FUEL ADDITIVES FOR IN-CYLINDER NO_x REDUCTION FROM DIESEL ENGINES

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INTRODUCTION

Heavy-duty vehicles contribute a significant portion to California's air pollution with over 50% of the oxides of nitrogen (NO_x) and over 84% of the particulate matter (PM). Environmental and health concerns have resulted in stringent emission standards which require heavy-duty diesel engines to meet a 4.0 g/bhp-hr NO_x standard in 1998 and potentially a further reduction down to 2 g/bhp-hr NO_x in the year 2004. There is a critical need for cost effective technologies to meet these mandates and to clean the air we breathe. One promising approach towards meeting these standards with minimal changes in the present infrastructure of the transportation industry is the use of fuel additives that when injected into the cylinder, along with the diesel fuel, can result in substantial NO_x reduction.

Previous in-cylinder studies have utilized water in-fuel microemulsions to lower combustion temperatures (adiabatic flame temperature) resulting in moderate NO_x reduction. These microemulsions involve the use of a surfactant which forms a reverse micelle entrapping the water phase into a homogeneous water/fuel blend. The NO_x reduction ability of these microemulsions can be augmented by additives (referred to as NO_x scavenger additives). These additives are derived from the class of chemicals that have demonstrated greater than 90% NO_x reduction in aftertreatment processes such as the selective non-catalytic reduction of NO_x. These scavengers are soluble in the aqueous phase of the water/fuel microemulsion and when used with the water-in-fuel microemulsion as a carrier, offer the potential for significant NO_x removal from diesel engine exhaust.

The primary purpose of this project was the characterization of these microemulsion fuel blends for NO_x reduction and as carriers for scavenger additives. Thirty-one fuel formulations were tested for NO_x removal effectiveness on a 1988 Cummins 200 hp C8.3 L engine. The effect of varying scavenger concentration on exhaust emissions and engine combustion was characterized by studying the effect of the various microemulsion components on emissions performance. The success of this approach can result in substantial reduction in diesel engine NO_x emissions with minimal engine modifications and economic impact.

BACKGROUND

NO_x Scavenger Chemistry

The heterogeneous combustion in a diesel engine is a complex sequence of events. The fuel burns in a diffusion type flame which is characterized by local high-temperature combustion zones around a cloud of vaporizing fuel droplets. The NO_x-formed in the cylinder is mainly due to reactions (1) and (2), according to the Zeldovich mechanism, and is often referred to as thermal No_x. In a diesel engine, the NO_x is considered to be predominantly formed on the outside of the flame front where, the 0_2 concentration is the highest.

$$N_2 + O \Leftrightarrow NO + N \quad (1)$$
$$N + O_2 \Leftrightarrow NO + O \quad (2)$$

There are two approaches to reducing the NO_x in the engine exhaust: (I) inhibit its formation by affecting the kinetics of reactions (1) and (2), or (ii) reduce its concentration by reaction with another species after it is formed. The addition of water is an example of the former approach while the addition of scavenger additives to the fuel results in NO_x reduction due to reaction between the NO_x formed and the additive.

While a reduction in combustion temperature by water addition and a reduction in cetane number of the fuel can be used to reduce NO_x formation, considerable fuel penalty is incurred. Hence the desired approach is the reduction of NO_x after it is formed without affecting the combustion characteristics of the engine.

The use of NO_x scavenger additives have been demonstrated to result in greater than 90% NO_x reduction at temperatures of 1400-15000 F and atmospheric pressure in aftertreatment processes such as the selective non-catalytic reduction (SNCR) of NO_x. Under these conditions, the scavenger molecules generate reactive species called free radicals which react with the NO to give N2. The reaction chemistry with one such scavenger additive, cyanuric acid (HNCO)3, is as shown in reactions (3)-(5).

$$(HNCO)_3 \Leftrightarrow 3HNCO \quad (3)$$
$$HNCO + OH \Leftrightarrow NCO + H_2O \quad (4)$$
$$NO + NCO \Leftrightarrow N_2 + CO + O \quad (5)$$

These water soluble scavenger additives can be injected in to the engine cylinder via the use of microemulsions; using less than 10 wt.% water, microemulsion fuel blends can serve as efficient carriers for these scavenger additives. Thus, this approach offers the potential to reduce NO_x with minimal changes to the fuel injection system.

Technical Challenges

Although the efficacy of scavenger additives in SNCR processes is well known, the behavior of these chemicals under the high temperature and pressure in the cylinder of a diesel engine is unknown. When injected with the fuel, the water encased scavenger needs to pass through the high temperature flame front and reduce NO_x in the oxygen rich exhaust stream. Limited data exists on the effect of scavenger and microemulsion concentration on NO_x reduction, fuel consumption, by-product formation and combustion characteristics across the engine load range. In addition, the shear, long-term stability and the pumping efficiency of the additized microemulsion needs to be characterized. Also, the effect on engine components such as gaskets, filters, fuel pump, piston rings and liners and fuel injectors needs to be examined to evaluate the suitability of this technology to present day engines.

Effect on Diesel Engine Combustion

Modern engines are optimized for fuel efficiency by careful control of air/fuel ratio, injection and cylinder pressures, fuel atomization, injection timing and ignition delay. These parameters are critically dependent on fuel quality. The addition of water, emulsifying agents and scavenger additives will likely result in the broadening of the pressure peak and a 'spreading out' of the combustion in the cylinder. These effects need to be examined in detail to achieve an understanding of the effect of the additized microemulsions on engine combustion characteristics.

Measurement of a number of critical combustion characteristics such as peak cylinder pressure, heat rise and rate, shape of injection and net mean crank angle point of heat rise envelope was planned but due to equipment hardware and hookup problems, these parameters could not be measured.

MICROEMULSIONS

An emulsion of water in fuel can be of two types: (I) microemulsion and (ii) macroemulsion. Microemulsion fuel blends consist of small droplets, usually 2 to 100 nanometers diameter of water as the noncontinuous phase dispersed in base diesel fuel. The water and fuel form a single phase by the use of a surfactant such as Emersol 315 (E315) with an alcohol such as methyl benzyl alcohol (MBA) added as a cosurfactant to increase stability. These surfactant/cosurfactant molecules form a reverse micelle structure with a polar core which entraps the water molecules and a lipophilic non-polar outer region which has affinity with the fuel. Macroemulsions fuel blends, on the other hand, consist of much larger droplets and approach more of a physical mixture of water with diesel fuel.

The formulation for the modified diesel fuel consisted of a base water-in-oil microemulsion with the secondary addition of NO_x scavengers as additives. A typical fuel composition was as follows:

- 70% D2 CARIB diesel fuel, * 10% water,
- Less than 10% surfactant that forms a reverse micelle structure entrapping the water,
- Less than 5% oxygenate to stabilize and increase the solubility of the surfactant,
- Less than 3 wt.% of an acid neutralizing agent.
- Desired amount of scavenger additive (dissolved in water).
- Required amount of cetane improver to bring the cetane value of the fuel to that of D2.

The microemulsions appeared as clear, one-phase solutions with minimal mixing and are thermodynamically stable towards phase separation once formed. The order of addition and mixing were not found to be critical. These fuel blends have certain desired properties: (I) flash point greater than 1400 F, (ii) temperature stability between -10 to +700 C, (iii) good shear stability in fuel handling system, and (iv) good long term storage stability (fuel tank storage).

EXPERIMENTAL

The engine used for the testing was a 1988 Cummins 200 hp, 8.3 L, with a turbocharger and an aftercooler. A fuel manifold system for injecting the microemulsions in the engine was constructed. This manifold system allows up to five different fuel blends at the same time without interrupting the engine steady state conditions. Microemulsions with different formulations were blended prior to the testing and stored in 30 gallon containers. Fuel consumption was measured by loss of weight using a Mettler weight balance. The test procedure included pre-blending of the fuels in thirty gallon containers which were mounted in the fuel manifold system. The engine rpm and the torque were set and CARIB D2 fuel injected to acquire an emissions baseline. Under steady state conditions, the fuel was switched to the desired fuel blend and the fuel consumption was measured. NO/NO_x were measured using a Thermo Environmental Chemiluminescence analyzer, CO by Teledyne NDIR analyzer, 0_2 by Teledyne electro-chemical cell and the hydrocarbons were measured using a Horiba FID analyzer. Ammonia measurements were made using Miran 1132 single beam IR instrument.

DISCUSSION

There are three primary methods of introducing water. These are (I) water/fuel emulsion, (ii) direct water injection into the cylinder, and (iii) fumigation of water into the air intake. In the first mode, water is introduced along the fuel side of the diffusion flame while the latter two modes result in water on the air side of the diffusion flame. The injection of water as an emulsion is preferred since it incurs minimal changes to the engine and also results in suppression of NO_x and particulate levels. It is believed that when water is introduced along with the fuel in a region which is O_2 deficient, there is an abundance of OH radicals which leads to particulate oxidation in addition to lower NO_x formation. If introduced via the air side, a reduction in the combustion temperature results in NO_x reduction but increases the soot in the exhaust.

Effect of Water Addition

Figure 1 shows the effect of water addition to diesel fuel on NO_x and CO concentrations at various engine loads. Water addition to the fuel results in a drop in the combustion temperature, resulting in a suppression of NO_x formation. However the fuel cetane number was lowered as a result of water addition. This resulted in an increase in the hydrocarbon levels (not shown in the figure). This effect could be controlled by advancing the engine timing. Water levels of 10% or less were selected for this study since the focus of this project was to provide a medium for transporting the NO_x scavenger.

Effect of SurfactantlCo-Surfactant

The surfactant serves as an interphase between two phases and is characterized by hydrophilic-lipophilic balance. A cosurfactant or compatibilizing agent is added to the blend to increase the solubility of the hydrocarbon phase, increase the hydrophilic-lipophilic balance of the surfactant phase and increase the stability of the microemulsion. The effect of surfactant concentration on the NO_x and CO reduction is shown in Figure 2. It is evident

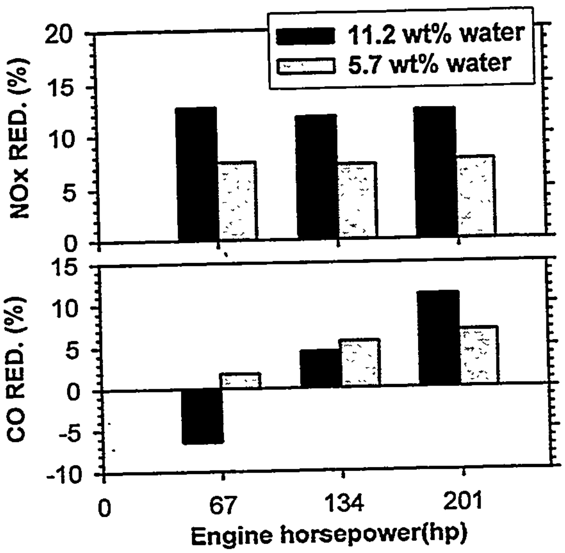

Figure 1: Effect of Water in Fuel on Exhaust Emissions at Various Engine Loads.

from the figure that the surfactant does not have any significant effect on the NO_x and CO levels in the exhaust, for the concentration levels tested. A similar set of experiments for the co-surfactant also revealed no effect on the NO_x and CO emissions. Based on these data it is clear that surfactant and cosurfactant do not participate in the NO_x reduction reactions.

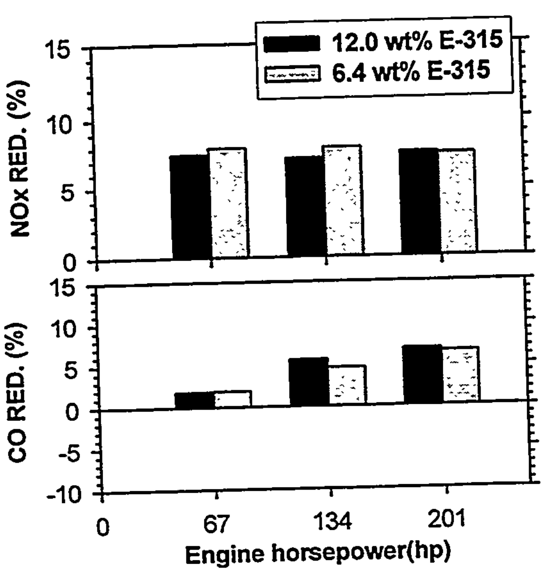

Figure 2: Effect of Surfactant on Exhaust Emissions at Various Engine Loads.

Effect of Cetane Improver

The effect of C1 as a cetane improver in both microemulsions as well as macroemulsions is shown in Figure 3. The improvement in the combustion characteristics of the fuel as a result of the cetane improver seems to lead to a small improvement in NO_x reduction in the case of the microemulsion fuel. The macroemulsion fuel showed a decrease in the NO_x reductions with increasing C11 concentration. The reason for this behavior is not clear, however, it is possible that the presence of nitrate compounds in C1 may have an influence on the formation or reduction of NO_x. The effect of C1 on other emissions such as CO, hydrocarbons and ammonia are plotted in Figure 4. It is clear from Figure 4 that there is no significant effect of the cetane improver on any of these emissions.

Effect of Scavenger Additive on NO_x *reduction*

All the data presented so far were obtained using microemulsions without the addition of a NO_x scavenger to enhance the NO_x reduction.

Figure 5 plots the results of the first series of tests at varying scavenger concentrations using

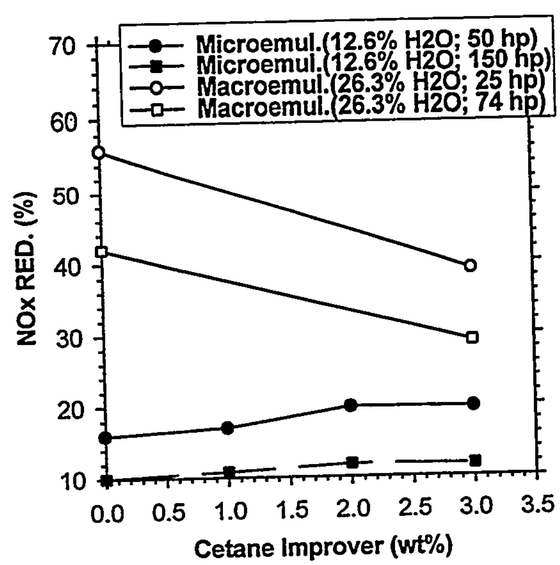

Figure 3. Effect of Cetane Improver C1 on No_x Reduction

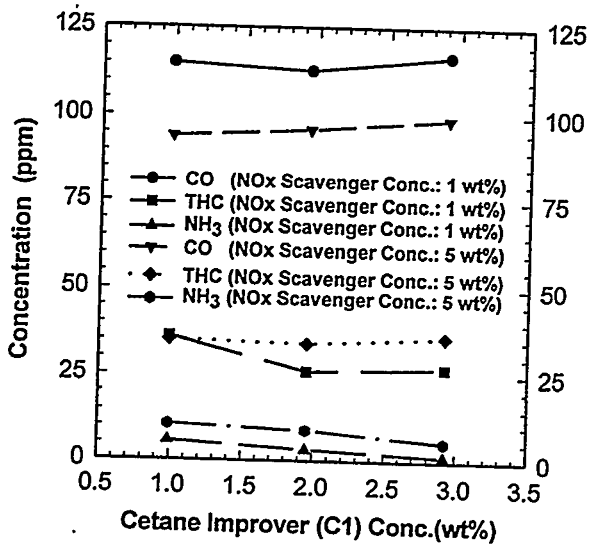

Figure 4: Effect of Cetane Improver C1 on CO and Hydrocarbon Reduction at Two Scavenger Levels

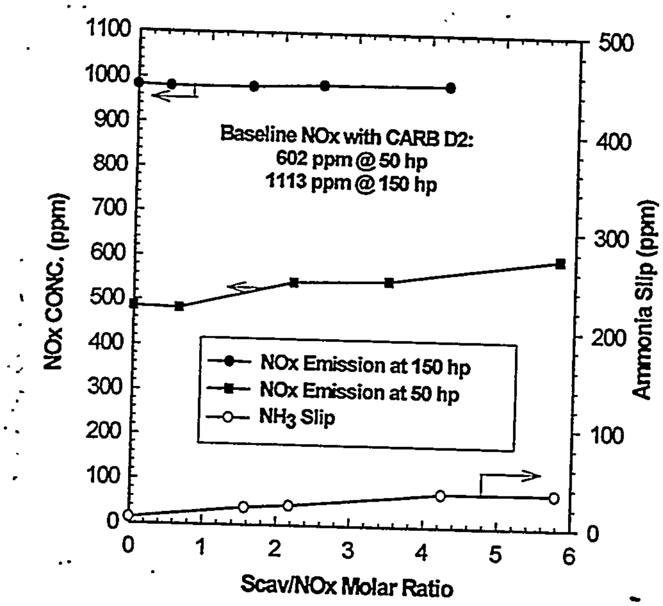

Figure 5: Effect of NO_x Scavenger Mole Ratio on NO_x Reduction. C1 as Cetane Improver

C1 as cetane improver. The scavenger concentration was varied between a scavenger/-NO_x molar ratio of 0 to 6 using 5 different fuel formulations. The scavenger concentration seemed to have little effect on the NO_x emissions and most of the NO_x reduction seemed to be a result of the microemulsion itself. However, up to 40 ppm unreacted ammonia (NI-13) slip was observed. One noteworthy feature is that although the exhaust NO_x concentration was not reduced, there was no substantial increase in NO_x in spite of the addition of large amounts of nitrogen containing additive. A possible explanation for this phenomenon could be that:

1 .the NO_x scavenger molecules were destroyed in the combustion process by pyrolysis in the fuel rich portion of the flame front with the survival of some residual NH_3 formed by a small amount of active scavenger only in cooler regions such as near the wall of the engine cylinders, or

2. the scavenger was indeed reactive but exhibited a low selectivity for NO_x reduction at the reaction conditions in the engine cylinder, i.e., possibly the formation of NO_x and its reduction proceeded at equal rates resulting in half the scavenger being responsible for reduring the NO_x formed by oxidation of the other half of the scavenger.

An additional complexity was the 41% decrease in cetane number of fuel, due to the addition of 3 wt.% of scavenger additive. The decrease in cetane number of fuel due to the addition of scavenger, possibly changed the nature of the combustion from that of a stratified charge, to premixed combustion. This makes it difficult to delineate the effect of scavenger from the effect of changing fuel cetane number. Moreover, the large drop in cetane number meant that large amounts of C1 had to be used to restore the cetane number, resulting in a possible influence of nitrates present in C1 on NO_x formation/reduction. Thus, to better understand the effect of additive concentration, its performance at constant cetane number of 50 was studied. To achieve this, the cetane improver was changed from C1 to C2 using the following criteria:

1 .The new cetane improver should have a substantially higher cetane value than 50 so that smaller quantities are sufficient to elevate the cetane value of the blend.

2..The molecular structure of the cetane improver should be similar to that of hydrocarbons present in diesel fuel so that the addition of which does not change the blend properties substantially.

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3. A cetane improver without any nitrates is preferable, so that there is no possible adverse effect on NO_x reduction.

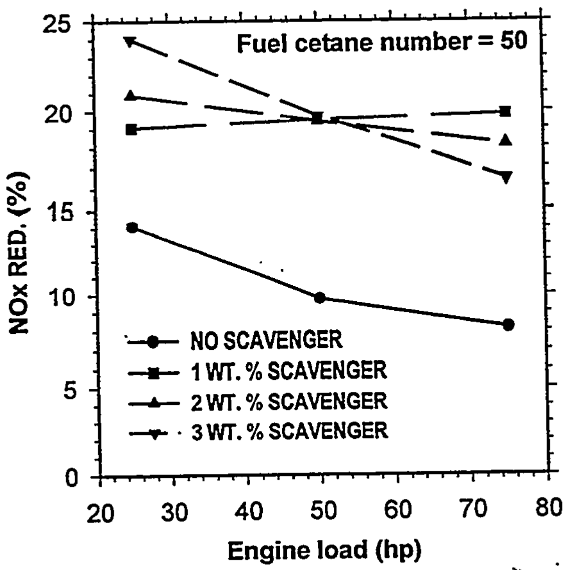

Figure 6: Effect of Scavenger Concentration on NO_x Reduction as a Function of Engine Load. C2 as a Cetane Improver.

Figure 6 shows the effect of varying scavenger concentration on NO_x reduction at a constant cetane number of 50. A considerable improvement in NO_x reduction is observed for the fuel with 1 wt.% scavenger in comparison to the fuel with no scavenger. This is in contrast to Figure 5 where the reduction seemed to be due to the microemulsion itself. Also, at low loads, there seems to be an improvement, with increasing scavenger levels, but this trend seems to reverse at the higher loads. The NH_3 levels in the exhaust were measured for the three scavenger concentrations and were found to be negligible. One possibility is that the improved cetane number of the fuel resulted in similar combustion characteristics in the cylinder and hence the scavenger survived the flame front and reacted with the NO_x formed downstream of the flame front. However, the addition of larger amounts of scavenger additive did not seem to linearly increase the amount of NO_x reduced.

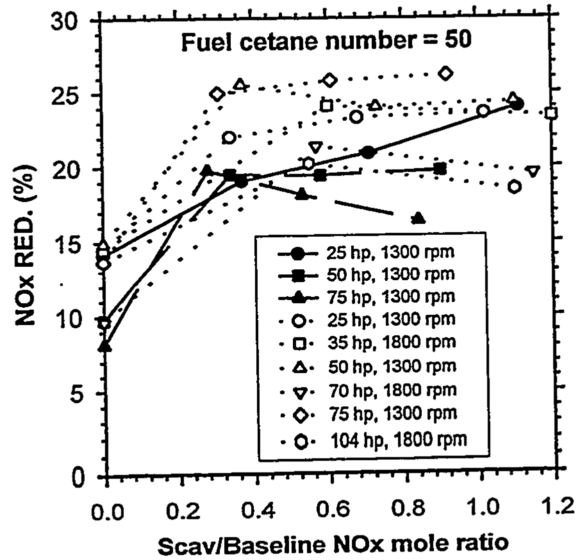

Figure 7: Effect of Scavenger to NO_x Molar Ratio on NO_x Reduction. C2 as Cetane Improver.

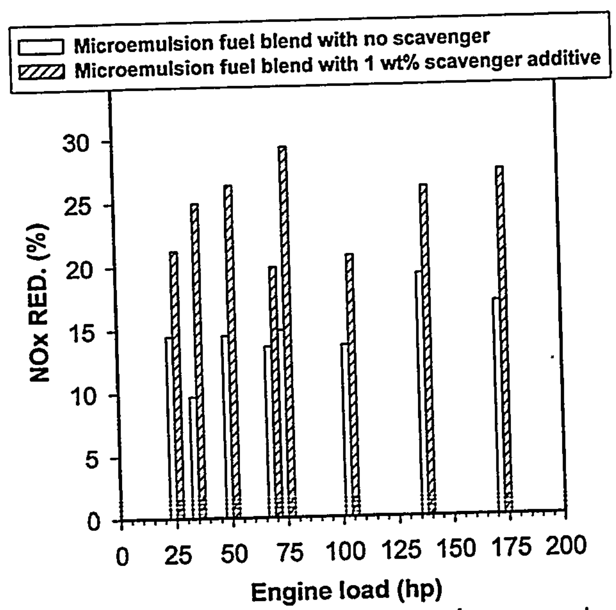

Figure 8: Summary of NO_x Reduction With and Without Scavenger at Various Loads. C2 as Cetane Improver.

The above results suggest that most of the scavenger is destroyed in the flame front and possibly a slightly larger amount compared to leads to NO_x reduction downstream of the flame. This effect needs to be examined in greater detail under varying combustion and injection conditions. Figure 8 compares the NO_x reduction obtained with the 1 wt.% fuel with that of the microemulsion itself at various loads under steady state conditions. A maximum of 15% improvement in NO_x reduction was observed over that of the microemulsion itself. No clear trend was observed as a function of load, but the increase in NO_x reduction over that of the microemulsion itself seemed to vary between 7-15% across the load range of the engine. Thus, for a typical fuel blend, consisting of 10 wt.% water, less than 10 wt% emulsifying agents and 1 wt% scavenger, almost 30 % reduction can be obtained across the load range of the engine.

SUMMARY

The use of microemulsions containing scab-Engen additives offers potential for substantial reduction in NO_x. The addition of water was limited to 10 wt% as Microemulsions containing less than 10 wt% water were found to be effective in carrying scavenger additives. A typical composition containing 10 wt% water, less than 10 wt% surfactant/ cosurfactant/neutralizing agent and 1 wt% scavenger additive reduced NO_x by almost 30% across the load range of the engine.

The addition of quantities greater than 1 wt% of the scavenger additive did not have a beneficial effect on NO_x reduction. This may be due to the additive being destroyed in the flame and not making it past the flame front for reaction with NO_x.

The use of scavenger additives leads to a severe depression in the cetane number of the fuel. Selection of a cetane improver is critical from both cost and NO_x reduction perspectives. For possible commercial application, an effective low cost cetane improver would have to be developed to increase the cetane number of the resultant fuel blend.

Assuming a cost of $0.60 per gallon of D2 diesel and using the microemulsion components and the scavenger additive used in this study, this approach is likely to add a cost of 280 (46.5%) to the cost of diesel fuel (cost includes the cost of cetane improver). More work needs to be done to lower the fuel formulation cost and to examine its effect on the combustion characteristics and mechanical wear and tear of the engine.

ACKNOWLEDGMENTS

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