An assessment of NO_x emissions during transient diesel engine operation with biodiesel blends

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Abstract: The target of the present work is to review the literature regarding the effects of biodiesel blends on nitrogen oxide (NO_x) emissions during the transient operation of diesel engines (acceleration, load increase, starting, driving cycles). The most important mechanisms are analyzed based on the fundamental aspects of transient conditions, and on the impacts the biodiesel physical and chemical properties have relative to the conventional diesel oil; emphasis is also placed on biodiesel feedstock and driving cycle effects. In parallel, a comprehensive statistical analysis is presented regarding biodiesel blends effects on NO_x emissions for engines running on transient cycles during the last 30 years. For the majority of the reviewed transients, an increasing trend in NO_x emissions is established when the biodiesel ratio in the fuel blend increases. Moreover, the biodiesel NO_x emission penalty seems to increase for more aggressive cycles and for increasing feedstock unsaturation.

Keywords: Diesel engine; Biodiesel; Transient operation; Nitrogen oxides; Driving cycle; Turbocharger lag

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Introduction

Depleting reserves and rising prices of crude oil, as well as gradually stricter emission regulations and greenhouse gas concerns have led to a growing effort to develop alternative fuel sources; the emphasis is on biofuels on account of their renewability (Couse 1992; Hansen et al. 2009). Particularly for the transportation sector, biodiesel (methyl or ethyl ester) has emerged as a very promising solution, since it possesses similar properties with the diesel fuel, it is miscible with diesel at any proportion, and is compatible with the existing distribution infrastructure (Demirbas 2007; Agarwal 2007; Giakoumis et al. 2012; Komninos and Rakopoulos 2012).

The use of biodiesel during diesel engine operation has been researched intensively during the last decades (e.g. Choi et al. 1997; Graboski and McCormick 1998; Rakopoulos et al. 2006; Agarwal 2007; Tsolakis et al. 2007; Lapuerta et al. 2008; Pinzi et al. 2009; Rakopoulos 2012). The majority of the researchers report decreases in the emitted particulate matter (PM)/soot, unburned hydrocarbons (HC) and carbon monoxide (CO). In contrast to the carbonaceous pollutants, however, slight to moderate increase of the nitrogen oxides (NO_x) is usually documented (Graboski and McCormick 1998; Lapuerta et al. 2008; Ayhan 2012). The exact percentage of emission change relative to the neat diesel operation depends on the biodiesel percentage in the fuel blend and the specific experimental schedule (US EPA 2002; Giakoumis 2012). One of the peculiarities of biodiesel with respect to other biofuels is the fact that it can be produced from a variety of feedstocks. Since each originating oil or fat is characterized by different composition, it is not surprising that the properties of the final ester differ substantially (Knothe 2005; Hoekman et al. 2012; Giakoumis 2013), as is representatively documented in Table 1 in comparison to the reference diesel fuel. Unsurprisingly, the disparity in the properties has also been found to influence the NO_x emissions from biodiesel-blended diesel engines (Graboski and McCormick 1998; Lapuerta et al 2008; Giakoumis et al. 2012).

The diesel engine has for many decades dominated the medium and medium-large transport sector. During the last years it is also rapidly establishing itself in the highly competitive automotive market (particularly in Europe) based on its reliability, fuel efficiency and turbocharging capability. Although the study of diesel engines usually focuses on the steady-state performance, it is its transient (dynamic) operation in the form of speed and load changes and starting that best illustrates the actual daily driving conditions (Watson and Janota 1986; Rakopoulos and Giakoumis 2006, 2009). The key influencing feature during dynamic operation is that both the engine speed and the fuel supply to the engine cylinders change continuously. Thus, the available exhaust gas energy varies, affecting the turbine enthalpy drop and, through the turbocharger shaft torque balance, both the boost pressure and the cylinder air-supply are influenced too.

Unfortunately, due to various dynamic, thermal and fluid delays in the system, mainly originating in the turbocharger moment of inertia ('turbocharger lag'), combustion air-supply is delayed compared to fueling. This affects adversely the torque build-up and ultimately worsens the vehicle driveability and increases considerably the exhaust emissions, in particular PM and NO_x (Wijetunge et al 1999; Hagena et al. 2006; Rakopoulos and Giakoumis 2006, 2009; Rakopoulos et al. 2010).

It is well established today that nitrogen oxides together with PM form the most harmful pollutants produced by diesel engines (Heywood 1988). NO_x consist mostly of nitric oxide NO and nitrogen dioxide NO_2, playing an important role in the atmospheric ozone formation. The production of nitrogen oxides is strongly dependent on temperature (thermal NO_x), residence time of the mixture at high temperatures, and local concentration of oxygen; other notable factors are the injection timing and the fuel properties. Since the gas temperature is the dominant contributor for the production of NO_x, the most successful reduction methods aim at lowering the (peak) cylinder temperatures. This is generally achieved by retarding the injection timing or applying exhaust gas recirculation (EGR). The latter, although very successful, is unfortunately associated with an increase in the amount of the emitted PM. Thus, the usual ECU (engine control unit) strategy during transients aims at shutting down the EGR valve in order to aid the build-up of the air–fuel ratio and boost pressure, and limit intolerable smoke emissions (Rakopoulos and Giakoumis 2009). It is not surprising then that during transients, an overshoot of NO_x emissions is usually experienced.

The target of the present work is to review the literature regarding the impacts of diesel-biodiesel blends on the transient NO_x emissions from diesel engines; the very critical (dynamic) conditions will be covered that are encountered during the daily engine/vehicle operation i.e., acceleration, load increase, starting and in the collective form of transient cycles. The analysis will focus on the differing physical and chemical properties of the various blends against those of the conventional diesel fuel. Moreover, emphasis will be placed on the specific discrepancies experienced during transients, most notably in the form of turbocharger lag. In order to support the arguments raised and further the analysis, the results from a recent detailed statistical analysis on biodiesel blends emissions during driving cycles (Giakoumis 2012a) will also be presented.

NO_x Emissions with Biodiesel Blends Combustion during Transients

Overall Results

In 2002, the US Environmental Protection Agency (EPA) published a comprehensive analysis of biodiesel impacts on exhaust emissions. The available at the time emissions data (mainly North-American manufactured, heavy-duty engines running on SME blends during the American FTP cycle) were statistically analyzed in order to quantify the effects of biodiesel blends on all regulated pollutants (US EPA 2002). Recently, an update of these formulas was accomplished (Giakoumis 2012). A large amount of data was carefully collected from 67 papers, published in international Journals, well established Conferences and final Reports issued by renowned research centers up to the end of 2011, all dealing with driving cycles experimentation. In order for the results to be representative of the true engine operation, hence be realistic and applicable to other engines/operating conditions, only those experiments that focused on transient cycles (i.e. truly transient conditions, as the ones experienced by the diesel-engined vehicles in their daily operating schedule) were taken into account. All of the studies concerned four-stroke, direct injection engines running on various chassis or engine dynamometer cycles. The database contains a representative mix of American, European and Japanese engines/vehicles and of real-world biodiesel feedstocks; details, as well as a complete list of the respective publications is available in Giakoumis (2012).

Figure 1 illustrates the complete set of the gathered transient NO_x observations corresponding to all types of engines, driving cycles, biodiesel feedstocks and blend ratios. Roughly two thirds (66.5%) of the measurements concerned positive (increasing) NO_x emissions with biodiesel in the fuel blend over the reference petrodiesel operation, and one third concerned decreases, as is further documented graphically in Fig. 2. Specific statistical data for the most investigated biodiesel blends are also provided inside Fig. 1. From this data it is made obvious that the standard deviation increases, almost steadily, as the biodiesel content in the fuel blend increases, a fact that highlights in an explicit way the observed differences within the biodiesel blends tested.

Moreover, Fig. 3 summarizes the cumulative effects of biodiesel blends on transient NO_x emissions by providing a best-fit approximation from all collected measurements of Fig. 1. From Fig. 3, a moderate increasing NO_x trend with rising biodiesel blend is established, as was also the result of the earlier EPA graph demonstrated in the same figure for comparison. It is surprising that although a considerable amount of new data (from 2000 up to 2011) has been included in the current statistical analysis, the earlier best-fit curve remains practically unchanged for blend ratios up to 50%. Nonetheless, due to the considerable disparity in the measured data, the coefficient of determination was found very low (0.13). Higher R^2 values were established however for specific engines or engine cycles or biodiesel feedstocks, as is documented in Table 2 that summarizes all best-fit curves data; the latter will be discussed later in the text.

Main Mechanisms and Trends during Transients

The higher cetane number of biodiesel in contrast to the conventional diesel is suspected to cause a decrease in the emitted NO_x for certain engines and originating biodiesel oils or under specific conditions, most notably premixed-controlled combustion typical under light-load operation (Zhang and Boehman 2007). This fact may be due to the relatively shorter ignition delay and thus shorter duration of premixed combustion. To this end also contributes the lower biodiesel volatility (which makes the evaporation process slower with respect to that of the diesel fuel) and the absence of aromatic compounds in the biofuel.

Nonetheless, the majority of researchers have argued towards an increasing NO_x production trend during transients, as has also been the (usual) finding during steady-state operation (Graboski and McCormick 1998; Lapuerta et al. 2008). Representative results are demonstrated in Fig. 4 for two typical discrete automotive transients, namely an acceleration and a hot starting. The reasons for this increasing trend of NO_x with rising biodiesel percentage are primarily temperature related, i.e. higher local gas temperatures with biodiesel are established compared with petrodiesel that originate in injection, combustion and engine calibration grounds (Mueller et al. 2009; Sun et al 2010; Giakoumis et al. 2012); a summarization and brief description follows.

Biodiesel fuels are characterized by higher bulk modulus of compressibility, speed of sound and surface tension. This means that when a diesel-tuned engine is run on biodiesel blends, a faster wave propagation and pressure rise inside the hydraulically operated injectors is experienced that leads to an earlier needle lift (of the order of 0.5–2^{o} crank angle) (Tat et al. 2000). This, in turn, increases the duration of the premixed combustion, the pressures and temperatures during diffusion combustion and ultimately the total residence time in the cylinder (Szybist et al 2007). Nonetheless, this injection advance effect appears to be applicable mostly to pump-line nozzle and unit injector systems (Tsolakis et al. 2007). Interestingly, Cheng at el. (2006) revealed that a hydrocarbon fuel with the same ignition delay, injected at the same timing as a neat biodiesel, still produced 10% lower load-averaged NO_x than the biodiesel. Hence, there are probably other, inherent in the biodiesel combustion, issues that may be be more influential than injection timing.

Musculus (2005) revealed another contributing cause for the high local gas temperatures with biodiesel combustion, by showing that actual flame temperatures inside the cylinder may be influenced by differences in soot radiative heat transfer. The formation of soot particles in the combustion chamber radiates heat that lowers the combustion temperatures, subsequently decreasing the emitted NO_x. Since the oxygen in a biodiesel blend is well known to decrease soot (Graboski and McCromick 1998; Agarwal 2007; Lapuerta et al. 2008; Giakoumis et al. 2012) thus reducing the radiative heat transfer term, higher local gas temperatures are expected that in turn favor greater NO_x penalty.

The fact that fuel injectors operate on a volumetric rather than gravimetric basis means that if a diesel-tuned engine runs on biodiesel blends, a larger mass of fuel will be injected (approximately 5% according to Table 1 for neat biodiesel combustion). At the same time, owing to its inherent oxygen concentration, biodiesel combustion will lead to an 10–12% increase in the available oxygen provided that the engine retains its diesel-fuel calibration. Consequently, an increase of the order of 6% in the air−fuel equivalence ratio (lambda) is expected. This can prove particularly influential for increasing NO_x emissions during transients, where lower than unity values of lambda are experienced. During a typical turbocharged diesel engine transient event (e.g. acceleration), the fuel pump rack responds almost instantly to the fueling increase command and shifts to its maximum position, leading to higher fueling. However, the increased exhaust gas power produced by the engine is not capable of instantly raising the turbine power output, largely (but not exclusively) owing to the turbocharger inertia (Watson and Janota 1986; Rakopoulos and Giakoumis 2006; 2009). Hence, the compressor operating point moves rather slowly towards the direction of increased boost pressure and air-mass flow rate; during this period, known as *turbocharger lag*, the engine is practically running in naturally aspirated mode or with very limited boost. As a result of this slow reaction, the air–fuel equivalence ratio during the early cycles of an acceleration event assumes very low values that are usually lower than stoichiometric. During biodiesel combustion, on the other hand, the excess oxygen inherent in the blend (numerator in the definition of lambda) vs. the increased mass of injected biodiesel blend (denominator) will lead to higher values of the air−fuel equivalence ratio values that will now be closer to stoichiometry. Consequently, higher gas temperatures will be promoted, since, as is well established (Law 2006), the adiabatic flame temperature peaks at conditions slightly rich of stoichiometric. Thus, higher NO_x emissions are more likely to be observed for biodiesel blended engines, at least when steep transients are involved as the ones illustrated in Fig. 4.

Another key contributing factor in modern engines is the ECU calibration that may dictate a different injection strategy (longer injection pulse-width) based on the lower heating value of biodiesel, if an engine that is tuned for diesel operation is required to run on biodiesel (Sun et al. 2010). An even more prominent demonstration of the ECU's influence is actually located in the exhaust gas recirculation (EGR) system. When an engine that has been calibrated for neat diesel operation runs on biodiesel, more fuel is required to achieve the demanded torque/vehicle speed, hence a lower EGR rate is established, elevating both the in-cylinder temperatures and the NO_x emissions (Lujan et al. 2009; Bannister et al. 2010). The experimental results from Sze et al. (2007) lend support to this argument. They found that the lower calorific value of biodiesel affected 'throttle' position up to 3.3% relative to the petrodiesel operation, which ultimately decreased the EGR rate up to 10.5% (depending on the driving cycle) for the cases examined, as is illustrated in the upper sub-diagram of Fig. 5. At the same time, other engine variables such as the fuel rail pressure, the VGT position and the boost pressure were influenced too.

Lastly, differences in the chemical kinetic pathways that are responsible for the production of prompt NO, when biodiesel is used have been reported that may contribute to the higher biodiesel NO_x emissions. Such arguments typically rely on increased levels of CH being produced at the auto-ignition zone during biodiesel combustion, which leads to the production of N-atoms in the jet core followed by prompt NO formation, once the mixture is convected to the diffusion flame, where O_2 and OH are present (Mueller et al. 2009).

Effects of Engine Type and Driving Cycle

The effect of the driving cycle's characteristics (i.e. its average power or its aggressiveness) on the NO_x emissions was investigated by Sze et al. (2007), who studied a 2006 MY (model year) engine operating on 7 different heavy-duty engine and chassis-dynamometer cycles. It was found that the changes in the emitted NO_x from biodiesel combustion correlated very well with the average cycle power (R^2=0.99) and the fuel consumption (R^2=1.0) of the engine. The results obtained from this study are reproduced in the lower sub-diagram of Fig. 5, documenting that higher NO_x penalty for biodiesel-fueled engines was experienced with increasing average transient-cycle power.

The apparent reasons for the higher biodiesel NO_x liability with increasing cycle power (or cycle aggressiveness) are located in the primary NO_x production mechanism. In a diesel engine for the torque to increase, higher amount of injected fuel is required. This in turn, leads to lower air−fuel equivalence ratios and finally higher gas temperatures. Likewise, a more aggressive cycle (or driving pattern in general) is characterized by more frequent and abrupt accelerations or load increases; the latter pave the way for higher NO_x too owing to the harsher (or more frequent) turbocharger lag phases and the lower EGR rates they induce (Wijetunge et al. 1999; Rakopoulos and Giakoumis 2009). Take for example the results in the upper sub-diagram of Fig. 5, where the more highly-loaded HWY (highway) cycle results also in greater EGR valve decreases with rising biodiesel blend than the lighter-loaded UDDS. Similar conclusions have been reached by many other researchers in the field, who almost regularly measured higher NO_x emissions over the more aggressive driving patterns compared to the 'softer' ones (summarized in Giakoumis et al. (2012)).

Figure 6 demonstrates the collective NO_x emissions results from the conducted statistical analysis regarding the effects of engine and dynamometer type and driving schedule. The light-duty results (almost exclusively NEDC) differentiate considerably from the rest of the engine-related curves in Fig. 6, exhibiting higher NO_x liability for all the tested biodiesel blends despite the NEDC's rather 'soft' profile. This behavior, that seems to contradict the previously discussed results from Sze et al. (2007), can be explained based on the following facts:

- most of the NEDC experiments include modern passenger car engines fitted with EGR (MY>2000), which tends to increase NO_x emissions, when an increasing biodiesel blend ratio is applied, and
- this cycle has a higher portion of extra-urban segment, where the majority of NO_x is emitted, a fact that actually strengthens the previous point.

The significant importance of EGR is reflected into the fact that the light-duty and the post 2000 MY results are quite similar in their trend and absolute values. This can be explained by the fact that engines manufactured during the 2000s were systematically equipped with EGR (see also the percentage of measurements reporting increasing NO_x emissions with biodiesel over petrodiesel in Fig. 2).

An even more prominent differentiation from the general 'average' NO_x trend in Fig. 6 is exhibited by the heavy-duty, chassis-dynamometer cycles (mostly the American UDDS), where, oddly, a moderately negative trend for NO_x emissions with biodiesel blending is established. This means that a NO_x benefit over the reference diesel operation was measured with biodiesel blends combustion. As mentioned earlier, the underlying reasons may be located in the light loading of the UDDS cycle, which tends to increase the premixed portion of combustion over the diffusion one, (where NO_x are primarily produced). Notice also the UDDS results in the upper sub-diagram of Fig. 5, where, interestingly, an increase in the EGR rate is evident. The latter arguments can be supported by the fact that 'only' 40% of the total NO_x measurements from heavy-duty, chassis-dynamometer cycles correspond to emission increases when biodiesel is added in the fuel blend (Fig. 2). This leaves an impressive 60% of the measurements showing NO_x benefits over the neat diesel operation. In contrast, as was demonstrated in Fig. 2, 66.5% from all data and 77.9% from heavy-duty, engine-dynamometer measurements concerned NO_x increases with biodiesel addition in the fuel blend.

On the other hand, it is the results from the heavy-duty, engine-dynamometer cycles that exhibit the highest cohesion (R^2=0.54 in Table 2 – incidentally, the same was found true for the PM, CO and HC emissions). This can be straightforwardly explained by the fact that these measurements have minimum disparity since they primarily concern north-American engines (from a handful of manufacturers) running on SME blends during the FTP cycle. In contrast, for the NEDC results, each investigation corresponds practically to a different engine/car, and there is a great variety of tested methyl esters. As a result, the obtained data are scattered and controversial (R^2=0.24 in Table 2).

Effects of Biodiesel Feedstock

The chemical composition of biodiesel is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. Acids may be saturated, which means that they contain only single bonds, or unsaturated, i.e. they contain at least one double bond (Graboski and McCormick 1998). A usual measure of the biodiesel's degree of unsaturation is the iodine number (IN) or iodine value (IV). Since the composition of the originating oils/fats varies considerably, it is not surprising that the physical and chemical properties of biodiesel differ substantially (Table 1). Hence, one of the most intriguing points regarding biodiesel, is the possible influence the different fuel properties may have on the (NO_x) emissions. In order to relate the differences in the molecular structure between the various methyl esters, the degree of unsaturation or the number of double bonds was chosen as the influential parameter. Table 3 provides relevant data (unsaturation level, chain length and iodine number (IN)) from a recently conducted statistical survey (Giakoumis 2013), useful for the discussion that follows.

Peterson et al. (2000) studied biodiesel blends from 6 different real-world feedstocks (safflower, rapeseed, soybean, mustard, coconut, hydrogenated soybean) during the hot UDDS chassis-dynamometer cycle, and identified a statistically significant correlation between iodine number and NO_x emissions (R^2=0.89 – upper graph in Fig. 7. This resulted in 29.3% increase in NO_x from IN=7.88 (coconut methyl ester) to 129.5 (SME) for the neat blends, and 8.3% increase for the B20 blends. Evidently, the higher order double bonds were increasingly important in producing NO_x. Comparable observations were valid for the cold UDDS although the feedstock sample was smaller. Recently, Mueller et al. (2009) found that B100 (steady-state) combustion conditions were closer to stoichiometric during ignition and in the standing premixed auto-ignition zone near the flame lift-off length at higher loads than was the case with petrodiesel. This finding might shed light into the fact why highly saturated biodiesels produce lower NO_x, since fuels with high cetane numbers (i.e. saturated) lead to mixtures farther from the stoichiometry.

In parallel, McCormick et al. (2001) studied a group of 21 different biodiesel fuels (comprising of 7 real-world feedstocks and 14 pure fatty acid methyl and ethyl esters) during the FTP cycle. A highly significant relation between NO_x and density was found (not confirmed, however, by subsequent research on an equally significant level), with the single parameter explaining 88% of the variance. The relationship between CN and NO_x emissions indicated that a NO_x-neutral biodiesel, relative to the certification diesel (used at the time of the measurements), would have a cetane number of 68. The dataset included also direct comparisons of fuels with differing numbers of double bonds in the fatty acid chain. A highly linear relationship (R^2=0.93) between IN and NO_x emissions during the FTP was established, as is illustrated in Fig. 7 (circular symbols); the regression predicted that a biodiesel with an IN=38 (i.e. 1.5 double bonds/molecule) would actually be NO_x-neutral relative to the certification diesel used.

It was concluded that high-stearate fuels with few double bonds produced significantly less NO_x than certification diesel. Unfortunately, these (saturated) materials have poor cold-flow properties and some are even solid at room temperature. Interestingly, a later study by McCormick et al. (2005), this time on a newer production engine, showed that

B100 tests, in general confirmed the above results, although the R^2 was found lower this time, of the order of 0.83 (Fig. 7); the latter implied EGR and fuel injection system effects too, primarily through the weaker influence of the biodiesel's higher bulk modulus of elasticity relative to the neat diesel fuel. Similar observations concerning the effect of unsaturation on NO_x emissions have been reported by Knothe et al. (2006) and Bakeas et al. (2011); the respective best-fit curves are also illustrated in Fig. 7.

Unfortunately no statistically significant direct comparison between the various biodiesel feedstocks is feasible from the available database in order to substantiate the previous findings. This is primarily due to the fact that although SME has been popular in all types of investigations (but mostly on the American FTP), the rapeseed methyl ester has been primarily employed in European studies of the NEDC, all of which have been conducted during the last years covering a great variety of modern, EGR equipped engines/vehicles (Giakoumis 2012; Giakoumis et al. 2012). Comparing the whole SME database with its RME counterpart would be, to a large extent, like comparing FTP with NEDC measurements, at least for the present level of statistical analysis. To this aim, the left sub-diagram of Fig. 8 only provides, for the sake of completeness, a comparison between the vegetable, SME and non-vegetable (i.e. animal fat but also waste cooking derived) data from all available transient studies and engines.

The only test cycle for which a healthy variety of methyl esters has been investigated is the NEDC, but the great disparity of the tested engines/vehicles, makes such a comparison dubious, that is why it has not been performed. Nonetheless, in the right sub-diagram of Fig. 8, a comparison is attempted as to the effect of biodiesel feedstock on NO_x emissions from all heavy-duty data (engine and chassis-dynamometer ones), which, have been found to exhibit the least data variance. It is the RME blends in heavy-duty experimentations that demonstrate the most 'erratic' behavior, with NO_x emission decreases (and PM increases) that differentiate considerably from the general tendency. For this trend, it is the results of Peterson et al. (2000), who systematically used RME blends in their research that are mostly responsible. Unfortunately, there are only a few RME FTP results available to confirm or refute this behavior. From the rest of the data, no clear conclusions can be reached as regards the effects of SME, animal fat (AFME) and waste cooking methyl esters (WCME) on the emitted NO_x.

Methods for Compensating the NO_x Increase

In view of the arguments discussed previously that correlate NO_x emissions with cetane number, some researchers investigated the effect of ignition improvers. For example, Sharp et al. (2000) found that the addition of ethyl-hexyl-nitrate (EHN) was unsuccessful for a B20 SME blend, whereas di-tert-butyl peroxide (DTBP) could lower NO_x by 6.2%, while maintaining the 9.1% PM reduction during the FTP. Nuszkowksi et al. (2009) measured decreasing NO_x with increasing both 2-EHN or DTBP, with the greater impact observed on older technology (1990s) engines; McCormick et al. (2003) too identified the positive effects of both additives during the FTP.

Graboski et al. (1996) proposed that NO_x-neutral blends with biodiesel could be produced by altering either the base-fuel aromatic content or the natural cetane number. To this aim, a low-aromatic fuel (23.9%) was treated with biodiesel (to make a B20 blend), and a small amount of cetane (n-hexadecane) was applied to raise the cetane number of the test blend to the same value as the reference fuel. The lower aromatic content of the fuel compared to the certification fuel was enough to offset the NO_x increase produced by the biodiesel. At the same time, the particulate matter was reduced relative to the certification fuel by 24%. It could be argued that the particulate benefit was due to the properties of the base stock and not the biodiesel, since reducing the aromatic content also reduces particulate matter. However, the particulate emission for the biodiesel/low aromatic blend was 14% below that from the low aromatic base stock alone. This suggested that fuel reformulation with oxygen and aromatic control is a route to producing NO_x-neutral and PM reducing fuels. The same research group in a more recent study (McCormick et al. 2003) found that lowering the base fuel aromatics content from 31.9% to 7.5% for a SME B20 blend managed to reduce NO_x by 6.5%. Linear interpolation of their results suggested that a B20 fuel based on petroleum diesel with 25.8% aromatics would be equivalent in NO_x emissions to a certification diesel fuel with 31.9% aromatics. From the same study it was also concluded that the use of kerosene as the base fuel could lead to a NO_x-neutral blend (this occurs at 40% biodiesel, assuming linearity). The antioxidant TBHQ was also effective, but NO_x reduction was small at the level tested, and TBHQ was suspected to increase PM emissions. It was concluded that the use of antioxidants as NO_x reduction additives was something that could be explored in more detail.

McCormick et al. (2001) performed also one direct comparison of the impact of chain length on NO_x emissions. A series of saturated methyl esters based on lauric, palmitic and stearic (all with zero double bonds) acids was prepared and tested; ethyl stearate was also examined. On the basis of this comparison, it was concluded that shorter chain esters produced higher NO_x emissions during the FTP; still the fully saturated methyl laurate produced NO_x at or below the certification fuel level. Therefore, it was postulated that shortening of the hydrocarbon chain may be a route to NO_x-neutral fuels with improved properties. In any case, although for the pure fatty acid esters, an inter-dependence between various properties and chain length is valid, this is barely the case for biodiesels. For the latter, which are mixtures of a variety of pure fatty acid esters, the correlation with chain length weakens considerably, as is documented in Table 3.

Based on the knowledge gained from the studies that correlated the biodiesel feedstock with the NO_x emissions, some researchers investigated the possibility of an ideal triglyceride feedstock design. A biodiesel with a combination of one or zero double bonds to minimize NO_x production, and a low pour point to improve cold weather operation would have both environmental and climatic advantages (Peterson et al. 2000). To this aim, Chapman et al. (2003) investigated two approaches in order to achieve the saturation of the biodiesel fuel: blending and hydrogenation. The blending approach involved the blending of short-chained, saturated methyl esters with biodiesel fuel, i.e. a blend of 60% capryllic acid methyl ester and 40% capric acid methyl ester, was chosen so that its short hydrocarbon chain length would help to offset the adverse effect of saturation on cold-flow properties. This approach was found to produce a 2.8% reduction in NO_x emissions over all examined modes, and also improved the fuel's cold flow property. Unfortunately, the high cost of the saturated methyl esters renders it economically unfeasible. The second approach was the hydrogenation of soybean oil prior to transesterification. To produce a blend that will reduce NO_x while not increasing the cloud point, a high selectivity must be achieved during hydrogenation. It was concluded that further research should be conducted to determine the exact conditions for hydrogenation, such as temperature, catalyst type and loading, and pressure in order to produce the desired fatty acid chains.

In modern, electronically controlled engines, a notable compensation of NO_x emissions could be achieved through a revised engine calibration with regards to the injection system or the EGR control. A notable example is provided by Magand et al. (2011), who studied the performance of an engine during the NEDC. They found that when the ECU is appropriately re-adjusted to cater for the different physical and chemical properties of their biofuel blend, the initially high NO_x penalty (60%) relative to the reference diesel fuel was reversed into an impressive benefit of almost 22%, without sacrifice in the PM reduction. Likewise, Ireland et al. (2009) applied both EGR and injection timing recalibration during steady-state tests in order to reduce NO_x from biodiesel combustion, while maintaining the PM at levels lower than that of petrodiesel operation, however at the expense of fuel efficiency.

Even though the use biodiesel alone cannot prove sufficient to achieve the current or future PM emission levels (i.e. without the need for DPF), the inherent capacity of methyl esters (and biofuels in general) to decrease PM by a large percentage, provides higher flexibility in controlling NO_x emissions. This can be accomplished, for example, by applying elevated EGR. In other words, a percentage of the high PM benefit with the use of biodiesel can be traded for higher EGR rates, hence lower or possibly zero NO_x levels.

Summary and Conclusions

The primary mechanisms of transient NO_x emissions with biodiesel blends were identified and discussed based on both the differing properties of biodiesel with respect to petrodiesel, but also with regard to the discrepancies observed during transients. At the same time, a detailed statistical analysis of all driving cycles emission data up to the end of 2011 provided best-fit curves that demonstrated the engine/vehicle, driving cycle and feedstock influence on NO_x emissions from biodiesel-blended fuels. The most important conclusions reached are:

- Confirming the principal observations during steady-state operation, for the majority of examined transients an increasing trend in NO_x emissions is established with increasing biodiesel ratio in the fuel blend.
- In particular, it is the earlier start of injection, the more-advanced combustion, the lower radiative heat transfer and the higher oxygen availability that contribute towards a rising trend relative to petrodiesel operation.
- Irrespective of driving cycle type, the biodiesel impact on NO_x emissions appears to be related to the fuel consumption or the average cycle load, with the emission penalty with biodiesel increasing for more aggressive cycles/driving patterns. This is due to the fact that steeper and more frequent accelerations or load increases lead to harsher turbocharger lag phases that provoke lower EGR rates.

- Biodiesels produced from unsaturated feedstocks appear to increase the NO_x emission penalty, at least for older production engines.
- The use of injection retard, low-aromatic diesel base-fuel, cetane improvers, and carefully ‘designed’ feedstock can all aid in (at least partial) abatement of the usual NO_x penalty observed with biodiesel combustion.

Owing to the lower calorific value of biodiesel, when an engine that has been calibrated for neat diesel operation runs on biodiesel, a lower EGR rate is achieved, therefore contributing towards an increase in NO_x emissions in relation to the petroleum diesel operation. Further, biodiesel’s lower heating value and exhaust gas temperatures also affect other engine subsystems operation (oxidation catalyst, VGT, diesel particulate filter). This highlights the need for a revised calibration strategy when a diesel-tuned engine is required to run on methyl ester (or any biofuel) blends. The same holds true for the injection system that requires a different optimization to compensate for biodiesel’s higher values of density, bulk modulus of elasticity and speed of sound.

Nomenclature

AFME	Animal fat methyl ester
CN	Cetane number
DPF	Diesel particulate filter
DTBP	Di-tert-butyl peroxide
ECU	Engine control unit
EGR	Exhaust gas recirculation
EHN	Ethyl-hexyl-nitrate
EPA	Environmental Protection Agency
EU	European Union
FAME	Fatty acid methyl ester
FTP	Federal Test Procedure (heavy-duty engines)
IN/IV	Iodine number/iodine value
MY	Model year
NEDC	New European driving cycle (light-duty vehicles)
NRTC	Non-road transient cycle
NO_x	Nitrogen oxides
PM	Particulate matter

R^2	Coefficient of determination
RME	Rapeseed methyl ester
SME	Soybean methyl ester
TBHQ	Tertiary-butyl-hydro-quinone
UDDS	Urban dynamometer driving schedule (heavy-duty vehicles)
VGME	Vegetable methyl ester
VGT	Variable geometry turbocharger
WCME	Waste-cooking methyl ester
WHTC	Worldwide harmonized transient cycle (heavy-duty engines)

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Table 1 Comparison of key physical and chemical properties between biodiesel (Giakoumis 2013) and automotive diesel fuel

	Low-sulfur automotive diesel fuel	Biodiesel
Density/15°C (kg/m^3)	835	870–890
Kinematic viscosity/40°C (cSt)	2–3.5	3.5–6.2
Cetane number	~50	46–65
Lower heating value (kJ/kg)	~43,000	36,500–39,500
Oxygen content (% weight)	0	10–12
Sulfur content (ppm)	<50 <15 for ultra-low sulfur diesel fuel	<10
Air–fuel equivalence ratio	14.5	12.5 *
Latent heat of evaporation (kJ/kg)	265	230 *
Molecular weight (kg/kmol)	~170	290 *
Surface tension/40°C (N/m)	0.026	0.0285 *
Boiling point (°C)	180–360	345 *
Bulk modulus of elasticity (bar)	16,000	17,500 *
Flash point (°C)	50–90	125–175

* average values

Table 2. Summarization of NO_x emissions best-fit quadratic curve coefficients A and B, coefficient of determination R^2 and standard error for all transient cycles, engine types and methyl esters (quadratic best-fit curve: $y=Ax+Bx^2$).

All data	A=0.106, B=–0.000318 R^2=0.13, Std. error=10.24
MY>2000	A=0.170, B=0.000384 R^2=0.48, Std. error=9.04
All heavy-duty cycles	A=0.007, B=0.000506 R^2=0.11, Std. error=8.15
All heavy-duty engine-dynamometer cycles	A=0.068, B=0.000491 R^2=0.54, Std. error=5.75
All heavy-duty chassis-dynamometer cycles	A=0.005, B=–0.000763 R^2=0.13, Std. error=7.87
All light-duty cycles	A=0.246, B=–0.00088 R^2=0.24, Std. error=13.3
All vegetable oils	A=0.103, B=–0.00031 R^2=0.13, Std. error=9.71
All SME	A=0.097, B=0.00014 R^2=0.30, Std. error=7.57

Table 3. Degree of unsaturation, chain length and iodine number of various methyl esters (average values from a statistical analysis of experimental data (Giakoumis 2013)).

Animal fat or vegetable oil	Percentage of unsaturated / saturated fatty acids	Degree of unsaturation (average number of double bonds)	Chain length	FAME iodine number
Beef tallow	52/ 48	0.59	17.37	54.5
Canola	92 / 8	1.33	17.99	104
Coconut	9 /91	0.12	13.12	7.8
Corn	86 / 14	1.45	17.79	120.3
Cottonseed	71 / 29	1.27	17.46	105.7
Jatropha	78 / 22	1.15	17.79	99
Karanja	75 / 25	1.04	18.08	85.2
Mahua	54 / 46	0.69	17.57	70.8
Palm	51 / 49	0.62	17.08	53.1
Peanut	82 / 18	1.16	18.04	80.5
Rapeseed	93 / 7	1.32	18.08	111.7
Safflower	90 / 10	1.65	17.85	136.7
Soybean	84 / 16	1.51	17.79	126.2
Sunflower	89 / 11	1.57	17.92	128.6
Waste cooking	76 / 24	1.09	17.69	85.2

Figure Captions

Fig. 1. NO_x data points (observations) from all available transient measurements up to the end of 2011.

Fig. 2. Percentage of positive (increasing) NO_x emission observations with biodiesel over the reference diesel operation.

Fig. 3. Collective statistical best-fit NO_x curve from biodiesel blends combustion during transient cycles.

Fig. 4. Development of NO emissions during a typical medium/heavy duty turbocharged diesel engine acceleration (left) and hot starting event (right) (6 cylinder engine; total displacement: 5,958 L; speed range: 800–2600 rpm; max. power: 177kW@2600rpm)

Fig. 5. Effect of driving cycle pattern on the EGR rate and the respective NO_x emissions for a 2006, medium-duty diesel engine (adapted from Sze et al. (2007)).

Fig. 6. Collective best-fit NO_x results for various transient cycles and engine model years.

Fig. 7. Effect of iodine number on NO_x emissions (adapted from Peterson et al. (2000); adapted from McCormick et al. (2001; 2005); data from Knothe et al. (2006); adapted from Bakeas et al. (2011)).

Fig. 8. Collective best-fit NO_x results for various biodiesel feedstocks.

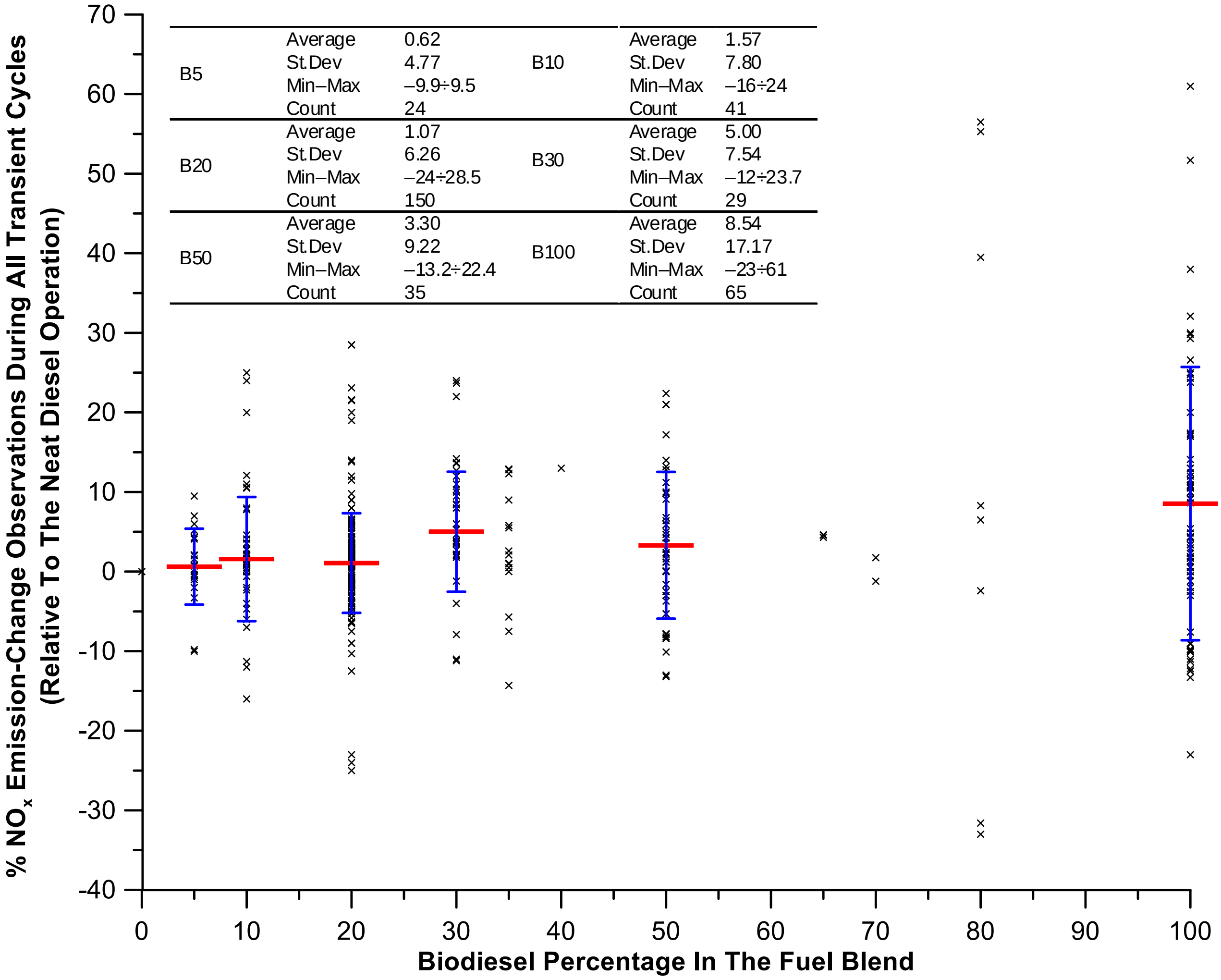


Figure 1.

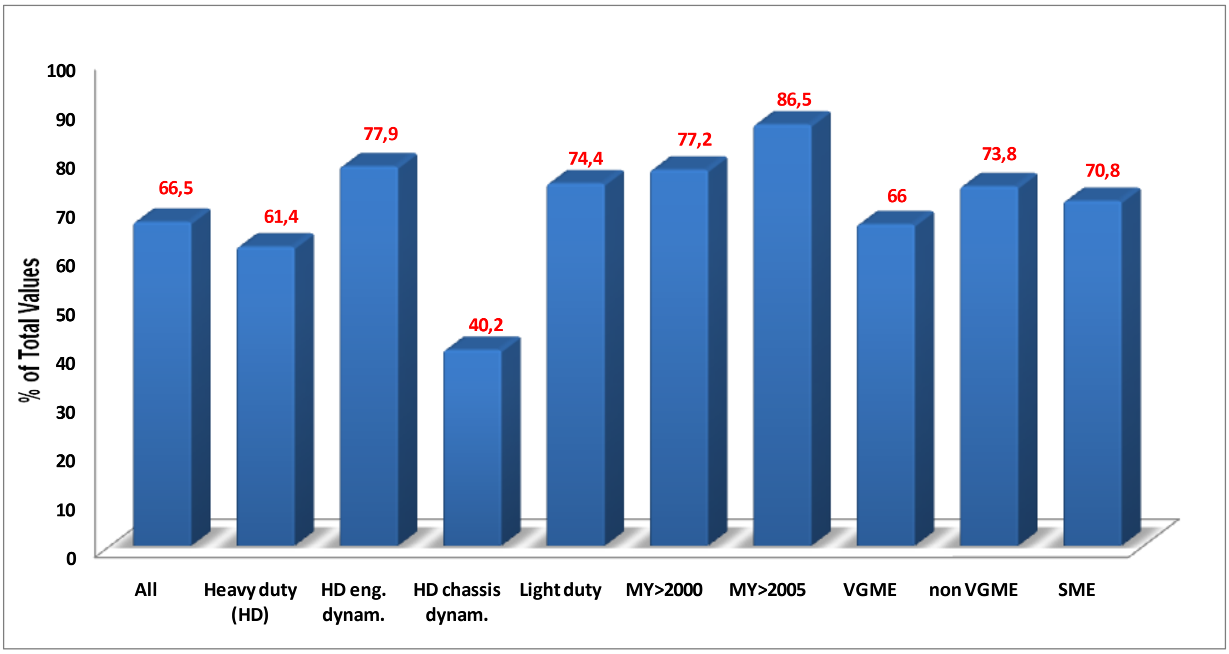


Figure 2.

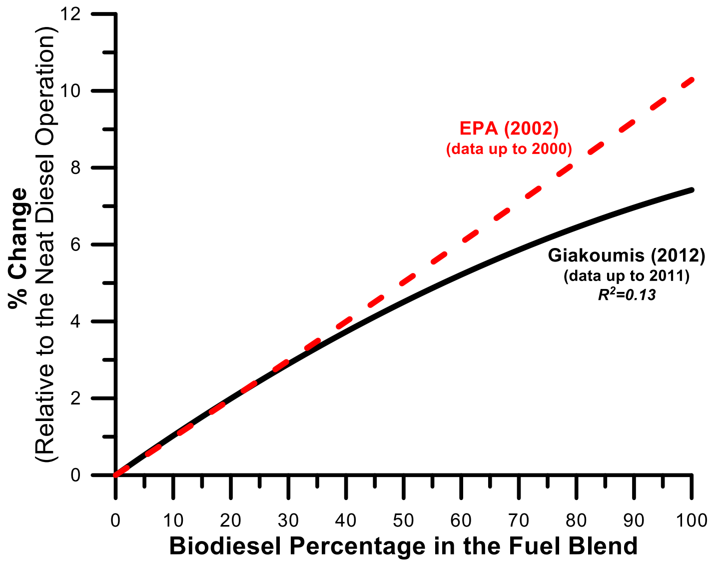


Figure 3.

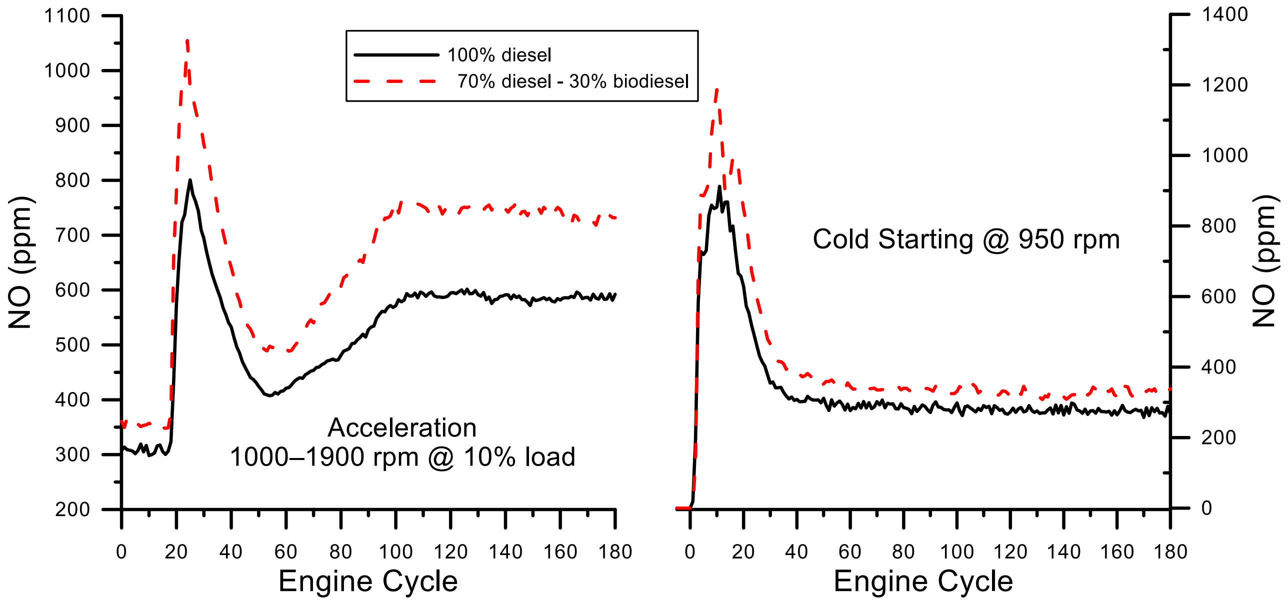


Figure 4.

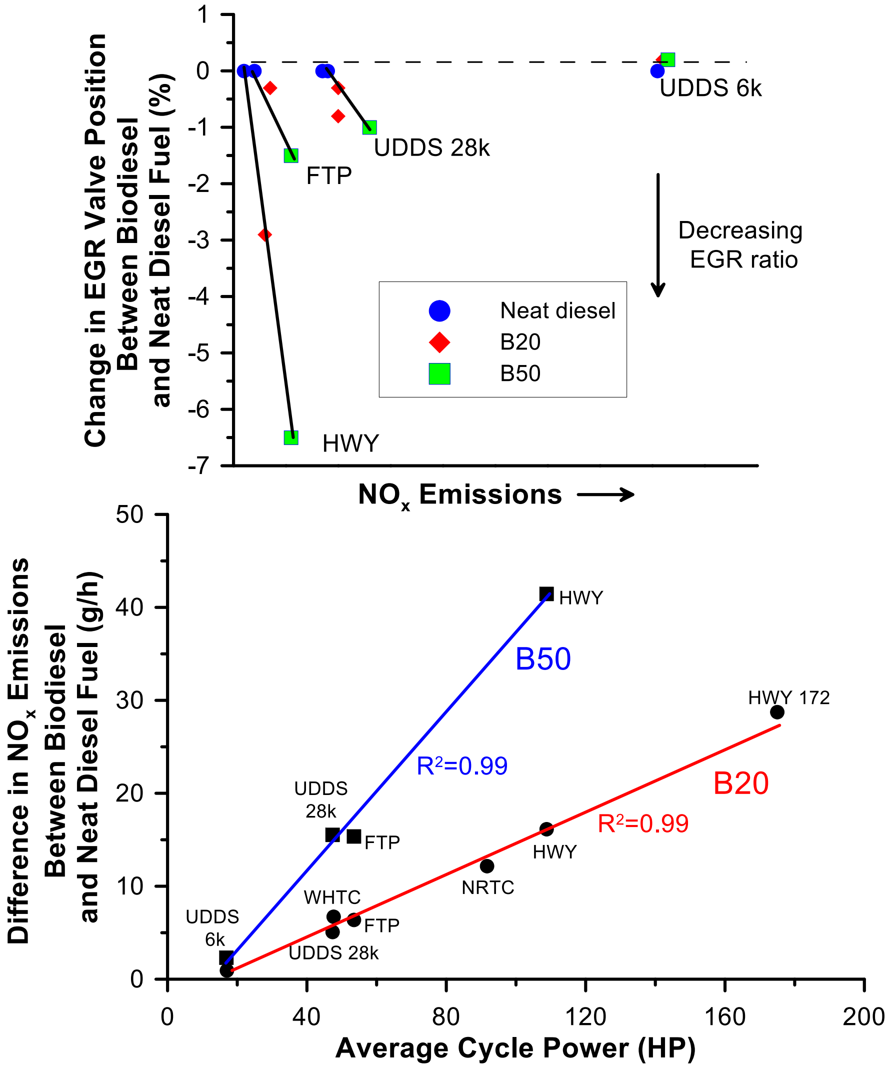
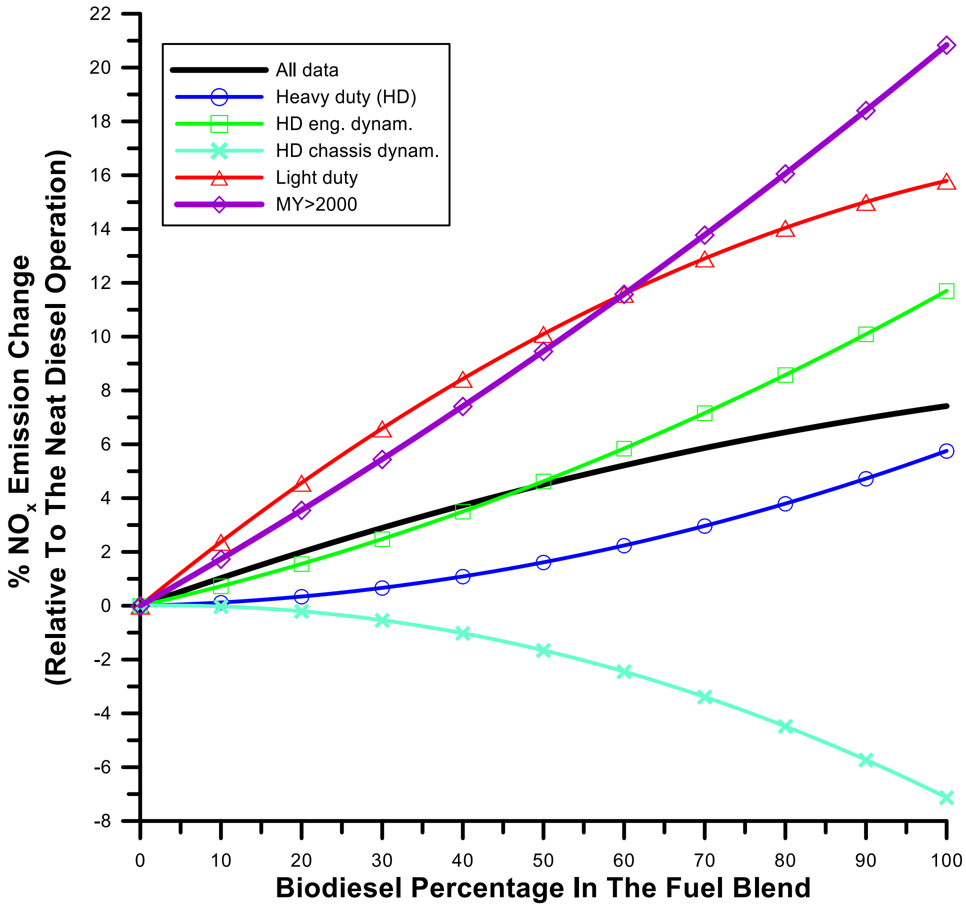

Change in EGR Valve Position
Between Biodiesel
and Neat Diesel Fuel (%)
1
0
-1
-2
-3
-4
-5
-6
-7
UDDS 6k
UDDS 28k
FTP
HWY
Decreasing
EGR ratio
Neat diesel
B20
B50
NOx Emissions
Difference in NOx Emissions
Between Biodiesel
and Neat Diesel Fuel (g/h)
50
40
30
20
10
0
HWY
B50
HWY 172
R²=0.99
B20
UDDS
28k
FTP
R²=0.99
HWY
NRTC
WHTC
FTP
UDDS
6k
UDDS 28k
0
40
80
120
160
200
Average Cycle Power (HP)

Figure 5.



All data
Heavy duty (HD)
HD eng. dynam.
HD chassis dynam.
Light duty
MY>2000
% NOx Emission Change
(Relative To The Neat Diesel Operation)
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
0
10
20
30
40
50
60
70
80
90
100
Biodiesel Percentage In The Fuel Blend

Figure 6.

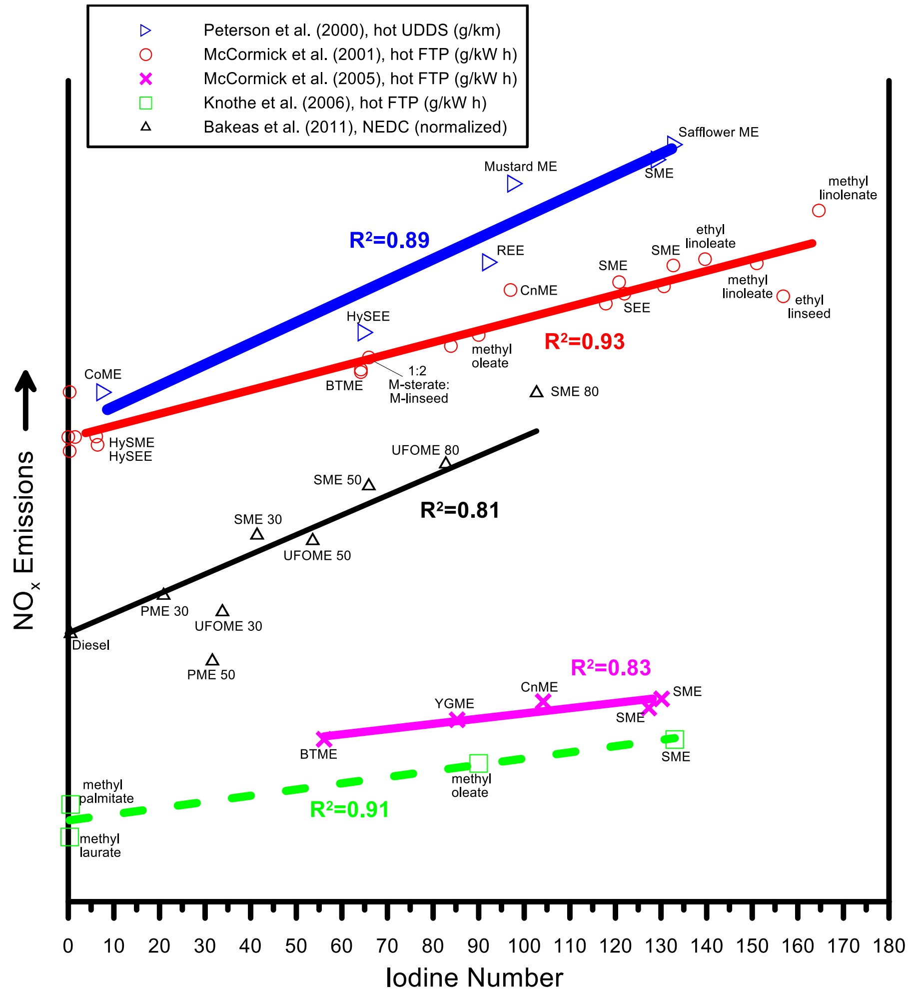


Figure 7.

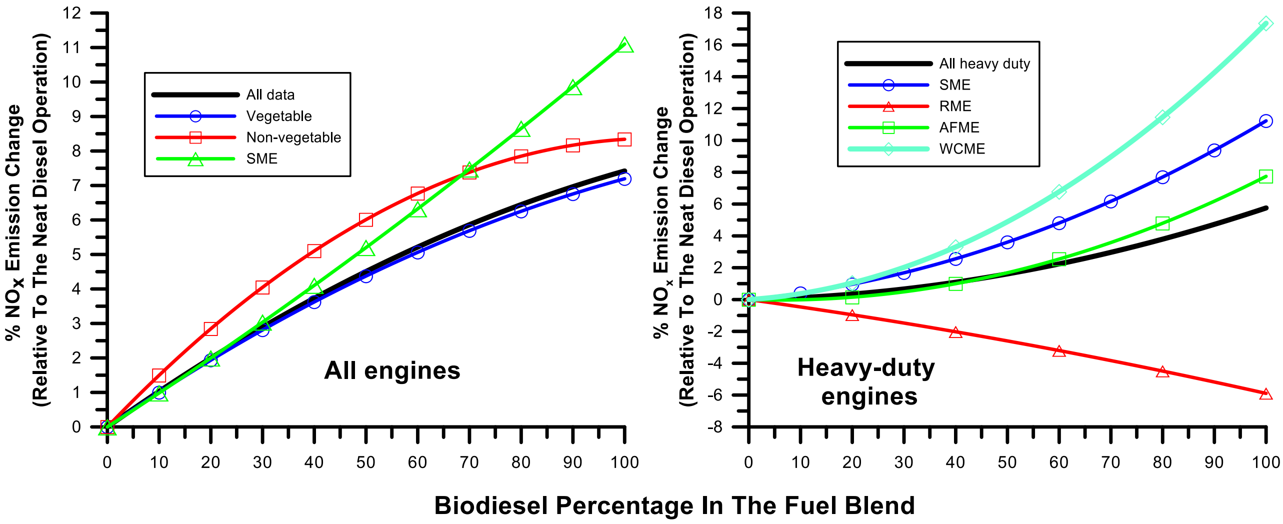


Figure 8.