

# Biodiesel Tech

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## NO<sub>x</sub> Emissions and Biodiesel

### What is NO<sub>x</sub>?

NO<sub>x</sub> is the name given to a class of gaseous chemicals that are formed by high temperature reactions of nitrogen and oxygen. It includes nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and a few other compounds such as nitrous oxide (N<sub>2</sub>O) that are present in very small quantities. Most of the NO<sub>x</sub> emitted by spark-ignited (gasoline) engines is NO. Diesel engines emit 10 to 30% of the NO<sub>x</sub> as NO<sub>2</sub> with the balance being NO. In the atmosphere, NO is gradually converted to NO<sub>2</sub>.

### Why do we care about it?

NO<sub>x</sub> is one of the compounds that are regulated by the Environmental Protection Agency (EPA). Engine and vehicle manufacturers are required to limit the NO<sub>x</sub> levels emitted from the engine and vehicle tailpipes to increasingly low levels. While both NO and NO<sub>2</sub> are irritants and will cause breathing difficulties, the primary concern with NO<sub>x</sub> is its involvement in smog formation reactions. Smog reactions are a complex series of reactions involving NO<sub>x</sub>, unburned hydrocarbons, and sunlight that produce many irritating chemicals. Ground-level ozone is one of these chemicals that is produced in considerable quantity. It is often used as a surrogate for smog intensity because it is easily measured. Ground-level ozone should not be confused with ozone in the upper atmosphere, which serves a useful function of limiting ultraviolet radiation. Ground-level ozone, NO<sub>2</sub>, and the other compounds that compose smog, are responsible for the brownish haze that often lingers over large cities such as Los Angeles. Smog has adverse health effects on everyone, but is a particular concern for asthmatics and other sensitive individuals.

NO<sub>x</sub> can also react with water in the atmosphere to form acids that have changed the pH of lakes in the northeastern United States, killing fish, and have caused other serious environmental degradation. Acid rain also damages automotive coatings and deteriorates marble and limestone on buildings.

Engines built since 2009 are equipped with devices in their exhaust pipes that dramatically reduces both NO<sub>x</sub> and particulates. These devices are known as aftertreatment. Aftertreatment-equipped engines have very clean exhaust but older engines can still emit high levels of pollutants. Since diesel engines can have lives of 30 years or more, these older engines can comprise a substantial portion of the fleet.

Engines fueled by 100% biodiesel (B100) are usually seen to have NO<sub>x</sub> emissions increases of 4 - 13% before aftertreatment. NO<sub>x</sub> emissions increases with B20 are usually only 2 - 4%. These increases could easily be eliminated by retarding the engine's fuel injection timing by 1 - 2 degrees of crankshaft angle.

While this would sacrifice a portion of biodiesel's particulate reduction due to the NO<sub>x</sub>-particulate trade-off described later, there would still be a significant improvement in the overall emissions from the engine. However, adjusting the engine defeats one of the most significant advantages of biodiesel - that it can be used in existing diesel engines without modifications. The engine's EPA emission certification may also be threatened if these types of modifications are made. The timing retard would also increase fuel efficiency.

### Where does it come from?

NO and NO<sub>2</sub> are formed inside the cylinders of internal combustion engines. Virtually all combustion processes will contribute somewhat to NO, the dominant species in NO<sub>x</sub>. Research has shown that there are three primary mechanisms for the formation of NO. The first mechanism is NO production from the nitrogen that is contained in the fuel. This mechanism can be important for coal and for liquid fuels that contain large amounts of nitrogen-based additives. However, most diesel fuels contain very small amounts of nitrogen. Even when nitrate-based cetane improvers are used, the amounts are usually so small that the fuel nitrogen does not seem to contribute to NO. The second mechanism is called *prompt* NO. This is NO that is formed by reactions involving hydrocarbons during the actual combustion process. While it is possible to design experiments that generate large amounts of prompt NO, the conditions needed do not appear to be present in diesel combustion.



The third and most important NO formation mechanism is called *thermal* NO. Thermal NO is produced following a chemical pathway called the Zeldovich mechanism. Use of this mechanism in modern computer models of engine combustion processes has provided good success in predicting measured NO levels. This has not only served to validate the Zeldovich mechanism itself but has also confirmed that in diesel engines, most NO<sub>x</sub> originates from the thermal mechanism. NO<sub>x</sub> control strategies such as injection timing retard and exhaust gas recirculation are successful because they reduce combustion temperatures and thus, thermal NO<sub>x</sub>. It has been shown that increasing the cetane number of the diesel fuel can decrease NO<sub>x</sub> emissions in some engines. The primary effect of a higher cetane number on diesel combustion is that the fuel self-ignites faster. This produces a seemingly contradictory situation where the combustion event is advanced, which would be expected to cause the higher NO<sub>x</sub> emissions usually associated with advanced combustion timing. However, faster ignition means that the amount of fuel that is involved in the initial self-ignition event is smaller and therefore the initial burning rate is lower, which tends to decrease NO<sub>x</sub> production. When both of these effects are compared, the effect of the lower initial combustion rate seems to dominate and most engines produce less NO<sub>x</sub> with higher cetane number diesel fuels. It should be noted that the effect of cetane enhancers is still believed to be a temperature effect. By shifting the timing and rate of the combustion process, the gas temperature in the cylinder is also changed. When the gas temperature increases, the NO<sub>x</sub> level increases. Unfortunately, the processes that affects NO<sub>x</sub> production also tend to affect production of soot. When something on the engine is changed to reduce NO<sub>x</sub> emissions, such as injection timing, air swirl, or fuel injection pressure, it tends to increase soot or particulate matter emissions. Engine designers know this phenomenon as the NO<sub>x</sub>-particulate trade-off.

Biodiesel made from highly saturated feedstocks, such as animal fats and recycled restaurant greases, tends to have a higher cetane number than that from vegetable oils (60 - 65 compared with 48 - 53) and this has been shown to reduce or even eliminate the NO<sub>x</sub> increase.

### **NO<sub>x</sub> reducing additives**

Fuel chemists have been searching for many years for an additive that could be used to reduce NO<sub>x</sub> emissions. This has turned out to be a very difficult task and except for the cetane improvers mentioned earlier, has been unsuccessful. When the origin of the NO<sub>x</sub> is considered, the reason for this difficulty becomes clear.

When the fuel is injected into the high temperature air in the engine cylinder, it does not ignite immediately. The fuel atomizes, vaporizes, and mixes with air. It undergoes preliminary chemical reactions that involve the fuel molecules breaking part and forming smaller, more chemically reactive molecules called radicals. These radicals engage in reactions that create more radicals. After some time, the concentration of radicals reaches a point where the reactions become very rapid and the fuel is said to autoignite. Up to this point, the temperature is low so the thermal NO<sub>x</sub> production is negligible. After ignition, the fuel burns quickly to create a mixture of very simple molecules that include carbon monoxide and hydrogen as well as simple radicals such as oxygen atom, nitrogen atom, and hydrogen atom. It is in this post-combustion soup of simple molecules that the nitric oxide is formed. Its formation is somewhat slow, so the longer the mixture is held at high temperature, the more NO that will be produced. As the engine cycle progresses, and the temperature in the cylinder decreases due to the expansion of the piston, the composition of the gases shifts toward product gas species such as carbon monoxide and water vapor. In theory, the nitric oxide should decompose to O<sub>2</sub> and N<sub>2</sub> as the temperature drops. However, the rate of this decomposition reaction becomes so slow that the level of NO stays high and is said to be frozen at the previous equilibrium level. The amount of NO formed in the near-equilibrium chemical soup depends only on the time, temperature, and the relative amounts of C, H, O, and N atoms present. For an additive to change the amount of NO formed, it must influence one of these variables. Additives are present at such a small levels that they usually do not have a significant effect on the relative amounts of C, H, O, and N atoms. The only way to affect the time and temperature is to change the combustion timing or rate. Cetane improvers act in this way by affecting the ignition process, but no way is known for an additive to change the combustion rate after the initial auto-ignition event since the combustion rate during this part of the combustion process is controlled by the air-fuel mixing process, not chemical effects.

So, after this somewhat technical explanation, the conclusion is that fuel additives are not available for NO<sub>x</sub> reduction except for cetane enhancers, and these compounds are only effective in fuels with naturally low cetane numbers and at engine operating conditions where the time delay before the start of combustion, called the ignition delay, is significant. These conditions are primarily at light and medium load levels, as most modern turbocharged engines have very short ignition delays (and little cetane number sensitivity) at high loads.

