Effect of 2-Ethylhexyl Nitrate Cetane Improver on NO_x Emissions from Premixed Low-Temperature Diesel Combustion

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Production implementation of premixed low-temperature diesel combustion (LTC) is highly attractive because it can lead to low engine-out particulate matter (PM) and NO_x emissions. It is important for LTC strategies to yield acceptable emissions while consuming commercially available fuel, whose properties vary substantially and which contains various additives. The chemical reactions of 2-ethylhexyl nitrate (2-EHN), an additive used to increase the cetane number of a diesel fuel, show potential to increase the NO_x emissions of a diesel engine. While 2-EHN has been widely shown to not affect the emissions of conventional diesel combustion, few results are available for LTC, which features different combustion characteristics and significantly lower NO_x emissions. This paper demonstrates the effect of using a fuel doped with 2-EHN cetane improver in a direct-injection, diesel-fueled LTC operating mode. Testing was conducted at a light-load condition on a modern single-cylinder engine, fueled with two sets of test fuels at matching cetane numbers (47 and 53), with some test fuels using 2-EHN cetane improver. The addition of 2-EHN to the fuel increases the engine-out NO_x for the tested LTC operating condition. Decomposition of the nitrate cetane improver forms NO and NO_2 in significant quantities relative to the low engine-out NO_x emissions from LTC.

Introduction

In response to the new restrictions on exhaust gas emissions, particularly to particulate matter (PM) and NO_x (NO + NO_2), new strategies for diesel combustion have been developed.[1,2] To achieve a simultaneous reduction in PM and NO_x emissions, these combustion strategies seek to exhibit two primary properties: a well-mixed cylinder charge prior to ignition to avoid unfavorable carbon−oxygen ratios that lead to PM formation and combustion temperatures that remain relatively low to minimize NO_x and PM formation. Commonalities between strategies, termed low-temperature diesel combustion (LTC), include heavy use of cooled exhaust gas recirculation (EGR) to increase the time available for fuel−air mixing and to lower combustion temperatures and altered fuel injection strategies to improve fuel−air mixing levels and slow initial combustion burn rates.[1−3] The combination of high flow rates of cooled EGR and increased injection pressures decreases soot formation by reducing the presence of mixture regions with locally rich equivalence ratios, locations which are known to produce soot.[4,5] Cooled EGR extends the ignition delay and increases the time available for fuel−air mixing, while increased injection pressure improves fuel spray breakup and reduces physical mixing time.[4] Further, the CO_2 in the recirculated exhaust gas slows the formation rate of soot precursors.[6] Cooled EGR reduces NO_x formation by dilution of the intake mixture[7] and absorbing energy released by the combustion process to decrease the combustion temperature.[8] Retarded injection timing phases combustion later in the cycle to lower peak combustion temperatures and restrict the available time for thermal NO_x formation.[9] While desirable to take advantage of the low soot and low NO_x characteristics of LTC over the entire engine operating range, LTC may only replace conventional diesel combustion in the light to midload operating ranges. The operable range of LTC is constrained by combustion stability and misfire at light load and emissions at high load.[10−12]

With strict emission regulations set to require very low PM and NO_x vehicle emission levels in the upcoming years, production implementation of LTC strategies is attractive. To enable production implementation, it is critical to characterize parameters which could increase PM and NO_x emissions with these combustion strategies. Variations in petroleum fuel properties such as cetane number have been shown to alter emissions by shifting combustion phasing[13] but can be compensated for using engine control parameters. However, the presence of additives in the fuel, specifically

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nitrate cetane improvers, may directly increase emissions levels.

A common cetane improving additive, 2-ethylhexyl nitrate (2-EHN, EHN), is used to improve diesel fuel ignitability. The chemical formula is $C_8H_{17}NO_3$, with the basic structure an ethyl hexane molecule with one of the hydrogen atoms replaced with an NO_3 nitrate radical. EHN is stable at room temperature conditions, and its decomposition reaction rates are even slower when in a fuel solution at high pressure.[14,15] Thus, EHN remains stable within the fuel injection system, only decomposing within the cylinder after injection. The addition of EHN improves ignitability, and therefore the cetane number, by increasing the stock of radicals (ignition precursors) participating in the ignition process.[16,17] However, once ignition occurs, the effect of the EHN is limited, and the combustion process is dictated by the properties of the bulk fuel.[18]

The cetane improving reaction process of EHN is identified and described in prior works.[14,19−23] EHN decomposes at temperatures in the range of 450−550 K, yielding, after secondary reactions, formaldehyde (CH_2O), nitroheptane ($C_7H_{15}NO_2$), nitrogen monoxide (NO), nitrogen dioxide (NO_2), and assorted radicals.[14,19−22] By 550 K, EHN is entirely decomposed.[22] As the temperature exceeds 650 K, the nitroheptane decomposes, further increasing the concentration levels of formaldehyde and NO_2.[21,22] The NO_2 reacts through two separate sets of reactions, one with the formaldehyde formed from EHN decomposition and the other with unburned diesel fuel, to form hydrogen nitrite, HNO_2. The HNO_2 dissociates into NO and the hydroxyl radical (OH).[19,21] The hydroxyl radical is the combustion precursor which has a role in the chemical reactions initiating combustion.[24−26] Increasing the concentration of hydroxyl radicals improves the likelihood of ignition, thereby improving the ignition quality, perceived ignitability, and measured cetane number of the fuel.[23]

Examination of the EHN decomposition process described indicates that NO and NO_2 are formed by the initial decomposition, and the final reaction products include NO. This implies that introducing EHN into the combustion process results in an additional (fuel-borne) NO_x formation mechanism that would otherwise not be present. Substantial prior research concludes that EHN addition does not increase NO_x emissions but in many cases actually decreases it.[18,27−36] However, these studies were carried out with conventional diesel combustion. Relative to the high levels of NO_x produced by conventional diesel combustion, the amount of NO_x resulting from EHN decomposition would be insignificant. Further, changes in conventional diesel combustion resulting from an increased fuel cetane number due to EHN usage can decrease NO_x emissions, overshadowing the direct NO_x production from EHN decomposition. Depending on the test structure used, this could be significant. Increasing fuel cetane number, which occurs when EHN is added, reduces the premixed burn fraction of conventional combustion, leading to lower peak combustion temperatures and decreased thermal NO_x formation.[37,38] This reduction would overshadow any NO_x directly formed by EHN decomposition. For combustion processes resulting in low engine-out NO_x levels, the amount of NO_x formed directly by EHN decomposition may be significant. One recent source reports that, based on a principal components analysis model of a limited set of engine data, adding EHN to the fuel may increase the NO_x emissions of a diesel-fueled, homogeneous charge compression ignition (HCCI) engine with low engine-out NO_x emissions.[39] With EHN fuel additive linked to increased NO_x emissions with HCCI combustion, it is imperative to quantify and understand the effect EHN has on other combustion modes producing low NO_x emissions levels, including LTC. Accordingly, this study examines the changes in NO_x emissions of an LTC operating mode caused by the addition of EHN additive to the fuel.

Experimental Methods

Experimental Setup. The experimental investigation was conducted on a single-cylinder engine,[12,13] one which is designed based on the production 1.7 L four-cylinder diesel engine used in prior LTC research at the University of Michigan.[3,40−44] The single-cylinder test engine has four valves per cylinder and a centrally mounted common rail fuel injector. The piston features a toroidal shaped combustion bowl yielding a 15:1 compression ratio.

Gaseous exhaust emissions were sampled with a Horiba Series 23 emissions bench featuring a chemiluminescent analyzer for

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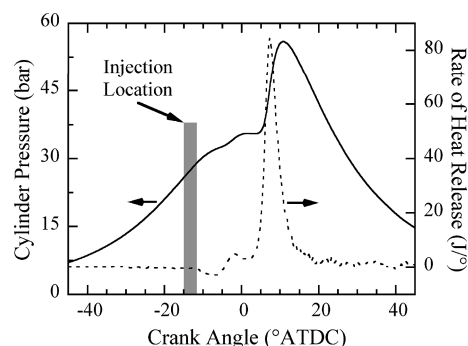
Figure 1. Characteristic example of the LTC strategy used in this study. MK1 fuel, 1500 rpm, 5 bar IMEP, 40% EGR, 15° BTDC injection timing.

measuring NO_x (NO and NO_2 only), a heated FID for hydrocarbons, infrared analyzers for CO and CO_2, and a paramagnetic analyzer for oxygen. The central focus of this work is NO_x emissions, which are reported on a per-mass-fuel basis (g/kg of fuel) as an emissions index,[45] denoted as EI-NO_x. EGR flow rates were calculated using measurements of intake and exhaust CO_2 concentration and reported on a wet mass-percent basis. Intake oxygen concentrations were derived from the calculated EGR flow rate and measured oxygen concentration in the exhaust. Equivalence ratios were computed from the measured exhaust emission concentrations.[45]

Cylinder pressure measurements were taken with a water-cooled Kistler 6041A pressure transducer at 0.2 degree intervals across 200 engine cycles. Calculation of cylinder pressure derived heat release was conducted with a single-zone ideal-gas model of combustion in the form published by Gatowski et al.[46] Heat release analysis was conducted on each recorded cycle individually, with the reported results being the average across 200 cycles. Mass of residuals was calculated using the expression published by Yun and Mirsky with final blowdown conditions specified in the same manner as the original publication.[47] Heat transfer was estimated using Hohenberg's correlation.[48] Heat losses were corrected so the sum of the apparent heat release and heat loss equals the total energy release expected from the fuel, found using the fuel flow rate and the lower heating value of the fuel.

Plotted data sets contain error bars representing 95% confidence. The uncertainty includes both experimental variation, represented by two standard deviations of the measured data, and instrument uncertainty based on the instrument specifications. Instrument and experiment uncertainties were combined using the Root Sum Squares method, and the uncertainties of calculated parameters were computed with sequential perturbation methods for uncertainty propagation.[49] Fit lines presented on plotted data are intended for clarity and visualization purposes only and are not intended to imply a mathematical correlation for the data.

Combustion Mode. The LTC strategy used in this paper was similar to prior studies[3,12,13,41] and features high rates (40% or 45%) of cooled EGR, along with a single direct fuel injection event. The resulting combustion exhibits behavior characteristic of LTC: an ignition delay substantially longer than the injection duration, presence of a cool-flame heat release, and a single sharp premixed main heat release. These attributes are visible in Figure 1, which features characteristic pressure and rate of heat release traces for the LTC strategy used in this study. The
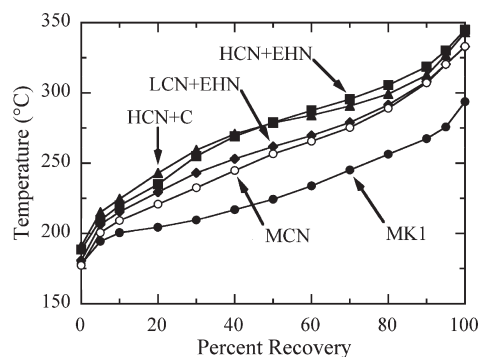
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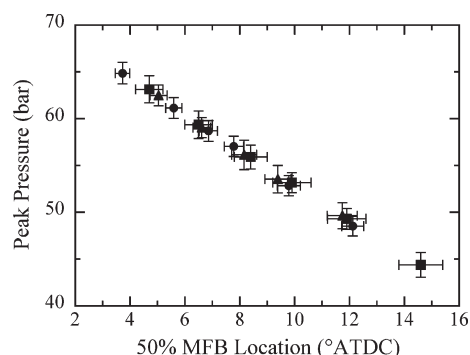(47) Yun, H.; Mirsky, W. *SAE Tech. Pap. 741015*. 1974.
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Table 1. General Properties of the Test Fuels

	MK1	HCN + EHN	HCN + C	MCN	LCN + EHN
cetane number (-)	53	54	53	47	47
sulfur (ppm)	12	16	14	8	8
density (g/mL)	0.81	0.85	0.84	0.85	0.85
LHV (MJ/kg)	43.5	42.4	43.0	42.8	42.5
T50 (°C)	224	279	279	262	257
alkanes (%)	95	72	75	80	72
olefins (%)	1	5	4	1	2
aromatics (%)	3	23	21	19	26

injection location shown stems from the commanded injector signal, with the start of injection defined as the time when the injector signal current reaches the opening current level. Measurements of injection line pressure show a one-degree phase lag from the commanded injection signal, so the actual injection event occurs with a lag of one degree or less after the commanded injection timing.

Developed as a part of previous research on LTC,[12,13] and derived from previous studies,[3,41] the operating condition used in this study is 1500 rpm with indicated mean effective pressure (IMEP) held constant at 5.00 ± 0.02 bar. This corresponds to a light midload operating condition representative of an average operating condition for LTC combustion. Intake and exhaust absolute pressures were fixed to 100 and 110 kPa, respectively. Coolant, oil, and EGR temperatures were maintained at 85 °C. The fuel rail pressure remained constant at 1000 bar. Primary engine variables in this investigation were EGR quantity and injection timing. EGR mass flow was held at either 40% or 45%. At this operating condition, a 40% EGR mass flow corresponds to an intake oxygen concentration of 15.2 ± 0.4% and an equivalence ratio of 0.79 ± 0.02, while a 45% EGR mass flow yields an intake concentration of 14.0 ± 0.4% and equivalence ratio of 0.89 ± 0.02. The timing of the single fuel injection was swept from an injection timing yielding slightly over 90 dB combustion noise back to the misfire limit. It is important to note that combustion remained stable in all cases: there was no misfire, and the coefficient of variation (COV), defined as the standard deviation of 200 cycles of data divided by the mean over the same period, of IMEP remained below 1.5% for all test points.

Test Fuels. Two sets of test fuels were used, centering on different matched cetane numbers. The first set of fuels, centering on a cetane number (CN) of 53, included a Swedish Environmental Class 1 fuel (MK1), along with two variations of a doped US certification fuel. The doped certification fuels were created by adding either 1150 ppm 2-EHN (HCN + EHN) or 15% *n*-cetane (HCN + C) to the same base fuel with a relatively high cetane number (HCN) of 48. The second set of fuels, centering around a CN of 47, was comprised of a US certification fuel naturally yielding 47 CN (midrange cetane, MCN) and a US certification fuel with an undoped CN of 42 (low cetane, LCN) which was doped with 900 ppm 2-EHN to yield the final 47 CN (LCN + EHN). Final fuel specifications are given in Table 1, and their distillation curves are shown in Figure 2. There is some spread between the distillation curves of the 53 CN fuels, with the MK1 fuel exhibiting a significantly lower distillation curve. However, within each fuel set, one petroleum-only fuel possesses a distillation curve which is very close to the EHN-doped fuels.

Testing of fuels within a fuel set was conducted within a short period of time for maximum consistency and comparability of measurements. However, direct comparison of emission magnitudes between the results of the 47 CN and 53 CN fuel sets should not be made since significant time passed between testing of the two fuel sets. Both injector condition and ambient air conditions can change over lengthy time periods, and emissions, most critically NO_x, are sensitive to these parameters.

Though CO, HC, and PM emissions are important for engine combustion studies, NO_x emission results are the focus of this

Figure 2. Distillation curves for different test fuels. Matched set of 53 CN fuels: (●) MK1, (■) HCN + C, (▲) HCN + EHN. Matched set of 47 CN fuels: (○) MCN, (◆) LCN + EHN. Testing conducted according to ASTM International Standard D86, with relevant uncertainty.
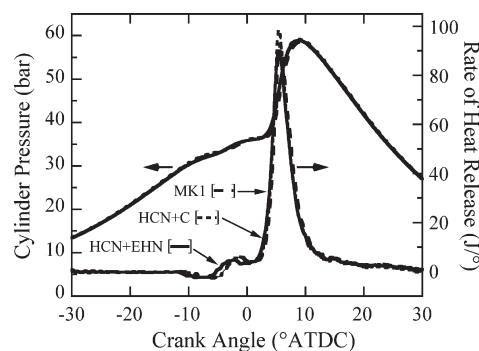

Figure 3. Matching peak cylinder pressure with matched combustion phasing across 53 CN fuels at 1500 rpm, 5 bar IMEP, 40% EGR condition. (●) MK1, (■) HCN + C, (▲) HCN + EHN. Other test fuel sets and EGR rates exhibit identical behavior.

Figure 4. Representative matching traces of cylinder pressure and rate of heat release for the 53 CN set of test fuels. 1500 rpm, 5 bar IMEP, 40% EGR, with start of injection timings as follows: MK1 fuel and HCN + C at 13° BTDC and HCN + EHN at 14° BTDC. Common location of 50% MFB is 6.7 ± 0.3° ATDC. Cylinder pressure and rate of heat release traces are averages over 200 engine cycles.

paper. Emissions of CO and HC follow the same trends identified in a prior study.[13] When combustion phasing and EGR level are matched for a given condition, there are no significant differences in CO and HC emissions between fuels, including those doped with EHN. Fuel-sourced variations in PM emissions are difficult to quantify within this experiment. Carbon soot emissions, measured with an AVL 415S smokemeter, are low for all tested conditions, and variance between fuels fall within the experimental uncertainty. The EHN-doped fuels appear to generally produce higher soot emissions, which may be the result of injector fouling which was more prevalent in the tests of EHN-doped fuels. However, with the available instrumentation and test structure, the magnitude could not be quantified nor the source directly identified. Given these notes on the other emissions, the results and discussion focus solely on NO_x emissions, where significant new results were found.

Results and Discussion

NO_x Emissions Trends. Results of a prior work[13] show that, for the given LTC operating mode, cylinder conditions are very similar when combustion phasing is matched. With the current sets of tests fuels, this holds true. In both studies, combustion phasing is defined as the location of 50% mass fraction burned (MFB), the point in the engine cycle when half of the apparent fuel energy has been released. This is a commonly used metric for specifying combustion phasing, and trends are consistent if alternative methods, including location of peak cylinder pressure or location of peak heat release, are used. As shown in Figure 3, peak cylinder

pressure correlates very well with combustion phasing, the location of 50% MFB, for all test fuels, indicating similar combustion conditions. Though illustrated with the 53 CN set of fuels at 40% EGR, the behavior shown is also present within the data taken at different EGR rates and with the lower cetane number fuel set. Giving confirmation of similar combustion conditions, there is very strong agreement between the cylinder pressure and heat release traces for the different test fuels when the combustion phasing is matched, as demonstrated in the representative set shown in Figure 4. The cool-flame heat release of the EHN-treated fuel (HCN + EHN) is advanced over the other fuels by one degree, the same increment that the injection timing was advanced to maintain the matching combustion phasing. The advance was necessary due to a shift in the combustion caused by injector fouling present in the tests of EHN-treated fuels.

When combustion phasing is aligned for this LTC condition, combustion generates virtually identical heat release and cylinder pressure behavior and should, based on prior research,[13] result in identical gaseous emissions, particularly NO_x, independent of fuel. However, fuels doped with 2-ethylhexyl nitrate produced significantly higher levels of NO_x emissions than the hydrocarbon-only fuels. The increase in NO_x emissions was present in the results of both sets of fuels and at both EGR levels tested, as shown in Figure 5. The 0.10−0.15 g/kg of fuel difference in NO_x emissions corresponds to approximately a 6 ppm increase in exhaust NO_x concentration, over a 5−15 ppm base level for the petroleum-only fuels. The NO_x increase is especially notable at the 45% EGR condition, where NO_x emissions are minimal and independent of combustion phasing. The NO_x concentrations at this EGR level are nearly double those from the petroleum-only fuels. Thermal NO_x formation should be identical since the pressure traces match. At 45% EGR, the combustion phasing independent NO_x levels indicate there is minimal thermal NO_x formation. Given the similar combustion behavior between the EHN-doped and petroleum-only fuels, it would be expected that the prompt NO_x formation would be similar, as well. If prompt NO_x formation is equivalent and thermal NO_x formation is equivalent (or nonexistent), the difference in NO_x emissions must result from a different mechanism than normally present. The indicated source of the increased NO_x emissions with the doped fuels is from the nitrogen found in the EHN cetane improver.
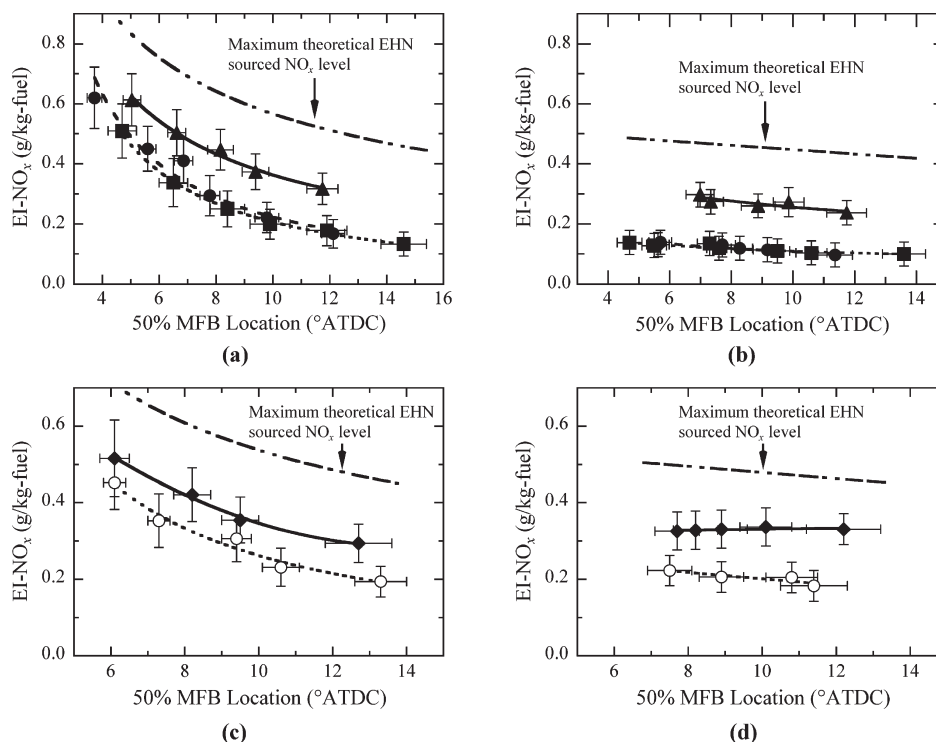
Figure 5. NO_x emissions versus combustion phasing, along with theoretical maximum NO_x produced from EHN decomposition—calculated assuming all nitrogen from EHN in fuel exits as NO_x. Operating condition is 1500 rpm, 5 bar IMEP, with (a) 53 CN test fuels, 40% EGR, (b) 53 CN test fuels, 45% EGR, (c) 47 CN test fuels, 40% EGR, (d) 47 CN test fuels, 45% EGR. (●) MK1, (■) HCN + C, (▲) HCN + EHN, (○) MCN, (◆) LCN + EHN.

Source of NO_x Increase. The overall maximum possible level of NO_x production from the EHN additive can be calculated from the decomposition reactions: every molecule of EHN contains one nitrogen atom, so each mole of EHN can yield at most one mole of NO. Using the EHN concentration of each fuel (1150 ppm by volume for the high cetane, 900 ppm by volume for the mid cetane), the calculated maximum possible mass of NO which can be created from the EHN is 0.34 g/kg of fuel and 0.27 g/kg of fuel, respectively. The increase noted in NO_x emissions (0.10−0.15 g/kg of fuel) is covered by both these formation levels, indicating the NO_x from EHN decomposition can account for the full difference in NO_x emissions. This relation is illustrated in Figure 5 with curves showing the maximum theoretical NO_x formed from the EHN. These curves for the 53 CN fuels result from adding the maximum possible NO_x increase (0.34 g/kg of fuel) to the average NO_x value at a given phasing from the two petroleum-only fuels (MK1 and HCN + C). For the 47 CN fuels, these curves result from adding the maximum possible NO_x increase (0.27 g/kg of fuel) to the NO_x values from the MCN fuel. The increase in engine-out NO_x emissions is about a third of the predicted maximum NO_x formation level. The difference between the maximum possible formation and measured NO_x emissions is accounted for by formation of nitrogen-containing compounds other than NO and NO_2 and shifts in NO_x equilibrium reactions. Incomplete decomposition of the EHN additive is not responsible for the discrepancy. Since complete EHN decomposition occurs as temperatures exceed 550 K[22] and heat release analysis of cylinder pressure indicates cylinder temperatures in excess of 900 K at the time of the direct fuel injection, complete eradication of EHN is assumed.

Formation of nitrogen-containing compounds other than the NO and NO_2 likely accounts for the difference between the maximum predicted NO_x emissions increase and the measured levels. Incomplete conversion of all nitrogen in EHN to NO_x has been documented in the literature. Results from flow reactor combustion of EHN-laced hydrocarbons suggest that nitrogen was not conserved across the reaction, even when the nitrogen in EHN was the only nitrogen present in the system.[22] This indicates that other nitrogen-containing compounds were present in the reaction products but were not able to be identified. However, compounds including HCN and HNCO were identified in the products.[22] These compounds were not quantified by the chemiluminescent NO_x analyzer used in the present study, and they also introduce alternative chemical mechanisms that form N_2 under certain conditions.[50] This reaction chemistry is heavily dependent on local reaction conditions, including equivalence ratio and the exact chemical species present, which are parameters that vary significantly within the cylinder. Overall, kinetics of these secondary reactions are not well understood, limiting prediction of their behavior during LTC.

Alternatively, shifts in NO_x equilibrium during combustion may account for the difference between engine-out NO_x levels and the theoretical maximum. The influx of NO from the fuel additive decomposition increases NO concentration, shifting the thermal NO_x reaction equilibrium to form less NO_x or destroy NO_x formed from EHN decomposition. Results of a prior study on a lean-burn natural gas engine illustrate NO_x emissions shift due to perturbing the NO_x equilibrium with additional sources of NO_x.[51,52] In the cited

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studies, NO_x was injected into the intake gas, albeit in significantly higher concentrations (0.6−2.7%) than are produced by the complete decomposition and reaction of all EHN to NO_x (15−20 ppm) in the present study. The resulting NO_x emissions were higher than baseline concentrations but less than the injected quantity, indicating destruction of NO_x within the combustion process.[51,52] The results mirror those of the present study. However, the combustion mode used in this prior study featured higher flame temperatures which yield faster NO_x chemistry and increased thermal NO_x formation, reflected by the NO_x emissions which are an order of magnitude higher than those of the present study. With the low temperatures in LTC, the reaction kinetics of the NO_x mechanisms will be slow, limiting their ability to alter NO_x levels.

Between the two mechanisms discussed, the dominant explanation for the offset between maximum potential NO_x formation and observed NO_x emissions is judged to be the formation of alternate, nonmeasured, nitrogen-containing compounds through secondary reactions. The low combustion temperatures imply NO_x reaction kinetics will be slow, which should mute the effect of the EHN sourced NO_x on equilibrium reactions. Alternately, the secondary reactions occurring during EHN decomposition occur prior to combustion at low temperatures, suggesting they will be less sensitive to combustion than the NO_x equilibrium reactions. Beyond this basic assessment, the low levels of NO_x emissions and the complexity of the secondary reaction chemistry make it impractical to conclusively quantify the relative importance of each effect.

Comparison to Prior Literature. These results indicating that EHN yields higher NO_x emissions contrast the findings of previous research, which conclude that EHN addition does not increase engine-out NO_x emissions and in many cases results in a slight decrease.[18,27−36] The principal differences between these published cases and the current research work are the magnitude of the engine-out NO_x emissions and the type of diesel combustion employed.

The magnitude of NO_x emissions in published studies is substantially higher than the range produced here. Normalizing the literature results into per-fuel-mass emissions indices demonstrates how much higher the NO_x levels in literature tests were. The NO_x emissions from tests conducted on older heavy-duty and industrial diesel engines[18,27−35] are in the range of 25−45 g/kg of fuel, 2 orders of magnitude higher than the test results of this work. A more recent test[36] using a heavy-duty diesel engine in a multimode test produced NO_x emissions of approximately 10 g/kg of fuel, still substantially more than the levels of NO_x (0.1−0.6 g/kg of fuel) found in this test. The amount of NO_x formed by EHN decomposition is insignificant compared to the overall emission level in the prior tests and would be usurped by experimental uncertainty and condition variation. However, in the current case, where high rates of EGR are used to minimize the thermal NO_x formation, the amount of NO_x formed by EHN decomposition becomes increasingly significant.

The combustion mode used in all these earlier studies is classified as conventional diesel combustion. Given the dates of publication and test engines used, it is unlikely any of these engines use significant quantities of EGR for NO_x reduction. With conventional diesel combustion, featuring both a premixed and diffusion portion of combustion, increasing fuel cetane number decreases mixing time and, as a result, the premixed portion of combustion.[37,38] By decreasing the amount of premixed combustion, overall peak pressures and temperatures decrease, causing decreased thermal NO_x formation. As such, the decrease in thermal NO_x formation, due to the higher cetane number causing a reduction in premixed fraction, likely overshadows any NO_x production from EHN decomposition. EHN did not alter the NO_x emissions of the more recent engines used in one reference.[36] The engines used in this test feature multiple fuel injections per cycle, and cetane number has been shown to have little effect on the combustion of engines using multiple injections.[53] The cetane improving quality of EHN therefore did not affect the combustion in a manner which would change the thermal NO_x formation.

However, one source in the literature indicates partial support for EHN doping leading to increased NO_x emissions for engines with low NO_x emissions. A principal component analysis (PCA) conducted on data from a diesel-fueled HCCI engine predicts that, for all other parameters held equal, increasing the concentration of EHN in the fuel will increase NO_x emissions.[39] However, though a positive correlation was presented, the study was not comprehensive enough to yield a reliable quantitative relationship between EHN concentration and NO_x emissions. The test fuels were not chosen to explicitly isolate the EHN effect, and the experimental test methods introduce dependent factors which obscure the results. Because of this, the base experimental data do not explicitly demonstrate a link between EHN and NO_x emissions, though the PCA model infers it.

Conclusions

On the basis of the results of this research work, one principal conclusion can be drawn: the use of 2-ethylhexyl nitrate cetane improver increases the engine-out NO_x for premixed low-temperature diesel combustion (LTC). It appears that decomposition of the nitrate cetane improver forms NO and NO_2, adding an additional NO_x formation mechanism, with approximately one-third of the nitrogen in the fuel additive contributing to additional NO_x in the exhaust. Nitrogen from the EHN which does not form NO_x likely yields, through secondary chemical reactions, other nitrogen-containing compounds not measured by the NO_x analyzer. The magnitude of the NO_x formation causing an increase in engine-out NO_x emissions is significant with respect to the low NO_x emissions produced by premixed low-temperature diesel combustion.

(53) Massa, C.; Diaz, M.; da Silva, R.; Ferreira, A.; Fontes, S. *SAE Tech. Pap. 2007-01-2000*. 2007.