NO_X REDUCTION FROM DIESEL FUEL AND BIODIESEL BY SELECTIVE NON-CATALYTIC REDUCTION

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Introduction

NO_x emissions are the major concern of automotive industry in general and biodiesel industry in particular, because biodiesel increases nitrogen oxides (NO_x) emissions. The present day technologies like NH_3-SCR are commonly used to fulfill the legal requirements. Beyond that, many researchers tried to reduce NO_x emissions using selective non-catalytic reduction (SNCR) by the introduction of cyanuric compounds. The key for successful reduction of NO_x emissions by SNCR technology lies in the use of specifically designed chemicals that are soluble in fuels and act as reduction agents with significant reduction of NO_x emissions. The tested additives are shown in Tab 1. The tests were carried out in an AFIDA combustion chamber basically designed to measure the cetane number of fuel. It was attached to the equipment to measure all major components of the exhaust gases.
Eventually, this preliminary study of the successful use of SNCR technology forwards a strong argument that SNCR could reduce the NO_x emissions from diesel engines in a most efficient way when proper compounds are chosen. It also opens up a new area of investigation into the combustion chemistry of diesel engines operated on biofuels.

1	1,2,3-tris-(diethylaminomethoxy)propane
2	1,2-Bis-(diethylaminomethoxy)-3-tert-butoxy propane
3	2,2-dimethyl-(4-diethylaminomethoxymethy)-1,3-dioxolane
4	(2,2-dimethyl-1,3-dioxolane)-4-methoxy-N-ethylcarbamate
5	3-tert-butoxy-propyl-2-ol-1-N-ethylcarbamate
6	3-tert-butoxy-propyl-1,2-bis-(N-ethylcarbamate)
7	n-Octadecanoic hydrazide

Table 4: The seven different compounds tested as additives

Results

The first type of additives used to test their ability to reduce NO_x emissions by SNCR were N,O-acetals containing a tertiary amine group.
The compounds 1, 2 and 3, added to diesel fuel in 2 % by weight, showed reduction of NO_x emissions of 22 %, 9 % and 3 %, respectively, as shown in Fig 1.

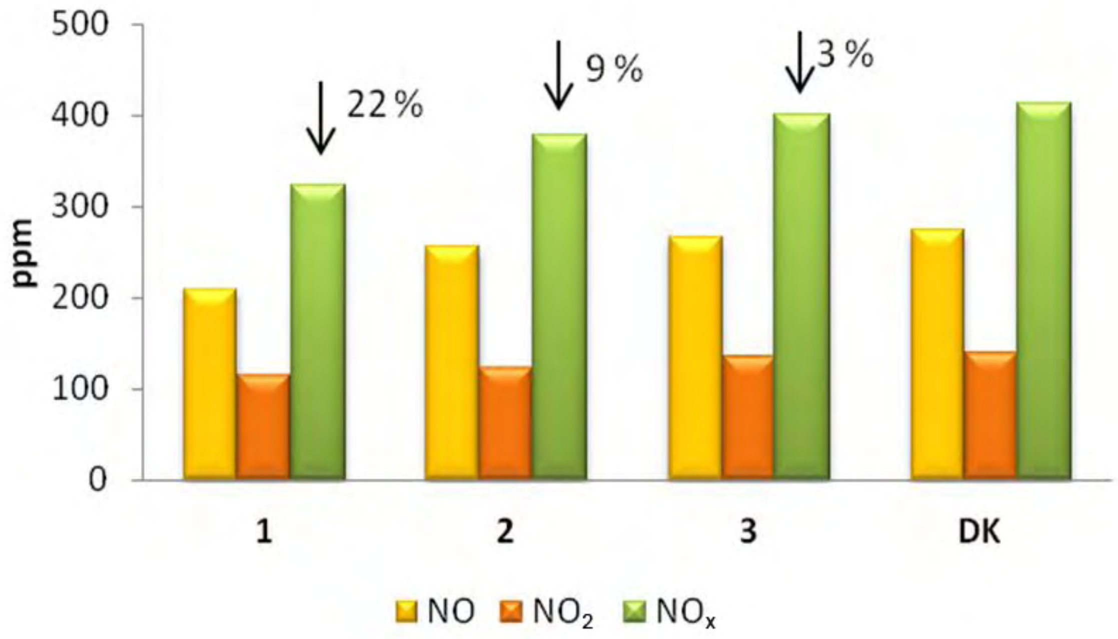

Figure 4: NO, NO_2 and NO_x emissions with 1, 2 and 3 as additives in diesel fuel

When added as an additive to RME, the compounds 1 and 3 showed an increase in NO_x emissions as shown in Fig 2. It could be postulated that the biodiesel is involved in the increase in concentration of oxygen atoms in the combustion zone which could be the same phenomenon that decreases PM emissions during the combustion.

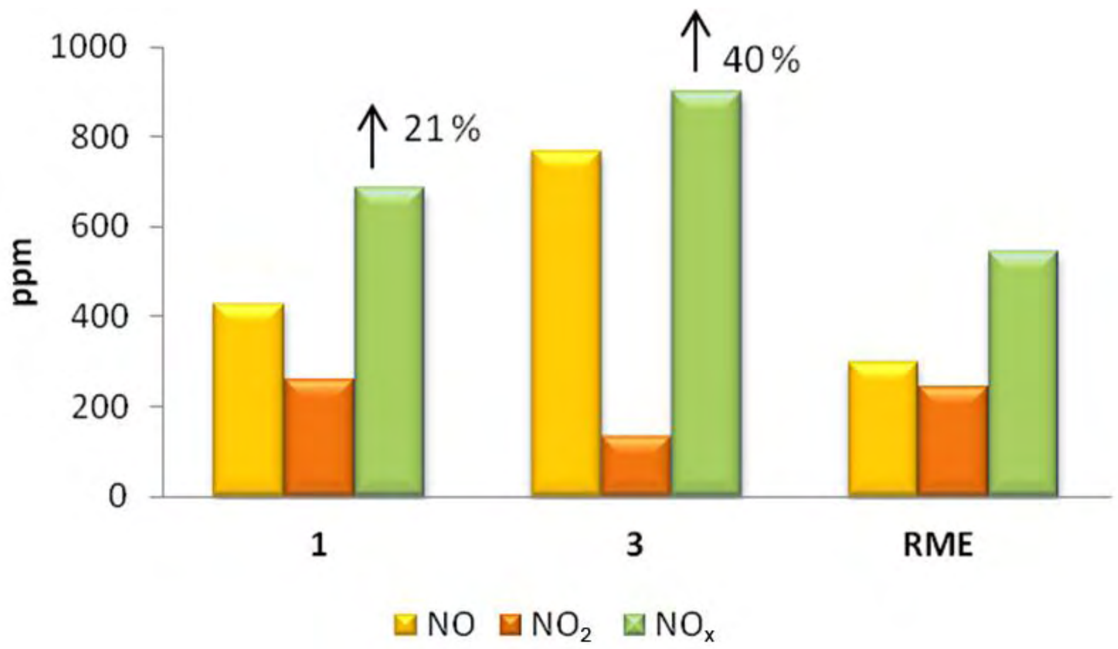

Figure 5: NO, NO_2 and NO_x emissions with 1 and 3 as additives in biodiesel fuel

It has been shown by Farber et al. [1954] and Fenimore et al. [1961] that the presence of OH radicals or oxygen atoms in excess above the thermodynamic equilibrium in the combustion zone may cause the oxidation of nitrogen containing additives leading to an increase in NO_x emissions. Such an environment is clearly created by biodiesel due to its oxygen content. However, the difference in increase of the NO_x emissions by compound **1** (21 %) and compound **3** (40 %) in biodiesel fuel could be explained firstly as the limitation of OH radicals and O atoms towards the oxidation of the additive, due to the competition between the additive and the carbon content of the fuel towards the oxygen atoms, and secondly the limitation in stripping of the compounds in the flame and the availability of $NH_{i,\ i=0,1,2}$ to reduce NO which is lower in the case of compound **3** compared to compound **1**.
The second type of compounds that were tested were carbamates. Three different compounds 4, 5 and 6 were tested as 2 wt. % additives in biodiesel fuel. Also these compounds showed an increase in NO_x of 16.5, 9.9 and 10.3 % compared to the biodiesel fuel. Unfortunately, the compounds could not be tested in diesel fuel because of the poor solubility.
In view of increased NO_x emissions from biodiesel fuel it was decided to use highly reactive compounds like hydrazid (7) in biodiesel fuel to reduce NO_x emissions. In order to enhance the solubility of compound 7, about 2 wt. % of compound 3 were added to RME. Compound **3** could not facilitate the solubility of compound **7** in diesel fuel at room temperature. This also hindered the testing of B10 and B20 where the additive precipitated. It is known that hydrazides undergo a thermal decomposition process and release hydrazine. Miller et al. [1981, 1989] have performed an extensive study on the NO reduction by hydrazine and shown that hydrazine acts much like ammonia in the reduction and formation of NO. The addition of these two compounds to the biodiesel showed reduction of NO_x emissions of 45%, as shown in Fig 3.

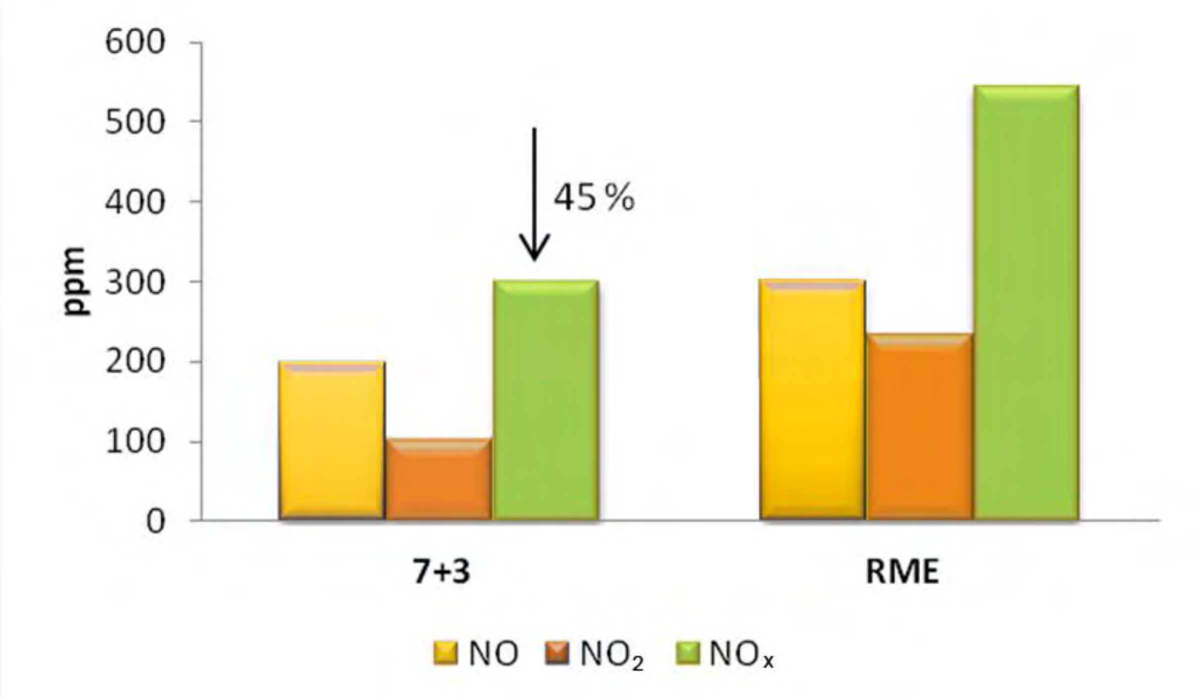

Figure 6: NO, NO_2 and NO_x emissions of 7+3 as additives in biodiesel fuel

Conclusion

Biodiesel has the advantage of lower PM, CO and HC production over petroleum diesel. Its only disadvantage regarding emissions is its higher NO_x emission. NO_x emissions from biodiesel can be reduced by the addition of 2-4 % of the above additives (named 7+3). However, using the specified additives in lower concentrations increased NO_x emissions due to the fuel nitrogen content. There are certain limitations in the addition of nitrogen containing blend components. Firstly, the limitation leading to the stripping process of the additive during combustion which must provide $NH_{i,\ i=0,1,2}$ and then the limitation of availability of thus produced ions to react with NO or to react with oxygen which would result in further NO_x redution or formation of NO_x. As shown by Fenimore et al. [1961] about 40 % of thus produced NH_i are oxidized to NO in NH_3/O_2 (a maximum limit) and later get reduced to produce nitrogen, as the rate of reduction of NO to N_2 is almost twice of its formation from NH_i ions. Therefore, the presence of NH_i in lower concentrations may affect the later process. However, it can be concluded that the above results constitute the primary steps of a new concept of SNCR by using amines in primary, secondary and tertiary state as additives to reduce NO_x emission from diesel engines. Most of the amines, carbamates and hydrazides can be successfully used in the future due to their solubility in ethanol which is being widely blended with gasoline fuels at present. Eventually, the combination of current SCR technology with SNCR use could be a successful attempt to reduce NO_x emissions from diesel engines.

Source:
J. Krahl, S. Tanugula, H. Hopf, Diesel Fuel Additives to Reduce NO_x Emissions from Diesel Engines Operated on Diesel and Biodiesel Fuels by SNCR**,** SAE Technical Paper 2010-01-2280, **2010**

References

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