

# Comparison of Diesel Fuel Oxygenate Additives to the Composition-Explicit Distillation Curve Method. Part 4: Alcohols, Aldehydes, Hydroxy Ethers, and Esters of Butanoic Acid

Jessica L. Burger, Evgenii Baibourine, and Thomas J. Bruno\*

Thermophysical Properties Division, National Institute of Standards and Technology (NIST), Boulder, Colorado 80305, United States

## Supporting Information

**ABSTRACT:** There is a great deal of interest in formulating oxygenated diesel fuels that produce low-particulate emissions. In this paper, the fourth in a series of papers on the properties of mixtures of diesel fuel with oxygenating additives, we present the volatility, as measured by the advanced distillation curve, of diesel fuels with potential fuel additives: butanal, pentanal, methyl butanoate, ethyl butanoate, 1-propanol, 1-butanol, 1-pentanol, 2-ethoxyethanol, and 2-butoxyethanol. As observed in earlier studies of oxygenate additive mixtures, the more volatile additives cause significant early departures from the distillation curves of diesel fuel, while the less volatile additives act more to displace the entire distillation curve. We also note that oxygenates with higher heat capacities caused greater variability among distillation curves. This is probably due to the onset of film boiling in the distillation flask. We present the results for the initial boiling behavior and the distillation curve temperatures and track the oxygenates throughout the distillations. These data will aid in determining the suitability of these types of compounds as oxygenates.

## INTRODUCTION

In parts 1 (10.1021/ef2003415), 2 (10.1021/ef2003427), and 3 (10.1021/ef200343a) of this series,<sup>1–3</sup> we presented and discussed the volatility behavior of mixtures of diesel fuel with linear, cyclic, and butyl glycerin oxygenated compounds, respectively. These measurements were performed with the composition-explicit (or advanced) distillation curve (ADC) method, which has been applied to numerous complex mixtures, including diesel fuels and oxygenates of diesel fuels.<sup>4–6</sup> In this part, we treat alcohols, aldehydes, hydroxyl ethers, and esters of butanoic acids, all of which have been suggested as diesel fuel oxygenates.<sup>7–10</sup> The compounds have one or two oxygen atoms and with normal boiling temperature ranging between 74.85 and 171.2 °C.

Butanal (CAS number 110-62-3) is an alkyl aldehyde used as an accelerator in the process of rubber vulcanization, a solvent, and a plasticizer. It is a clear colorless liquid with a pungent odor. It is used as a flavoring agent and is considered generally recognized as safe (GRAS).<sup>11</sup> Butanal has been listed as a possible oxygenate but may be unacceptable because of its low flash point (−11 °C).<sup>11</sup> Pentanal (CAS number 110-62-3) is an alkyl aldehyde and is used in flavors, resins, and rubber accelerators. Pentanal has been suggested to reduce soot-forming emissions.<sup>9</sup> Methyl butanoate (CAS number 623-42-7) is an ester used as a solvent and also as a flavoring and fragrance agent. It is a clear colorless liquid with a strong apple-like odor. Methyl butanoate has been used as a model compound for biodiesel fuels.<sup>12–15</sup> Ethyl butanoate (CAS number 105-54-4) is an ester used as a flavoring and fragrance agent, with a strong pineapple-like odor. Methyl and ethyl esters are of interest in the study of biofuels, but oxidation and ignition delays sometimes occur.<sup>10,13,16</sup> 1-Propanol (CAS number 71-23-8) is

a primary aliphatic alcohol used as a solvent, antiseptic, and chemical intermediate and also as a component in inks, pesticides, and lacquers. It is a clear colorless liquid with a mild alcoholic odor. Propanol is a co-product of glycerol formed during the production of biodiesel fuel and has been suggested as an attractive oxygenate because of the increasing production of that fluid.<sup>7,17</sup> 1-Butanol (CAS number 71-36-3) is a primary aliphatic alcohol used as a solvent and chemical intermediate. It is a clear colorless liquid with a sweet rancid odor. 1-Butanol has been used in blends with conventional diesel fuel in a high-speed, direct-injection diesel engine to test performance and particulate emission.<sup>16–18</sup> 1-Pentanol (CAS number 71-41-0) is a primary aliphatic alcohol used as a solvent for resins and gums, lubricants, frothers in an ore-flotation process, plasticizers and solvents, corrosion inhibitors, and anti-oxidants. Blends of various alcohols, including 1-pentanol, have been studied with diesel fuel for their capacity to reduce soot formation.<sup>8,17</sup> 2-Ethoxyethanol (CAS number 110-80-5) is an aliphatic glycol ether used as an anti-icing fuel additive and an industrial solvent for coatings, inks, adhesives, textile dyes, lacquers, and epoxy resins. 2-Ethoxyethanol has been suggested as a potential oxygenate based on multiple criteria, including its flash point and solubility in low aromatic diesel fuel.<sup>11</sup> 2-Butoxyethanol (CAS number 111-76-2) is also listed as a possible oxygenate but did not meet all of the criteria.<sup>11</sup> 2-Butoxyethanol is an aliphatic ether alcohol used as a solvent in surface coatings and in hydraulic fluids, glass cleaners, and

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leather cleaners. Some basic information on the properties of these additives, from the NIST Chemistry WebBook, is provided in Table S1 of the Supporting Information.

## ■ EXPERIMENTAL SECTION

The diesel fuel used in this work was obtained from a commercial source and was stored at 7 °C to 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. 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 μm, with a temperature program from 90 to 275 °C, at 9 °C per minute) with flame ionization detection (FID) and mass spectrometric (MS) detection. Samples were injected with a syringe into a split/splitless injector set with a 0:1 split ratio. The injector was operated at a temperature of 325 °C with a constant head pressure of 55.2 kPa (8 psig). A temperature program was used from 60 °C for 1 min, followed by temperature ramping at 10 °C/min to 275 °C, with a hold at 275 °C for 3 min, with FID and MS detection. Mass spectra were collected for each peak from 15 to 550 relative molecular mass (RMM) units. Peaks were identified with guidance from the NIST/EPA/NIH Mass Spectral Database and also based on retention indices.<sup>19–21</sup> This analysis was unremarkable in that the typical pattern of commercial petroleum-derived diesel fuel was observed.

The oxygenates used in this work were obtained as pure fluids from a commercial source. All were reagent-grade fluids with reported purities of 98–99% (mass/mass). These fluids were analyzed with chromatographic methods (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1 μm, with temperature programs appropriate to each fluid). These analyses revealed that the purities of the fluids were in fact higher than specified.

As mentioned in parts 1 (10.1021/ef2003415), 2 (10.1021/ef2003427), and 3 (10.1021/ef200343a) and other distillation work, our study of a particular mixture ratio does not imply that mixtures with very high oxygenate concentrations are practical formulations for fuel.<sup>1–3,19–23</sup> Our mixtures were chosen to cover as large of a range of composition as practical for the purpose of modeling the results with equations of state.

The method and apparatus for the distillation curve measurement has been reviewed in a number of sources; therefore, an additional general description will not be provided here.<sup>24–30</sup> The required volume of fluid for the distillation curve measurement (in each case, 200 mL) was placed into the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor the temperature in the liquid phase,  $T_L$ , and the temperature at the bottom of the takeoff position in the distillation head,  $T_h$ . Enclosure heating was then commenced with a four-step program based on previously measured distillation curves.<sup>31</sup> Volume measurements were made in a level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock.<sup>30</sup> In the course of this work, we measured between three and six complete distillation curves for each of the fluid samples.

Because 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 (1 atm = 101.325 kPa). This adjustment was performed with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000 109.<sup>32–35</sup> This value corresponds to a carbon chain of 12. In the chemical analysis of the diesel fuel sample (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, not accounting for the presence of the oxygenate

additive. The magnitude of the temperature adjustment is of course dependent upon the extent of departure from standard atmospheric pressure.<sup>36</sup> 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 adjustment of approximately 8 °C. The actual measured temperatures are easily recovered from the Sydney Young equation at each measured atmospheric pressure.

## ■ RESULTS AND DISCUSSION

As mentioned in parts 1 (10.1021/ef2003415), 2 (10.1021/ef2003427), and 3 (10.1021/ef200343a), diesel fuel is a commodity fluid with seasonal and regional variations, although the degree of variability is not as great as that encountered with gasoline. We have found that the diesel fuel that we have used here (winter grade, low wax, ultralow sulfur, and red dye for off-road use) is representative of many diesel fuels that we have examined. As stated previously, we measured from three to six complete distillation curves for the diesel fuel and each of the 10, 20, and 30% (v/v) mixtures of diesel fuel with each of the oxygenates.

**Initial Boiling Temperatures.** During the initial heating of each sample in the distillation flask, the behavior of the fluid was carefully observed. Direct observation through the flask window or through the borescope allowed for the measurement of the temperature at the onset of boiling for each of the mixtures (measured with  $T_k$ ). Typically, to ascertain the initial boiling behavior, we measure the onset of bubbling, the temperature at which bubbling is sustained, and the temperature at which the vapor rises into the distillation head. We have shown that this last temperature is actually the initial boiling temperature (that is, an approximation of the bubble point temperature at ambient pressure) of the starting fluid mixture. This measurement is significant for a mixture because it can be modeled with an equation of state. The measurement of these temperatures with mixtures of commercial diesel fuel is complicated by the presence of the dye mentioned above. As a result, we only report the onset and vapor rise temperatures here. Vapor rise is accompanied by a sharp increase in  $T_b$ , is therefore far less subjective to ascertain, and thus, is less uncertain than the onset of bubbling. Experience with previous mixtures, including *n*-alkane standard mixtures that were prepared gravimetrically, indicates that the uncertainty in the onset of the bubbling temperature is approximately 1 °C. The uncertainty in the vapor rise temperature is 0.3 °C.

In Table 1, we present the initial temperature observations for mixtures of diesel fuel and diesel fuel with 10, 20, and 30% (v/v) each of the oxygenates, except butanal. Butanal was measured at 2, 5, and 10% (v/v) because of the relatively low solubility of butanal in diesel. As a consequence of the low solubility of butanal in diesel, we were unable to observe the changes in volatility over as wide of a range of concentrations. These values have been adjusted to atmospheric pressure with the modified Sydney Young equation, as mentioned earlier. The initial boiling temperature (IBT) of the base diesel fuel itself, also adjusted, was 216.8 °C, with an uncertainty of 0.3 °C. We note that the addition of even 10% (v/v) of these oxygenates significantly decreased the IBT of the mixtures relative to base diesel fuel. The magnitude of the departure is directly correlated with the normal boiling temperature of the oxygenate and the concentration of the oxygenate in

**Table 1. Summary of the Average Initial Boiling Behavior of the Diesel Fuel Mixtures with the Oxygenate Additives<sup>a</sup>**

observed temperature (°C)		diesel fuel (83.63 kPa)	
vapor rise		218.6	
observed temperature (°C)	diesel fuel + 2% (v/v) butanal (82.70 kPa)	diesel fuel + 5% (v/v) butanal (82.66 kPa)	diesel fuel + 10% (v/v) butanal (82.55 kPa)
onset	127.8	118.6	82.3
vapor rise	176.8	138.9	113.4
observed temperature (°C)	diesel fuel + 10% (v/v) pentanal (83.45 kPa)	diesel fuel + 20% (v/v) pentanal (83.56 kPa)	diesel fuel + 30% (v/v) pentanal (84.05 kPa)
onset	141.3	127.0	119.8
vapor rise	154.8	134.8	125.7
observed temperature (°C)	diesel fuel + 10% (v/v) methyl butanoate (83.55 kPa)	diesel fuel + 20% (v/v) methyl butanoate (82.76 kPa)	diesel fuel + 30% (v/v) methyl butanoate (83.07 kPa)
onset	141.8	106.0	94.4
vapor rise	155.7	132.0	121.4
observed temperature (°C)	diesel fuel + 10% (v/v) ethyl butanoate (82.92 kPa)	diesel fuel + 20% (v/v) ethyl butanoate (83.03 kPa)	diesel fuel + 30% (v/v) ethyl butanoate (82.89 kPa)
onset	165.4	140.5	137.2
vapor rise	176.1	155.3	145.5
observed temperature (°C)	diesel fuel + 10% (v/v) 1-propanol (83.24 kPa)	diesel fuel + 20% (v/v) 1-propanol (83.73 kPa)	diesel fuel + 30% (v/v) 1-propanol (82.90 kPa)
onset	98.6	95.5	86.5
vapor rise	112.2	105.8	100.8
observed temperature (°C)	diesel fuel + 10% (v/v) 1-butanol (83.19 kPa)	diesel fuel + 20% (v/v) 1-butanol (83.39 kPa)	diesel fuel + 30% (v/v) 1-butanol (82.64 kPa)
onset	107.0	100.3	99.0
vapor rise	128.7	115.2	109.5
observed temperature (°C)	diesel fuel + 10% (v/v) 1-pentanol (83.04 kPa)	diesel fuel + 20% (v/v) 1-pentanol (83.24 kPa)	diesel fuel + 30% (v/v) 1-pentanol (83.59 kPa)
onset	158.2	126.6	141.3
vapor rise	168.6	154.4	152.8
observed temperature (°C)	diesel fuel + 10% (v/v) 2-ethoxyethanol (83.35 kPa)	diesel fuel + 20% (v/v) 2-ethoxyethanol (82.87 kPa)	diesel fuel + 30% (v/v) 2-ethoxyethanol (83.06 kPa)
onset	109.2	116.6	103.7
vapor rise	157.4	150.4	139.7
observed temperature (°C)	diesel fuel + 10% (v/v) 2-butoxyethanol (82.25 kPa)	diesel fuel + 20% (v/v) 2-butoxyethanol (82.81 kPa)	diesel fuel + 30% (v/v) 2-butoxyethanol
onset	131.4	128.4	128.3
vapor rise	192.7	183.9	180.7

<sup>a</sup>The vapor rise temperature is that at which vapor is observed to rise into the distillation head, considered to be the IBT of the fluid. These temperatures have been adjusted to 1 atm with the Sydney Young equation. the average experimental atmospheric pressures are provided to allow for recovery of the average measured temperatures. The uncertainties are discussed in the text.

diesel fuel. The most striking reduction is seen with the addition of 1-propanol; a 10% (v/v) addition to diesel fuel reduced the IBT by 106.4 °C. At 30% (v/v), this reduction was 117 °C. The effect on the IBT because of the addition of the higher boiling point oxygenates is of lower magnitude

but nevertheless pronounced. This is similar to what was observed for the linear and cyclic oxygenates presented in the other parts of this work.

**Distillation Curves.** During the measurement of the distillation curves, both the kettle and head temperatures were recorded ( $T_k$  and  $T_h$ , respectively). The ambient atmospheric pressure was also recorded and used to adjust the temperatures to what would be obtained at sea level atmospheric pressure by use of the modified Sydney Young equation, as mentioned earlier. The uncertainty in temperature,  $T_k$ , was approximately 0.3 °C. The lone exceptions to this were the curves of 30% 2-butoxyethanol; the average standard deviation between these measurements was 2.9 °C. It is likely that the variability was due to the onset of film boiling in the kettle, making the heating of the mixture less uniform.<sup>37</sup> The heat capacity of 2-butoxyethanol liquid is  $2.70 \times 10^5 \text{ J kmol}^{-1} \text{ K}^{-1}$  (20.0 °C), the highest heat capacity of the oxygenates used in this part of the study. We have noted in prior work that fluids with relatively high heat capacities undergo film boiling in the kettle.<sup>38</sup> The repeatability of the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) was 0.001 kPa. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction was 0.05 mL in each case. Average head and kettle temperatures, as well as the average measured atmospheric pressure, are presented as a function of the distillate cut for a representative measurement for each mixture (at 10, 20 and 30%, v/v, of oxygenate) in parts a–i of Table 2. These data are also represented graphically in Figures 1–9. On each of the figures, the IBT is indicated as a hatch mark on the temperature axis. The behavior of the distillation curves is consistent with that of the IBT data. The magnitude of the departure from neat diesel fuel that is caused by the oxygenate is correlated to its normal boiling temperature; the largest displacements in the distillation curves are observed in the mixtures with oxygenates having lowest normal boiling temperatures. We also note that the largest displacement is caused by the addition of the first 10% (v/v) of the oxygenating additive; the addition of 20 and 30% displaces the curves to a far lesser extent. These changes are most striking with the additive having the lowest boiling temperature, becoming subtler with the additive having the boiling temperature closest to that of the diesel fuel.

As we noted in parts 1 (10.1021/ef2003415), 2 (10.1021/ef2003427), and 3 (10.1021/ef200343a) of this series, the addition of 10% (v/v) of the oxygenates to diesel fuel produces a distillation curve that is still sigmoidal over the entire curve, despite the initial steep displacement to lower temperatures. For the 20 and 30% (v/v) mixtures, a somewhat different shape is apparent, with an initial flattening of the curve in response to the high concentration of a single component. Subsequent to this flattening, the curve once again becomes sigmoidal. Finally, we note that an examination of the behavior of the temperatures  $T_k$  and  $T_h$  revealed no convergence; thus, we find no indications of azeotropy among the oxygenates and the components of the base diesel fuel, even though there has been previous work indicating azeotropes of 2-butoxyethanol with alkyl benzenes.<sup>39</sup>

**Composition Channel Information.** While the examination of the distillation curves is instructive and valuable for

**Table 2. Representative Distillation Curve Data (Given as the Average of Four Distillation Curves) for Mixtures of Diesel Fuel with the Oxygenate Additives<sup>a</sup>**

a		diesel fuel + 2% (v/v) butanal (82.70 kPa)	diesel fuel + 5% (v/v) butanal (82.66 kPa)	diesel fuel + 10% (v/v) butanal (82.55 kPa)			c		diesel fuel + 10% (v/v) methyl butanoate (83.55 kPa)	diesel fuel + 20% (v/v) methyl butanoate (82.76 kPa)	diesel fuel + 30% (v/v) methyl butanoate (83.07 kPa)
distillate volume fraction (%)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)	
5		224.6	188.3	219.4	178.8	151.7	95.0		291.5	273.1	285.5
10		230.1	209.6	228.3	206.3	217.5	124.8	65	299.0	280.7	294.6
15		236.0	216.6	234.5	215.5	230.2	195.4	70	308.6	290.1	304.3
20		241.3	222.0	240.0	223.4	236.4	205.5	75	317.0	298.6	312.8
25		245.8	227.3	244.9	227.3	241.7	212.5	80	328.6	305.4	326.2
30		251.3	234.2	250.0	233.1	247.8	222.2	85	diesel fuel + 10% (v/v) ethyl butanoate (82.92 kPa)	diesel fuel + 20% (v/v) ethyl butanoate (83.03 kPa)	diesel fuel + 30% (v/v) ethyl butanoate (82.89 kPa)
35		256.2	238.9	255.4	238.5	252.9	228.4				
40		261.7	244.9	261.8	244.6	259.2	232.6				
45		267.8	251.4	268.0	251.5	265.8	239.7				
50		273.0	256.7	273.8	257.5	272.1	246.1				
55		278.4	262.8	279.9	262.0	278.5	254.7				
60		285.1	269.6	287.6	271.3	286.2	263.7				
65		291.9	277.1	295.9	277.6	294.0	269.0				
70		299.0	282.5	305.4	286.3	301.3	276.2				
75		307.1	291.5	313.4	293.3	311.4	285.8				
80		314.4	299.6	322.9	300.2	319.6	294.6				
85		324.4	310.3	336.2	303.6	330.8	293.2				
b		diesel fuel + 10% (v/v) pentanal (83.45 kPa)	diesel fuel + 20% (v/v) pentanal (83.56 kPa)	diesel fuel + 30% (v/v) pentanal (84.05 kPa)			diesel fuel + 10% (v/v) 1-propanol (83.24 kPa)		diesel fuel + 20% (v/v) 1-propanol (83.73 kPa)	diesel fuel + 30% (v/v) 1-propanol (82.90 kPa)	
distillate volume fraction (%)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)	
5		174.0	100.6	143.0	102.8	129.9	103.1	5	144.0	98.4	108.6
10		198.9	106.3	152.9	104.4	134.4	104.5	10	224.8	174.8	115.6
15		225.2	142.9	171.7	114.4	141.6	106.3	15	232.0	197.6	144.9
20		234.7	169.7	195.5	92.9	153.6	108.7	20	237.1	210.4	228.1
25		241.2	185.9	225.6	113.9	169.5	107.4	25	243.0	211.4	235.7
30		247.4	194.9	237.0	141.8	198.7	71.7	30	248.4	214.5	241.4
35		252.5	204.5	244.0	160.7	227.8	77.1	35	253.8	224.5	247.5
40		258.5	209.8	250.4	182.7	242.4	117.3	40	259.7	230.7	254.5
45		265.0	215.5	256.4	189.8	250.9	137.8	45	265.9	240.0	259.7
50		270.6	218.4	263.0	193.8	257.9	140.4	50	273.0	247.8	267.9
55		277.5	220.4	269.8	195.3	264.4	151.6	55	279.5	255.2	274.0
60		285.2	222.3	277.6	194.8	273.2	154.6	60	286.5	267.5	282.1
65		291.7	227.3	284.3	193.7	281.5	154.6	65	295.0	276.7	289.3
70		299.7	231.9	292.5	195.7	290.2	150.2	70	303.0	283.9	298.6
75		309.1	232.4	299.1	199.9	301.7	148.5	75	312.1	291.0	308.5
80		318.8	248.9	308.8	200.6	311.8	150.3	80	321.4	293.0	318.0
85		329.2	251.3	322.2	202.9	324.4	158.2	85	332.3	299.8	330.5
c		diesel fuel + 10% (v/v) methyl butanoate (83.55 kPa)	diesel fuel + 20% (v/v) methyl butanoate (82.76 kPa)	diesel fuel + 30% (v/v) methyl butanoate (83.07 kPa)			diesel fuel + 10% (v/v) 1-butanol (83.19 kPa)		diesel fuel + 20% (v/v) 1-butanol (83.39 kPa)	diesel fuel + 30% (v/v) 1-butanol (82.64 kPa)	
distillate volume fraction (%)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)	
5		179.3	119.7	142.1	95.0	127.9	104.3	5	155.4	102.8	119.7
10		202.5	147.5	152.8	104.3	132.6	105.7	10	211.6	99.7	130.0
15		227.1	762.7	170.8	116.1	140.7	108.3				
20		236.3	202.4	201.0	108.1	153.4	122.5				
25		243.8	207.5	226.0	131.7	171.1	135.9				
30		247.0	214.5	238.2	187.0	203.6	132.7				
35		252.2	223.3	244.9	217.7	233.0	153.7				
40		257.5	233.4	252.0	226.3	243.4	214.6				
45		264.2	240.1	258.8	226.3	251.4	225.6				
50		270.1	248.5	264.5	925.6	257.4	232.3				
55		276.1	256.7	271.5	230.0	264.7	241.0				
60		283.9	265.6	278.8	216.5	273.7	252.2				
f		diesel fuel + 10% (v/v) 1-butanol (83.19 kPa)	diesel fuel + 20% (v/v) 1-butanol (83.39 kPa)	diesel fuel + 30% (v/v) 1-butanol (82.64 kPa)			distillate volume fraction (%)		$T_k$ (°C)	$T_h$ (°C)	
distillate volume fraction (%)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)		$T_k$ (°C)	$T_h$ (°C)	$T_k$ (°C)	$T_h$ (°C)	
5		144.0	98.4	108.6	98.0	103.9	96.4	5	155.4	102.8	119.7
10		224.8	174.8	115.6	66.8	105.5	97.3	10	211.6	99.7	130.0
15		232.0	197.6	144.9	52.9	110.2	97.7				
20		237.1	210.4	228.1	83.1	121.6	98.8				
25		243.0	211.4	235.7	134.3	190.9	91.9				
30		248.4	214.5	241.4	142.9	234.5	195.6				
35		253.8	224.5	247.5	151.7	241.0	205.5				
40		259.7	230.7	254.5	155.5	247.7	215.9				
45		265.9	240.0	259.7	158.7	253.5	223.6				
50		273.0	247.8	267.9	162.1	261.9	232.9				
55		279.5	255.2	274.0	170.9	270.6	180.2				
60		286.5	267.5	282.1	177.2	278.7	249.3				
65		295.0	276.7	289.3	180.8	288.6	265.2				
70		303.0	283.9	298.6	177.7	298.2	266.2				
75		312.1	291.0	308.5	187.2	308.8	271.1				
80		321.4	293.0	318.0	187.6	319.4	282.8				
85		332.3	299.8	330.5	174.9	334.7	281.0				

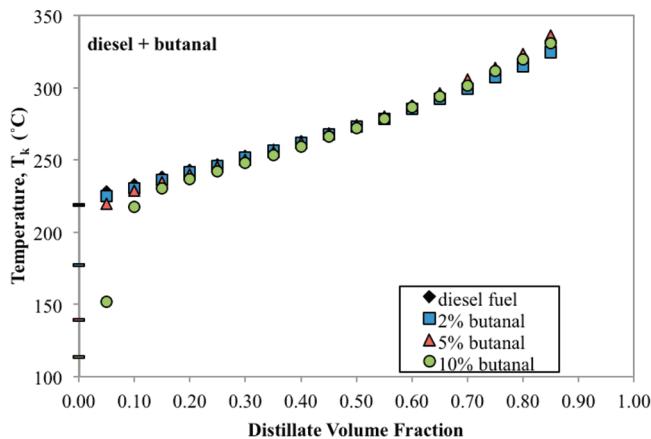
Table 2. continued

f	diesel fuel + 10% (v/v) 1-butanol (83.19 kPa)		diesel fuel + 20% (v/v) 1-butanol (83.39 kPa)		diesel fuel + 30% (v/v) 1-butanol (82.64 kPa)		h	diesel fuel + 10% (v/v) 2-ethoxyethanol (83.35 kPa)		diesel fuel + 20% (v/v) 2-ethoxyethanol (82.87 kPa)		diesel fuel + 30% (v/v) 2-ethoxyethanol (83.06 kPa)	
	distillate volume fraction (%)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	distillate volume fraction (%)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)
15	230.3	174.6	154.7	109.3	118.6	101.2	5	170.9	150.1	152.9	137.1	145.4	135.4
20	237.0	351.8	217.7	96.2	126.7	102.8	10	188.3	157.0	158.1	143.7	147.6	159.7
25	242.9	213.7	233.9	171.0	151.0	115.4	15	213.7	169.5	165.7	156.6	149.9	136.7
30	247.5	222.9	240.1	193.2	210.5	104.5	20	232.6	210.3	180.4	161.0	153.6	138.6
35	252.9	226.0	245.4	200.4	235.3	200.5	25	239.3	221.4	202.5	178.6	159.8	145.9
40	258.5	233.8	251.0	209.3	242.8	213.2	30	245.7	229.6	228.3	205.4	171.4	159.6
45	264.6	242.1	256.9	211.2	249.3	221.7	35	251.2	235.4	242.3	228.7	196.0	170.1
50	271.2	248.2	264.1	218.6	256.4	230.6	40	256.9	240.6	249.7	236.5	232.7	203.3
55	278.0	256.6	271.0	221.9	263.4	236.5	45	263.0	246.7	256.0	242.3	248.0	230.6
60	286.7	267.3	278.6	226.7	271.8	247.1	50	269.3	252.7	263.2	249.1	255.7	239.0
65	293.4	274.8	286.2	230.6	279.5	252.7	55	275.9	260.1	269.7	255.4	263.4	246.6
70	301.3	281.4	295.2	268.5	290.4	261.7	60	282.4	266.2	276.4	263.0	271.1	253.8
75	310.9	288.6	305.9	274.0	300.5	274.4	65	289.6	273.9	284.7	271.3	280.3	262.8
80	320.4	296.5	313.5	279.7	309.9	284.9	70	298.3	281.6	293.9	279.4	289.2	272.0
85	331.4	304.5	325.9	289.0	320.1	294.8	75	307.2	290.4	303.6	194.6	299.4	281.1
g	diesel fuel + 10% (v/v) 1-pentanol (83.04 kPa)		diesel fuel + 20% (v/v) 1-pentanol (83.24 kPa)		diesel fuel + 30% (v/v) 1-pentanol (83.59 kPa)		80	316.5	300.1	314.1	296.9	310.4	292.4
	distillate volume fraction (%)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	85	325.2	310.8	326.1	307.7	324.1
i	diesel fuel + 10% (v/v) 2-butoxyethanol (82.25 kPa)		diesel fuel + 20% (v/v) 2-butoxyethanol (82.81 kPa)		diesel fuel + 30% (v/v) 2-butoxyethanol		distillate volume fraction (%)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)
	distillate volume fraction (%)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	T <sub>k</sub> (°C)	T <sub>h</sub> (°C)	5	200.6	175.2	188.1	162.6	185.4
10	194.0	158.7	164.4	150.3	155.5	139.8	10	207.0	180.8	191.3	171.6	186.7	171.2
15	212.0	175.9	171.9	156.6	158.7	140.3	15	213.4	189.6	195.2	178.3	188.8	174.1
20	229.4	199.9	184.6	165.7	163.1	142.3	20	222.3	202.2	200.7	184.4	192.4	177.0
25	239.3	214.4	202.3	177.7	170.1	144.9	25	231.0	211.8	207.6	192.2	197.7	180.0
30	246.3	221.1	225.8	200.5	181.8	152.9	30	240.4	221.0	216.2	198.9	202.7	184.5
35	252.0	227.2	239.9	222.7	199.7	162.1	35	248.8	230.2	227.8	207.8	209.0	189.5
40	258.1	233.9	246.7	233.6	229.1	211.9	40	255.9	235.4	241.2	219.4	217.7	194.1
45	263.9	240.8	252.6	241.0	245.3	209.6	45	262.8	244.3	252.2	230.5	231.3	207.6
50	270.1	247.1	259.6	248.2	254.0	223.4	50	269.6	252.6	261.8	241.6	248.1	220.4
55	276.4	254.3	266.8	255.4	261.2	233.4	55	276.3	258.0	269.2	250.2	262.5	238.2
60	284.1	264.0	274.9	262.2	268.9	244.7	60	283.2	265.0	277.1	258.2	273.5	250.9
65	291.4	269.4	281.6	269.6	276.9	251.0	65	290.7	272.7	284.3	264.7	281.5	260.1
70	299.7	279.4	290.6	278.0	286.1	258.6	70	299.2	280.1	292.5	271.7	290.7	268.9
75	308.5	286.8	300.5	286.2	296.1	268.3	75	307.7	288.2	302.4	281.0	301.4	279.2
80	316.9	295.9	310.0	297.1	306.7	280.4	80	317.1	295.8	313.2	290.7	313.6	291.3
85	327.3	308.7	322.9	308.3	319.4	291.9	85	328.4	306.4	328.4	300.9	326.4	304.3

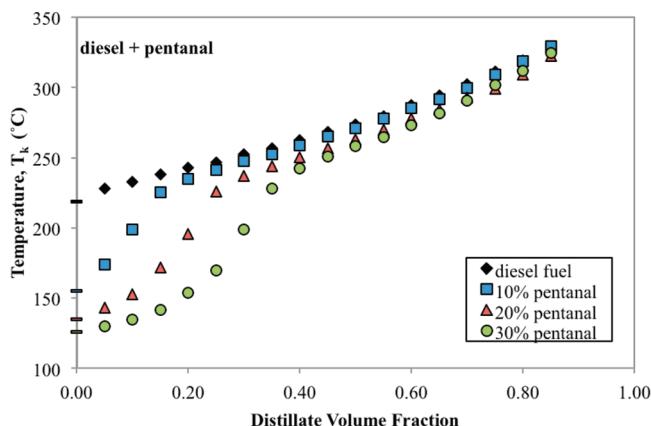
<sup>a</sup>The uncertainties are discussed in the text. These temperatures have been adjusted to 1 atm with the Sydney Young equation. The experimental atmospheric pressures are provided to allow for recovery of the actual measure temperatures.

many design purposes, the composition channel of the ADC approach can provide an even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser, as discussed in the Experimental Section. Following the analytical procedure described in the Experimental Section, 7  $\mu\text{L}$  samples were collected in autosampler vials containing a known mass of *n*-hexane solvent. Chemical analyses of each fraction were performed by gas chromatography with MS detection or with gas chromatography with FID. Calibration was performed by the external standard method, with four solutions of known concentration (prepared gravimetrically) of the oxygenate, also prepared in *n*-hexane. The chromatographic

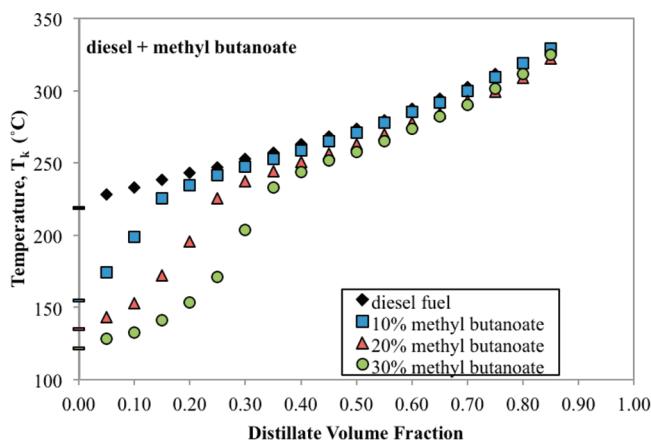
conditions were optimized for each oxygenate, as summarized in Table 3. In most cases, baseline resolution was easily obtainable for each oxygenate fluid, and the mass spectrometer was operated in scan and selected ion monitoring (SIM) mode. The measured concentrations of the oxygenates are presented in Figures 10–18 as histograms and in Table S2 of the Supporting Information, representing the mass percent of the additive as a function of the distillate cut. The uncertainty bars represent the propagated uncertainties of the sample and standard measurements and incorporate a coverage factor  $k = 2$ .<sup>40</sup> While not explicitly measured, we essentially recovered all of the oxygenate additive in the distillate or residue.



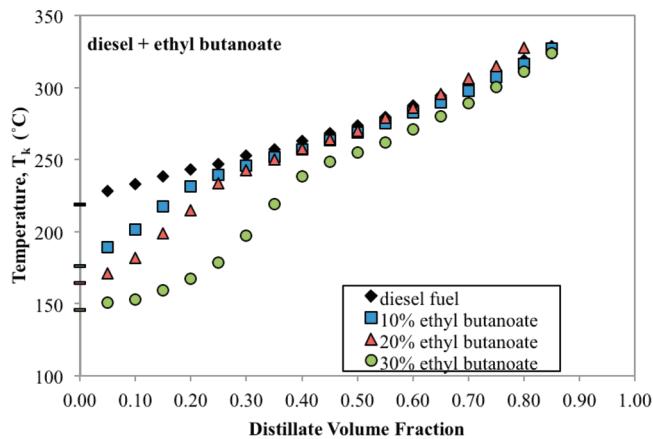
**Figure 1.** Distillation curves of diesel fuel with mixtures of butanal. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the  $y$  axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



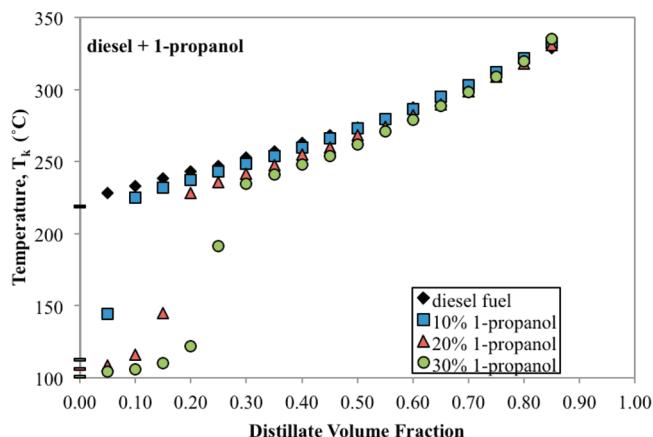
**Figure 2.** Distillation curves of diesel fuel with mixtures of pentanal. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the  $y$  axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



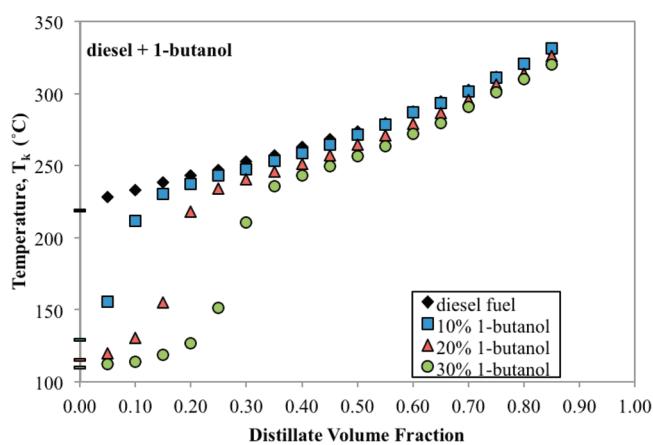
**Figure 3.** Distillation curves of diesel fuel with mixtures of methyl butanoate. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the  $y$  axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



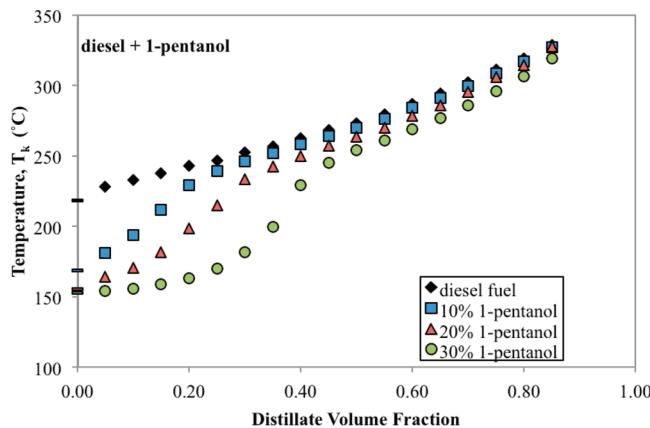
**Figure 4.** Distillation curves of diesel fuel with mixtures of ethyl butanoate. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the  $y$  axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



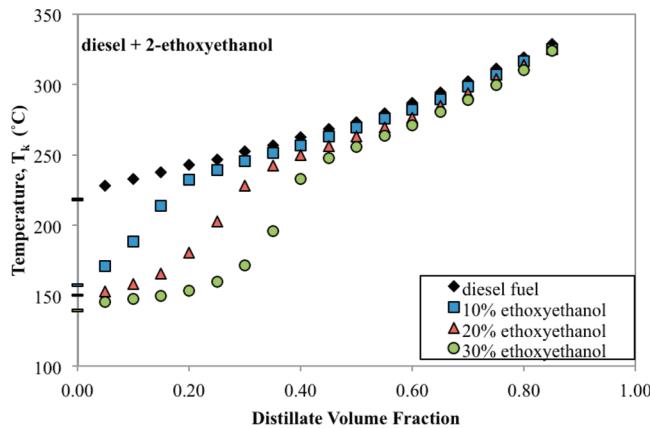
**Figure 5.** Distillation curves of diesel fuel with mixtures of 1-propanol. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the  $y$  axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



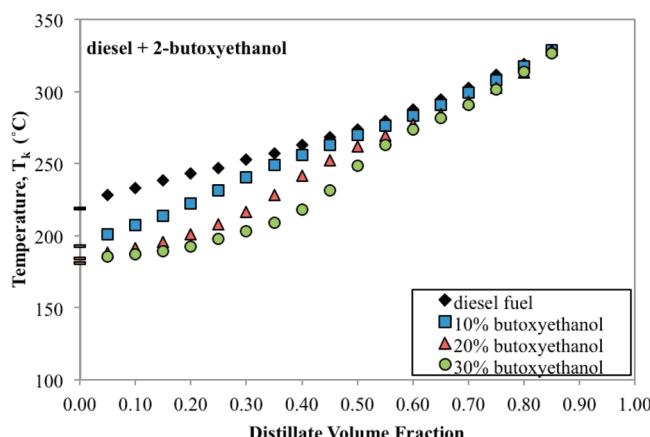
**Figure 6.** Distillation curves of diesel fuel with mixtures of 1-butanol. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the  $y$  axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



**Figure 7.** Distillation curves of diesel fuel with mixtures of 1-pentanol. 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 of each mixture. The uncertainties are discussed in the text.



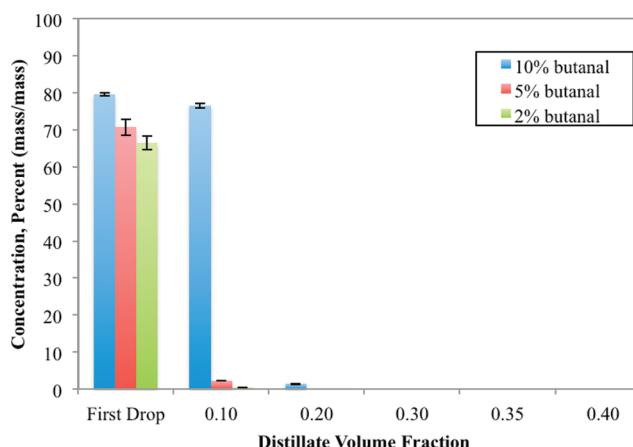
**Figure 8.** Distillation curves of diesel fuel with mixtures of 2-ethoxyethanol. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the y axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.



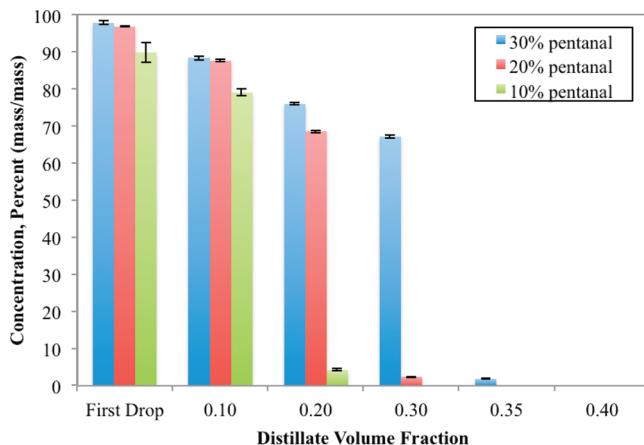
**Figure 9.** Distillation curves of diesel fuel with mixtures of 2-butoxyethanol. Here, we present  $T_k$ , the temperature measured directly in the liquid phase. The tick marks on the y axis represent the initial boiling point of each mixture. The uncertainties are discussed in the text.

**Table 3. Summary of the Analytical Conditions Used for the Samples Withdrawn as a Function of the Distillate Cut**

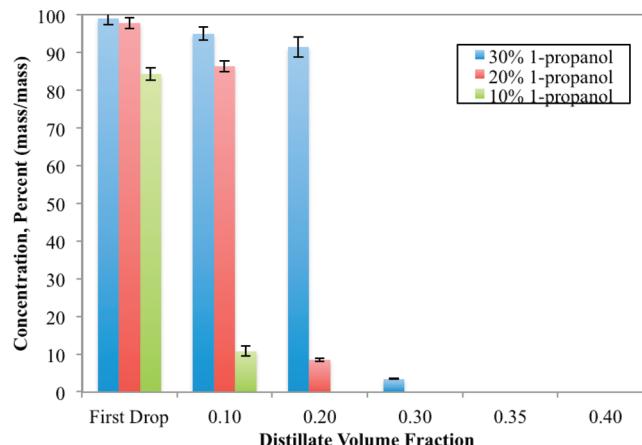
oxygenate	chromatographic method	analysis time (min)
butanal	40 °C for 2 min then 30 °C/min to 200 °C for 0 min then 60 °C/min to 275 °C for 2 min SIM: $m/z$ 72.1, 72.1, and 73.1	10.58
pentanal	50 °C for 0 min then 3 °C/min to 62 °C for 0 min then 60 °C to 275 for 2 min SIM: $m/z$ 69.0, 71.0, and 86.0	9.55
methyl butanoate	40 °C for 2 min then 30 °C/min to 200 °C for 0 min then 60 °C/min to 300 °C for 3 min SIM: $m/z$ 41.4, 43.2, 59.4, 71.2, 74.2, and 87.2	12
ethyl butanoate	40 °C for 2 min then 30 °C/min to 200 °C for 0 min then 60 °C/min to 300 °C for 3 min SIM: $m/z$ 43.2, 71.15, 88.10, and 101.1	12
1-propanol	45 °C for 2 min then 30 °C/min to 200 °C for 0 min then 30 °C/min to 300 °C for 3 min SIM: $m/z$ 31.1, 39.1, 42.1, 59.1, and 60.1	13.5
1-butanol	40 °C for 2 min then 30 °C/min to 200 °C for 0 min then 60 °C/min to 300 °C for 3 min SIM: $m/z$ 31.1, 45.1, and 59.1	12
1-pentanol	40 °C for 2 min then 30 °C/min to 200 °C for 0 min then 60 °C/min to 300 °C for 4 min SIM: $m/z$ 29.1, 31.1, 42.1, 55.1, and 70.1	13
2-ethoxyethanol	50 °C for 2 min then 30 °C/min to 275 °C and held for 3 min	12.5
2-butoxyethanol	50 °C for 2 min then 30 °C/min to 275 °C and held for 3 min	12.5
FID		



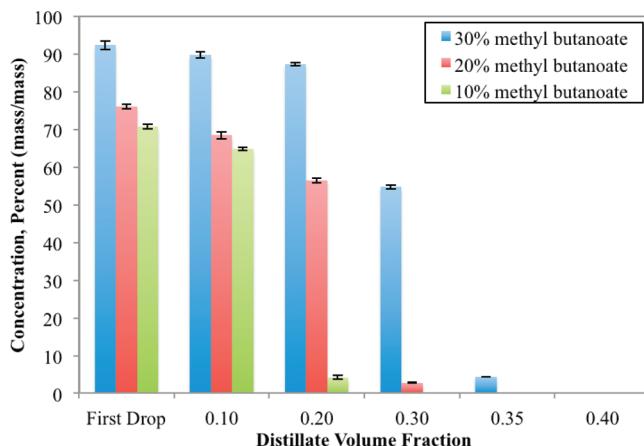
**Figure 10.** Histogram plot showing the results of the analysis for butanal as a function of the distillate volume fraction for the three diesel fuel starting mixtures (2, 5, and 10%, v/v).



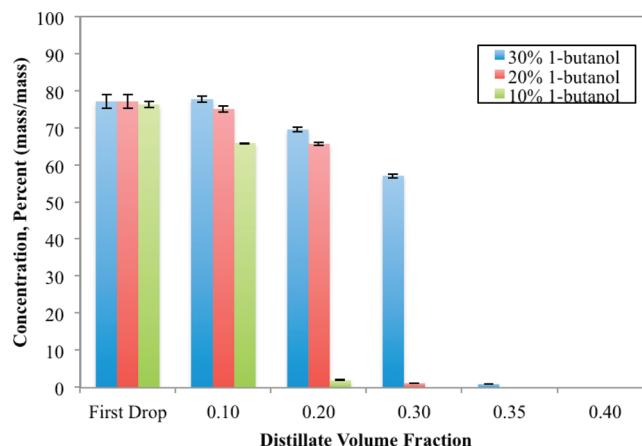
**Figure 11.** Histogram plot showing the results of the analysis for pentanal as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



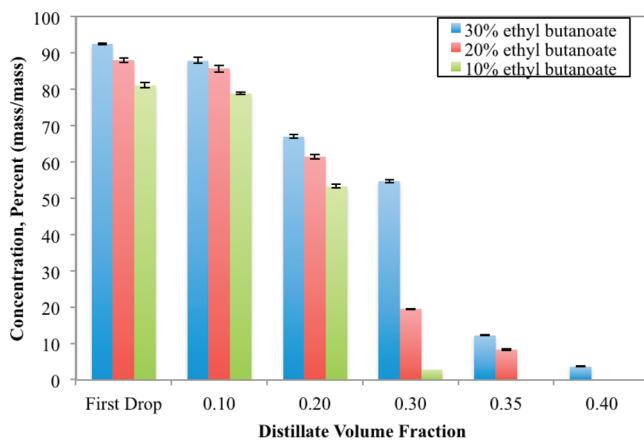
**Figure 14.** Histogram plot showing the results of the analysis for 1-propanol as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



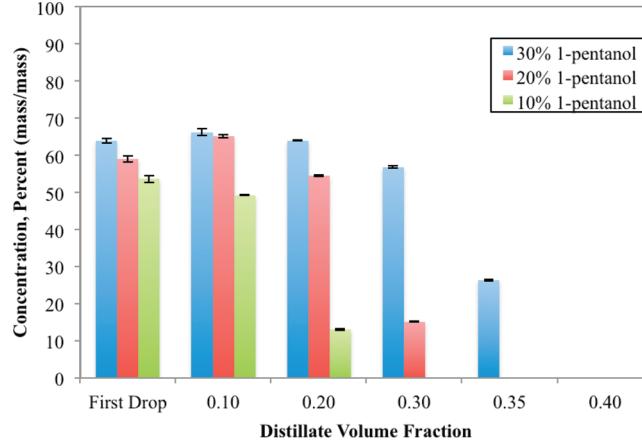
**Figure 12.** Histogram plot showing the results of the analysis for methyl butanoate as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



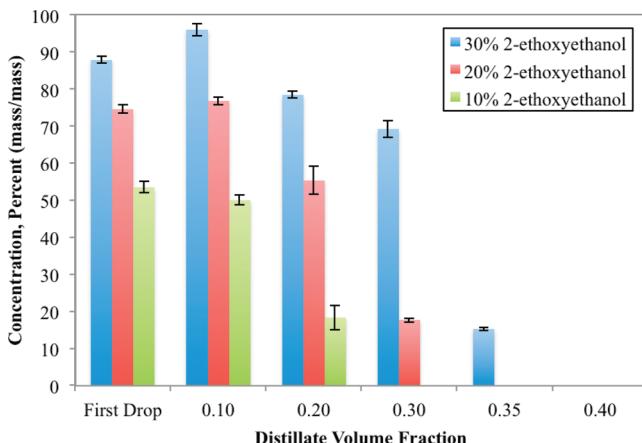
**Figure 15.** Histogram plot showing the results of the analysis for 1-butanol as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



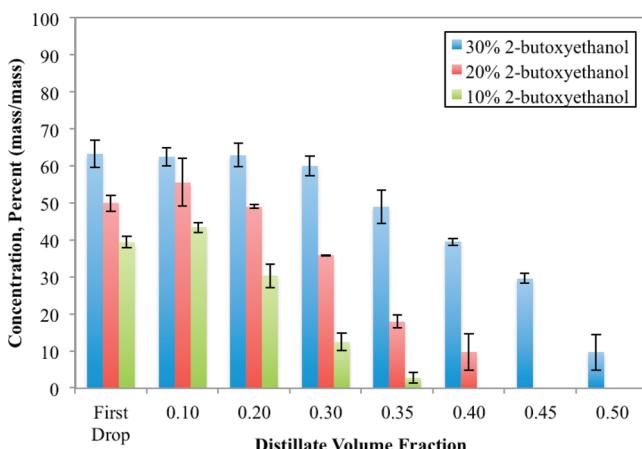
**Figure 13.** Histogram plot showing the results of the analysis for ethyl butanoate as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



**Figure 16.** Histogram plot showing the results of the analysis for 1-pentanol as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



**Figure 17.** Histogram plot showing the results of the analysis for 2-ethoxyethanol as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).



**Figure 18.** Histogram plot showing the results of the analysis for 2-butoxyethanol as a function of the distillate volume fraction for the three diesel fuel starting mixtures (10, 20, and 30%, v/v).

## CONCLUSION

In this paper, we have used the ADC approach to characterize the vapor liquid equilibrium of mixtures of alcohols, aldehydes, and butanoic acid oxygenates with a base diesel fuel. All of the additives studied here affect the distillation curve significantly, always resulting in an increase in volatility in the early part of the distillation curve. This effect is seen to persist later in the distillation curve as the normal boiling temperature of the oxygenate additive increases. The data presented here can be used for the development of equations of state for the mixtures.

## ASSOCIATED CONTENT

### Supporting Information

Data on the oxygenate additive fluids studied in this work (Table S1) and summary of the distillate volume fraction analysis (also shown in histogram plot form in Figures 10–18) of the diesel fuel mixtures with the oxygenate additives (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*Telephone: 303-497-5158. Fax: 303-497-5044. E-mail: bruno@boulder.nist.gov.

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### REFERENCES

- Bruno, T. J.; Lovestead, T. M.; Riggs, J.; Jorgensen, E.; Huber, M. L. *Energy Fuels* **2011**, *25* (6), 2493–2507.
- Bruno, T. J.; Lovestead, T. M.; Riggs, J. *Energy Fuels* **2011**, *25* (6), 2508–2517.
- Lovestead, T. M.; Bruno, T. J. *Energy Fuels* **2011**, *25* (6), 2518–2525.
- Bruno, T. J.; Ott, L. S.; Smith, B. L.; Lovestead, T. M. *Anal. Chem.* **2009**, *82* (3), 777–783.
- Bruno, T. J.; Ott, L. S.; Lovestead, T. M.; Huber, M. L. *J. Chromatogr., A* **2010**, *1217* (16), 2703–2715.
- Bruno, T. J.; Ott, L. S.; Lovestead, T. M.; Huber, M. L. *Chem. Eng. Technol.* **2010**, *33* (3), 363–376.
- Fernando, S.; Adhikari, S.; Kota, K.; Bandi, R. *Fuel* **2007**, *86* (17–18), 2806–2809.
- Lapuerta, M.; Garcia-Contreras, R.; Campos-Fernandez, J.; Dorado, M. P. *Energy Fuels* **2010**, *24* (8), 4497–4502.
- Bowman, C. T.; Golden, D. M.; Hanson, R. K.; Pitsch, H.; Davidson, P. D. F.; Bardos, A.; Cook, R.; Hong, Z.; Jampani, S.; Pang, G. *Optimization of Synthetic Oxygenated Fuels for Diesel Engines*; Global Climate and Energy Project (GCEP) at Stanford University: Stanford, CA, 2006; GCEP Technical Report.
- Um, S.; Park, S. W. *Fuel* **2010**, *89* (7), 1415–1421.
- Natarajan, M.; Frame, E. A.; Naegeli, D. W.; Asmus, T.; Clark, W.; Garbak, J.; Gonzalez, D. M.; Liney, E.; Piel, W.; Wallace, J. P. *SAE Trans.* **2001**, *110* (4), 2221–2245.
- Gail, S.; Thomson, M.; Sarathy, S.; Syed, S.; Dagaut, P.; DiÈvart, P.; Marchese, A.; Dryer, F. *Proc. Combust. Inst.* **2007**, *31* (1), 305–311.
- Hakka, M.; Bennadji, H.; Biet, J.; Yahyaoui, M.; Sirjean, B.; Warth, V.; Coniglio, L.; Herbinet, O.; Glaude, P.; Billaud, F. *Int. J. Chem. Kinet.* **2010**, *42* (4), 226–252.
- Walton, S.; Wooldridge, M.; Westbrook, C. *Proc. Combust. Inst.* **2009**, *32* (1), 255–262.
- Walton, S. M.; Karwat, D. M.; Teini, P. D.; Gorny, A.; Wooldridge, M. S. *Fuel* **2011**, *90* (5), 1796–1804.
- Graboski, M. S.; McCormick, R. L. *Prog. Energy Combust. Sci.* **1998**, *24* (2), 125–164.
- Kohse Höninghaus, K.; Olfwald, P.; Cool, T. A.; Kasper, T.; Hansen, N.; Qi, F.; Westbrook, C. K.; Westmoreland, P. R. *Angew. Chem., Int. Ed.* **2010**, *49* (21), 3572–3597.
- Lujaji, F.; Kristóf, L.; Bereczky, A.; Mbarawa, M. *Fuel* **2011**, *90* (2), 505–510.
- Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; CRC Press (Taylor and Francis Group): Boca Raton, FL, 2006.
- Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 3rd ed.; CRC Press (Taylor and Francis Group): Boca Raton, FL, 2011.
- Standard Reference Data (SRD) Program, National Institute of Standards and Technology (NIST). *NIST/EPA/NIH Mass Spectral Database*; SRD Program, NIST: Gaithersburg, MD, 2005.
- Bruno, T. J.; Wolk, A.; Naydich, A. *Energy Fuels* **2009**, *23* (2), 2295–2306.
- Ott, L. S.; Smith, B. L.; Bruno, T. J. *Energy Fuels* **2008**, *22* (4), 2518–2526.

- (24) Smith, B. L.; Ott, L. S.; Bruno, T. J. *Environ. Sci. Technol.* **2008**, 42 (20), 7682–7689.
- (25) Bruno, T. J. *Ind. Eng. Chem. Res.* **2006**, 45 (12), 4371–4380.
- (26) Bruno, T. J.; Smith, B. L. *Ind. Eng. Chem. Res.* **2006**, 45 (12), 4381–4388.
- (27) Smith, B. L.; Bruno, T. J. *Ind. Eng. Chem. Res.* **2007**, 46 (1), 297–309.
- (28) Smith, B. L.; Bruno, T. J. *Ind. Eng. Chem. Res.* **2007**, 46 (1), 310–320.
- (29) Smith, B. L.; Bruno, T. J. *Int. J. Thermophys.* **2006**, 27 (5), 1419–1434.
- (30) Bruno, T. J. *Sep. Sci. Technol.* **2006**, 41 (2), 309–314.
- (31) Bruno, T. J.; Smith, B. L. *Energy Fuels* **2006**, 20 (5), 2109–2116.
- (32) Ott, L. S.; Bruno, T. J. *Energy Fuels* **2008**, 22 (4), 2861–2868.
- (33) Young, S. *Proc. Chem. Soc.* **1902**, 81, 777.
- (34) Young, S. *Fractional Distillation*; Macmillan and Co., Ltd.: London, U.K., 1903.
- (35) Young, S. *Distillation Principles and Processes*; Macmillan and Co., Ltd.: London, U.K., 1922.
- (36) Ott, L. S.; Smith, B. L.; Bruno, T. J. *J. Chem. Thermodyn.* **2008**, 40 (9), 1352–1357.
- (37) Halliday, D.; Resnick, R.; Walker, J. The Leidenfrost effect. *Fundamentals of Physics*, 4th ed.; John Wiley and Sons: New York, 1993.
- (38) Bruno, T. J.; Wolk, A.; Naydich, A. *Energy Fuels* **2009**, 23 (6), 3277–3284.
- (39) Kieffer, W. F.; Holroyd, R. A. *Ind. Eng. Chem.* **1955**, 47 (3), 457–458.
- (40) Taylor, B. N.; Kuyatt, C. E. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; National Institute of Standards and Technology (NIST): Gaithersburg, MD, 1994; NIST Technical Note 1297.