Both of these two competing additives have a significant impact on the distillation curve. This is particularly evident in the regions close to each additives boiling temperature. Again, the initial depression in the distillation curve is consistent with what has been seen previously when ethanol is added to diesel. Since the mixtures here also contain biodiesel, a much earlier convergence toward higher temperatures is observed. Lastly, we would like to comment that an inspection of the temperatures T_k and T_h revealed no convergence; therefore, there is no indication of azeotropy in these mixtures.

One noteworthy feature of the distillation curves presented here is that even following the complete vaporization of the oxygenates from the sample being distilled, the vaporization temperatures did not completely merge with the vaporization temperatures of the base diesel fuel. This trend has been noted in many of our earlier publications and it is particularly evident in mixtures where the oxygenate concentration used is relatively high.^{38–41} This is an effect of the vapor liquid equilibrium that is established between the constituents of the fuel blends when one of the constituents (in this case the oxygenate) is more volatile than other constituents. The energy being applied is used to vaporize the most volatile component early in the distillation. Hydrocarbon components with a lower volatility that would have started to vaporize early in the distillation are forced to remain in their kettle liquid and the vaporization is postponed. Therefore, the vaporization temperatures from blends with increasing concentrations of volatile oxygenates are seen to be consistently lower than those of the base diesel fuel, even though the most volatile constituents (such as ethanol) have been distilled out of the kettle liquid.

Composition Channel Information

As discussed in the Experimental Section, the composition channel of the ADC method permits one to collect and study specific fractions as they come out of the condenser and provides a superior understanding of the properties of the fuel blends. Following the analytical procedure described above, 7 μ L aliquots were placed in autosampler vials with a known mass of acetone. Compositional analyses of the distillate cuts were performed by both GC-MS and GC-FID. The external standard method was used for calibration using

eight solutions of known concentrations (all standards were prepared gravimetrically with four containing the oxygenate of interest and four containing octane). All standards were also prepared in acetone (chosen because it will not interfere with the components in diesel fuel). The chromatographic conditions used were the same as discussed above and baseline resolution was achieved for each oxygenate fluid. Figures 4–6 gives the measured concentration of the oxygenates as histograms and the uncertainty bars in these figures show the propagated uncertainties of the sample and standard measurements and incorporate a coverage factor $k = 2$. In addition to these figures, Table S2 of the Supporting Information provides the mass percent of the oxygenate as a function of the distillate cut. Even though not explicitly measured, we effectively recovered all of the additive blends in the distillate or residue.

Ethanol, the oxygenate with the lowest boiling temperature in this study, was only detectable in the first drop and 0.10 distillate volume fraction. This agrees with the early substantial displacement seen in the distillation curves with ethanol/B100 oxygenate blends. Methyl linoleate (boiling point 192 °C), a major component of B100, was also tracked during the distillation. Methyl linoleate was seen in the distillate cuts starting at the 0.20 distillate volume fraction and continued to be present throughout the rest of the distillation and into the residue. The highest concentration of methyl linoleate was in the 0.90 distillate volume fraction. TOU and TOD were present in early distillate cuts (up to 0.70 distillate volume fraction for TOU with none being observed in the later distillate cuts) with the highest concentrations being around the 0.10 and 0.20 distillate volume fractions. This is also in agreement with the distillation curves. The largest displacements with the addition of TOU and TOD were seen in the first half of the distillation curve. It is apparent when comparing the distillation curves to the histograms that the largest displacements to the distillation curve corresponds closely to changes in the composition channel information. For diesel oxygenates the largest displacement from the diesel fuel distillation curves are seen to correspond to a high concentration of oxygenate in the distillate volume fractions.

CONCLUSIONS

In the work presented here, the ADC method was used to characterize the vapor-liquid equilibrium of blends of TOU, TOD, and ethanol/FAME blends with a prototype diesel fuel. Such mixtures with polar and moderately polar compounds have proven to be challenging in the past. Therefore, measurements that explicitly address the properties of these mixtures (not simply the properties of the pure components) are exceptionally important and informative. These blends have a number of interesting thermodynamic properties that have not been seen in our previous oxygenate studies. As discussed above, we were able to examine the distillation curves with blends of diesel fuel and ethanol/B100, which have competing effects on the distillation curve. Ethanol, as discussed above, reduces the temperatures observed early in the distillation (near ethanol's boiling temperature). After these early distillation points (once the ethanol has distilled out), B100 has the greatest impact on the remaining distillation curve and shifts the curve to higher temperatures than what is seen for diesel fuel/ethanol blends. In fact, for the 15% B100 mixture the majority of the distillation curve reaches temperatures higher than those seen diesel fuel alone. In addition, blends with TOU and TOD also exhibited uncommon characteristics. These

additives are unusual because they distill over the majority of the distillation curve (up to 70%). The effects of this can be seen both in histograms of oxygenate concentration in the distillate cuts and in the distillation curves. The greatest deviations from diesel fuel alone in the distillation curves are seen at around the 0.40 distillate volume fraction and slightly before that for the concentration of oxygenate in the distillate cut due to the well-known lag between composition and distillation temperature. It would be very interesting to use distillation curves to examine the effect of molecular interactions, however, we would first need to study this effect with surrogate mixtures with known molecular interaction behavior to draw useful conclusions. These measurements provide a comparison of uncommon oxygenate-blended samples allowing one to more fully grasp properties of fuel blends in general, which may in the future lend itself to the development of more efficient and clean combusting diesel fuels. In addition, the work given here can be used for the development of equations of state for diesel fuel blends.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

The distillation curves of diesel fuel mixtures with TOU. Here we present T_k , the temperature measured directly in the liquid phase. The tick marks on the y-axis represent the initial boiling point (IBT) of each mixture. The uncertainties are discussed in the text.

Figure 2.

The distillation curves of diesel fuel mixtures with TOD. Here we present T_k , the temperature measured directly in the liquid phase. The tick marks on the y-axis represent the initial boiling point (IBT) of each mixture. The uncertainties are discussed in the text.

Figure 3.

The distillation curves of diesel fuel mixtures with ethanol and B100. Here we present T_k , the temperature measured directly in the liquid phase. The tick marks on the y-axis represent the initial boiling point (IBT) of each mixture. The uncertainties are discussed in the text.

Figure 4.

Histogram plot showing the results of the analysis for TOU as a function of distillate volume fraction for the three diesel fuel starting mixtures (10 %, 20 %, and 30 %, vol/vol).

Figure 5.

Histogram plot showing the results of the analysis for TOD as a function of distillate volume fraction for the three diesel fuel starting mixtures (10 %, 20 %, and 30 %, vol/vol).

Figure 6.

Histogram plot showing the results of the analysis for diesel blends with ethanol and B100 as a function of distillate volume fraction for the three diesel fuel starting mixtures (5 % ethanol/15 % B100, 10 % ethanol/10 % B100, 15 % ethanol/5 % B100, vol/vol). The histogram plot for ethanol can be seen in (a), and the histogram plot for methyl linoleate (a major component of B100) can be seen in (b).

Table 1

A summary of the average boiling behavior of the diesel fuel with oxygenates studied in this work. The vapor rise temperature is that at which vapor is observed to rise into the distillation head, considered to be the initial boiling point (IBT) of the fluid (highlighted in bold print). These temperatures have been adjusted to 1 atmosphere with the modified Sydney Young equation; the average experimental atmospheric pressures are provided to allow recovery of the average measured temperatures. The uncertainties are discussed in the text.

Samples	Avg. Pressure (kPa)	Sustained (°C)	Vapor Rise (°C)
diesel fuel	82.9	211.2	216.2
10 % TOU	83.2	180.8	206.0
20 % TOU	83.0	175.1	203.8
30 % TOU	82.7	166.9	200.5
10 % TOD	83.3	193.6	199.8
20 % TOD	83.7	189.5	192.1
30 % TOD	84.0	184.0	186.4
5 % ethanol/15 % B100	83.3	82.9	95.4
10 % ethanol/10 % B100	83.4	77.4	85.9
15 % ethanol/5 % B100	83.5	78.1	83.4

Table 2

Representative distillation curve data (given as the average of three distillation curves) for the diesel fuel with novel oxygenates. The uncertainties are discussed in the text. These temperatures have been adjusted to 1 atm with the modified Sydney Young equation; the average experimental atmospheric pressures are provided to allow recovery of the actual average measured temperatures.

	diesel fuel 83.5 kPa		diesel fuel + 10 % TOU (vol/vol) 83.2 kPa		diesel fuel + 20 % TOU (vol/vol) 83.0 kPa		diesel fuel + 30 % TOU (vol/vol) 82.7 kPa		diesel fuel + 10 % TOD (vol/vol) kPa		diesel fuel + 20 % TOD (vol/vol) kPa		diesel fuel + 30 % TOD (vol/vol) kPa		5 % ethanol/15 % B100 (vol/vol) 83.3 kPa		10 % ethanol/10 % B100 (vol/vol) 83.4 kPa		15 % ethanol/5 % B100 (vol/vol) 83.5 kPa	
	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)	T _k (°C)	T _h (°C)
DVF (%)																				
5	228.3	195.0	219.2	199.4	212.2	199.9	208.8	196.5	208.7	188.3	198.1	179.8	192.0	182.5	229.7	174.8	100.9	82.7	86.7	83.8
10	234.6	201.7	225.1	203.6	216.2	204.9	211.5	200.6	214.2	197.8	202.2	184.8	194.6	183.3	237.9	210.6	227.6	163.9	95.0	83.7
15	240.4	203.1	228.9	204.3	219.8	208.0	214.4	203.7	221.4	202.2	206.4	185.7	197.4	186.1	244.6	221.6	236.4	211.9	190.9	69.6
20	245.8	207.3	232.8	211.5	223.0	211.6	216.7	206.2	227.9	209.1	211.3	188.8	199.9	188.2	251.6	230.8	243.6	222.8	234.5	213.5
25	257.4	217.5	239.5	217.9	227.5	213.6	219.7	210.6	236.1	219.0	217.7	196.7	204.3	195.2	259.2	237.5	250.8	230.5	241.7	224.7
30	262.6	222.0	244.6	220.9	231.8	219.9	222.9	213.4	244.2	224.4	224.9	200.8	209.2	198.8	265.9	244.8	257.2	238.3	247.8	231.9
35	268.3	228.7	251.8	231.4	237.2	224.0	226.7	217.7	252.4	228.7	233.1	208.2	215.2	204.3	273.8	251.2	264.8	244.3	255.5	239.6
40	274.0	235.3	259.5	240.5	244.1	229.9	231.5	222.3	261.4	239.5	245.0	217.1	223.7	212.5	282.0	258.0	272.7	252.2	262.8	247.4
45	280.6	245.5	267.1	249.3	252.1	241.9	237.8	227.2	269.8	249.5	256.3	231.0	234.7	222.3	290.2	266.2	281.1	256.9	270.7	254.7
50	286.5	253.8	274.1	258.5	260.2	252.8	244.9	233.4	276.1	258.6	266.1	239.3	247.1	234.3	297.8	272.6	288.3	266.9	277.6	260.3
55	293.4	265.3	281.9	268.5	270.2	260.0	254.7	243.9	283.6	267.1	275.9	251.9	261.5	249.4	306.1	282.4	297.2	272.4	286.0	267.9
60	300.3	269.1	289.6	278.6	280.9	270.1	266.7	253.6	291.0	277.0	284.5	259.7	274.5	264.9	314.1	292.8	305.4	282.1	294.7	275.4
65	306.7	279.2	296.8	286.5	288.7	276.6	279.1	264.1	297.9	281.1	292.8	270.5	283.9	274.8	321.1	298.3	313.3	289.0	302.4	282.5
70	314.2	289.1	304.7	297.0	298.6	289.6	293.0	280.7	306.0	286.9	301.6	281.1	294.6	282.2	328.8	307.1	322.3	298.7	311.7	293.2
75	321.8	288.6	311.1	303.7	307.5	300.2	304.2	293.6	314.2	295.9	310.2	283.5	303.7	295.2	335.2	317.5	330.2	306.7	320.6	300.1
80	329.9	293.7	319.3	310.5	317.2	309.5	315.1	304.0	323.8	303.7	320.5	290.5	314.2	305.3	341.1	325.1	337.4	313.8	329.5	307.1
85	339.9	304.8	329.1	316.1	326.7	317.7	327.1	315.9	332.7	302.7	330.6	300.3	325.4	317.5	348.0	331.2	345.9	322.0	339.0	319.4