

Composition-explicit Distillation Curves for Mixtures of Diesel Fuel with Dimethyl Carbonate and Diethyl Carbonate

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We have recently introduced several important improvements in the measurement of distillation curves of complex fluids. The modifications to the classical measurement provide for (1) a composition-explicit data channel for each distillate fraction (for qualitative, quantitative, and trace 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; and (6) a corrosivity assessment of each distillate fraction. We have applied the new method to the measurement of rocket propellant, gasolines, jet fuels, and hydrocarbon crude oils. In this paper, we present the application of the technique to representative batches of ultra low sulfur diesel fuel (ULSD) and mixtures of this diesel fuel with two of the more promising oxygenating agents; namely, dimethyl carbonate and diethyl carbonate. The addition of oxygenates, although more familiar in gasoline fuel systems, is also of great interest in the diesel fuel community, since it provides an opportunity to decrease particulate emissions. The potential of designing new fuel mixtures critically depends on knowledge of the thermophysical properties of the fluids. The volatility, as provided by the distillation curve method we apply, is part of that knowledge base. We present herein the distillation curves as a function of additive starting concentration and the concurrent analytical information. We noted that even after the oxygenates have distilled out of the mixtures, there is a persistent depression in the temperature. An explanation in terms of the Helmholtz free energy equation of state model is advanced.

Introduction

Diesel Fuel Oxygenates. Diesel engine designers have increasingly come under pressure to improve the environmental performance of compression ignition (CI) engines.^{1–6} Although very efficient, diesel engines have had difficulties achieving desirable emission targets, especially for soot and NO_x formation. Over the years, improvements have been made in the design of fuel systems, combustion chambers, and engine control. Indeed, catalytic after-treatment of diesel exhaust has become common on large diesel power plants. More recently, reformulation of diesel fuel has been given renewed attention.^{7–10} This has focused on two aspects of the fuel: (1) reformulation

to lower the sulfur specification and (2) reformulation to incorporate oxygenates into the fuel.^{7,11–30}

The first aspect (lowering the sulfur specification) is more related to issues of acid precipitation rather than to soot and NO_x formation. Indeed, this goal has substantially been met as of 2007, with the introduction of ultra low sulfur diesel (ULSD)

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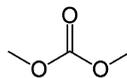
fuels that meet the target 15 ppm (mass/mass) specification. The second goal, on the other hand, is still the subject of research.

Reformulation of diesel fuel to include oxygenates has proven to be an effective way to reduce soot and NO_x emissions, to enhance the ability to recirculate exhaust gases (EGR) and to reduce in-cylinder radiative heat transfer (and thereby improve efficiency). Moreover, reformulation may enable the application of more sophisticated aftertreatment technologies. Since the reformulation is usually done by mixing oxygenates directly into the diesel fuel, such reformulations are applicable to biodiesel as well. Several major classes of chemical additives have been considered for diesel oxygenates: alcohols, ethers, glycol ethers, glycol esters, lactones, and carbonates. There are indications that it might be possible to produce completely smoke-free operation of a diesel engine by the incorporation of 38% (mass/mass) of oxygen into the fuel.³¹ Other authors have argued that the addition of more than 5% of any oxygenating additive would be cost prohibitive, or that supplies would prevent such a level of addition in the fleet.^{32,33} Some potential oxygenates for diesel fuel can be derived from biomass.³⁴ In any case, the potential of designing new fuel mixtures that incorporate oxygenates critically depends on knowledge of the thermophysical properties of the fluids. The volatility, as provided by the distillation curve method we apply, is part of that knowledge base. In this paper, we present measurements on mixtures of diesel fuel with dimethyl carbonate and diethyl carbonate, fundamental data for which are provided in Table 1. These data were obtained from the literature sources indicated except for the refractive index of dimethyl carbonate, which was measured for this work with a Abbe-type refractometer thermostatted with a circulating bath.

Dimethyl carbonate is used extensively as a methylating agent in organic synthesis and is preferred in this role because of lower toxicity than the other common reagents (such as iodomethane

Table 1. Data^a on the Additives Studied in This Work^{76,77}

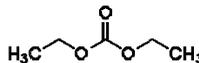
dimethyl carbonate:



CAS No. 616-38-6
 INChI = 1/C3H6O3/c1-5-3(4)6-2/h1-2H3
 RMM = 90.08
 T_{boil} = 90.25 °C
 T_{fus} = -5.6 °C
 Density = 1.07 g/mL (20 °C)
 Refractive index, n_D²⁰ = 1.3701 (20.0 °C)
 Flash Points: Closed Cup: 18 °C, Open Cup: 21.7 °C
 Flammable Limits: Lower: 4.22% Upper: 12.87%
 Vapor density (relative to air) 3.1

Synonyms: methyl carbonate; DMC; dimethyl ester of carbonic acid.

diethyl carbonate:



CAS No: 105-58-8
 INChI = 1/CSH10O3/c1-3-7-5(6)8-4-2/h3-4H2,1-2H3
 RMM = 118.13
 T_{boil} = 126.8 °C
 T_{fus} = -43 °C
 Density = 0.975 g/mL (25 °C)
 Refractive index, n_D²⁵ = 1.384 (20 °C)
 Flash point: Closed Cup: 25 °C
 Flammable Limits: Lower: 1.4 % Upper: 11 %
 Vapor density (relative to air) 4.1

Synonyms: Ethyl carbonate; Diatol; Eufin; ethoxyformic anhydride; diethylcarbonat; DEC; diethylester kyseliny uhlicite; diethylkarbonat; diethyl ester of carbonic acid.

^a In this table INChI is the International Chemical Identifier, a textual identifier for chemical substances, designed to provide a standard and human-readable way to encode molecular information and to facilitate the search for such information in databases and on the web, developed by IUPAC and NIST during 2000–2005. RMM is the relative molecular mass.

and dimethyl sulfate).^{35,36} It is biodegradable and is insoluble in water. Diethyl carbonate is also used as an ethylating reagent in synthetic processes (it is used in the synthesis of the anticonvulsant drug Phenobarbital³⁷), and it is also used extensively as a solvent in the textile industry. Like dimethyl carbonate, it is also biodegradable and insoluble in water. Investigations into the applications of these fluids as oxygenates or extenders for fuels has been ongoing for approximately a decade.

The applicability of a particular additive mixture is judged mainly by operational parameters of engines. In diesel engines, it is possible to use the distillation curve to design fuels for operability.^{38,39} Especially important with diesel fuels are the latter regions of the distillation curve, which describe the high relative molecular mass components of the fuel. It is also possible to correlate the distillation curve of fuels with exhaust emissions, a fact that is especially important with diesel engines. The emissions that have been studied include carbon monoxide, particulates, nitrogen oxides, and unburned hydrocarbons. These parameters are typically measured in studies performed on

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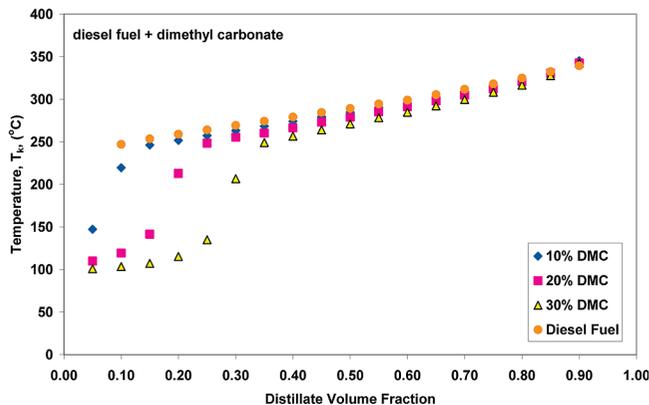


Figure 1. The distillation curves of diesel fuel with mixtures of DMC. Here we present T_k , the temperature measured directly in the fluid. The uncertainties are discussed in the text.

Table 2. A Summary of the Initial Behavior of the Diesel Fuel Mixtures with the Carbonate Additives (Dimethyl Carbonate = DMC, Diethyl Carbonate = DEC)^a

observed temperature, °C	diesel fuel 83.5 kPa		
vapor rise	233.4		
observed temperature °C	diesel fuel + 10% (v/v) DMC 83.49 kPa	diesel fuel + 20% (v/v) DMC 83.56 kPa	diesel fuel + 30% (v/v) DMC 83.74 kPa
onset vapor rise	118.9	100.9	96.6
	122.0	103.9	98.9
observed temperature °C	diesel fuel + 10% (v/v) DEC 83.52 kPa	diesel fuel + 20% (v/v) DEC 83.42 kPa	diesel fuel + 30% (v/v) DEC 83.47 kPa
onset vapor rise	169.0	150.8	141.5
	173.5	154.2	144.5

^a The vapor rise temperature is that 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 adjusted 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.

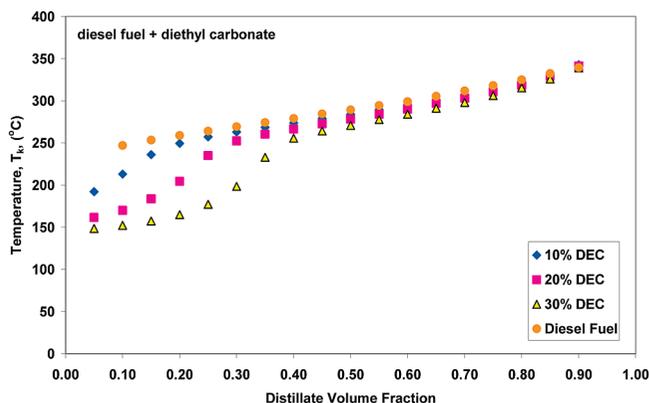


Figure 2. The distillation curves of diesel fuel with mixtures of DEC. Here we present T_k , the temperature measured directly in the fluid. The uncertainties are discussed in the text.

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.^{40,41} 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.

Advanced Distillation Curve Measurement. In earlier work, we described a method and apparatus for an advanced distillation

curve (ADC) measurement that is especially applicable to the characterization of fuels. This method is a significant improvement over current approaches,⁴² 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 assessment of the energy content of each distillate fraction; (6) trace chemical analysis of each distillate fraction; and (7) corrosivity assessment of each distillate fraction.^{43–56} This approach also provides important advantages over other methods such as the simulated distillation method embodied in procedures such as ASTM D-2887.⁵⁷ 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 the ability to model the distillation curve resulting from our metrology with an equation of state based model.^{58,59} Such thermodynamic model development is simply impossible with the classical approach to distillation curve measurement, or with any of the other techniques that are used to assess fuel volatility or vapor liquid equilibrium.

We have applied this metrology to gasolines, aviation fuels, and rocket propellants.^{50–56,60} 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 diesel fuels used today, for example, it is usually unnecessary to assess corrosivity as a function of distillate fraction.^{61,62} In the work reported here, we have applied the advanced distillation curve technique to diesel fuel and oxygenates of diesel fuel made with methyl carbonate and ethyl

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Table 3. Representative Distillation Curve Data^a for Mixtures of Diesel Fuel with Dimethyl Carbonate (DMC) and Diethyl Carbonate (DEC) in 10, 20, and 30% (v/v) Concentrations^b

distillate volume fraction, %	diesel fuel + 10% (v/v) DMC 83.49 kPa		diesel fuel + 20% (v/v) DMC 83.56 kPa		diesel fuel + 30% (v/v) DMC 83.74 kPa	
	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C
	Dimethyl Carbonate (DMC)					
5	146.2	103.4	109.9	95.1	102.5	95.5
10	219.1	106.4	119.2	99.4	105.1	97.1
15	246.1	225.5	141.5	107.8	108.7	100.9
20	251.6	233.8	212.8	110.6	116.9	84.2
25	257.4	241.7	248.5	228.9	136.6	109.9
30	263.1	248.5	255.3	238.7	205.0	116.2
35	268.2	254.2	260.2	244.8	251.0	229.5
40	273.8	260.4	266.5	252.0	259.3	241.5
45	279.4	266.2	273.1	259.2	266.6	250.2
50	284.5	271.5	278.8	265.4	273.8	258.4
55	290.2	277.9	285.0	272.1	281.0	266.2
60	295.7	283.7	291.1	278.5	287.4	272.8
65	301.9	289.6	298.1	285.3	295.3	281.2
70	308.3	297.1	304.7	292.3	302.8	288.2
75	315.6	283.6	312.0	299.6	311.4	296.4
80	323.4	309.5	320.9	306.6	319.7	304.2
85	332.3	316.8	330.5	316.1	330.6	312.8
90	345.4	327.5	342.5	327.9	345.3	326.8
	Diethyl Carbonate (DEC)					
5	192.2	155.0	161.5	140.3	148.5	134.6
10	213.0	172.0	170.0	147.1	152.2	138.2
15	236.2	197.1	183.6	155.7	157.3	141.9
20	249.5	228.1	204.4	167.2	164.9	146.8
25	257.3	240.7	235.0	191.0	177.2	153.7
30	263.0	248.8	252.4	229.9	198.4	163.6
35	268.4	254.8	260.3	244.0	232.9	177.7
40	273.9	260.9	266.6	252.2	255.7	234.0
45	278.9	266.7	272.7	259.4	264.2	248.5
50	284.1	272.3	278.3	265.9	270.9	256.3
55	289.5	275.2	284.2	274.1	277.8	264.3
60	294.9	283.5	290.0	278.4	283.9	270.9
65	300.9	289.3	296.7	285.1	291.3	278.6
70	307.0	294.9	303.2	291.5	298.0	285.0
75	313.9	301.1	310.5	298.1	306.1	292.6
80	321.5	307.7	318.5	304.8	315.3	299.8
85	331.3	314.8	328.9	311.9	325.9	308.8
90	342.7	324.9	341.4	323.0	339.1	316.8

^a Given as the average of between 4 and 6 distillation curves. ^b 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 recovery of the actual measured temperatures.

carbonate. These measurements will be helpful in the application and adoption of oxygenated diesel fuels.

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, ULSD 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.^{63,64}

The dimethyl carbonate and diethyl carbonate fluids were obtained from commercial sources as reagent grade fluids. The purity of these fluids was verified with a chromatographic method similar to that specified above for the diesel fuel. A moisture analysis was done with Karl Fisher Coulombic titrimetry. No more

than 10 ppm (mass/mass) water was found. Care was taken in the handling of these fluids to minimize any additional moisture uptake. Mixtures of these oxygenates with diesel fuel were prepared gravimetrically in mixing cylinders at room temperature in concentrations of 10, 20, and 30% (v/v). We note that these mixture concentrations may or may not result in a practical fuel for CI engines, as discussed in the introduction. Our purpose here is to provide the property measurement infrastructure for the development of equation of state based models that will represent such mixtures. For this reason, a wide coverage in terms of oxygenate concentration is desirable.

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.^{43,45,46} 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 T_k , (signifying placement in the kettle) the temperature in the fluid and T_h , the temperature at the bottom of

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Table 4. Constituents and Mole Fractions Used in the Simple Surrogate Models Developed to Simulate the Behavior of the Distillation Curves of Diesel Fuel with DMC

compound	mole fraction composition		
	10% (v/v) DMC mixture	20% (v/v) DMC mixture	30% (v/v) DMC mixture
n-nonane	0.0200	0.0160	0.0140
n-decane	0.0400	0.0310	0.0280
n-undecane	0.1000	0.0790	0.0700
n-dodecane	0.4046	0.3178	0.2848
n-tridecane	0.1000	0.0790	0.0700
n-tetradecane	0.0400	0.0310	0.0280
n-pentadecane	0.0400	0.0310	0.0280
n-hexadecane	0.0200	0.0160	0.0140
dimethyl carbonate	0.2354	0.3992	0.5368

the takeoff position in the distillation head. Enclosure heating was then commenced with a four-step 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.

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 done with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000109. 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.⁶⁵ 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.^{66–70}

Results and Discussion

Diesel fuel is a commodity fluid with seasonal and regional variations, although the degree of variability is not as great as with gasoline. We have found that the diesel fuel that we have used here (winter grade, low wax, ultra low sulfur, red dye for off-road use) is representative of many diesel fuels that we have examined. We performed between four and six complete distillation curve measurements for the diesel fuel and the 10, 20, and 30% (v/v) mixtures of diesel fuel with dimethyl and diethyl carbonate.

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 bore scope allowed measurement of 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. This can be noted visually or by the rapid increase in temperature of the thermocouple that monitors T_h . We have shown that this last temperature is actually the initial boiling temperature (the IBT, an approximation of the bubble point temperature at ambient pressure) of the initial fluid.⁴³ This measurement is significant for a mixture because it can be modeled with an equation of state. 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_h and 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 bubbling temperature is approximately 1 °C. The uncertainty in the vapor rise temperature is 0.3 °C.

In Table 2, we present the initial temperature observations for mixtures of diesel fuel with 10, 20, and 30% (v/v) each of dimethyl carbonate and diethyl carbonate. These values have been adjusted to atmospheric pressure with the Sydney Young equation, as mentioned earlier. The initial boiling temperature of the base diesel fuel itself, also adjusted, was 233.4 °C.

When we examine the initial boiling temperatures of the diesel fuel and carbonate mixtures, we note that the addition of the oxygenate dramatically decreases the initial boiling temperatures by between 12 and 22%, even for the 10% (v/v) mixtures, as reflected in the column labeled “vapor rise”. Note that for this comparison we have used absolute temperature to preserve thermodynamic consistency. As we have noted for all other fluids measured with the ADC 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. Those values, being obtained as the first drop of distillate enters the receiver, are 7–13 °C too high. As expected, the largest decrease in initial boiling temperature is produced by the mixtures with dimethyl carbonate.

Distillation Curves. Representative distillation curve data (presented as T_k , measured directly in the fluid) for the diesel fuel and diesel fuel with 10, 20 and 30% (v/v) of the carbonates are presented in Tables 3a and 3b, respectively. In these tables, the estimated uncertainty (with a coverage factor $k = 2$) in the temperatures is 0.3 °C. 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. We note from the data that there is always an appreciable difference in the temperatures measured at the T_h and T_k positions. This difference ranges from approximately 10 to 40 °C and averages approximately 20 °C. These observations indicate the absence of azeotropy between either dimethyl or diethyl carbonate and the major constituents of the diesel fuel. This result is consistent with the known (albeit sparse) literature on the occurrence of azeotropes with these compounds. Azeotropes have been observed in mixtures of dimethyl carbonate with n-hexane, cyclohexane, methylcyclopentane, and 1-hexene, but mixtures with higher hydrocarbons such as n-octane and n-decane were

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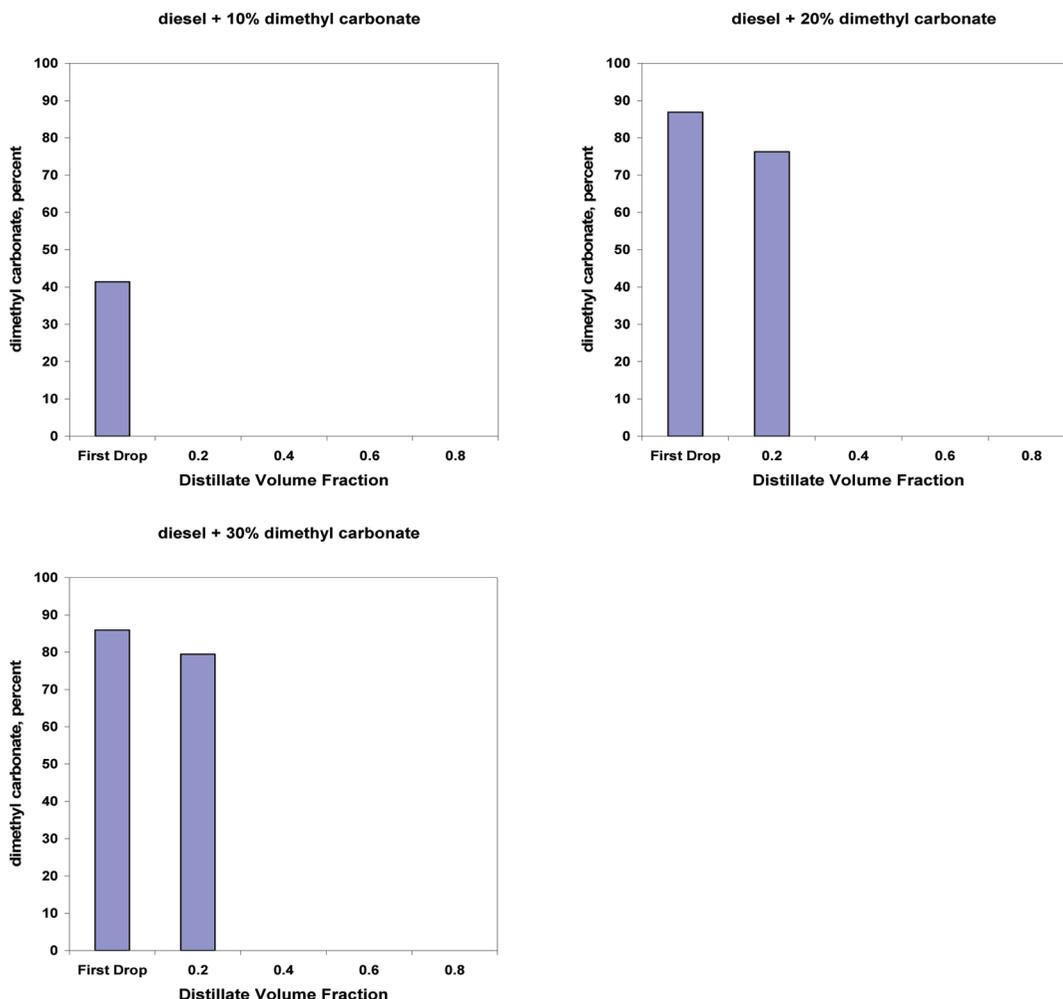


Figure 3. Histograms represent the measured distillate concentration in percent (mass/mass) of DMC as a function of distillate fraction. The uncertainty is discussed in the text.

found to be zeotropic.⁷¹ No literature could be found on azeotropy with diethyl carbonate.

The distillation curves are presented in Figures 1 and 2. A gross examination of the distillation curves for each of the carbonates shows that the early behavior of the curves (for distillate volume fractions up to 0.15) are consistent with the observed initial boiling points described earlier. Both of the carbonates are far more volatile than diesel fuel and significantly depress the boiling temperature relative to diesel fuel up to a distillate volume fraction of approximately 0.4. After this point, the curves closely approach that of diesel fuel, although the convergence is not completed until much later in the distillation, at a distillate fraction of 0.9. Not surprisingly, the effect on the distillation curve is more persistent for DEC than for DMC, even well after the 0.4 distillate volume fraction. The lower volatility of this additive causes its effect to be more pronounced with higher concentrations of additive throughout the curve. Thus, the curves of 30% (v/v) DEC are below those of diesel fuel until convergence at the 0.9 distillate volume fraction. As we will see below when we discuss the composition explicit data channel, this effect occurs although no carbonate can be found in the distillate beyond the 0.4 distillate volume fraction. The behavior described above is not unusual, and was observed with other volatile additives as well. For example, in our earlier measurements of gasoline with methanol and the butanols,⁷²

we noted that the additives caused a persistent offset, although the additive itself had been boiled out earlier in the distillation.

Composition Channel Information. While the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of the ADC approach can provide even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser, as discussed in the Introduction. Following the analytical procedure described in the experimental section, samples were collected and prepared for analysis. Chemical analyses of each fraction were done by gas chromatography with flame ionization detection and mass spectrometric detection. Calibration was done by the external standard method in which four solutions each of DMC and DEC were prepared in toluene. The results are presented in Figures 3 and 4 as histograms representing the mass percent of the DMC and DEC additives, respectively. While not explicitly measured, we essentially recover all the oxygenate.

For the mixtures of diesel fuel with both of the carbonate additives, we note that the carbonate emerges very early in the distillations. In the case of mixtures with DMC, for the 10% (v/v) starting mixture, we note that by the 0.2 distillate fraction, only traces of the additive can be found, and subsequent to this, none can be detected. For the 20 and 30% (v/v) mixtures, appreciable DMC is observed in the 0.2 fraction. This explains the structure of the curves presented in Figures 1 and 2. We

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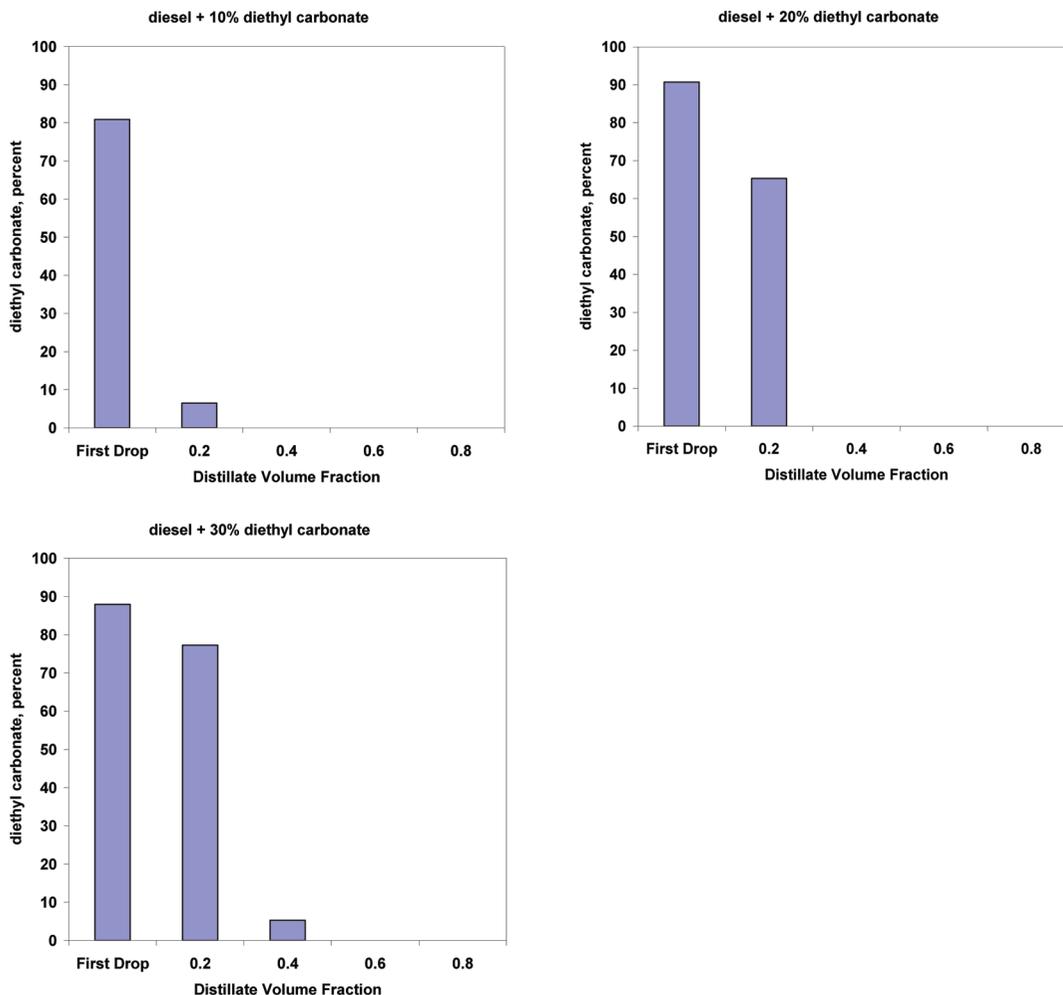


Figure 4. Histograms represent the measured distillate concentration in percent (mass/mass) of DEC as a function of distillate fraction. The uncertainty is discussed in the text.

note, for example, that for the 10% mixture, the distillation curve has nearly merged with that of diesel fuel, since only traces of DMC remain. For the higher concentrations, the curves have nearly merged by a distillate volume fraction of 0.4, after which no DMC can be detected in the distillate. In the case of mixtures of diesel fuel with DEC, which are less volatile than mixtures with DMC, we note that even for the 10% (v/v) starting mixture, we observe appreciable additive at a distillate volume fraction of 0.2, and nothing is subsequently detected. This is consistent with the distillation curve. For the 30% (v/v) starting mixture, we find appreciable DEC through the 0.4 distillate fraction.

We note that although the carbonate additives are removed relatively early in the distillations, their effects can be seen almost until the 0.9 distillate fraction. As mentioned earlier, this effect also occurred with other volatile additives and is a consequence of the vapor–liquid equilibrium established between the volatile additives and the less-volatile fuel constituents. Early in the distillation, the applied energy is being used to preferentially evaporate the additive. Hydrocarbon constituents that are less volatile and would otherwise begin to vaporize early in the distillation remain in the liquid phase. Their evaporation is delayed, thus the distillation curves of the 20 and 30% starting mixtures are seen to lie below that of diesel fuel although the carbonate additives are no longer present in the liquid. The absence of the additive and the increased presence of the hydrocarbons can be observed experimentally with the composition explicit data channel.

One can also model this behavior with an equation of state. For calculations of the thermodynamic properties of mixtures, we use a mixture model explicit in Helmholtz energy that can utilize any equation of state, provided that it can be expressed in terms of the Helmholtz energy. This form of model has been used successfully for refrigerant mixtures and for natural gas mixtures.^{73,74} We have adapted this approach to calculate the distillation curve of complex mixtures. As we have done for aviation and rocket kerosenes, we can devise a suite of components that is representative of the constituents of the fluid.^{58,59,75} We typically start with a comprehensive chemical analysis of the fluid to develop a list of potential constituents (for example, between 6 and 12) to include in the mixture model. Provided sufficient data are available on those constituents, pure fluid equations of state are developed for each. Then, using the mixture model mentioned above the distillation curve of a

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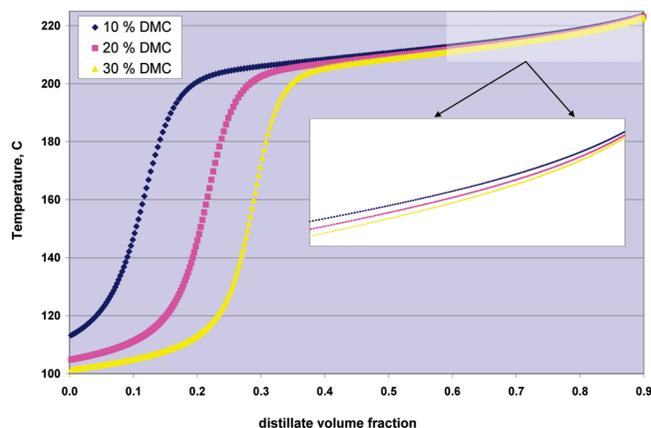


Figure 5. Calculated distillation curves of the three mixtures summarized in Table 4. This figure shows that the distillation curve for the 30% (v/v) mixture with DMC is below that of 10 and 20% (v/v) mixtures, although no DMC remains after a distillate volume fraction of 0.4. The magnified inset shows this for distillate volume fractions from 0.6 to 0.9.

mixture of those constituents is calculated and refined with other thermophysical property information that includes density, speed of sound, viscosity, thermal conductivity, etc.

Here, our goal is not a comprehensive equation of state for mixtures of diesel fuel with the carbonates, but rather we desire to further explain the distillation curve structures, and how the composition explicit channel explains those structures. Specifically, we seek to demonstrate theoretically that although the additive has been boiled out of the mixture by a distillate volume fraction of 0.4, the effect of its presence persists much later, as observed experimentally. To do so we construct very simple, rough surrogate mixtures for diesel fuel with DMC at approximately 10, 20, and 30% (v/v). The components and their mole fractions are provided in Table 4. Note that we have taken no pains to make this surrogate physically authentic. There is a complete absence of aromatics and cyclics in this surrogate mixture, and we have not fit any thermophysical property data such as density or the transport properties. We merely seek to examine the behavior that is predicted over the distillation curve.

The distillation curves calculated with the model for the mixtures provided in Table 4 are presented graphically in Figure 5. This figure shows that the distillation curve for the 30% (v/v) mixture with dimethyl carbonate is below that of 10 and 20% (v/v) mixtures, although no DMC remains after a distillate volume fraction of 0.4. The magnified inset shows this for distillate volume fractions from 0.6 to 0.9. We note that although the exact curvature and inflection of the measured distillation curves are not completely replicated by those calculated by the simple models we have used here, the calculated curves are very instructive. We note that the calculated curves do not merge in the latter stages of the distillations, even after the total depletion of the additive. This result is the same as that observed on the temperature profiles of the experimental distillation curves, and also by the information provided by the composition explicit channel.

Figures 6 and 7 show further calculations from our simple surrogate model, specifically tracking how the composition of the liquid and vapor phases change as the distillation proceeds. The compositions of DMC, n-nonane (the lightest component in the surrogate diesel), and n-hexadecane (the heaviest component in the surrogate diesel) are shown. The distillation process is modeled as a simple distillation with no reflux; as vapor is produced it is removed at a constant flow rate as described earlier. Figure 6 demonstrates that the concentration

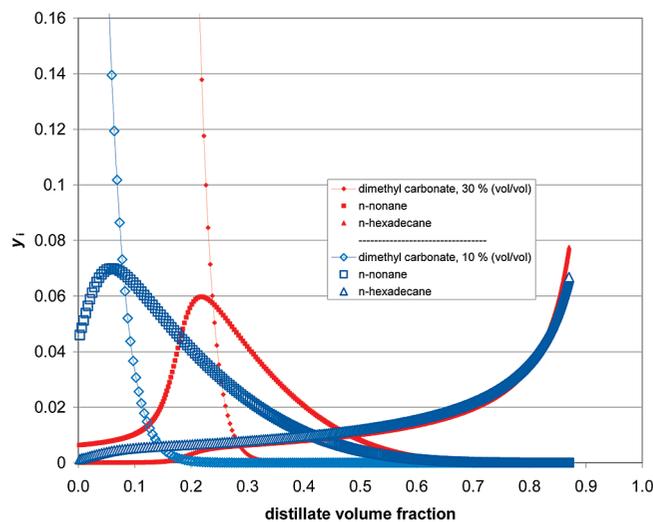


Figure 6. Calculated distillation curves (expressed as mole fractions of vapor, y_i) for the mixtures of 30 and 10% (v/v) DMC in the surrogate summarized in Table 4. We observe the changes in composition of DMC, n-nonane, and n-hexadecane in the vapor phase as the distillation proceeds.

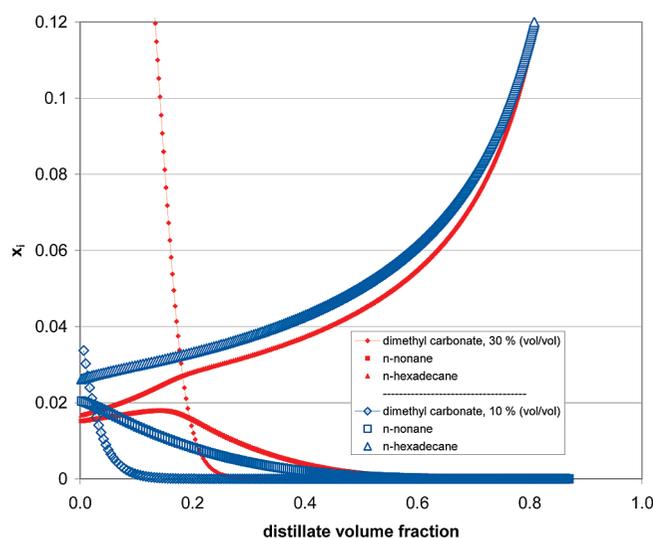


Figure 7. Calculated distillation curves (expressed as mole fractions of liquid, x_i) for the mixtures of 30 and 10% (v/v) DMC summarized in Table 4 showing the changes in composition of DMC, n-nonane, and n-hexadecane in the liquid phase as the distillation proceeds.

of the lightest component in the diesel surrogate (n-nonane) is affected more than the heavy component with the addition of DMC. This behavior is shown for two initial concentrations of DMC (30 and 10% (v/v)) as described in Table 4. In Figure 6, the peak in the vapor phase concentration of nonane is delayed, so that the removal of nonane from the liquid phase is also delayed. The difference in the 10 and 30% mixtures is dramatic, with the vaporization of n-nonane being delayed much longer into the distillation than the 10% mixture. The higher concentration of nonane in the liquid phase, shown in Figure 7, leads to the depression of the distillation curve seen in Figure 5 earlier, even though the DMC itself has boiled off.

We emphasize that the simple model presented above is not intended to serve as a proposed equation of state for diesel fuel. Indeed, when we develop such complex fluid equations of state, we begin with a comprehensive chemical analysis, then the distillation curve, then measurements on density (in the compressed liquid), heat capacity, and speed of sound. For the transport model we also measure viscosity and thermal conductivity, also in the compressed liquid. Thus, the process of

developing an equation of state for a complex fluid such as diesel fuel requires the distillation curve, but far more in addition.

Conclusions

In this paper we have presented measurements of the volatility of a typical petroleum derived diesel fuel with mixtures of DMC and DEC. The significance of these mixtures is that they anticipate part of the thermophysical property knowledge that will be required if the carbonates were to be adopted as an oxygenate for diesel fuel. These data have been developed by the application of the advanced distillation curve metrology. The temperature data are thermodynamically consistent, and can therefore be used in the development of equations of state

models for these complex fluids as we have demonstrated for other mixtures. These temperature data are augmented by the compositional information provided by the ADC approach. We observed that the distillation curves for increasing concentration of carbonate additive show an increased volatility, despite the fact that the additive has been boiled out. This behavior is a consequence of the vapor liquid equilibrium established among the components, and has been reproduced with a mixture equation of state model.

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