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Characterization of the Effects of Cetane Number Improvers on Diesel Fuel Volatility by Use of the Advanced Distillation Curve Method

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Supporting Information

ABSTRACT: The cetane number (CN) is a measure of the ignition quality of a fuel for compression-ignition engines according to the self-ignition delay. If the CN of a fuel is too low, chemical compounds known as CN improvers may be added to increase both the CN and performance of the fuel. The addition of CN improvers is dependent upon the detailed properties of the particular fuel. While many fuel properties are important for design, the vapor—liquid equilibrium, as described by volatility, is very sensitive to composition. In this work, we measured blends of diesel fuel with the following CN improvers: amyl nitrate, isoamyl nitrate, 2-ethylhexyl nitrate, and the multi-component CN improver PM-1, in diesel fuel by use of the advanced distillation curve (ADC) method to determine the amount of CN improver in the various distillate volume fractions. Tracking the CN improver throughout the volatility profile of diesel fuels provides valuable information for determining structural property relationships, and moreover, it provides the basis for the development of equations of state that can describe the thermodynamic properties of these complex mixtures, with specific attention paid to additives. We have found that the addition of CN improver significantly decreases the temperature at which boiling begins and that the majority of the CN improver is thermolytically degraded before the first drop can be collected. These observations are supported by low-pressure ADC, where the CN improver was found in fractions up to 30%. These results have implications in the prediction of thermophysical properties of diesel fuel with CN improvers.

INTRODUCTION

The cetane number (CN) is a measure of the ignition quality of a fuel for compression-ignition engines, tracking the selfignition delay and serving a function similar to that of the antiknock index (or octane rating method) for spark-ignition engines. Ignition delay is determined by two factors: the time that it takes the fuel to be vaporized and to mix with the air in the cylinder and the time that it takes for the vaporized fuel to react with oxygen through free radical processes.¹ In many instances, if the ignition delay is too long in a diesel engine, the results are unburned fuel, low power, and particulate formation and may increase engine noise and wear.²

Internationally, the CN of commercial diesel fuels varies from 55 to 35 depending upon the composition of the fuel.² Fuels containing a higher percentage of *n*-paraffin have a higher CN because combustion proceeds faster through mechanisms involving free radicals, whereas diesel fuels with a higher aromatic content have a lower CN because of their more stable ring structures, which require higher temperatures and pressures to initiate ignition.³

Various strategies exist to increase the CN, including blending diesel fuel with Fischer–Tropsch liquids⁴ and modifications to the petroleum stream to limit aromatics.^{5–9} If the CN of a fuel is too low, molecules known as CN improvers may be added to increase its CN and increase the performance of the fuel. CN improvers currently in use are frequently organic nitrates, which act by facilitating chain-initiation radicals to improve subsequent autoignition reactions.^{5,10,11} Nevertheless, organic nitrates have significant drawbacks, such as toxicity (LD₅₀ of

cyclohexyl nitrate of 425 mg/kg) and corrosivity.¹² Other commercial or proprietary formulations include mixtures with β -carotene; the operational mechanism of this additive is suggested to be the enhanced interaction of oxygen (from the fuel–air mixture).¹³

As new fuels develop in the changing political, environmental, and economic climate, the addition of alternative feedstocks will likely increase the variability in CN of fuels for compression ignition engines. This makes the manipulation of CN and the understanding of CN improvers even more important than previously thought. To obtain data critical for understanding the effects of minor constituents on fuel properties, most importantly the volatility or VLE, we applied the advanced distillation curve (ADC) method to diesel fuel blends containing "therapeutic" amounts (500-1000 ppm), that is, the typical treatment levels of CN improvers: amyl nitrate, isoamyl nitrate, isoamyl nitrite, and 2-ethylhexyl nitrate, and the newly introduced commercial, multi-component CN improver, designated herein as PM-1. Our purpose in doing so, consistent with our vision for replacing fit-for-purpose properties with fundamental properties, is 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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EXPERIMENTAL SECTION

Materials. The diesel fuel used in this work was obtained from a commercial source; fuel from this source has been used in much of our measurements with diesel fuel. The fuel was stored at room temperature. No phase separation was observed as a result of the storage conditions. The fuel was a winter-grade, low-wax, ultralowsulfur diesel fuel that incorporated a red dye (specifying off-road use) and was refined locally from petroleum of the Denver-Julesburg field. The fuel had a relatively high CN of 45 (the average for the United States is approximately 41). This fluid was used without any purification or modification. The composition was studied with a gas chromatographic (GC) method (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane, having a thickness of 1 μ m and temperature program from 90 to 275 °C, at 9 °C/min) with flame ionization detection (FID) and mass spectrometric (MS) detection. Samples were injected with a syringe into a split/splitless injector set with a 100:1 split ratio. The injector was operated at a temperature of 325 °C and with a constant head pressure of 55.2 kPa (8 psig). Mass spectra were collected for each peak from 15 to 550 relative molecular mass (RMM) units. Peaks were identified with guidance from the National Institute of Standards and Technology (NIST)/United States Environmental Protection Agency (EPA)/National Institutes of Health (NIH) Mass Spectral Database and also on the basis of retention indices.^{14,15} This analysis was unremarkable in that the typical pattern of commercial petroleum-derived diesel fuel was observed.

The CN improvers (amyl nitrate, isoamyl nitrite, isoamyl nitrate, and 2-ethylhexyl nitrate) and solvent used in this work (acetone) 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 μ m and temperature programs appropriate to each fluid) and were not purified further. A proprietary CN improver, PM-1, which was formulated to contain by mass 39.0% cyclohexanone, 59.9% 2-ethylhexyl nitrate, 0.1% β -carotene, and 1% Santoquin (1,2-dihydro-6-ethoxy-2,2,4-trimethylquinoline), was blended according to the given formulation from pure fluids from a commercial source. Data on these CN improvers and the components of PM-1 are presented in Table S1 of the Supporting Information.

Concentrations of CN improvers ranged from 500 to 2000 ppm (v/v). This falls within the normal range used for CN improvers.³ To gain additional insight into the properties of PM-1, higher concentrations from 2.5 to 5% (vol/vol) (25 000–50 000 ppm, vol/vol) were used for composition studies. Our study of a particular mixture ratio does not imply that mixtures with these concentrations are practical formulations for fuel.^{16–19} Our mixtures were chosen to cover as large of a range of compositions to serve our ultimate purpose of modeling the results with an equation of state. This is the same philosophy that we applied in our study of diesel fuel oxygenates.^{16–24}

ADC Measurements and Sampling. The ADC apparatus and procedure have been described previously;²⁵⁻³¹ thus, only a brief description, as it applies to this study, will be given here. For each measurement, 200 mL of diesel fuel or diesel fuel blend with CN improver 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 $(T_{\rm h})$, 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 $T_{\rm h}$ approximates what might be obtained from the classical distillation measurement procedure. Enclosure heating was then commenced with a model-predictive temperature controller.³² The heating profile was designed to be of similar shape to that of the distillation curve, but it leads the distillation curve by approximately 20 °C. Volume measurements were made in a level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock.³⁰

Because the measurements of the distillation curves were performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were adjusted 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.^{33–35} This value corresponds to a compound with a straight 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 could indeed represent the fluid as a very rough surrogate. The magnitude of the temperature adjustment is of course dependent upon the extent of departure from standard atmospheric pressure.^{30,31} The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level, resulting in a typical temperatures are easily recovered from the modified Sydney Young equation at each measured atmospheric pressure.

The composition of each distillate volume fraction of diesel fuel or fuel blend was studied by a GC method (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane, with a thickness of 0.25 μ m) with MS detection.¹⁴ The GC analysis of all samples was performed with helium carrier gas at 55.2 kPa (8 psig) and column temperature programming appropriate for each fluid. MS was used with the aid of the NIST/EPA/NIH Mass Spectral Database following column separation to provide compositional information by identification of peaks in the resulting chromatogram.¹⁴ These analytical results (compositions and relative quantities of components) are consistent with our prior knowledge of each fuel.

 β -Carotene Stability by Nuclear Magnetic Resonance (NMR) Spectroscopy. As mentioned earlier, the proprietary formulation PM-1 that we examined contains $\beta\text{-carotene}$ as a component. It is wellknown from kinetic studies that β -carotene degrades during thermal processing and storage and that this degradation may be described as a first-order reaction.³⁶ The exact rate is dependent upon many factors, including the solvent system.³⁶ To further characterize the samples of fuel blends with this additive, we used a 600 MHz NMR spectrometer to obtain proton spectra of β -carotene heated in *n*-dodecane (used here as a surrogate diesel fuel).³⁷ A solution containing approximately 0.1 mg of β -carotene was dissolved in 1 mL of *n*-dodecane at 50 °C. This concentration provided a strong NMR signal while still being soluble in n-dodecane. This solution was incubated at 100, 125, 150, 175, and 200 °C for approximately 1 h at each temperature. NMR samples were prepared by mixing approximately 40 μ L of the β -carotene solution in 1 mL of acetone- d_6 . The samples were maintained at 30 °C for NMR measurements. One-dimensional (1D) proton spectra were obtained for each sample under standard conditions (acquisition time of 2.7 s, delay time of 1 s, and 2 dummy scans), and spectra were the result of 1024 scans.

RESULTS AND DISCUSSION

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 boroscope allowed for 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 (IBT) (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, and it is the only point at which the temperature, pressure, and liquid composition are known. Measurement of these temperatures with mixtures of commercial diesel fuel is complicated by the presence of the dye mentioned above. As a result, we report only the onset and vapor-rise temperatures here. Vapor rise is accompanied by a sharp increase in $T_{\rm h}$ and is, therefore, far less subjective to

ascertain and, thus, 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 and the uncertainty in the vapor rise temperature is approximately 0.3 °C. Nevertheless, the addition of CN improvers to diesel fuel further complicates the measurement of onset and vapor rise temperatures. In Table 1, we

Table 1. Summary of the Average Initia	l Boiling Behavior of
the Diesel Fuel Mixtures with CN Imp	rovers Added ^a

observed	temperature (°C)	diesel fuel, 83.5 kPa					
	onset	204.2					
	vapor rise	218.8					
observed temperature (°C)	diesel fuel + 500 ppm amyl nitrate, 83.7 kPa	diesel fuel + 1000 ppm amyl nitrate, 83.2 kPa	diesel fuel + 2000 ppm amyl nitrate, 84.2 kPa				
onset	197.4	197.4 184.0					
vapor rise	218.6	217.5	215.1				
observed temperature (°C)	diesel fuel + 500 ppm isoamyl nitrite, 82.7 kPa	diesel fuel + 1000 ppm isoamyl nitrite, 83.3 kPa	diesel fuel + 2000 ppm isoamyl nitrite, 83.5 kPa				
onset	172.7	178.4	177.3				
vapor rise	216.9	216.8	216.7				
observed temperature (°C)	diesel fuel + 500 ppm 2-ethylhexyl nitrate, 82.7 kPa	diesel fuel + 1000 ppm 2-ethylhexyl nitrate, 83.1 kPa	diesel fuel + 2000 ppm 2-ethylhexyl nitrate, 82.9 kPa				
onset	189.5	173.1	180.4				
vapor rise	218.2	218.8	218.4				
observed temperature (°C) diesel fuel + 2000 ppm isoamyl nitrate, 82.8 kPa							
onset		184.2					
vapor r	ise	212.1					
observed temp	perature (°C) d	diesel fuel + 2000 ppm PM-1, 83.8 kPa					
onset	:	184.5					
vapor	rise	216.9					

^{*a*}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 modified 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.

present the initial temperature observations for mixtures of diesel fuel with CN improvers. The onset of boiling is consistently lowered by the addition of CN improvers, but it was slightly more difficult to determine the exact onset because the bubbles are typically small and occur with less frequency. In addition, when 1000 and 2000 ppm of the CN improvers were added, we frequently observed a rapid unpredictable boiling between the onset of bubbling and the vapor rise temperature. In particular, in the 2000 ppm isoamyl nitrate mixture, this phenomenon and vapor rise temperatures overlapped such that the vapor rise temperature appeared to be significantly lower than what was seen for any of the other mixtures. Thus, the uncertainty in the initial boiling temperatures of diesel fuel with CN improvers is 2 °C, which is somewhat higher than previously reported uncertainties for diesel fuel and mixtures of diesel fuel with oxygenate additives. This phenomenon is likely coincident with the thermolytic degradation of the CN. To further characterize CN degradation, a low-pressure distillation was performed and is discussed in detail below.

Distillation Curves. During the measurement of the distillation curves, both the kettle and head temperatures were recorded (T_k and T_b , respectively) at predetermined distillate volume fractions. The ambient atmospheric pressure was also recorded and used to adjust the temperatures to their atmospheric pressure equivalent by use of the modified Sydney Young equation, as mentioned earlier. The uncertainty in temperature, $T_{\rm k}$ measurements was approximately 0.3 °C. 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 volume fraction for a representative measurement for each mixture in parts a-d of Table 2. These data are also represented graphically in Figure 1. The $T_{\rm h}$ and $T_{\rm k}$ distillation curves were compared, and no azeotropic behavior was observed. This is in agreement to what is indicated by the literature.³⁸ The IBT is indicated as a hatch mark on the temperature axis. Except for the IBT, there is no significant displacement in the distillation curves with the addition of CN improvers in the range measured. This result is not surprising because these compounds are added to initiate radical reactions during combustion and, therefore, have the greatest effect on thermophysical properties early in the distillation. The distillation curves for amyl nitrate, isoamyl nitrite, and 2-ethylhexyl nitrate were remarkably similar, showing no significant deviation from the distillation curve of neat diesel fuel. Therefore, for isoamyl nitrate and PM-1 only, the distillation curves of 2000 ppm are presented in Figure 1.

While the distillation curves of the mixtures discussed above are similar, the composition-explicit feature of the ADC reveals that changes in composition occur nonetheless. This is discussed more fully below.

Distillate Composition. 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 μ L samples were collected in autosampler vials containing a known mass of acetone solvent. Chemical analyses of each fraction were performed by GC–MS. Calibration was performed by the external standard method, with four solutions of known concentration (prepared gravimetrically) of the CN improver, also prepared in acetone. The chromatographic parameters were optimized for each CN improver, as summarized in Table 3. In most cases, baseline resolution was easily obtainable for each fluid and the mass spectrometer was operated in scan mode. The measured concentrations of the CN improvers are presented in Figures 2-6 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 = 2.40 The evolution of the 2-ethylhexyl nitrate concentration during the distillation of PM-1 shows that the maximum concentration occurs at the 10% volume fraction and continues to decrease until 2-ethylhexyl nitrate has been completely vaporized (or thermolytically degraded). Because the boiling temperature of 2-ethylhexyl nitrate is less than of the vapor rise temperature of the neat diesel fuel, one would expect the first drop to contain the highest concentration of 2-ethylhexyl nitrate (as it did in the lower concentration distillations of 2-ethylhexyl nitrate in

Table 2. Representative Distillation Curve Data (Given as the Average of Three Distillation Curves) for Mixtures of Diesel Fuel with (a) Amyl Nitrate, (b) Isoamyl Nitrite, and (c) 2-Ethylhexyl Nitrate at 500, 1000, and 2000 ppm and (d) Isoamyl Nitrate and PM-1 at 2000 ppm^a

(a) amyl nitrate	diesel 500 pp nitrate,	fuel + m amyl 83.7 kPa	diesel 1000 pp nitrate,	fuel + om amyl 83.2 kPa	diesel fuel + 2000 ppm amyl nitrate, 84.2 kPa (c)		diesel fuel + 2000 ppm amyl nitrate, 84.2 kPa		diesel fuel + 2000 ppm amyl nitrate, 84.2 kPa		+ diesel fuel + 2000 ppm amyl hPa nitrate, 84.2 kPa		diesel f 500 p (c) 2-ethylhexyl 2-ethyl nitrate nitrate, 8		uel + pm hexyl 2.7 kPa	- diesel fuel + 1000 ppm l 2-ethylhexyl Pa nitrate, 83.1 kPa		diesel fuel + 2000 ppm 2-ethylhexyl nitrate, 82.9 kPa	
distillate volume fraction (%)	$(^{\circ}C)$	$\binom{T_{\rm h}}{(^{\circ}{ m C})}$	$\binom{T_k}{(^{\circ}C)}$	$\binom{T_{\rm h}}{(^{\circ}{ m C})}$	$\begin{pmatrix} T_k \\ (^{\circ}C) \end{pmatrix}$	$(^{\circ}C)$		distillate volume fraction (%)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	T_k (°C)	$(^{\circ}C)$	T_k (°C)	$T_{\rm h}$ (°C)					
5	228.0	182.8	227.7	183.5	227.1	160.2		5	227.6	100.0	227.6	108.8	227.0	100 1					
10	234.6	202.1	234.0	197.2	234.0	181.2		10	227.0	208.3	227.0	208.0	227.9	200.7					
15	240.8	209.4	240.2	206.3	240.1	196.0		10	234.1	208.5	233.0	200.9	234.3	209.7					
20	246.8	219.8	246.6	216.4	246.1	206.9		20	239.0	217.2	239.7	210.7	246.4	210.5					
25	253.1	225.8	253.3	225.2	252.8	213.8		20	252.0	223.2	273.9	223.5	240.4	220.2					
30	259.5	234.2	259.2	232.4	258.4	215.0		25	255.0	231.0	252.0	230.5	255.5	232.0					
35	265.4	240.3	265.0	240.7	264.5	228.3		30	250.5	237.3	230.3	230.7	256.0	240.0					
40	272.0	246.0	271.4	241.8	270.8	233.9		33	204.9	245.0	204.4	245.1	204.2	240.5					
45	278.4	250.9	278.1	249.0	277.1	239.3		40	2/1.5	255.1	270.0	250.9	270.4	232.5					
50	285.2	258.6	284.7	256.1	283.8	250.4		43	277.0	239.4	202.0	250.0	2/7.1	200.5					
55	291.3	264.1	290.9	261.3	290.1	255.5		30	204.1	2/1.0	203.9	200.2	205.2	200.5					
60	298.0	268.4	297.3	267.1	296.8	263.6		55	290.7	280.2	291.0	2/3.3	289.9	2/2.6					
65	305.5	274.5	304.6	273.5	304.2	268.9		60	297.2	280.7	290.0	280.8	296.1	280.0					
70	312.4	281.2	311.4	280.6	311.7	276.4		65	305.2	296.3	304.0	288.4	304.5	287.5					
75	319.8	285.9	319.1	281.2	319.5	282.8		70	311.6	302.7	311.4	296.6	311.6	294.5					
80	327.4	291.7	326.4	283.8	327.0	289.6		75	319.5	309.2	318.9	303.8	319.1	301.1					
85	335.1	296.1	334.5	291.1	336.1	304.4		80	327.1	313.7	326.2	311.8	327.3	315.3					
(b) isoamyl nitrite	diesel 500 ppn nitrite, 3	fuel + n isoamyl 82.7 kPa	diesel 1000 isoamyl 83.3	fuel + ppm nitrite, kPa	diesel 2000 isoamy 83.5	fuel + ppm l nitrite, kPa		(d) isoamyl nitrate	200 ate and PM-1 ni		diesel fuel + 2000 ppm isoamyl 1 nitrate, 82.8 kPa		diesel 2000 ppr 83.8	515.8 fuel + n PM-1, kPa					
distillate volume fraction (%)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)	$T_{\rm k}$ (°C)	$T_{\rm h}$ (°C)		distillate volume fr	action (%)	$T_{\rm k}$ (°C) T _h	(°C)	T_{k} (°C)	$T_{\rm h}$ (°C)					
5	230.5	207.4	228.0	199.1	227.2	197.2		5		227.5	19	92.8	227.5	202.1					
10	235.1	215.9	220.0	210.3	227.2	206.8		10		234.3	20	\$7.3	233.7	211.6					
15	233.1	213.9	234.5	210.5	230.0	214.6		15		240.7	21	17.1	239.6	220.1					
20	247.5	221.0	246.9	224.0	237.7	222,0		20		246.5	22	24.2	246.4	227.1					
20	253.0	237.3	2533	231.0	252.5	230.2		25		253.0 232.		32.1	253.1	235.7					
30	259.0	237.3	255.5	238.0	252.5	238.2		30		258.1	23	38.2	258.4	241.5					
35	257.2	240.8	264.9	230.0	250.2	230.2		35		264.4	24	14.8	264.4	248.0					
33 40	203.4	256.8	204.9	277.5	204.4	243.0		40		270.5	25	51.6	270.7	255.3					
40	271.1	250.0	271.4	252.5	271.5	252.2		45		277.4	25	58.1	276.8	261.0					
43 50	278.2	202.5	277.4	239.0	277.5	257.9		50		283.8	26	55.2	283.3	267.7					
50	204.0	200.1	204.5	200.8	203.5	200.3		55		291.0	27	71.4	290.3	274.7					
55 40	270.5	2/4.7	270.4 204 4	270.0	270.7	272.0		60		297.1	27	77.3	296.2	282.6					
0U (5	297.5	280.9	290.0	2/9.9	290.5	2/8.0		65		305.0	28	35.3	304.5	290.8					
05	304.0	288.5	304.5	288./	304.0	285./		70		312.4	29	93.7	311.1	296.8					
/0	312.3	295.2	311.7	295.9	311.1	293.3		75		319.5	30)1.2	318.4	305.4					
/5	319.7	301.2	319.2	303.4	319.0	299.9		80		326.9	30)6.5	326.9	313.7					
80	328.0	307.8	327.2	310.4	326.6	305.8		85		336.7	31	2.0	335.2	320.9					
85	557.4	319.3	333.5	319.0	335.2	313.0													

^aThe 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 for recovery of the actual measure temperatures.

diesel alone). The diesel fuel and other components of PM-1 contain small amounts of components that have boiling points lower than that of 2-ethylhexyl nitrate (such as cyclohexanone) or that may decrease the rate of thermolytic breakdown of 2-ethylhexyl nitrate (such as 3-ethoxy-2,2,4-trimethyl-1*H*-quinoline). The presence of these fluids therefore decreases the concentration of 2-ethylhexyl nitrate in the first drop.

It should be noted that the percent of CN improvers recovered through distillation was lower than what would be expected on the basis of mass balance. Indeed, it is likely that these compounds are thermolytically degraded during the measurement, possibly coincident with the rapid boiling phenomena observed between the onset of bubbling and vapor rise. To confirm that this is the case, additional experiments were performed with amyl nitrate in diesel fuel. A solution containing approximately 0.11% (mass/mass) of amyl nitrate in diesel fuel was held at a given temperature for 1 h and then analyzed by GC–MS in the manner discussed above. It was found that the concentration of amyl nitrate remains at approximately 0.11% (mass/mass) and does not degrade below 166 °C. Between 166 and 171 °C, the mass percent decreases to 0.05%, and between 170 and 175 °C, it continues to decrease to 0.03% (all temperatures have been adjusted with the modified Sydney Young equation as described earlier).





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Figure 1. Distillation curves of diesel fuel with the addition of CN improvers. 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.

These observations are in agreement with known thermolysis conditions.³⁹ To further study this change, amyl nitrate was added to *n*-dodecane (a surrogate for diesel fuel) at a high concentration (8% by mass). This mixture was heated until to the onset of bubbling, but heating was stopped at 206 °C, before vapor rise could occur. Between 196 and 204 °C, the mixture changed color from clear to dark brown. GC–MS analysis showed that there was a 90% reduction in the amyl

Figure 2. Histogram plot showing the results of the analysis for amyl nitrate as a function of the distillate volume fraction for the three diesel fuel starting mixtures (500, 1000, and 2000 ppm).

nitrate concentration between the original mixture and the mixture after being brought to 206 °C. The degradation product was identified as 1-pentanol. The GC–MS analyses also shows evidence of higher molecular weight compounds (found at longer retention periods). These peaks were not baseline-resolved and, thus, not identified. Because the CN improvers studied were mainly nitrates and nitrites, it is likely that the other CN improvers would be similarly degraded near the boiling temperature of diesel fuel.

Table 3. Summary of the Analytical Conditions Used for the Diesel Fuel/CN Improver Analyses as a Function of Distillate Cut

CN improver	chromatographic method	analysis time (min)
amyl nitrate	40 °C for 2 min	26.5
	then 10 °C/min to 275 °C for 1 min	
	SIM: <i>m/z</i> 60.0 and 76.0	
isoamyl nitrite	40 °C for 5 min	30.7
	3 °C/min to 60 °C for 1 min	
	then 15 °C/min to 300 °C for 2 min	
	SIM: <i>m/z</i> 60.0	
2-ethylhexyl nitrate	40 °C for 2 min	36.9
	then 3 °C/min to 120 °C for 1 min	
	then 25 °C/min to 300 °C for 0 min	
	SIM: <i>m</i> / <i>z</i> 72.0 and 99.0	
isoamyl nitrate	40 °C for 5 min	30.7
	then 30 °C/min to 60 °C for 1 min	
	then 15 °C/min to 300 °C for 2 min	
	SIM: <i>m</i> / <i>z</i> 71.0	
PM-1	60 °C for 2 min	29.0
	then 10 °C/min to 300 °C for 3 min	
	SIM, group 1: <i>m/z</i> 80.0 (cyclohexanone)	
	SIM, group 2: m/z 72.0 and 128 starting at 5.20 min (2-ethylhexyl nitrate)	
	SIM, group 3: <i>m</i> / <i>z</i> 174.0, 175.0, 202.0, 203.0, and 217.0 starting at 15.05 min (Santoquin)	



Figure 3. Histogram plot showing the results of the analysis for isoamyl nitrite as a function of the distillate volume fraction for the three diesel fuel starting mixtures (500, 1000, and 2000 ppm).



Figure 4. Histogram plot showing the results of the analysis for 2-ethylhexyl nitrate as a function of the distillate volume fraction for the three diesel fuel starting mixtures (500, 1000, and 2000 ppm).

It is of value to examine the behavior of the distillation curve and distillate fraction composition in the absence of the thermolytic breakdown of the CN improver. One approach for this is low-pressure ADC, as described in previous papers.^{40–42} Diesel fuel with 2.5 vol % of amyl nitrate was distilled at a pressure of 900 Pa. Figure S1 of the Supporting Information



Figure 5. Histogram plot showing the results of the analysis for isoamyl nitrate as a function of the distillate volume fraction for the three diesel fuel starting mixtures (500, 1000, and 2000 ppm).



Figure 6. Histogram plots showing the results of the analysis for the components of PM-1 as a function of the distillate volume fraction for the three diesel fuel starting mixtures [5% (50 000 ppm), 2.5% (25 000 ppm), and 0.5% (5000 ppm) (v/v)]. β -Carotene is not shown but is discussed in the text.

shows the distillation curve for the first 30% of this lowpressure distillation. If the distillation curve is adjusted with the modified Sydney Young equation, it may be compared to the distillation curve for diesel fuel. It appears that, without the



Figure 7. Distillation curves of diesel fuel performed at atmospheric pressure and diesel fuel with the addition of CN improver amyl nitrate distilled under low pressure (900 Pa). Here, we present temperature as $T_{\rm k}$, the temperature measured directly in the liquid phase. These temperatures have been adjusted to 1 atm with the modified Sydney Young equation. The uncertainties are discussed in the text.

thermolytic breakdown of the CN improver, the distillation curve is shifted to lower temperatures (Figure 7). Following the analytical procedure described in previous papers,^{40–42} 7 μ L distillate fraction samples were collected at 9, 14, 19, 24, and 29 vol % and from the cold trap (which contained approximately 4 mL of liquid). Chemical analyses of each fraction were performed by GC–MS. Calibration was performed by the external standard method, in which four solutions of known concentration (prepared gravimetrically) of amyl nitrate were prepared in acetone. The measured concentrations of amyl nitrate are presented in Figure 8 as a histogram. It should be



Figure 8. Histogram plot showing the results of the analysis for amyl nitrate as a function of the distillate volume fraction for the low-pressure distillation (900 Pa).

noted that, under the low-pressure conditions, amyl nitrate was not degraded and 90% of amyl nitrate was recovered in the first 30 vol % of the distillation (126 °C).

Hydrocarbon Classification. An analytical technique that complements the detailed analyses of distillate composition examines the diesel fuel blends for hydrocarbon types by use of a MS classification method similar to that summarized in ASTM D2789.^{43,44} The procedures, uncertainty, and potential

pitfalls of this method have been discussed previously.²⁷ This analysis was applied to the diesel fuel/CN improver blends with unremarkable results. The typical trends for hydrocarbon type analyses can be seen in Figure S2 of the Supporting Information, which shows the average of results from the CN improver blends.

β-Carotene Degradation as Observed by 1D Proton NMR. The multi-component CN improver, PM-1, contains β-carotene in addition to cyclohexanone, 2-ethylhexyl nitrate, and Santoquin. It is well-known that β-carotene can undergo thermal degradation at temperatures as low as 85 °C.³⁶ We were able to observe the degradation of β-carotene in *n*-dodecane (a simple surrogate for diesel fuel) by proton NMR by observing the 6.0–7.0 ppm region, which corresponded to the conjugated double bonds. The β-carotene spectrum at 50 °C (Figure 9) indicates that the majority of β-carotene in the sample



Figure 9. One-dimensional proton NMR spectrum of β -carotene dissolved in *n*-dodecane (surrogate diesel fuel) at 50 °C.



Figure 10. Thermal degradation study of the area of the NMR spectra corresponding to the conjugated double bonds in β -carotene. β -Carotene was dissolved in *n*-dodecane at 50 °C and then held at elevated temperatures for 1 h at each temperature. These spectra show significant degradation between 100 and 125 °C and almost complete degradation of these signals by 150 °C.

is in an all-*trans* confirmation.⁴⁵ Figure 10 is a comparison study by 1D NMR of the conjugated double bonds. It can be seen that changes begin to occur between 50 and 100 °C (the number of peaks in the 6.0–7.0 ppm region increases), serious degradation happens between 100 and 125 °C, and the signal is almost entirely lost by 150 °C. Thus, because β -carotene degrades before

the first drop temperature is reached, we were unable to trace it through the distillation. As a CN improver, however, the addition of Sanotquin (commonly used to prevent oxidative rancidity in feed, fat, and meal) and rapid heating in combustion settings may allow β -carotene in PM-1 to survive long enough to aid in ignition and improve the CN of the fuel. This will have to be studied in the future.

CONCLUSION

In this paper, we have reported the application of the ADC method to a number of mixtures of diesel fuel with CN improvers. Most importantly, the addition of CN improvers significantly changes the chemistry occurring around the onset of boiling and vapor rise. Indeed, the majority of the CN improver thermolytically degrades before the first drop is even collected. IBT comparison of a number of CN improvers allows us to better understand the variability in additive packages, which in the future will lead to a more comprehensive modeling system. Indeed, modeling of this system by use of our surrogate mixture approach will require the component slate to be modified as one desires predictions at higher and higher temperatures. In particular, as one attempts to predict thermophysical properties at temperatures approaching the IBT and then up to 10-20 distillate volume fraction, the contribution of the CN improver molecule will have to be gradually "tuned out" out of the property calculations. We note also that this strictly thermodynamic consideration ignores the kinetics of the thermolytically changing concentration. Only the combination of the decomposition kinetics and the vaporization thermodynamics will enable a true predictive picture, in which time is an additional independent variable. We note that, in other work on aviation turbine kerosenes,⁴⁶ our efforts to develop a general tunable model that will account for the variability of the fluid required a compositionbased parameter that is easily available. We chose the CN as one candidate parameter; while a gas turbine is very different from a compression-ignition engine, the CN is generally measured for jet fuels as a fit-for-purpose property. The work on this generalized model is ongoing. The complication with the addition of CN improvers to diesel fuel is that, as mentioned above, the contribution will have to be gradually tuned out as the additive reacts.

ASSOCIATED CONTENT

S Supporting Information

Distillation curve of diesel fuel with the addition of 2.5% amyl nitrate performed under low-pressure conditions (900 Pa) to avoid thermolytic breakdown of amyl nitrate (Figure S1), average plots, of all the blends, of the hydrocarbon family types resulting from the moiety family analysis performed on CN improver blends and diesel fuels (Figure S2), data on the CN improvers and the components of the CN improver PM-1 studied in this work (Table S1), and summary of the distillate volume fraction analysis (also shown in histogram plot form in Figures 2–6) of the diesel fuel mixtures with the CN-improving additives (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Disclaimer: To describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the NIST, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

The authors declare no competing financial interest.

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