Exhaust emissions of diesel engines operating under transient conditions with biodiesel fuel blends

by

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Abstract

The transient operation of turbocharged diesel engines can prove quite demanding in terms of engine response, systems reliability and exhaust emissions. It is a daily encountered situation that drastically differentiates the engine operation from the respective steady-state conditions, requiring careful and detailed study and experimentation. On the other hand, depleting reserves and growing prices of crude oil, as well as gradually stricter emission regulations and greenhouse gas concerns have led to an ever-increasing effort to develop alternative fuel sources, with particular emphasis on biofuels that possess the added benefit of being renewable. In this regard, and particularly for the transport sector, biodiesel has emerged as a very promising solution.

The target of the present work is to review the literature regarding the effects of diesel-biodiesel blends on the regulated exhaust emissions of diesel engines operating under transient conditions (acceleration, load increase, starting and transient cycles). The analysis focuses on all regulated pollutants, i.e. particulate matter, nitrogen oxides, carbon monoxide and unburned hydrocarbons; results are also presented for combustion noise

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and particle size concentration/distribution. The most important mechanisms of exhaust emissions during transients are analyzed based on the fundamental aspects of transient operation and on the impacts the physical and chemical properties of biodiesel have relative to conventional diesel oil. Biodiesel feedstock, transient cycle and fuel injection system effects are also discussed.

For the majority of the reviewed transients, a decreasing trend in PM, HC and CO, and an increasing trend in NO_x emissions is established when the biodiesel ratio in the fuel blend increases. Irrespective of driving cycle type, the NO_x emission penalty and the PM benefit with biodiesel seem to increase for more aggressive cycles/driving patterns. Moreover, biodiesels produced from unsaturated feedstocks tend to increase the NO_x emission liability, at least for older production engines; no such correlation has been established for the emitted PM, HC or CO. Since the research so far stems from engines optimized for diesel fuel, application of revised engine calibration (e.g. EGR, injection system) can prove very useful in eliminating, at least in part, any inefficiencies caused by the use of biodiesel.

Based on a large amount of published data over the last twenty years, best-fit correlations are deducted for quantification of biodiesel benefits or penalties on all regulated pollutants during various transient/driving cycles. Also, a detailed list is provided summarizing data from all published works on the subject during the last two decades.

Keywords: Diesel engine; Biodiesel; Transient operation; Exhaust emissions; Turbocharger lag; Transient cycle

Contents

1. Introduction

Energy security is a key ingredient for the economic stability of every country, particularly for those countries that do not have adequate fossil or nuclear resources. In this regard, depleting reserves and rising prices of crude oil, having placed negative loads on the trade balances of the non-oil producing countries, are posing a severe threat to the world economy since petroleum prices form the basis of the world industrialization. These facts, coupled with the continuously growing concern over global warming and environmental degradation in general (e.g. acid rain, smog, climate changes), have accentuated the public and scientific awareness and led to a substantial effort to develop alternative fuel sources. Among those, biofuels have assumed a leading role since they possess the critical benefit of being renewable, showing thus an ad hoc advantage in reducing the emitted carbon dioxide (CO_2) [1]. One of the most prominent areas where the high demand for petroleum-based fuels manifests itself is the transportation and agricultural sector, which collectively form not only one of the main consumers of fossil fuels but also one of the major contributors to environmental pollution. Thus, automotive, truck and non-road engines/vehicles constitute an important field, where the use of alternative fuels emerges as a very promising, long-term, alternative solution in order to achieve the desired diversification from petroleum products. Motivated by these facts, the European Union (EU) issued a directive on the use of biofuels accounting to at least 5.75% of the market for gasoline and diesel fuel sold as transport fuels by the end of 2010, and 10% up to 2020 (EU Directive 2009/28/EC). Likewise, a commitment by the US government in the early 2000s to increase bio-energy three-fold in ten years enforced the search for viable biofuels and led to a rapid growth in the share of biofuels, which is expected to be boosted in the next years following the most recent US EPA RFS2 act (Renewable Fuels Standard version 2).

In parallel during the last decades, the increasingly stringent exhaust emission regulations have dominated the automotive industry and forced manufacturers to new developments. More than in the past, a combination of both internal measures and efficient exhaust after-treatment devices will be required; an environmentally friendly solution, even though on a supplementary basis, can be the use of biofuels [2].

The term biofuel refers to any fuel that is derived from biomass, such as sugars, vegetable oils, animal fats, etc. Biofuels made from agricultural products (oxygenated by nature) reduce the countries' dependence on oil imports, support local agricultural industries and enhance farming incomes, while offering benefits in terms of sustainability and reduced particulate matter (PM) emissions. What is equally important, from an economic point of view, is that they are more evenly distributed than fossil or nuclear resources, since they can be produced domestically. Consequently, they constitute a long-term measure to, at least in part, increase energy security and diversity. Among the biofuels currently in use or under consideration, biodiesel (methyl or ethyl ester) is considered as a very promising fuel for the transportation sector since it possesses similar properties with diesel fuel, it is miscible with diesel practically at any proportion, and is compatible with the existing distribution infrastructure; moreover, biodiesel is less toxic than petrodiesel and is also bio-degradable [3,4]. Biodiesel is produced by transesterification of vegetable oils, animal fats or recycled cooking oils, and consists of long-chain alkyl esters, which contain two oxygen atoms per molecule [4−7]. The more widely used biodiesels are rapeseed methyl ester (RME) in Europe and soybean methyl ester (SME) in the US; other popular biodiesels are palm, sunflower, cottonseed, waste cooking and tallow methyl esters, collectively known as fatty acid methyl esters (FAME).

The major biodiesel advantage relative to diesel fuel is its renewability. Relevant life cycle assessment (LCA) analyses, although highly dependent on the methodology employed and hence usually variable in their results, have shown that the 'source-to-wheel' CO_2 emissions from neat biodiesel combustion account for at least 50% savings with respect to petroleum diesel fuel. This is an extremely promising fact with regards to increasing global warming concerns from the transport sector but other issues should not be ignored, such as food prices and biodiversity. In view of these concerns, it is not surprising that 'second-generation' biodiesels from non-edible feedstock (e.g. algae) are under development [4,5,7]. On the other hand, the major technical barriers associated with the use of biodiesel are its higher production cost (largely owing to the cost of the feedstock, except, of course, for the case where waste cooking oils are used), its susceptibility to oxidation as well as its poor low-temperature properties. It is also highly doubtful that biodiesel could ever be available in sufficient quantities to offset the use of petrodiesel.

The use of biodiesel during steady-state operation has been researched heavily during the last decades [e.g. 4,6−14]. For example, a search in the Elsevier database at the end of 2011 with the term 'biodiesel' returns more than 2000 papers that contain this word in the article's keywords. The majority of the researchers report decrease in the amount of emitted soot (this decrease is roughly proportional to the increase in the biodiesel ratio in the fuel blend), decrease in unburned hydrocarbons (HC) and carbon monoxide (CO - both already low enough for most turbocharged DI diesel engines), and slight to moderate increase of nitrogen oxides (NO_x). The exact percentage of emission change relative to the neat diesel operation varies considerably; it depends on the originating vegetable oil or fat as well as the biodiesel percentage in the fuel blend and the examined test conditions as demonstrated, for example, by a statistical analysis published by EPA in 2002 [15]. Another comprehensive study has been reported in [12] comparing various methyl esters with their originating vegetable oils (blends of 10 and 20% v/v with diesel fuel), and four reviews (none of which focused on transient conditions) are available regarding performance, combustion, emissions and emission control during diesel engine operation [6,8,16,17].

Although the diesel engine has for many decades dominated the medium and medium-large transport sector based on its reliability, fuel efficiency and the ability to operate turbocharged, discrepancies in the form of increased exhaust smokiness and noise have delayed its infiltration (and popularity) in the highly competitive automotive market. Traditionally, the study of diesel engine operation has focused on the steady-state performance. However, the majority of daily driving schedules involve transient conditions. In fact, only a very small portion of a vehicle's operating pattern is true steady-state; one notable example is when cruising on a motorway.

The fundamental aspect of turbocharged transient conditions lies in their operating discrepancies compared with the respective steady-state ones. Whereas during steady-state operation, engine speed and fueling, hence all the other engine and turbocharger properties remain essentially constant, under transient conditions both the engine speed and fuel supply change continuously. Consequently, the available exhaust gas energy varies, affecting the turbine enthalpy drop and, through the turbocharger shaft torque balance, the boost pressure and the air-supply to the engine cylinders are influenced too. However, due to various dynamic, thermal and fluid delays, mainly originating in the turbocharger moment of inertia, combustion air-supply is delayed compared with fueling, adversely affecting torque build-up and vehicle driveability [2]. As a result of this delay in the response between air-supply and fueling, particulate and gaseous emissions peak way beyond their acceptable, steady-state values [2,18,19]. Acknowledging these nowadays well established facts, various legislative directives in the EU, the US and Japan, have drawn the attention of manufacturers and researchers to the transient operation of diesel engines in the form of transient cycles certification for new vehicles [20,21]. Not surprisingly, the research on transient diesel engine operation has also expanded [e.g. 18,19,22–25], emphasizing on the (experimental) investigation of exhaust emissions.

The target of the present work is to review the literature regarding the impacts of diesel-biodiesel blends on the (regulated exhaust) emissions of compression ignition engines under the very critical transient conditions encountered in the every-day engine/vehicle operation i.e., acceleration, load increase, starting and in the collective form of transient cycles. The analysis that follows will primarily focus on the two most influential diesel engine pollutants, PM and NO_x, but results will be also presented for the other two regulated pollutants CO and HC, as well as for particle size concentration and combustion noise radiation.

The usual approach when analyzing alternative fuels impacts on exhaust emissions is by discussing the differing physical and chemical properties of the various blends against those of the reference fuel. Consequently, the composition and properties of biodiesel, together with its combustion and emission formation mechanisms, will form the basis for the interpretation of the experimental findings. What is equally important is that, for the first time, emphasis will be placed on the specific attributes and discrepancies encountered during transients too (most notably in the form of turbocharger lag), which may enhance or alleviate the differences observed between the biodiesel blends and the neat diesel operation. Through the analysis that follows it is believed that

- Light will be shed into the underlying exhaust emission trends under transient conditions,
- Possible differentiations in the emission mechanisms with respect to steady-state conditions will be identified,
- Valuable relations will be proposed based on the large amount of experimental data surveyed regarding the quantitative effect of biodiesel blend on engine emissions during transient cycles,
- Potential problems or inefficiencies associated with biodiesel use will be highlighted,

- Conclusions will be derived that can prove valuable to both engine manufacturers, (inter)national administrations and institutions, and finally
- Interesting areas for future research will be located.

2. Historical overview

Despite the plethora of published papers on steady-state diesel engine emissions when using biodiesel, the inherent difficulties in measuring and analyzing exhaust emissions during transients has led to a narrower investigation in this subject so far. Table A in the Appendix provides a list of the published papers in international Journals and well established Conferences, as well as reports from renowned research centers in chronological order that all deal with exhaust emissions during (truly) transient conditions, when the engine runs on various biodiesel blends [26–103]. A few comments and conclusions derived from the list of the surveyed publications are summarized.

- All the investigations in Table A deal with four-stroke passenger cars and medium/heavy-duty or non-road engines/vehicles. This is not unexpected since four-stroke engines have dominated the vehicular industry during the last decades. To this end, earlier two-stroke studies have been excluded from the current analysis and the quantitative results that will be presented later in the text. The same holds for indirect injection engines, minimal data from which are included, only for the sake of completeness. Moreover, to the best of the authors' knowledge, there are no works available in the open literature concerning industrial, locomotive or marine engines (load increase) transient emissions with biodiesel.
- The research was initiated in the early 90s mainly in the US on heavy-duty, highway engines, and has intensified heavily in the recent years, as is documented in Fig. 1, particularly with respect to light-duty engines/cycles.
- The impacts of biodiesel blends on engine emissions during various legislative transient cycles constitute the most prolific segment of the research (Fig. 2). Only a few publications [e.g. 50,63,73,75,84,103] investigated discrete transient schedules, i.e., specific acceleration, load increase and starting events. The obvious advantage of the latter category is that instantaneous transient emissions were measured applying high-response exhaust analyzers.

- All researchers of the former category (transient cycles) treated and analyzed their measurements in a ‘quasi’ steady-state manner by providing cumulative emission values throughout the cycle (recall that this is actually the objective of a legislated driving cycle), without provision of the parts of the cycle or its particular transient schedules that contribute mostly, although ‘instantaneous’ emissions were sometimes gathered too, e.g. [34,35,49,65,71], however on a second by second basis. Nonetheless, these investigations fall technically into the transient category too, and will actually comprise a very important part of the discussion that follows owing to their popularity and vast amount of published results.
- As is also documented in Fig. 2, roughly 30% of the experimentations focused on the American FTP heavy-duty transient cycle, and another one quarter on the European passenger car NEDC. Paradoxically, the American light-duty cycles and the European ETC heavy-duty one have only sporadically been dealt with.
- The most investigated biodiesel blends are B20 (i.e. 20% v/v biodiesel blended with 80% conventional diesel) and B100 (neat biodiesel) (Fig. 3). The most popular methyl ester in the research so far is soy-derived; it has been the subject in half of the studies and 40% of all investigated biodiesels during transients (Fig. 2).

3. Biodiesel physical and chemical properties

In this section, the most important biodiesel physical and chemical properties will be briefly discussed with respect to the reference diesel fuel; these properties are summarized in Table 1. The discussion will provide some valuable information for the analysis that follows, since many of the emission mechanisms are based on the different attributes between biodiesel and petrodiesel. From the data provided in Table 1 it can be concluded that biodiesel with respect to the reference diesel fuel contains/has:

1. 10−12% by wt. oxygen (leads to proportionally lower energy density, necessitating greater mass of fuel to be injected in order to achieve the same engine power output).
2. ultra-low natural sulfur content (considered a soot precursor too), with vegetable derived methyl esters having practically zero sulfur content, and animal based ones extremely small; however, this advantage seems to gradually fade owing to the continuous desulfurization of the petroleum diesel fuel.

3. higher cetane number (represents the ignitability of the fuel, with higher CN leading to shorter ignition delay); cetane number decreases as the number of double bonds increases, i.e. as the methyl ester becomes more unsaturated. Highly saturated esters such as those derived from coconut, palm, tallow and used cooking oil have the highest cetane numbers.
4. lower heating value owing to oxygen content (greater mass needs to be injected in order to assume the same engine power).
5. higher viscosity (leads to less accurate operation of the fuel injectors, and to poorer atomization of the fuel spray, increase in the Sauter mean diameter of the fuel droplets and of the break-up time; viscosity is related to the degree of unsaturation and to the fatty acid chain length (the latter varies considerably in the pure esters but barely in the final biodiesels).
6. higher density (volumetrically-operating injectors inject greater mass of biodiesel than conventional diesel fuel).
7. higher bulk modulus of compressibility (at least in part, owing to the presence of oxygen in the fuel structure, which creates a permanent dipole moment in the molecule).
8. higher flash point (is a measure of the temperature to which a fuel must be heated such that the mixture of vapor and air above the fuel can be ignited); neat biodiesel is thus much safer than diesel in this regard.

Moreover, biodiesel has no aromatic or poly-aromatic hydrocarbons (considered a soot precursor), and also exhibits better lubricity (decreases wear, particularly in rotary and distributor-type fuel injection pumps, which employ a fuel-based lubrication).

Due to its chemical structure (it usually contains a high percentage of unsaturated fatty acids, such as oleic, linoleic and linolenic), biodiesel is more prone to oxidation compared with conventional diesel fuel, particularly for long term storage. Thus, additives in the form of anti-oxidants are usually required. It is the more saturated biodiesels, e.g. from palm, coconut or tallow, that exhibit better oxidative behavior but still inferior to mineral diesel. Moreover, biodiesel exhibits worse cold-flow properties (pour point and cloud point) than petrodiesel requiring cold-flow improvers. Contrary to the oxidation stability, it is the more saturated esters that suffer from poor low-temperature attributes. On the other hand, the best pour and cloud point are to be found in highly saturated FAMEs, particularly RME.

Differences in the fuel properties (viscosity, density, surface tension, boiling point and oxygen content) between biodiesel and conventional diesel fuel are expected to affect the fuel spray penetration and evaporation rate although the trends reported are not always consistent [17]. Thus, the air−fuel mixing and flame temperatures can be affected too, as reported, for example, by Choi and Reitz [104]. Specifically, a marked difference between biodiesel and neat diesel combustion occurs in the atomization process, given that the mean droplet size is larger when biodiesel is used owing to its a higher kinematic viscosity and surface tension. Both factors are well known to affect the Sauter mean diameter of the fuel droplets, which were reported by Allen and Watts to be up to 40% higher for biodiesel compared to petrodiesel [105]. This fact and the different distillation curves, i.e., higher distillation curve for biodiesel than that of the neat diesel fuel, indicate that the evaporation process will be slower for the biodiesel, and thus could affect the combustion process by reducing the fraction of fuel burned in the premixed combustion phase in favor for the diffusion portion. On the other hand, the fact that biodiesel contains oxygen may, under circumstances, lead to enhance the reaction rate during the premixed phase, hence lead to quicker evolution of diffusion combustion too under higher temperatures.

Not always consistent results have been reported as regards both the ignition delay and the duration of combustion between biodiesel and petrodiesel. The influence of the engine operating conditions and the originating feedstock appears to be important for both combustion properties [17].

4. Effects of biodiesel blends during transient operation

4.1. Nitrogen Oxides

4.1.1. Main mechanisms and trends during transients

Nitrogen oxides together with particulate matter are the most critical pollutants produced by diesel engines; they consist mostly of nitric oxide NO and nitrogen dioxide NO_2 (referred to, collectively, as NO_x), and play an important role in the atmospheric ozone formation. Formation 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 injection timing and fuel properties. The most successful method of NO_x emissions abatement is by lowering the peak cylinder temperature through a) retarded injection timing (this may, however, affect engine efficiency), or b) exhaust gas recirculation. The latter has been rendered very popular in recent years as an effective means for reducing the emitted NO_x from both spark and compression ignition engines on account of the increasingly stringent emission regulations. However, the usual ECU strategy during transients aims at shutting down the EGR valve in order to help build-up of air–fuel ratio and boost pressure, and limit intolerable smoke emissions [2]. It is not surprising then that during this phase an overshoot of nitrogen oxides is generally noticed.

The somewhat higher cetane number of biodiesel in contrast to the neat diesel fuel may decrease NO_x emissions under certain conditions (e.g. premixed-controlled combustion typical under light-load operation [106]), engines and originating biodiesel oils, as will be detailed later in the text. 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. This decreasing trend was reported for example in [28,31,36,46,47,60,70,74].

On the other hand, a long series of points has been raised by many researchers that argue towards an increasing NO_x production trend during transients, as has also been the usual finding during steady-state operation. In fact, the majority of published works report slight to moderate increases in transient NO_x with biodiesel addition in the fuel blend (from the statistical analysis of the data from Table A, it was found that 66.5% of all available transient measurements concerned positive (increasing) NO_x emissions with biodiesel in the fuel blend – see also Fig. 11 later in the text). Representative results during three different transient schedules are documented in Fig. 4 that illustrates two typical low-load discrete accelerations of a medium-duty turbocharged diesel engine; in Fig. 5 which demonstrates cumulative results from a heavy-duty cycle; and in Fig. 6 which focuses on a light-duty driving schedule. The reasons for this increasing trend of NO_x with rising biodiesel percentage in the fuel blend have been classified into two categories, namely injection and temperature-related (although sometimes no clear distinction can be made, or other classifications can be used, e.g. combustion or fundamental and calibration reasons); these mostly derive from fundamental (steady-state) spray studies, and are summarized below based on the dominance of the thermal NO_x production over the prompt-NO or the fuel-bound nitrogen mechanisms [17]. It is important to note that none of these mechanisms appears to be prevailing for all engines and operating conditions, but rather their synergistic effect produces the higher NO_x trend with biodiesel; a thorough discussion of the subject is provided in [17,107].

Injection-related factors

a) Owing to biodiesel's higher bulk modulus of compressibility, speed of sound and surface tension (Table 1), when a diesel-tuned engine is run on biodiesel blends, a faster wave propagation and pressure rise inside the hydraulically operated injectors are experienced resulting in earlier needle lift (of the order of 0.5–2^o crank angle) [108–111]. This advance of injection timing increases the duration of the premixed phase and the total residence time in the cylinder, and mostly the pressures and temperatures during diffusion combustion [16] (hence it is a temperature-related argument too). The reason for the increase in the duration of the premixed-portion of combustion lies in the fact that when the fuel is injected earlier in the cylinder, the surrounding conditions are less favorable for mixture preparation. Thus, as the start of injection (SOI) timing is advanced, the phasing of the combustion event is advanced too and more time is spent at elevated temperature conditions that promote the production of (thermal) NO_x [16]. It should be pointed out, however, that this injection advance effect appears to be applicable mostly to pump-line nozzle and unit injector systems, and would not appear to be that relevant to high-pressure common rail systems, where rapid transfer of a pressure wave does not occur [106]. Nevertheless, an interesting study by Cheng at el. [112] 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. Similarly, Zhang and Boehman [106] used engine controls to eliminate injection timing differences between B40 and petrodiesel, and found that B40 produced slightly lower NO_x emissions under low load but higher NO_x under high loads; these findings probably entail that other, inherent in the biodiesel combustion, issues might be more influential than injection timing.

b) 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, which is more likely to promote NO_x emissions as it is expected to lower the local air−fuel equivalence ratio and increase the respective local gas temperatures (hence it is temperature-related too).

c) Moreover, the reduced fuel leakage losses in the (mechanical) fuel pump owing to the higher kinematic viscosity of biodiesel compared with the neat diesel fuel, lead to higher injection pressures [17] and, hence, mass of injected fuel, a fact that acts in parallel to (and strengthens) the previous point.

d) Lastly, the ECU calibration 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 [17].

ii. Temperature-related factors (thermal NO)

a) Local conditions during biodiesel combustion are nearer to stoichiometric compared with the neat diesel operation. This fact can prove quite influential during transients, particularly during the crucial turbocharger lag cycles, where the air–fuel equivalence ratio is expected to be lower than unity. The underlying mechanism here is the promoted increase in the adiabatic flame temperature, which is well known to peak around stoichiometric conditions [113]. In other words, for the duration of the turbocharger lag, whereas during diesel combustion the air–fuel equivalence ratio might be below unity, for biodiesel combustion, the excess oxygen inherent in the blend leads to higher values that are now closer to stoichiometry, and hence promote higher gas temperatures. Interestingly, similar arguments have been raised by Mueller et al. [107] during steady-state operation. They concluded that the combustion process generally progressed more quickly for the biodiesel fuels and test engine conditions examined than for the hydrocarbon reference fuels. Specifically, owing to its high oxygen content, biodiesel premixes more fully during the ignition delay, and a larger fraction of its heat release occurs during the premixed phase of combustion. To the extent that this leads to higher in-cylinder temperatures and longer residence times at high temperature, this would be expected to also increase NO_x emissions for the biodiesel blends.

b) A common belief about biodiesels is that they have higher adiabatic flame temperatures (the existence of double bonds in the fuel molecule has been associated with high flame temperatures [113]), which is expected to increase accordingly the emitted (thermal) NO_x. Steady-state [114] and transient

[36,40,48,51] emission findings from many studies lend support to this argument; biodiesels produced from unsaturated feedstocks such as soybean or rapeseed have been found to emit higher NO_x compared with the more saturated esters, such as those derived from palm or tallow. However, adiabatic flame temperatures do not usually vary much with biodiesel feedstock, and measured peak temperatures show even less variation [17,107], so the underlying mechanism behind the unsaturation effects remains open for speculation. Mueller et al. [107] 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 might explain the fact why highly saturated biodiesels produce also lower NO_x, since fuels with high cetane numbers lead to mixtures farther from stoichiometric.

c) Another contributing cause for elevated local gas temperatures with biodiesel combustion has been revealed by Musculus [115]. In his experimental study it was shown that actual flame temperatures inside the cylinder may be influenced by differences in soot radiative heat transfer, i.e. the heat radiation in the combustion chamber from the formation of soot particles lowers the combustion temperatures, subsequently decreasing the emitted NO_x. Since the oxygen in a biodiesel blend is well known to decrease soot (Section 4.2.1), thus reducing the radiative heat transfer term, higher local gas temperatures are expected that in turn will favor greater NO_x penalty, even for fuel blends for which the equilibrium calculations have not revealed a difference in the stoichiometric adiabatic flame temperatures. Similar findings have been reported in a comprehensive, experimental study by Mueller et al. [107].

d) An essential factor for the NO_x emissions behavior in modern engines is the exhaust gas recirculation (EGR) system. Although this is not a combustion but rather an engine-calibration effect, it nonetheless results in temperature impacts, hence it is discussed here. Bannister et al. [76] found that the increase of the biodiesel percentage in the fuel blend led to an approximately linear reduction in the maximum tractive force at any given speed owing to the lower energy density of methyl esters. Consequently, 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 (fueling is an input to the EGR control strategy), escalating in-cylinder temperatures and NO_x emissions. For example, Lujan et al. [65] measured NO_x emissions 20.6%, 25.9% and 44.8% higher for B30, B50 and B100 blends respectively compared with the neat diesel case (Fig. 6). An even more comprehensive approach was conducted by Sze et al. [54], who actually quantified the EGR effect. They found that the lower calorific value of biodiesel affected 'throttle' position (up to 3.3% relative to the petroleum diesel operation), and subsequently other relevant engine parameters, such as the fuel rail pressure, VGT position and boost pressure, and ultimately decreased the EGR rate up to 10.5% (depending on the cycle) for the cases examined. Typical results from their study are reproduced in Fig. 7 that illustrates the EGR valve position change for B20 and B50 SME blends relative to mineral diesel fuel for various transient cycles of a heavy-duty diesel engine. Apart from the most light-loaded cycle, biodiesel addition in the fuel blend resulted in noteworthy reduction in the EGR valve position.

Lastly, differences in the chemical kinetic pathways that form NO_x when biodiesel is used have been reported, that may contribute to the higher biodiesel NO_x emissions. Arguments based on differences in prompt NO formation seem to be the most common in this category. Such arguments typically rely on increased levels of CH being produced at the auto-ignition zone during biodiesel combustion (e.g. [116]), 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 oxygen and OH are present [107].

It should be mentioned that many of the issues discussed above arise when diesel-tuned engines are tested/run on a fuel that has different properties; consequently, many of these issues could be dealt with applying an appropriate re-calibration of the engine. Supporting evidence to this has been provided, for example, by Szybist et al. [16], who showed that once the inadvertent advance in SOI timing is corrected for, the NO_x emissions were no longer fuel composition dependent. Thus, application of a different injection strategy e.g. in the form of a different timing and duration of injection could compensate for biodiesel's higher values of density and bulk modulus of elasticity, and address the primary mechanism of NO_x emission increase (earlier start of injection), at least for mechanically-controlled fuel injection systems.

4.1.2. Parametric investigation

4.1.2.1. Impact of biodiesel feedstock

One of the most intriguing points regarding the biodiesel impact on NO_x emissions is the effect of fuel properties and molecular structure. Since biodiesel can be produced from a variety of vegetable or animal feedstocks, it seems reasonable to assume that the different chemical composition and structure of the originating oil or fat may influence the engine processes and exhaust emissions. It is Peterson et al. [36] and McCormick et al. [40,48], who have conducted the most illuminating research on the subject so far, demonstrating the relation between nitrogen oxides and degree of unsaturation, both studying the performance of heavy-duty diesel engines during transient cycles.

McCormick et al. [40] 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 on a 1991 MY engine. The left sub-diagram of Fig. 8 shows the regression model reached for NO_x emissions with density (R^2=0.88); the relationship between cetane number and NO_x emissions is shown in the right sub-diagram of Fig. 8. Since the impact of molecular structure is implicit in either the density or cetane number, more saturated esters which have higher cetane numbers and lower densities than less saturated esters emitted the lowest NO_x. A highly linear relationship (R^2=0.93) between iodine number (a usual measure of the fuel's unsaturation) and emissions of NO_x during the FTP was also established, as is illustrated in Fig. 9.

In general, it was found that high stearate fuels with few double bonds produced significantly less NO_x than certification diesel. Unfortunately, these materials have poor cold-flow properties and some are even solid at room temperature. Interestingly, a later study by McCormick et al. [48], this time on a common rail, heavy-duty diesel engine, showed that B100 blend tests, in general, confirmed the above results, although the R^2 was found lower this time, of the order of 0.83 (Fig. 9); the latter implies fuel injection system effects too, primarily through the weaker influence of the biodiesel's higher bulk modulus of elasticity relative to neat diesel fuel as was discussed previously, but EGR definitely had an important role too. On the other hand, the B20 test results were not found statistically significant, possibly owing to the much lower absolute values of NO_x, which made feedstock effects more difficult to observe.

In parallel, Peterson et al. [36] studied biodiesel blends from 6 different real-world feedstocks during the hot UDDS cycle for a medium-heavy duty diesel engine, and identified a similar statistically significant correlation between iodine number and NO_x emissions (Fig. 9). Again, no association could be established between unsaturation and PM, or between NO_x emissions and cetane number (right sub-diagram of Fig. 8), but a satisfactory correlation was found between NO_x and density (left sub-diagram of Fig. 8).

Similar observations concerning the effect of unsaturation on NO_x emissions have been reported by Knothe et al. [51], Fontaras et al. [74] and Bakeas et al. [81]. The latter additionally identified the glycerol content in the biodiesel blend as suspect for higher NO_x.

4.1.2.2. Impact of the transient cycle pattern

Another important objective is the investigation of the effect of the transient cycle's characteristics on the exhaust (and in particular NO_x) emissions. An elucidating analysis on this subject was conducted by Sze et al. [54], who studied a 2006 MY engine operated on 7 different heavy-duty engine and chassis-dynamometer cycles. The fundamental conclusion reached from their analysis was that higher NO_x penalty was observed for biodiesel-fueled engines with increasing average transient cycle power. Based on several observations, the changes in NO_x mass emission rate due to biodiesel was found to correlate well with the average cycle power (R^2=0.99) and the fuel consumption (R^2=1.0) of the engine. The results obtained are reproduced in Fig. 10. The apparent reasons for the higher biodiesel NO_x liability with increasing cycle power lies in the primary NO_x production mechanism. For a diesel engine, increasing power results in higher amount of injected fuel, lower air−fuel equivalence ratios and finally higher (peak) gas temperatures. Likewise, a more aggressive cycle 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. For example, in Fig. 10 the more highly-loaded HWY cycle results in greater EGR decreases with rising biodiesel blend than the lighter-loaded FTP or UDDS ones.

Comparable results have been reached in various investigations a) by the research group of Professor Stournas [52,70,81,88], who regularly measured higher NO_x emissions over the more aggressive (non-legislated) Artemis or Athens driving cycles relative to the 'softer' NEDC, b) by Wang et al. [35], who measured higher NO_x on the more aggressive 5 mi route cycle over the lighter-loaded 5 mi peak one, and c) by Durbin et al. [53], who measured higher NO_x liability on the more aggressive US06 cycle relative to the FTP75. Lopez et al. [71], who found similar results, concluded also that an SCR-based deNOx system behaved more efficiently as regards the NO_x liability for low biodiesel percentages. Whereas the NO_x emissions increase with a DPF-EGR system was 19.3% and 23.9% for B20 and B100 respectively relative to diesel fuel, when an urea-based SCR was applied the respective differences were remarkably reduced for the small percentage (6.4%) but also remarkably increased for the neat biodiesel (38%). On the other hand, Peterson et al. [28,36] systematically measured lower NO_x (and sometimes higher PM) emissions with various biodiesel blends relative to their reference diesel fuel, which has been, at least in part, attributed to the fact that the UDDS chassis-dynamometer cycle studied was less aggressive than the heavy-duty, FTP engine-dynamometer cycle (for which NO_x increase with biodiesel blends is the common case). This 'reverse' behavior of NO_x emissions under light-loaded conditions (recall that low loading results in higher amount of premixed-burn combustion) has been partially confirmed by Fontaras et al. [64] regarding the equally light-loaded urban part of the NEDC (for B50 blends only, another B100 fuel behaved differently), at steady-state conditions [106], and is also evident in the right-hand values of Fig. 10.

4.1.2.3. Impacts of the fuel injection system

Finally, the engine fueling system, e.g. high-pressure, electronically controlled or pump-line-nozzle might also be related to the NO_x emission trend; unfortunately, owing to the inherent difficulties involved, there are few studies that have focused on different engine technologies, which could substantiate this hypothesis. A first finding has already been discussed in section 4.1.2.1 as regards iodine number impacts on NO_x emissions between electronic unit injector [40] and common rail engines [48]. Another interesting finding was reported by Sharp et al. [37], who found that for two electronically controlled engines running on the FTP cycle, the NO_x emissions increase depended almost linearly on the fuel blend's oxygen content, but this was not the case for a third, pump-line-nozzle fuel injected engine (operating at a much lower injection pressure), which exhibited much lower sensitivity to B20 and B100 runs. Although the test sample was very narrow, there is a possibility that a trend might apply here, a fact, however, which definitely requires further testing in order to prove the validity (or not) of this argument. To this aim, Yanowitz and McCormick [117] gathered data from various B20 investigations and fuel injection systems that are reproduced in Table 2; they concluded that common rail systems might be liable to higher NO_x (and lower PM) relative to conventional diesel fuel, but the dataset was not adequate enough (and the standard deviations observed high, suggesting variance of the data) to justify an unequivocal trend. Moreover, modern engines that are systematically equipped with common-rail injection systems employ also EGR and other antipollution control, which affect the emission trend significantly. Hence, the effect of the injection system alone cannot be easily isolated from the interaction of the other engine sub-systems.

4.1.3. Overall results

In 2002, EPA published a comprehensive analysis of biodiesel impacts on exhaust emissions, with a large amount of emissions data from the 1980s and early 1990s gathered and analyzed in order to quantify the effect of biodiesel blends on all regulated pollutants [15]. Those data comprised many two-stroke engine results, some steady-state cycles, and were limited to north-American engines, primarily heavy-duty highway ones tested during the FTP cycle with SME blends. For the current survey, an update of the EPA formulas has been performed for all regulated pollutants in order to also include measurements from the last decade from

- newer engines with modern injection systems and EGR control,
- passenger car and light-duty engines running on chassis-dynamometer cycles,
- European and Japanese engines/vehicles, and
- a wider range of real-world biodiesel feedstocks.

To this aim, all transient measurements reported in Table A were collected and analyzed. Figure 11 summarizes the effects of biodiesel blends on transient NO_x emissions by providing a best-fit approximation to the collected measurements. From Fig. 11, a moderate increasing trend is established with rising biodiesel blend ratio as was also the result of the earlier EPA report demonstrated in the same figure. It is surprising that although a considerable amount of new data has been included in the current statistical analysis, the earlier EPA best fit curve remains practically unchanged for blend ratios up to 50% despite the diversity in the investigated engines, vehicles, feedstocks and cycles. This result can be explained as follows. On the one hand the majority of the newer production engines are equipped with EGR, which as was discussed previously tends to increase the NO_x emission penalty. On the other hand, these newer production engines that are included in the dataset are primarily passenger cars tested on the relatively light-loaded NEDC. Most probably, the synergistic effect of these two contradicting factors produces a cancel-out result and practically maintains the anticipated biodiesel NO_x liability to the extent of the earlier investigations for 5-50% v/v blends. However, since the NEDC (from which many data are included) rather underestimates real-world driving conditions by incorporating soft and linear accelerations, it is speculated that higher biodiesel NO_x penalty will be actually encountered during real-life driving.

4.1.4. Methods for compensation of the NO_x increase

Owing to the (usual) NO_x emission liability with biodiesel against conventional diesel fuel, it is reasonable to suggest that an injection retard in order to delay the ignition timing might prove beneficial; this was, for example, the focal point of the work conducted by Starr studying a heavy-duty engine running on SME blends during the hot FTP cycle [31].

Based on the fact that NO_x emissions seem to correlate with cetane number, some researchers investigated the effect of ignition improvers. For example, Sharp et al. [100] 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; similar observations were made by Starr [31] for each timing tested. Nuszkowksi et al. [101] measured decreasing NO_x with increasing both 2-EHN or DTBP, with the greater impact observed on older technology (1990s) engines. McCormick et al. [43] confirmed the above results of DTBP, but they too later [48] argued that the success might be actually lower for newer engines.

Graboski et al. [29] proposed that NO_x neutral blends with biodiesel could be produced by altering either the base-fuel aromatic content or natural cetane number. To this aim, a low aromatic fuel (23.9%) was treated with biodiesel (to make B20) and a small amount of cetane (n-hexadecane) to raise the cetane number of the test blend to the same value as certification fuel. The lower aromatic content of the fuel compared to 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 was argued that fuel reformulation with oxygen and aromatic control is a route to producing NO_x–neutral but PM–reducing fuels. The same research group in a more recent study [43] 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%.

Based on the information gained from the studies that concentrated on the biodiesel feedstock impact on NO_x emissions (section 4.1.2.1), an alternative route for compensating the NO_x liability is revealed, by designing the ideal triglyceride feedstock for biodiesel. 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 [36]. In view of this, Chapman et al. [118] investigated a blending approach that 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 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.

In most modern engines, a variety of operating parameters such as the EGR system and the injection timing are electronically monitored and adjusted by the engine ECU. Thus, a notable compensation of NO_x emissions could be achieved through a revised engine calibration with regards to the injection system (discussed in Section 4.1.1) or the EGR control, as has been revealed, for example, by Eckerle et al. [119] in their simulation approach. In view of the required ECU calibration when using biofuel blends, an interesting study was conducted by Magand et al. [120] studying the performance of an engine during the NEDC running on a mixture of Fischer-Tropsch, ethanol and RME. 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 of the order of 60% relative to the reference diesel fuel was reversed into an impressive benefit of almost 22% without sacrifice in the PM reduction. Likewise, Zhang and Boehman [106] and Ireland et al. [121] applied both EGR and injection timing recalibration during steady-state tests in order to reduce NO_x from biodiesel combustion, while maintaining PM at levels lower than that of petrodiesel operation, however at the expense of fuel efficiency. On the other hand, Tat and van Gerpen [122] proposed a technique for the detection of the biodiesel presence in the fuel, which was to be accompanied by a retard of the static injection timing.

4.2. Particulate matter and smoke

4.2.1. Main mechanisms and trends during transients

As mentioned in the Introduction, biodiesel-blended (oxygenated) fuels have been found capable of (substantially) decreasing particulate matter during steady-state operation. In general, similar results have been reported during transient conditions too for both passenger cars and heavy-duty diesel engines. Figure 12 illustrates typical sunflower biodiesel effects on smoke opacity development during a load increase transient event at constant engine speed of a passenger car engine; smoke opacity measurement was accomplished applying a high response analyzer particularly suited to transient experimentation. Clearly, smoke was found to decline the higher the biodiesel content in the fuel blend with remarkable decrease observed for the B70 or B100 blends. Similar results have been reported for various acceleration transients by Rakopoulos et al. [73].

Returning to Fig. 5, we can expand on the latter remarks by observing cumulative PM emissions from a heavy-duty diesel engine during the FTP cycle with respect to the biodiesel percentage fuel blend. Reduction up to 66% (hot start) or 63% (cold start) was measured when running the engine with 100% SME compared with petroleum diesel fuel, without sacrifice in engine efficiency. Interestingly, PM emissions were reduced proportionally to the oxygen content of the fuel blend (oxygen content being 0.21%, 2.37%, 4%, 7.24% and 11.03% respectively for the 0, 20, 35, 65 and 100% by volume biodiesel-diesel blends). Similar results for the emitted PM were documented in Fig. 6, this time regarding the NEDC (cold starting effects are incorporated here).

Based on the research conducted so far, the beneficial effect of biodiesel blend on smoke opacity values/PM emissions during transients, as has been documented in the representative Figs 5, 6 and 12 can be, primarily, attributed to the following factors:

- Increased oxygen concentration in the biodiesel blend, which aids the soot oxidation process, irrespective of fuel composition. Soot formation, caused by high temperature decomposition, mainly takes place in the fuel-rich zone at high temperatures and pressures, specifically within the core region of each fuel spray, effectively preventing carbon atoms from participating in soot–precursor reactions. If the fuel is partially oxygenated, as is the case with biodiesel, it possesses the ability to reduce locally fuel-rich regions and limit soot nucleation early in the formation process, thus reducing PM emissions and smoke opacity. Further, the formation of soot is strongly dependent on engine load, with higher loads (e.g. cruising portions of the driving cycle) promoting higher temperature, longer duration of diffusion combustion (where particles are mostly formed) and lower overall oxygen availability (air–fuel equivalence ratio). The locally very low values of air–fuel ratio experienced during turbocharger lag at the onset of each acceleration and load increase, enhance the above mechanism, which is more pronounced the higher the engine rating, i.e., the higher the full-fueling to no-fueling difference. The excess oxygen of biodiesel aids in maintaining these air–fuel equivalence ratio discrepancies during turbocharger lag (where soot is primarily produced [2]) milder relative to the neat diesel transient operation, however, at the expense of NO_x as was argued in the previous section. Despite the significant positive effect of biodiesel on PM emissions, it has been reported in the literature that the biodiesel-bound oxygen may be under-utilized. This is due to the fact that methyl esters undergo decarboxylation, which yields a CO_2 molecule directly from the ester [16,123]. Thus, the oxygen in the biodiesel blend is used less effectively to remove carbon from the pool of soot precursors (compared, for example, with ethanol- or ether-diesel blends);

- Combustion with biodiesel shifts to more controlled mode, which means that there is more time available after diffusion combustion for soot oxidation at a high temperature environment. In other words, the previously mentioned injection and combustion advance acts in favor of the soot destruction process;
- Biodiesel is characterized by lower air−fuel equivalence ratio (Table 1), which reduces the possibility of fuel-rich regions in the non-uniform fuel−air mixture [8];
- Different structure of soot particles (see Section 4.2.2);
- Longer carbon chains of the biodiesel compared with the diesel fuel;
- Absence of aromatic (primarily) and sulfur (secondarily, owing to the continuously decreasing sulfur content in conventional diesel fuel) compounds that are generally considered to act as soot precursors.
- Further, and in order to account for the lower heating value of biodiesel, fuel consumption must increase for the same demanded engine torque. Hence, the ECU strategy may dictate an earlier start of injection and a decrease in the exhaust gas recirculation (EGR) rate, both of which result in elevated temperatures inside the cylinder that promote soot oxidation (again at the expense of NO_x).

In view of these strong PM-decreasing mechanisms during biodiesel blends combustion, it is not surprising that 90% of all transient measurements correspond to PM reduction when adding biodiesel in the fuel blend. However, there have been a few exceptions too. For example, Fontaras et al. [64] reported an impressive 177% increase of PM emissions over the NEDC (it was postulated that this was due to the increase in the SOF), Peterson and Reece [28] reported a 19.2% increase of PM emissions when a rapeseed derived neat biodiesel was tested compared with the neat diesel fuel during the UDDS chassis dynamometer cycle, and similar trends were reached by Durbin et al. [38].

Most of the studies so far have also concluded that, despite the sometimes substantial PM decrease, biodiesel-fueled engines produce a higher fraction of SOF in their exhausted PM than when petroleum-based diesel fuel is used; a typical summary of composite transient particulate composition is provided in Table 3 for a heavy-duty diesel engine running on the FTP transient cycle for two biodiesel blends and the nominal diesel fuel. As is made obvious in Table 3, SOF emissions generally increased with increasing biodiesel content, although it has been claimed that the exact percentage actually varies from engine to engine. Moreover, the lube-oil portion of the SOF was found to be unaffected by the biodiesel content. Although the exact mechanism is not absolutely clear, this higher SOF percentage of biodiesel has been attributed to its lower volatility (higher boiling point) as well as to heavy fuel-related organic compounds that remain intact through combustion [37,51,52].

There are two important issues that need to be addressed too:

a) Contrary to NO_x emissions (Section 4.1.2.1), no correlation could be established between biodiesel feedstock and transient PM emissions; the latter suggests that the positive impacts of biodiesel on PM are most probably not associated with specific ‘internal’ physical or chemical properties or attributes of the fuel, such as, for example, the number of double bonds, but rather depend on the oxygen content. On the other hand, a dependence on density and cetane number has been claimed in one study, namely with cetane number lower than 45 and density higher than 895 kg/m^3, PM emissions were substantially elevated [40]; nonetheless no explicit trend has been established, and this finding has not been confirmed in subsequent studies.

b) The transient cycle’s characteristics do not seem to correlate that well with PM as was the case with NO_x (in Section 4.1.2.2, R^2 for NO_x had an impressive value of 0.99); from the same study of Sze at el. [54], a lower but still healthy value of 0.87 was established for the coefficient of determination of PM emissions with respect to the average power cycle. It seems then that the higher the average cycle power (i.e. the more aggressive the cycle), the higher the benefit of biodiesel-blended fuels on PM emissions relative to neat diesel oil. Obviously, the higher the loading or the aggressiveness of a cycle, the lower the air–fuel equivalence ratios or the harsher and the more frequent the turbocharger lag phases induced respectively; both lead to more intense soot production, where the beneficial effects of biodiesel (most notably its increased oxygen content) prevail over the neat diesel operation. Moreover, high loadings and abrupt accelerations both dictate lower EGR rates through the usually applied ECU calibration, which again act in favor of lower PM emission rates at the expense of NO_x.

Despite the well established positive effects of biodiesel on PM emissions during fully-warmed up transients discussed so far, its use during cold starting has been found to exhibit an adverse behavior. This has been primarily attributed to the higher initial boiling point of biodiesel with respect to conventional diesel fuel, which leads to more difficult fuel evaporation at low ambient temperatures, and the higher viscosity of biodiesel, which reduces the rate of spray atomization. Both phenomena, which are enhanced with very high biodiesel blends, lead to worse fuel–air mixing and, thus, more intense soot formation at low temperatures; the latter increase was measured up to 80% for an automotive, HSDI diesel engine, when comparing B100 with neat diesel operation [50]. Later in the warm-up phase, when the engine assumes its normal operating temperature, the advantages of biodiesel combustion prevail, and soot emissions decrease compared with neat diesel fuel. These cold-starting results have been confirmed by Rakopoulos et al. [84] during various hot-starting tests performed on an engine dynamometer for a medium-duty turbocharged bus/truck engine, as is demonstrated in Fig. 13, where it is made clear that starting not only increases the peak in smoke opacity but also the duration of unacceptable black smoke emissions. Interestingly, extended pressure variability was also noticed for the diesel-biodiesel blend during the starting event of Fig. 13 compared with the neat diesel operation. Likewise during transient cycles, for the previously mentioned example of Fontaras et al. [64], the increase actually rose to 278% when only the cold (urban) ECE15 was isolated. Similar observations were made by Macor et al. [86] again for the cold-started ECE-15. On the other hand, Graboski et al. [29] measured higher PM emissions during the cold-started runs of the heavy-duty FTP compared with the hot ones, but in either case a significant benefit relative to neat diesel operation was established for each biodiesel blend tested. Bearing in mind the arguments raised in the last paragraphs, it seems that it is the fully warmed-up, urban engine operation that mostly benefits as regards PM emissions reduction from the use of biodiesel.

4.2.2. Diesel particulate filter regeneration rate

Application of a modern, high-efficiency exhaust after-treatment system (e.g. diesel particulate filter - DPF) being capable of reducing soot emissions to negligible levels, can practically downgrade to a large extent the biodiesel beneficial effects on PM [46,65]. Moreover, since Euro 5 specifications are even stricter regarding PM, it seems that the use of biodiesel alone is not enough to conform to these standards (as could have been the case with previous specifications), requiring a DPF in any case.

An important factor affecting the DPF regeneration rate is the oxidative reactivity of particulate matter. Boehman et al. [124] found that the use of a B20 blend during steady-state operation can significantly lower the balance point temperature (BPT; is the DPF inlet temperature at which the rate of particle oxidation approximately equals the rate of particle collection). They presented results showing that it is not the increased availability of NO_2 that is responsible for the decrease in BPT but rather the inherent differences in soot reactivity for different fuels, and specifically for B20, the more highly disordered soot nanostructure, such that the soot is more reactive or it is reactive at lower temperatures. The same research group [16,125] further concluded that the more reactive toward oxidation behavior of biodiesel soot derives from enhanced incorporation in the soot of surface oxygen functionality. These results were confirmed by Williams et al. [126], again during steady-state operation, who showed that on average, the BPT is 45°C and 112°C lower, respectively, for B20 blends and neat biodiesel, than for 2007 certification diesel fuel. Filter regeneration rate measurements indicated that biodiesel causes a significant increase in regeneration rate, even when B5 blends are employed. Overall, their results suggested significant benefits from the use of biodiesel blends in engines equipped with DPFs. It was argued that this decrease of BPT and the subsequent increase in regeneration rate might allow passive DPFs to be used in lower-temperature engine cycles, avoiding the need for actively regenerated filters and their associated fuel economy penalty. In parallel, actively regenerated systems might require less frequent regeneration, perhaps resulting in a lower fuel economy penalty.

There are few studies available that investigated the effects of biodiesel on DPF regeneration during transients in order to confirm the above significant (steady-state) findings. Tatur et al. [102] found that under normal operating conditions, a SME B20 blend had marginal impact on both DPF regeneration rate and NO_x adsorption catalyst lean-rich cycle development for a passenger car running on various American, light-duty cycles. On the other hand, Muncrief et al. [60], concluded that a diesel vehicle operating under low-load conditions (as the refuse truck studied) with neat cottonseed or soybean derived biodiesel had relatively cool exhaust to adequately oxidize the accumulated soot on the DPF with NO_2. It was speculated, however, that this might be counter-balanced by the lower emitted PM from biodiesel combustion.

4.2.3. Overall results

The statistical analysis of all transient measurements from the studies of Table A yields the quadratic best-fit curve illustration presented in Fig. 14, where the effects of biodiesel blends on PM emissions are documented. Again, although rather high degree of variation was observed, and documented in the R^2 value (due to the fact that data from all kinds of cycles, engines, and originating oils have been included), a compelling decreasing trend of PM emissions with rising biodiesel blend ratios can be established, confirming in the most explicit way the results during steady-state operation.

Finally, Fig. 15 documents the, well established during steady-state operation, trade-off between PM and NO_x. The latter, although not statistical significant, seems to apply reasonably well to transient cycles emissions too for the two most investigated biodiesel blend ratios B20 and B100, particularly for the neat blend (R^2=0.46). It seems reasonable then to modify the engine calibration by applying a slightly higher level of EGR during biodiesel combustion, in order to trade off some of the significant PM benefit for lower NO_x emissions.

4.2.4. Particle number concentration and distribution

Currently, diesel particulate matter legislation is primarily based on emitted particle mass. However, particle size distribution is gaining increasing attention in terms of air quality, as it is believed that the toxicity increases as the particle size decreases; in fact, a correlation between elevated ambient particulate matter concentration and hospital admissions has been suggested [127,128]. To this aim, the EU has legislated an intermediate Euro 5b specification level that also includes a particle number limit of the order of $6x10^{11}$/km over the NEDC for both passenger car (category M) and light-duty vehicles (categories N_1 and N_2), applicable from September 2011.

There is an increasing amount of recent research, based on steady-state experimentation, that inter-relates the decrease in PM emissions from biodiesel use with an increase in the number of the more toxic nanoparticles [e.g. 16,128], although the trend is not unambiguous [8]; similar contradicting observations hold during transients. Fontaras et al. [64] found that the use of neat SME increased total particle number up to 200% compared with the neat diesel operation during the NEDC (measured with a CPC); a B50 blend behaved similarly. This increase in the particle number arose from a general shift towards smaller-diameter (nano)particles and was evident for all transient cycles examined (the transient results were confirmed for three steady-state runs at 50, 90 and 120 km/h). The increased viscosity of biodiesel, as well as the increase of SOF, and of the injection pressure and the advance in injection timing with rising biodiesel percentage in the fuel blend have been identified as possible causes for this behavior. Likewise, Tinsdale et al. [78] reported a 25% increase in the nucleation mode particle number over the NEDC for a B30 blend compared with the neat diesel case, and Chien et al. [68], using MOUDI and nano-MOUDI devices, concluded that as the (waste-cooking derived) biodiesel percentage increased, the ultra-fine and nanoparticles number increased too; in fact, when neat biodiesel was used, nanoparticles dominated the size distribution. The calculated median mass diameters for their examined blends were: 0.146, 0.144, 0.134 and 0.124 μm, for neat diesel, B20, B60 and B100 respectively.

On the other hand, Macor et al. [86] found that the total number of emitted particles decreased for both tested vehicles between 10−20% over the examined driving cycles (NEDC, Artemis) relative to the neat diesel case. A possible explanation that has been argued by some researchers in such cases is the absence of sulfur in the biodiesel. The respective size distribution profiles from the same study revealed that the larger-diameter particles (for all fuel blends) were produced during those sections that include frequent accelerations or high power. This behavior can be explained by the fact that generally the trend is towards larger particles with increasing load, whereas nanoparticles are favored mainly at idling conditions [2]. As the load increases, more fuel is injected; this favors the formation of larger particles primarily owing to the longer diffusion combustion duration, to the higher combustion temperatures, and to the reduced oxidation rate of the soot in the expansion stroke, since there is less time available after the end of the diffusion combustion and also lower oxygen availability. Fontaras et al. [74] expanded on the previous studies by including also biodiesel feedstock effects on the particle number concentration. It was found that the effect of biodiesel on total particle number, including volatile and semi-volatile particles, was variable. Although reductions were observed over the low-power (sections of the) cycles, and for sunflower and unused frying methyl esters, the PME and the very popular in Europe RME blends were associated with up to 3 times higher particle number emissions than the base diesel fuel over the Artemis Motorway test.

4.3. Carbon monoxide and unburned hydrocarbons

Carbon monoxide emissions depend mainly on the air–fuel equivalence ratio, being usually of low significance during steady-state diesel engine operation. For fuel-rich mixtures, such as those experienced during the turbocharger lag phase at the onset of an acceleration or load increase event, CO concentration in the exhaust increases steadily with decreasing air−fuel ratio. The use of biodiesel in engines is capable of reducing CO emissions primarily owing to the higher oxygen content of the fuel blend that favors more complete combustion. As was the case with PM, the higher biodiesel cetane number and the advanced injection may also contribute towards lower (engine-out) emitted CO. These arguments (primarily the increased oxygen content) explain the clear behavior illustrated in Fig. 5 during the (hot) FTP heavy-duty transient cycle; likewise, Bakeas et al. [81] reported a 10% reduction in (the already low emissions of) CO from a B20 blend with respect to the neat diesel operation for a passenger car tested during the NEDC. Similar results have been reported, among many others, in [27–29,34,36,48,52, 60,66,71,81,82,85].

In Fig. 6 in contrast, a slightly increasing trend of CO emissions is observed with increasing biodiesel percentage in the fuel blend. This was also the result reached by Rose et al. [79], Macor et al. [86], Bermudez et al. [90] and Fontaras et al. [64]; the latter reported a 54% increase in CO emissions during the NEDC for a B50 fuel blend, which was even higher, of the order of 95%, when neat biodiesel was tested compared with diesel fuel. Durbin et al. [53] reported similar results (increase of CO (and HC) emissions with rising biodiesel blend ratio) when an engine fitted with oxidation catalyst was tested, whereas for another, older production, engine without oxidation catalyst the trend was reversed. In all these experimentations, the CO increase (which was even higher during the cold-started runs or segments of the cycle) was attributed to the oxidation catalyst's limited efficiency during the early minutes before reaching its light-off temperature, backed up by EGR and injection timing strategy effects.

An instructive comparative study that supports this argument was conducted by Bannister et al. [76]; they reported lower engine-out CO (and HC) emissions, whereas their tailpipe counterparts were higher relative to neat diesel, and this was too attributed to a reduction in the catalyst conversion efficiency with increasing blend ratio, as is demonstrated in Fig. 16. The latter effect was most probably owing to the lower biodiesel exhaust gas temperature (illustrated in the right sub-diagram of the same figure). The average exhaust gas temperature was measured 2.3% lower between B50 and neat diesel fuel during the NEDC. Similar results were reached by Muncrief et al. [60] and by Sze et al. [54], who found the mean exhaust gas temperature from a B50 SME blend to be 2.5% or 16^{o}C lower than that from reference diesel fuel during a highway cycle, and around 1% for lighter-loaded cycles such as the FTP and the UDDS. The lower gas exhaust temperature is responsible for lower available exhaust gas energy that in turn can explain the extended catalyst light-off time but also its reduced efficiency throughout the whole cycle. Bannister et al. [76] also speculated that this decrease in exhaust gas temperature might be responsible for the lower boost pressures measured, since their variable geometry turbocharger operated on lower available exhaust gas energy (this was confirmed by Sze et al. [54]). This fact further highlights the unexpected impacts and interactions which result from changes in the fuel properties, demonstrating the need for revised calibration strategies (as is notably the case with EGR control), when a diesel-tuned engine is required to run on biodiesel blends.

The effect of biodiesel feedstock on CO emissions during transients is not clear. As was the case with PM, the EPA study [15] concluded that soy-derived (i.e. highly unsaturated) biodiesel led to higher CO than RME or TME (both with much fewer data available), implying a correlation between unsaturation (or higher density or lower cetane number) and elevated CO, which has not, however, been confirmed by subsequent studies, at least on a statistically significant level. Further, from Table 2 it seems that the older rotary and pump-line-nozzle injection systems promote a higher CO benefit with biodiesel blends relative to neat diesel fuel than their modern electronic and common rail counterparts, but no unambiguous trend can be confirmed.

Hydrocarbons form during the ignition delay period as the result of either very low air–fuel ratios or, mainly, under-mixing of fuel that cannot ignite or support a flame.

Contrary to soot, NO_x or CO that peak only during load increase or acceleration, turbocharged diesel engine HC emissions are noticed at the onset of deceleration or load decrease too, since in the latter case, turbocharger lag effects lead to instantaneously very high air–fuel equivalence ratios [2].

The absence of aromatic content as well as the advanced injection and combustion timing and the higher oxygen concentration of biodiesel, all promote more complete combustion reducing accordingly the level of unburned HC. Moreover, the higher cetane number of biodiesel contributes to the reduction of the ignition delay, where an important amount of HC is formed. For example, Karavalakis et al. [52] reported a 20% reduction in HC from a B20 blend compared with the neat diesel operation for a passenger car tested during the NEDC, and similar reductions have been measured by almost all researchers regarding hot tested transient cycles. Nonetheless, as was also the case with CO, the first minutes of the cycle, where the engine is still cold, may influence the HC emissions remarkably, reducing the exhaust gas temperatures and the DOC efficiency, and resulting in higher emissions the higher the biodiesel percentage in the fuel blend (see Fig. 16) [46,61,67,74,79]. Interestingly, possible sampling line issues have also been identified by some researchers as causes for the lower HC level in the exhaust compared with the neat diesel operation. For example the lower volatility of biodiesel may lead to hydrocarbons of high molecular weights being condensed in the exhaust pipe [37,129]. Lastly, as was the case with PM and CO (and unlike NO_x), it has not been feasible to statistically correlate the biodiesel feedstock with the HC emissions.

Figures 17 and 18 summarize the quantitative effects of biodiesel blends on HC and CO emissions during all transient cycle studies from Table A, where, despite the scattered and sometimes controversial data measured, a clear decreasing tendency is established with increasing biodiesel blend ratio. Both the CO and HC best-fit curves are comparable in their trend and development with the older data, the biodiesel benefit however has somewhat faded during the last years. It seems then that inclusion of many data from

a) newer production, European engines with after-treatment control in the form of diesel oxidation catalysts, which seem to operate less efficiently with biodiesel,
b) many light-loaded passenger car cycles, and, predominantly,
c) cold-started runs

has gradually shifted the overall trends to lower CO and HC emission benefits. In fact, many of the researchers from light-duty engines/cycles actually report increases in both CO and HC with the use of biodiesel.

Finally, with regards to CO_2 emissions, the majority of the studies concluded that no statistically significant changes were measured during transients between biodiesel blends and petroleum diesel fuel, with both moderate increases and decreases reported depending on the specific engine, blend and cycle examined. The latter finding practically confirms the results during steady-state operation that engine efficiency is, effectively, not altered with the addition of biodiesel in the fuel blend.

4.4. Combustion noise

The three primary sources of noise generation in a diesel engine are gas-flow, mechanical processes and combustion [130,131]. The origin of combustion noise radiation lies in the (high) rate of cylinder pressure rise, mainly after the ignition delay period, which causes discontinuity in the cylinder pressure frequency spectrum and increase in the level of the high-frequency region, resulting in vibration of the engine block and, ultimately, in combustion noise radiation (the characteristic diesel combustion 'knock'). This combustion noise radiation manifests itself in the domain from a few hundred up to a few thousand Hz.

There is only a handful of works available regarding biodiesel effects on noise radiation during steady-state engine operation, and with contradicting results. Nabi et al. [132] reported overall noise reduction for a naturally aspirated engine operating at high loads, ranging from 1 dBA for a B10 blend up to 2.5 dBA for neat karanja biodiesel (B100). Although the reduction was, in a rather simplistic manner, attributed to the oxygen content of the biofuel, it was most probably the higher cetane number of biodiesel that was responsible for a shortening of the ignition delay period that ultimately reduced the cylinder pressure rise rate and the combustion noise contribution to the total emitted noise. On the other hand, Haik et al. [133] found that the algae oil methyl ester was responsible for higher cylinder pressure rise rates $dp/d\varphi$ (a typical 'surrogate' property of combustion noise) compared with the neat diesel fuel or the raw algae oil for their indirect injection diesel engine. Although Anand et al. [134] did not specifically measure combustion noise, they too reported on the cylinder pressure rise rate for neat karanja biodiesel fuel blends, and concluded that the trend vs. neat diesel fuel was not clear; in fact the contributing factors acted in favor or against each fuel blend depending on the speed or load conditions.

The only comprehensive analysis regarding biodiesel impacts on combustion noise development during transients has been reported by Giakoumis et al. [103], and is depicted in Fig. 19 that illustrates noise development during three different accelerations of a medium-duty engine. Although biodiesel is characterized by slightly higher cetane number, its acceleration response compared with the neat diesel operation was proven marginally noisier, and this was attributed to its higher density that increased the total injected mass and the fuel mass burnt during the influencing premixed combustion phase. However, the trend was not clear throughout each acceleration, and sometimes the differences were very small, within the measuring unit's accuracy. It is thus suspected that higher blends might be required in order to establish a possibly unambiguous trend. Hot starting tests by the same research group revealed even more conflicting trends [84].

5. Summary and conclusions

A survey and an assessment were conducted of the literature concerning regulated emissions of diesel engines when running on biodiesel blends during transient conditions. The majority of the published work has focused on four-stroke engines or vehicle transient cycles (most notably the American heavy-duty FTP and the European passenger car NEDC), and for B20 and B100 blends of soybean or rapeseed-derived methyl esters. Based on a large amount of published data from four-stroke engines during the last two decades, correlations were reached for quantification of biodiesel benefits (or penalties) on regulated emissions relative to the neat diesel operation, updating an earlier EPA approach. The primary mechanisms of transient exhaust emissions when using biodiesel blends were identified and discussed for all regulated pollutants, and, for the first time, many of these mechanisms were inter-related with the inherent discrepancies observed during transients, most notably turbocharger lag. The most important of the conclusions derived are summarized below:

- Confirming the principal observations during steady-state operation, for the majority of examined transients a decreasing trend in PM, HC and CO, and an increasing trend in NO_x emissions is established when the biodiesel in the fuel blend ratio increases.

- For PM emissions, the increased oxygen concentration in the biodiesel-blend, which aids the soot oxidation process (most prominently during the critical turbocharger lag cycles), has been identified as the key contributor for the benefits of biodiesel blends relative to neat diesel operation.
- On the other hand for NO_x emissions, 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. This higher trend is more evident during combustion of biodiesels produced from highly unsaturated feedstocks, and does not seem to be dominated by any of the previously mentioned factors, but is rather dependent on the combination of most of them according to the specific operating conditions.
- Although CO and HC engine-out emissions have been found to, generally, decrease with increasing biodiesel blends, the oxidation catalyst's limited efficiency during cold starting as well as its decreased overall efficiency owing to the biodiesel-blends' lower exhaust gas temperatures often leads to a reverse emission behavior that might determine the whole emission pattern during transients.
- Irrespective of driving cycle type, the biodiesel impact on NO_x and PM emissions appears to be related to the fuel consumption or the average cycle load, namely the NO_x emission penalty and the PM benefit with biodiesel seem to increase for more aggressive cycles/driving patterns that incorporate steeper and more frequent accelerations or load increase events, hence harsher turbocharger lag phases that also provoke lower EGR rates.
- Biodiesels produced from unsaturated feedstocks (higher iodine number) contain a higher proportion of unsaturated components relative to the more saturated feedstocks or the neat diesel fuel, which appear to increase the NO_x emission penalty at least for older production engines. No such correlation could be established for the emitted PM, HC or CO, most probably because the oxygen content of the biodiesel, which is responsible for the reduction in the latter pollutants, remains practically unaffected by the degree of unsaturation.
- Biodiesel-blended engines produce a higher fraction of soluble organic fraction in their exhausted particulate matter during transients than when petroleum-based diesel fuel is used, even when the total particulate emissions are lowered.

- 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.
- There is no unanimous trend with regards to the effects of biodiesel on particle number concentration and distribution, as is also the result during steady-state conditions; a slight majority (in the limited number of transient investigations so far) suggests that an increase in the number of nanoparticles is observed with increasing biodiesel blend.
- Combustion noise radiation during acceleration or hot starting does not exhibit any clear trend compared with the reference diesel operation, as has also been the result reached during the limited steady-state experimentation.
- 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 and decrease in PM in relation to the petroleum diesel operation. Further, biodiesel’s lower heating value and exhaust gas temperatures affect also other engine subsystems operation (oxidation catalyst, VGT, DPF), highlighting the need for a revised calibration strategy when a diesel-tuned engine is required to run on methyl ester 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.

6. Future research directions

From the conducted review of the published work on transient diesel engine emissions with biodiesel blends, the following interesting topics for future work and research can be identified:

- Investigation of injection system effects on NO_x emissions, a subject that might reveal some unknown or masked, at the moment, production mechanisms or trends.
- Investigation of combustion noise radiation (an unexplored territory during steady-state conditions too), which is expected to gain interest in the next years with the

development of alternative diesel combustion technologies such as HCCI and PCCI.

- Investigation of the inter-relation between biodiesel and modern catalytic devices, such as DPF, SCR and NO_x adsorber catalysts, especially with respect to particle number concentration and distribution, but also to possible durability issues.
- More intense research on fundamental discrete transient schedules (acceleration, load increase, cold starting) that are inherently better suited to reveal fundamental aspects of the biodiesel blends combustion and emissions in contrast to the cumulative effects of transient cycles.
- Research on industrial or marine engines transient performance; these engines are characterized by different combustion systems, lower rotational speeds, lower swirl ratios and greater dimensions, all of which might influence the emission pattern.
- Development of a ‘perfect’ feedstock with the ‘appropriate’ molecular structure and chemical properties for compensation of the NO_x increase with biodiesel combustion while maintaining the PM reduction benefit.

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Nomenclature

Abbreviations

AFME	animal fat methyl ester
B20	20% biodiesel-80% diesel v/v
B100	neat biodiesel
BTME	beef tallow methyl ester
CME	cottonseed methyl ester
CN	cetane number
CnME	canola methyl ester
CVS	constant volume sampling
CPC	condensation particle counter
CoME	coconut methyl ester
DI	direct injection
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
DTBP	di-tert-butyl peroxide
ECE15	urban part of NEDC
ECU	engine control unit
EGR	exhaust gas recirculation
EHN	ethyl-hexyl-nitrate
EPA	environmental protection agency
EU	European Union
EUDC	extra urban driving cycle
FAME	fatty acid methyl ester
FTP	federal test procedure
HCCI	homogeneous charge compression ignition
HD	heavy-duty
HSDI	high-speed direct injection
HWFET	highway fuel economy test cycle
HySME	hydrogenated soybean methyl ester
IN	iodine number
LCA	life-cycle assessment

LD	light-duty
LHV	lower heating value
MOUDI	micro-orifice uniform deposit impactor
MY	model year
NAC	NO_x adsorption catalyst
NEDC	new European driving cycle
NRTC	non-road transient cycle
PAHs	polycyclic aromatic hydrocarbons
PCCI	premixed charge compression ignition
PnME	peanut methyl ester
PM	particulate matter
PME	palm methyl ester
REE	rapeseed ethyl ester
RME	rapeseed methyl ester
SCR	selective catalytic reduction
SI	spark ignition
SME	soybean methyl ester
SOF	soluble organic fraction
SOI	start of injection
SuME	sunflower methyl ester
TME	tallow methyl ester
UDC	urban driving cycle
UDDS	urban dynamometer driving schedule
UFOME	unused frying oil methyl ester
US06	supplemental federal test procedure
VGT	variable geometry turbocharger
v/v	per volume
WCME	waste cooking methyl ester
WHTC	world-wide harmonized transient cycle
WVU	West Virginia University
w/w	per weight
YGME	yellow grease methyl ester

Table 1

Comparison of key physical and chemical properties between biodiesel and automotive diesel fuel

	Low-sulfur automotive diesel fuel	Biodiesel
Density/15°C (kg/m^3)	820–850	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	~15	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	140–180

* average values

Table 2

Average B20 emissions change relative to neat diesel operation for north-American only, 4-stroke engines during transient cycles by fuel injector type (standard deviation in parentheses; from Yanowitz and McCormick [117])

Fuel Injector Type	Count	NO_x (%)	PM (%)	CO (%)
Common rail	4	4 (1)	-23 (10)	-13 (6)
Electronic unit	15	1 (3)	-18 (13)	-13 (8)
Hydraulic unit	2	1 (15)	7 (16)	-12 (29)
Mechanical	1	8	6	-17
Pump-line-nozzle	6	0 (2)	-13 (6)	-25 (5)
Rotary	8	-1 (4)	-21 (11)	-19 (6)

Table 3

Summary of composite transient particulate composition from a 1997, heavy-duty diesel engine during the FTP transient cycle (adapted from Sharp et al. [37])

Fuel	DOC	Volatile Organic Fraction (g/kW h)				Non-volatile (g/kW h)	
		Total	Oil	Fuel & Other	PM	SO_3+H_2O	Soot
Diesel	No	0.0039	0.023	0.016	0.137	0.013	0.084
B20	No	0.0044	0.024	0.020	0.118	0.009	0.064
B100	No	0.0043	0.024	0.019	0.070	0.001	0.024
Diesel	Yes	0.0027	0.009	0.017	0.101	0.001	0.071
B20	Yes	0.0024	0.008	0.016	0.079	0.004	0.051
B100	Yes	0.0020	0.009	0.011	0.040	0.003	0.017

Figure Captions

Fig. 1. List of published papers/reports on transient diesel engine emissions with biodiesel blends in a chronological order

Fig. 2. Quantification of investigations on transient diesel engine emissions based on the type of transient schedule (bar chart - left), the specific transient cycle employed (bar chart - right) and the specific biodiesel studied (pie chart)

Fig. 3. Quantification of investigations on transient diesel engine emissions based on the biodiesel blend applied

Fig. 4. Development of NO emissions during two low-load, dynamometer accelerations of a medium-duty turbocharged diesel engine for neat diesel and B30 operation [73]

Fig. 5. Effect of soybean biodiesel content on averaged cumulative PM emissions during the (hot) EPA Transient Cycle for a 1991 calibrated, heavy-duty diesel engine (experimental data adapted from Graboski et al. [29])

Fig. 6. Effect of biodiesel content on cumulative emissions during the NEDC for a Euro 4 passenger car (experimental data adapted from Lujan et al. [65])

Fig. 7. Effect of biodiesel content on EGR valve position for a heavy-duty diesel engine operating on SME blends and various transient cycles (experimental data adapted from Sze et al. [54])

Fig. 8. Effects of density and cetane number on NO_x emissions during transient cycles from four different heavy-duty diesel engines (data from Peterson et al. [36]; adapted from McCormick et al. [40]; data from McCormick et al. [48]; data from Knothe et al. [51])

Fig. 9. Statistically significant effects of iodine number on NO_x emissions during the UDDS, FTP and NEDC cycles for five different diesel engines/vehicles (adapted from Peterson et al. [36]; adapted from McCormick et al. [40,48]; data from Knothe et al. [51]; adapted from Bakeas et al. [88])

Fig. 10. Effect of average cycle power on NO_x emissions for a 2006, medium-duty diesel engine (adapted from Sze et al. [54])

Fig. 11. Collective NO_x emission change when using various biodiesel-diesel blends (data from all transient cycles of Table A)

Fig. 12. Smoke opacity development during a 26–90 Nm load increase transient event at 1661 rpm for various diesel–sunflower biodiesel blends (adapted from Armas et al. [50])

Fig. 13. Development of smoke opacity during hot starting of a medium-duty turbocharged diesel engine for neat diesel and B30 operation [84]

Fig. 14. Collective PM reduction when using various biodiesel-diesel blends (data from all transient cycles of Table A)

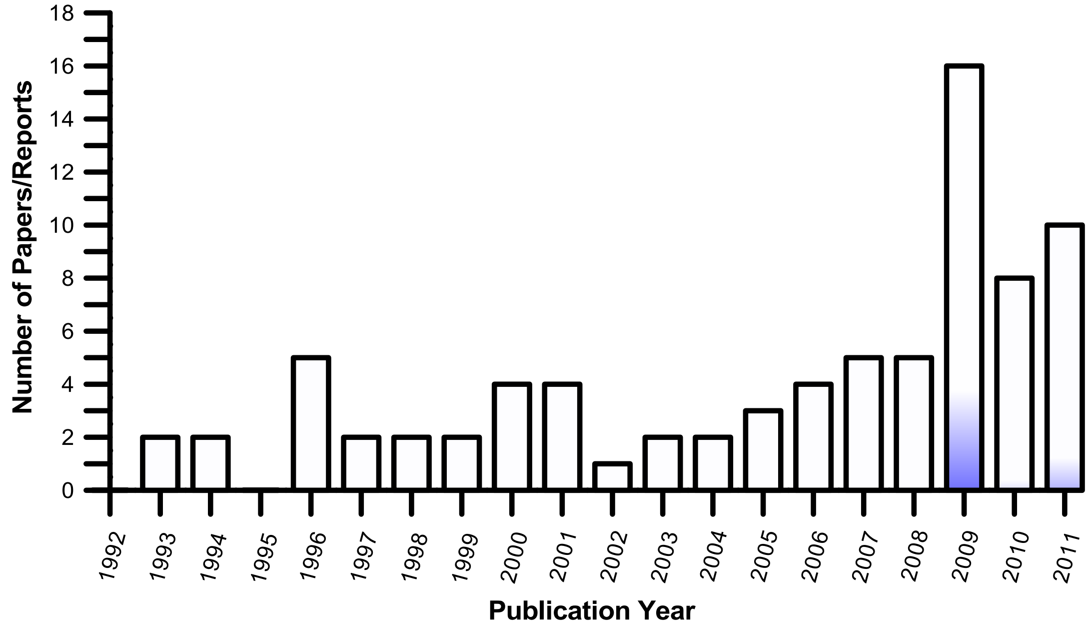
Fig. 15. PM-NO_x trade-off for B20 and B100 blends (data from all transient cycles of Table A)

Fig. 16. CO and HC diesel oxidation catalyst efficiency for two ambient temperatures (left), and average exhaust gas temperature (right) during the NEDC (adapted from Bannister et al. [76])

Fig. 17. Collective CO emission change when using various biodiesel-diesel blends (data from all transient cycles of Table A)

Fig. 18. Collective HC emission change when using various biodiesel-diesel blends (data from all transient cycles of Table A)

Fig. 19. Difference in the combustion noise between diesel fuel and a B30 blend throughout three acceleration tests [103]



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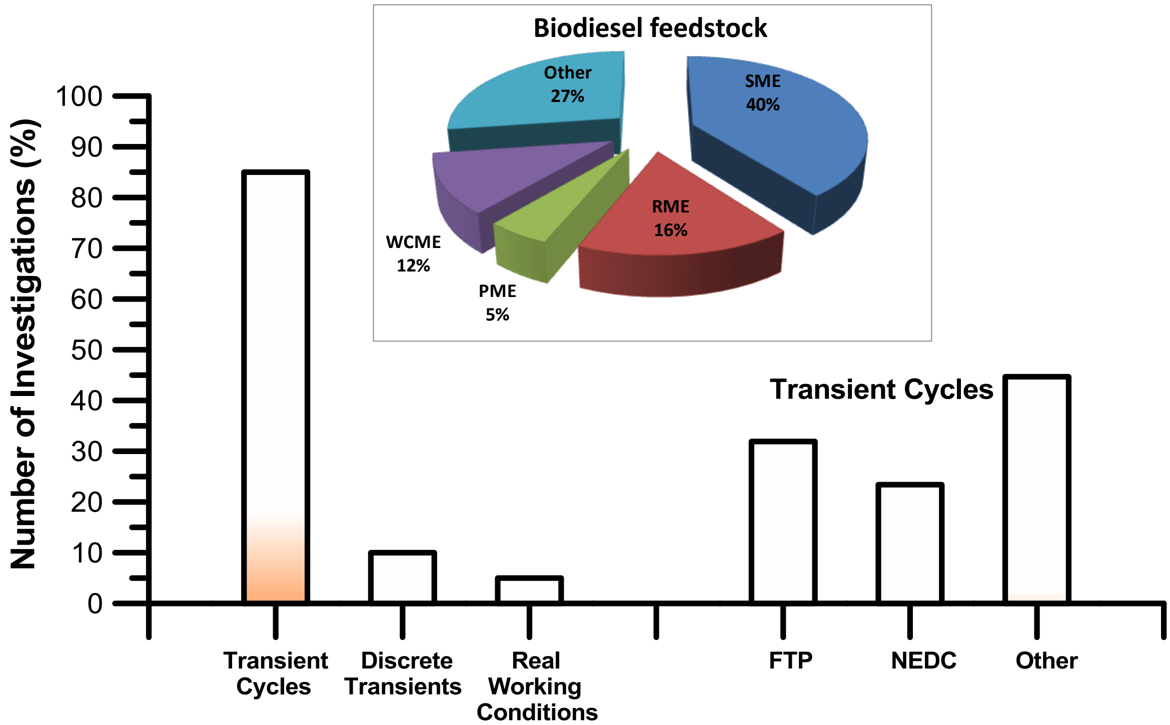

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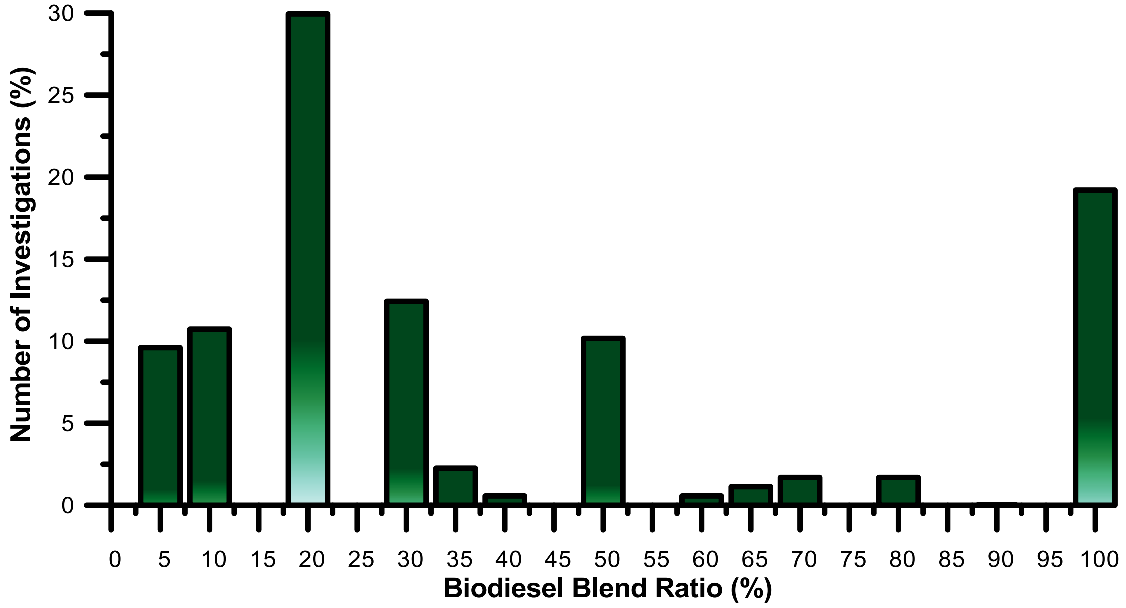


Fig. 3. Quantification of investigations on transient diesel engine emissions based on the biodiesel blend applied

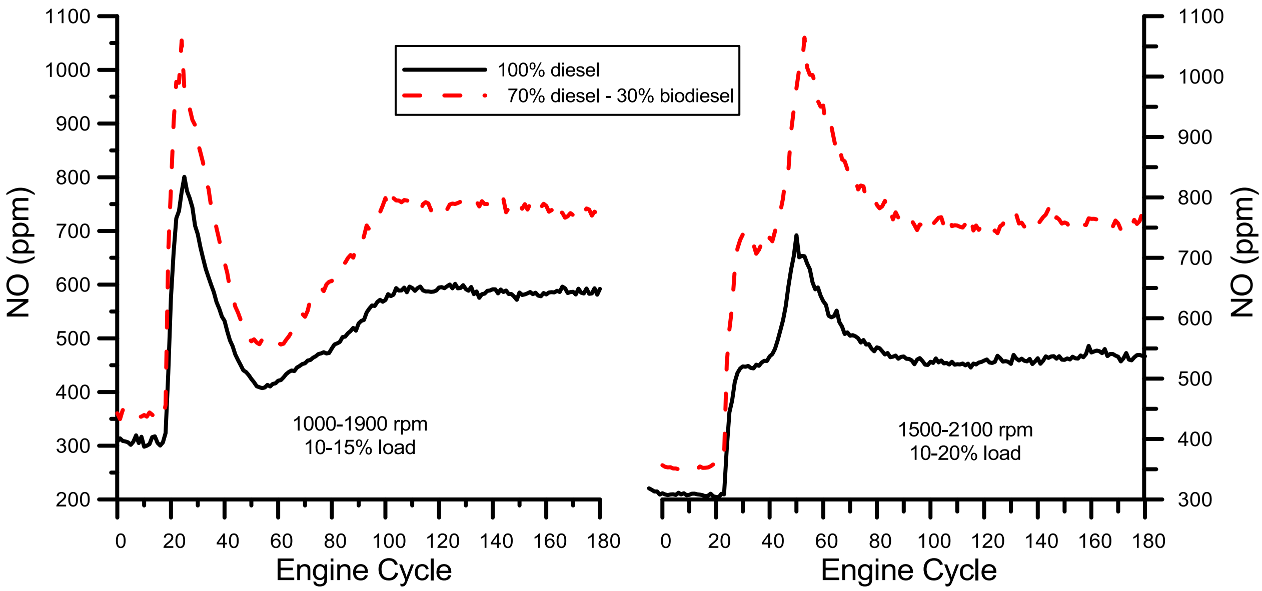


Fig. 4. Development of NO emissions during two low-load, dynamometer accelerations of a medium-duty turbocharged diesel engine for neat diesel and B30 operation [73]

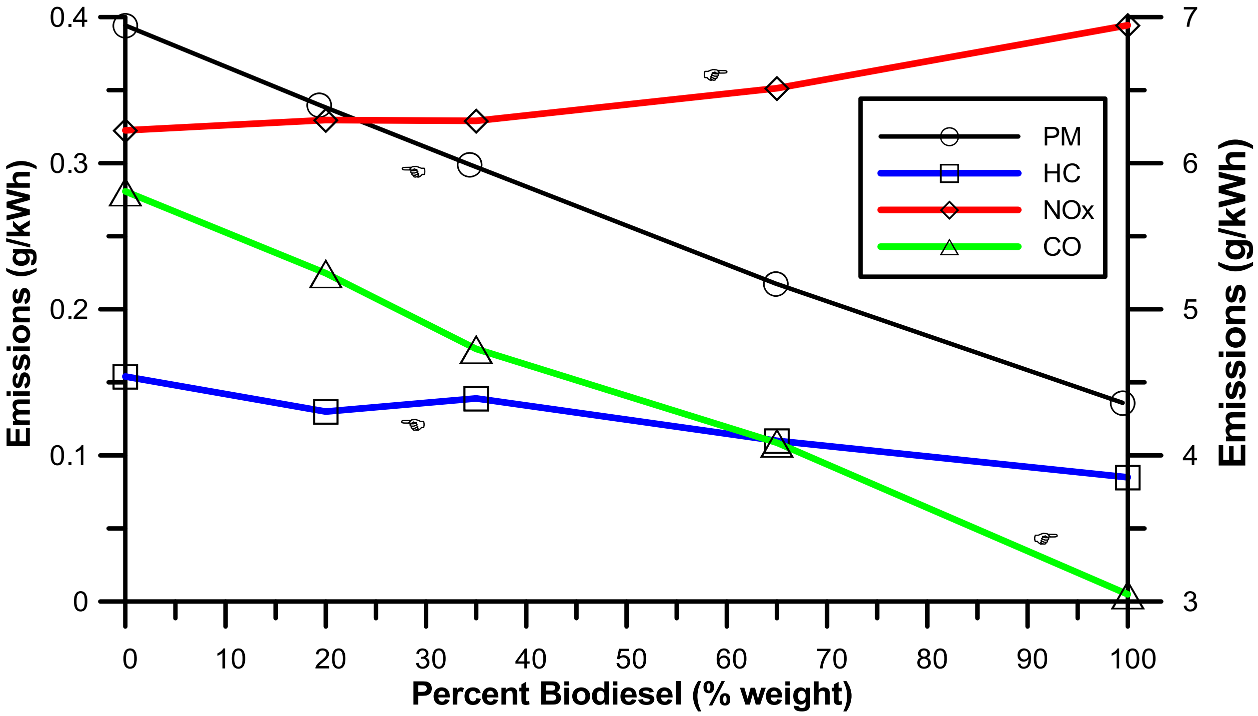


Fig. 5. Effect of soybean biodiesel content on averaged cumulative PM and gaseous emissions during the (hot) EPA Transient Cycle for a 1991 calibrated, heavy-duty diesel engine (experimental data adapted from Graboski et al. [29])

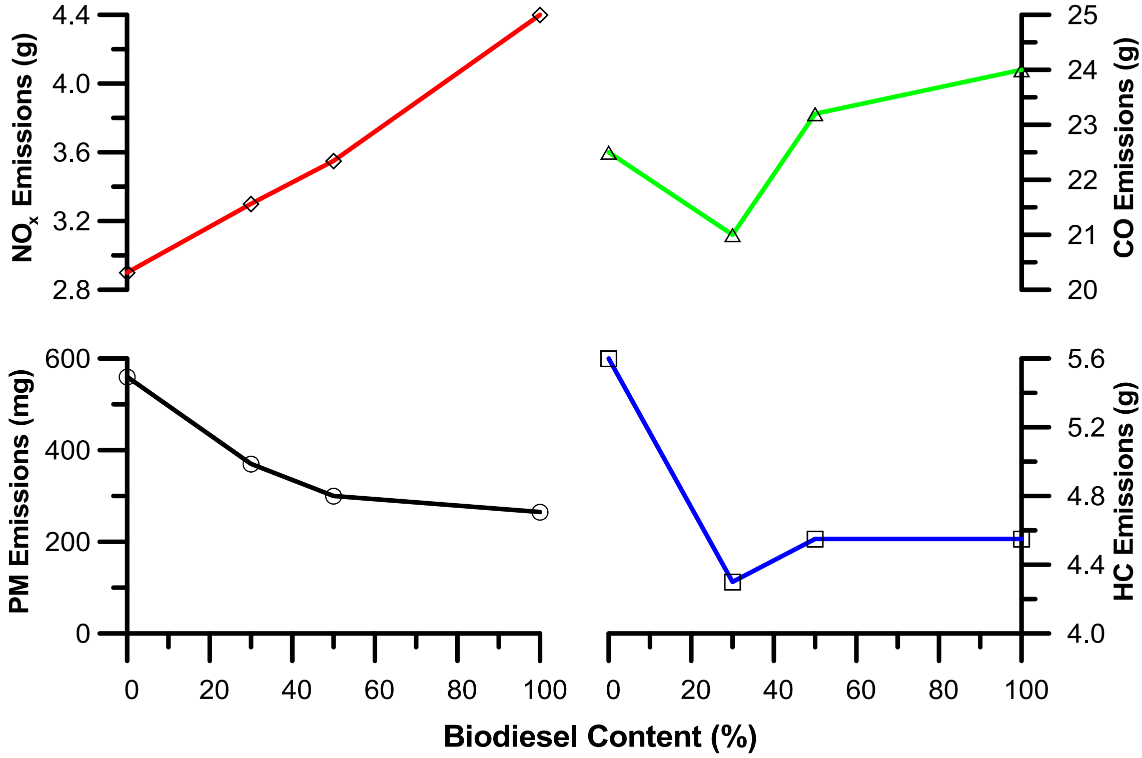


Fig. 6. Effect of biodiesel content on cumulative emissions during the NEDC for a Euro 4 passenger car (experimental data adapted from Lujan et al. [65])

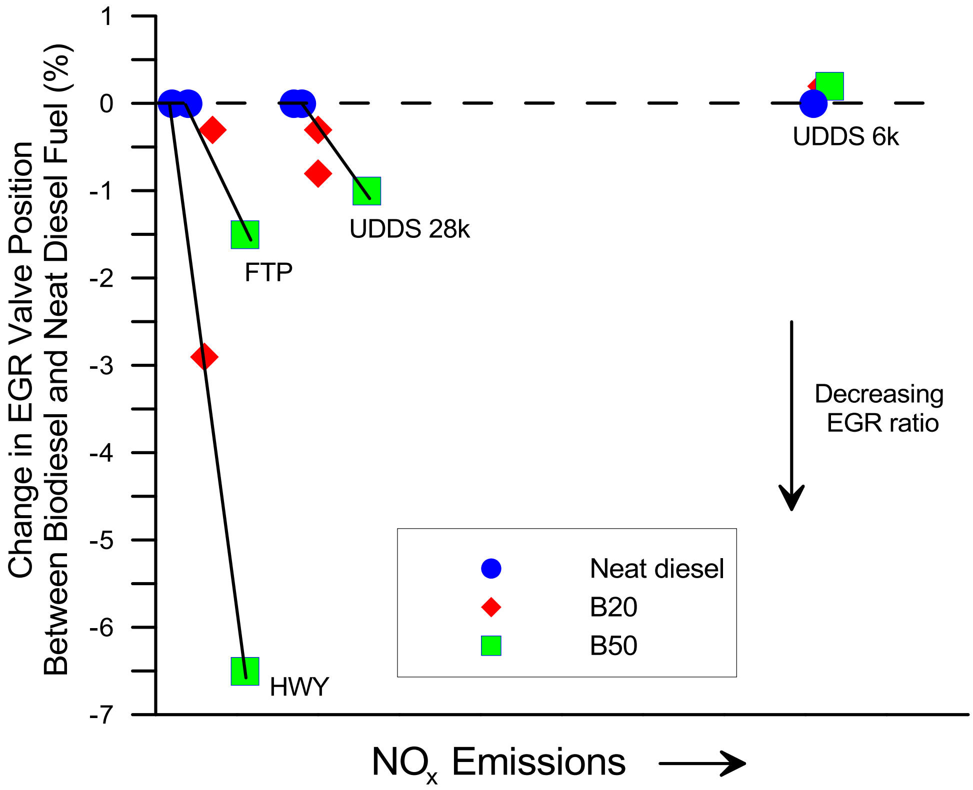


Fig. 7. Effect of biodiesel content on EGR valve position for a heavy-duty diesel engine operating on SME blends and various transient cycles (experimental data adapted from Sze et al. [54])

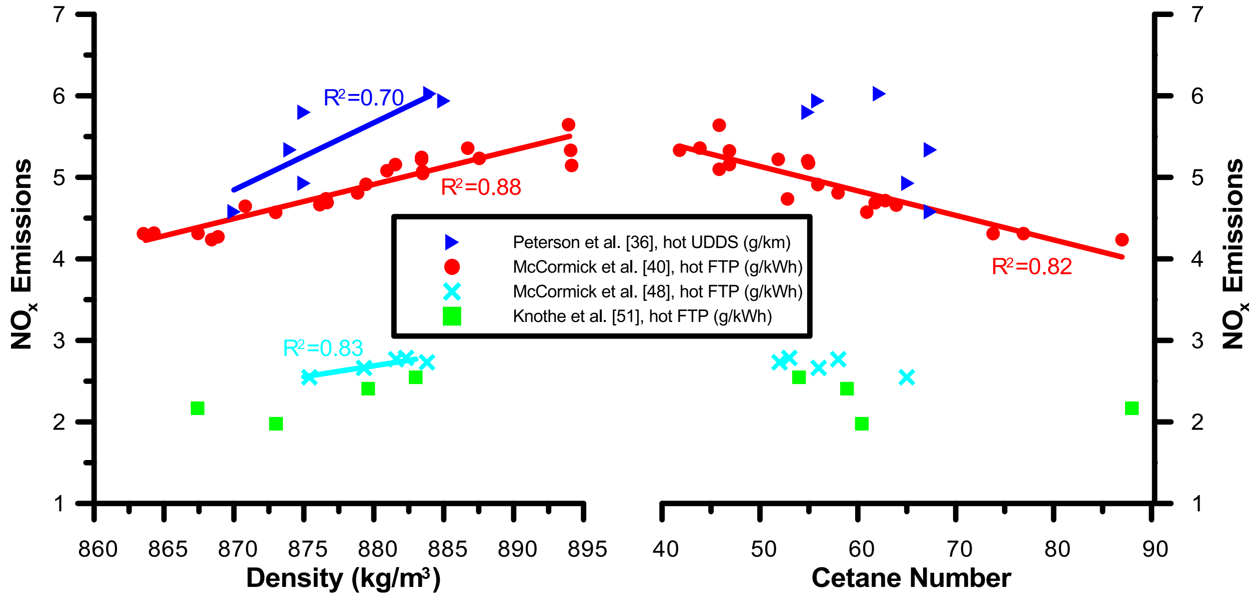
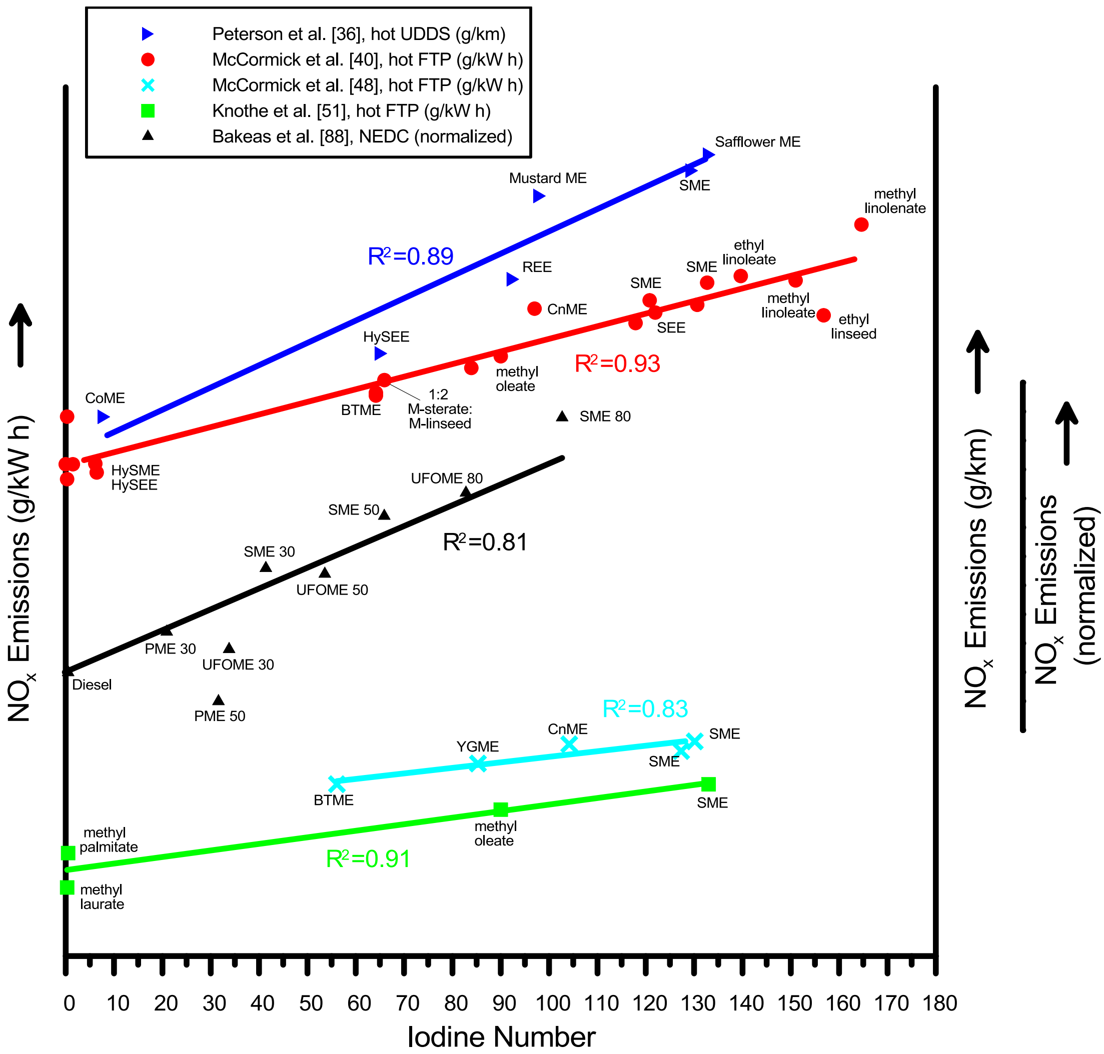


Fig. 8. Effects of density and cetane number on NO_x emissions during transient cycles from four different heavy-duty diesel engines (data from Peterson et al. [36]; adapted from McCormick et al. [40]; data from McCormick et al. [48]; data from Knothe et al. [51])



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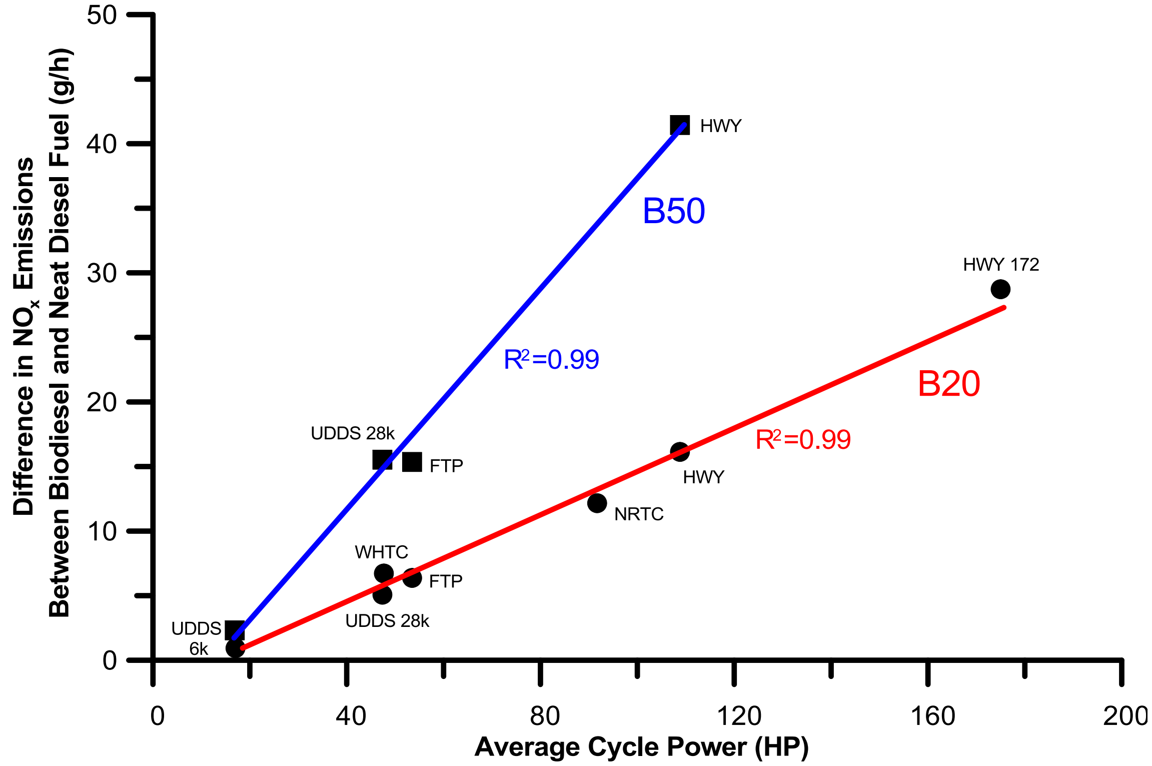

Fig. 10. Effect of average cycle power on NO_x emissions for a 2006, medium-duty diesel engine (adapted from Sze et al. [54])

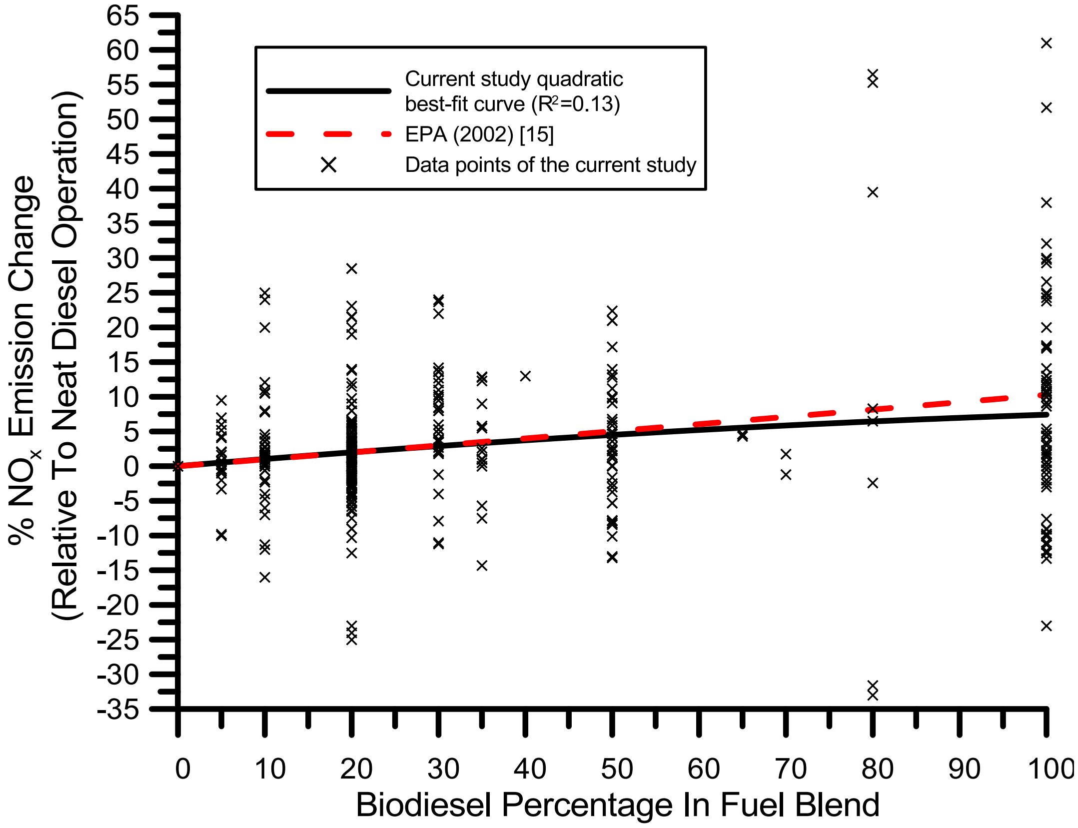

Fig. 11. Collective NO_x emission change when using various biodiesel-diesel blends (data from all transient cycles of Table A)

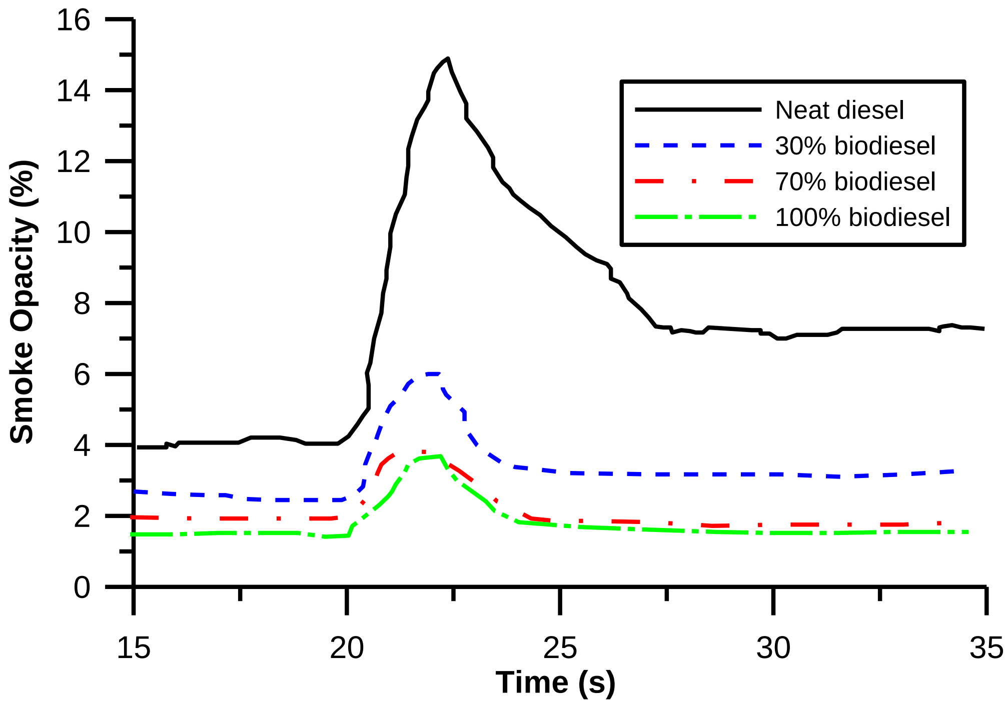

Fig. 12. Smoke opacity development during a 26–90 Nm load increase transient event at 1661 rpm for various diesel–sunflower biodiesel blends (adapted from Armas et al. [50])

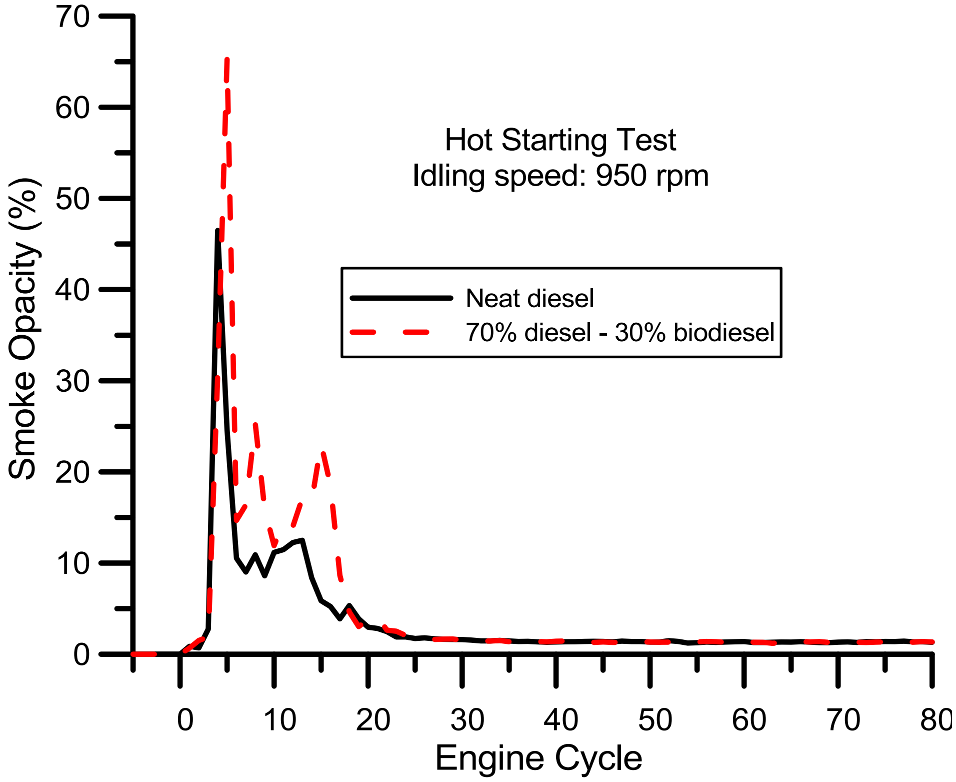

Fig. 13. Development of smoke opacity during hot starting of a medium-duty turbocharged diesel engine for neat diesel and B30 operation [84]

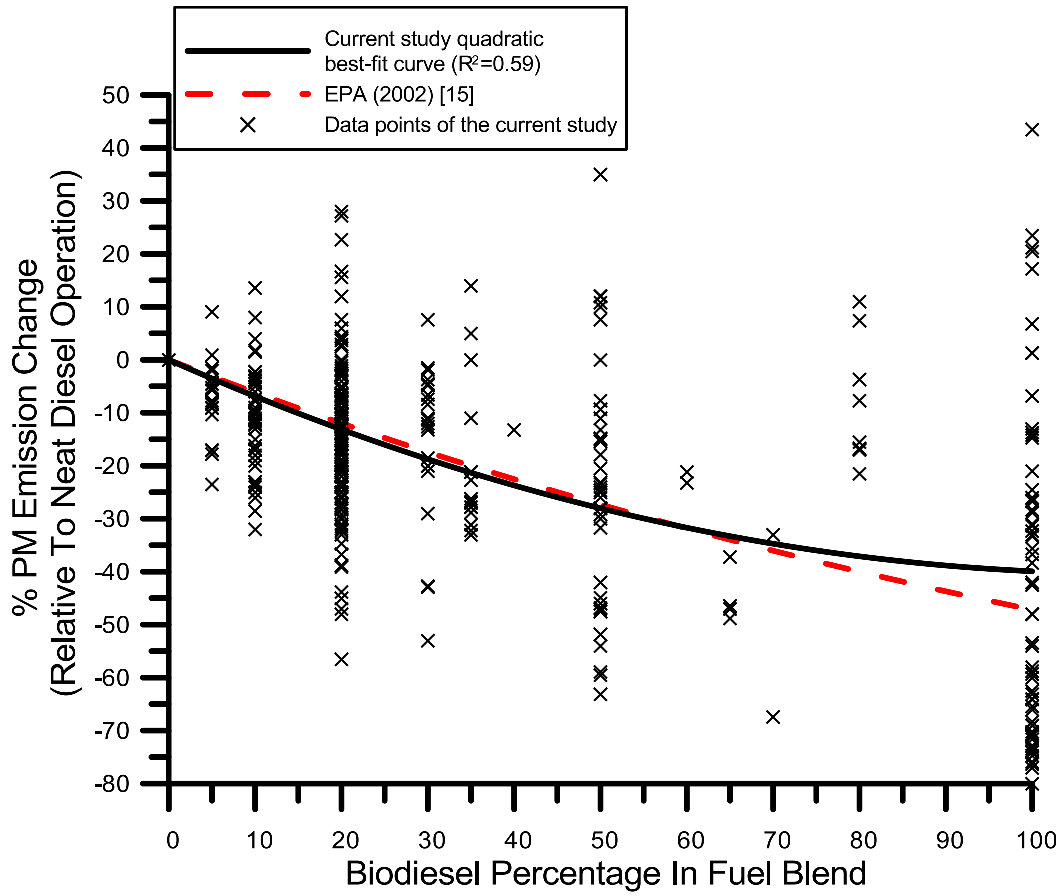

Fig. 14. Collective PM reduction when using various biodiesel-diesel blends (data from all transient cycles of Table A)

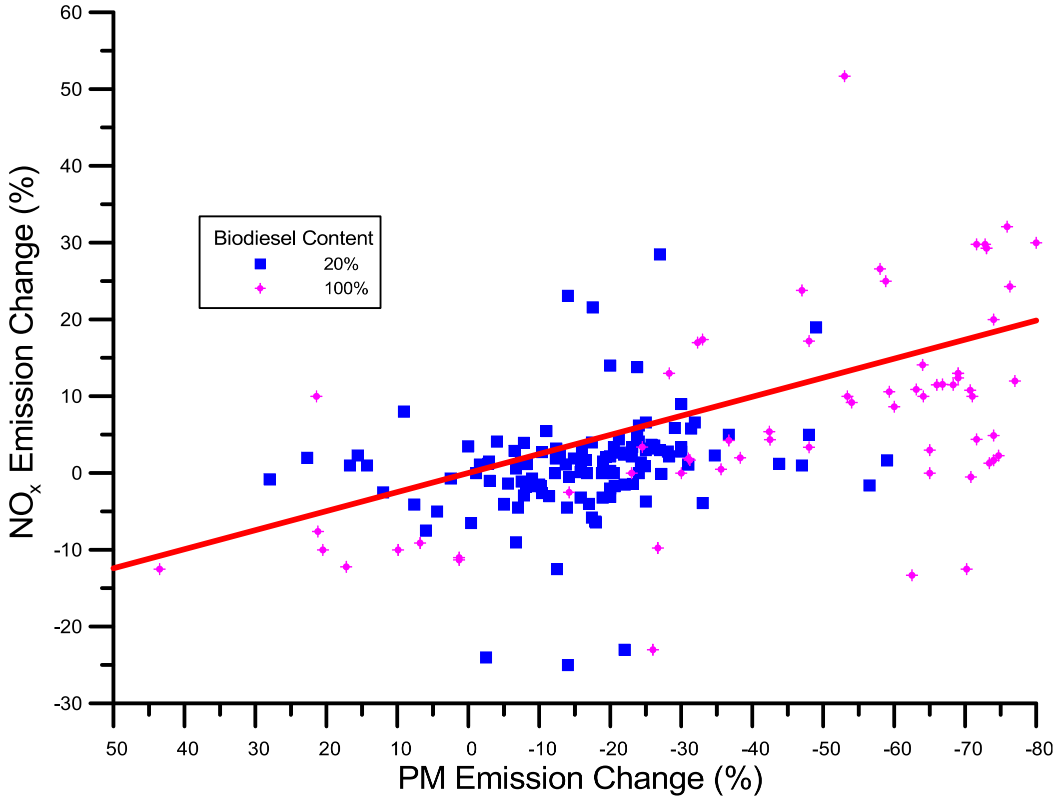

Fig. 15. PM-NO_x trade-off for B20 and B100 blends (data from all transient cycles of Table A)

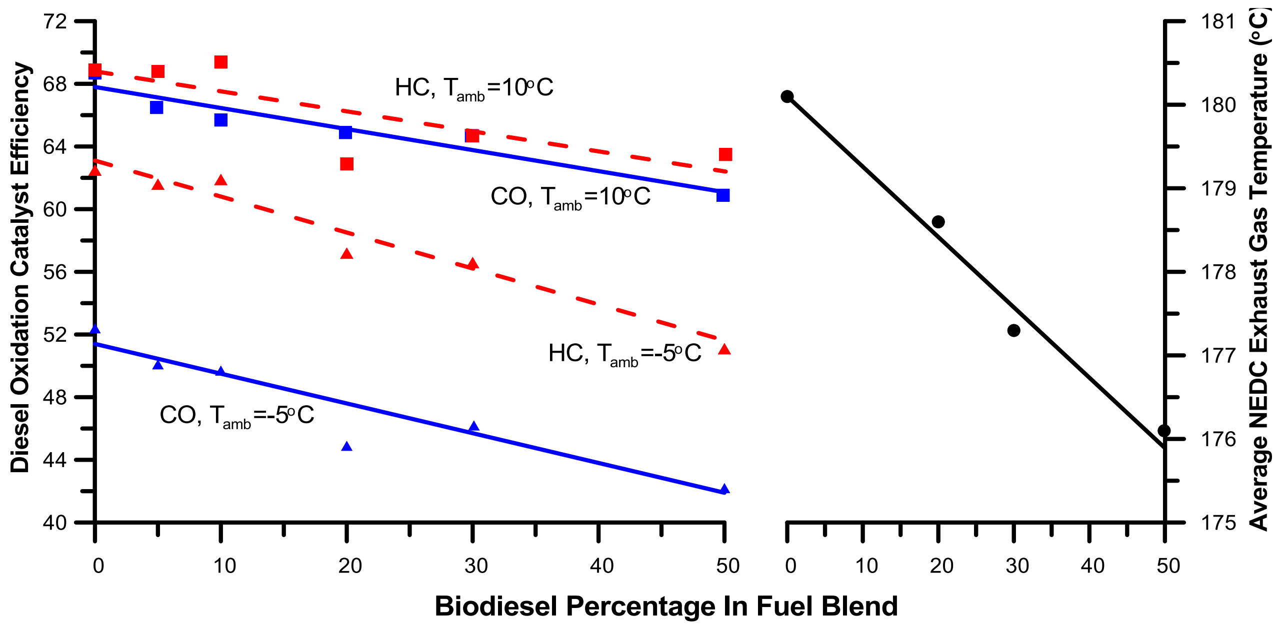

Fig. 16. CO and HC diesel oxidation catalyst efficiency for two ambient temperatures (left), and average exhaust gas temperature (right) during the NEDC (adapted from Bannister et al. [76])

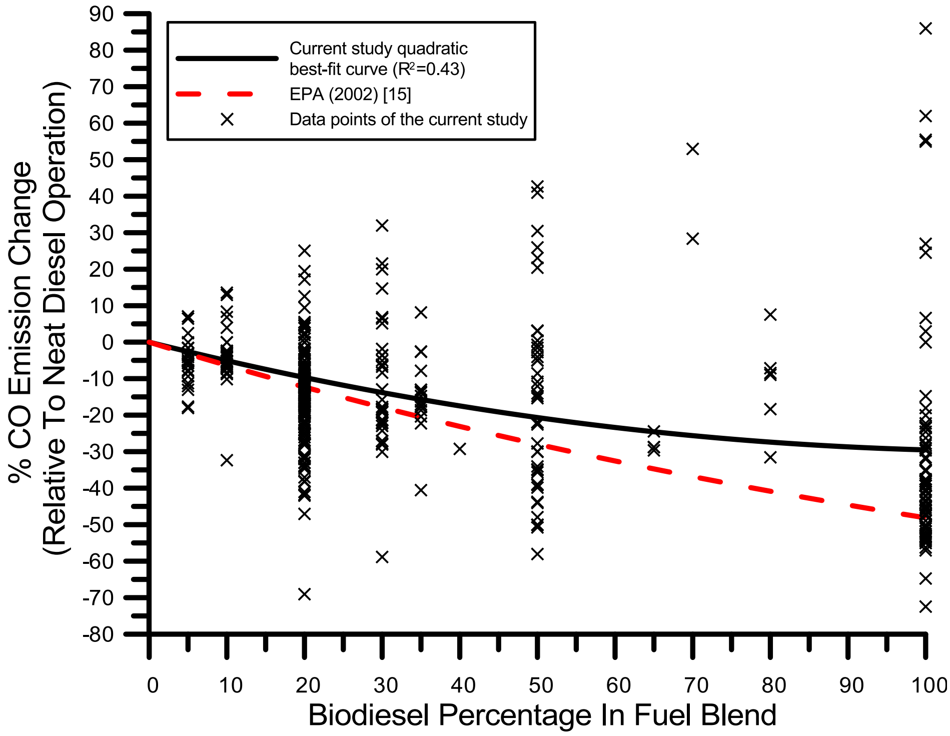

Fig. 17. Collective CO emission change when using various biodiesel-diesel blends (data from all transient cycles of Table A)

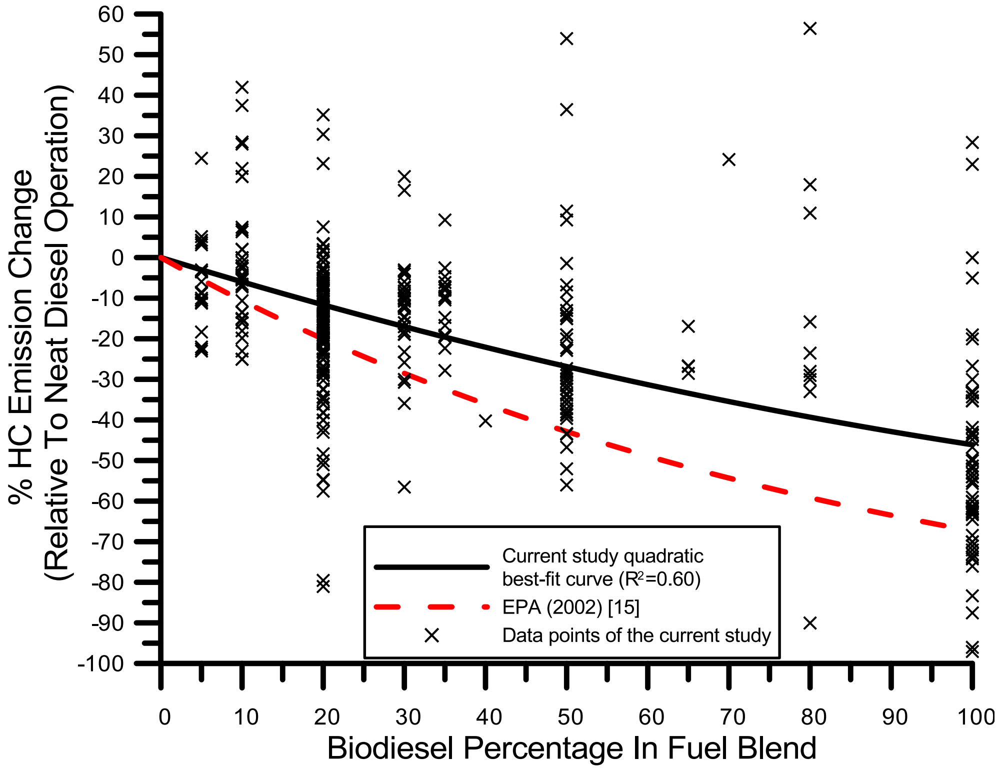

Fig. 18. Collective HC emission change when using various biodiesel-diesel blends (data from all transient cycles of Table A)

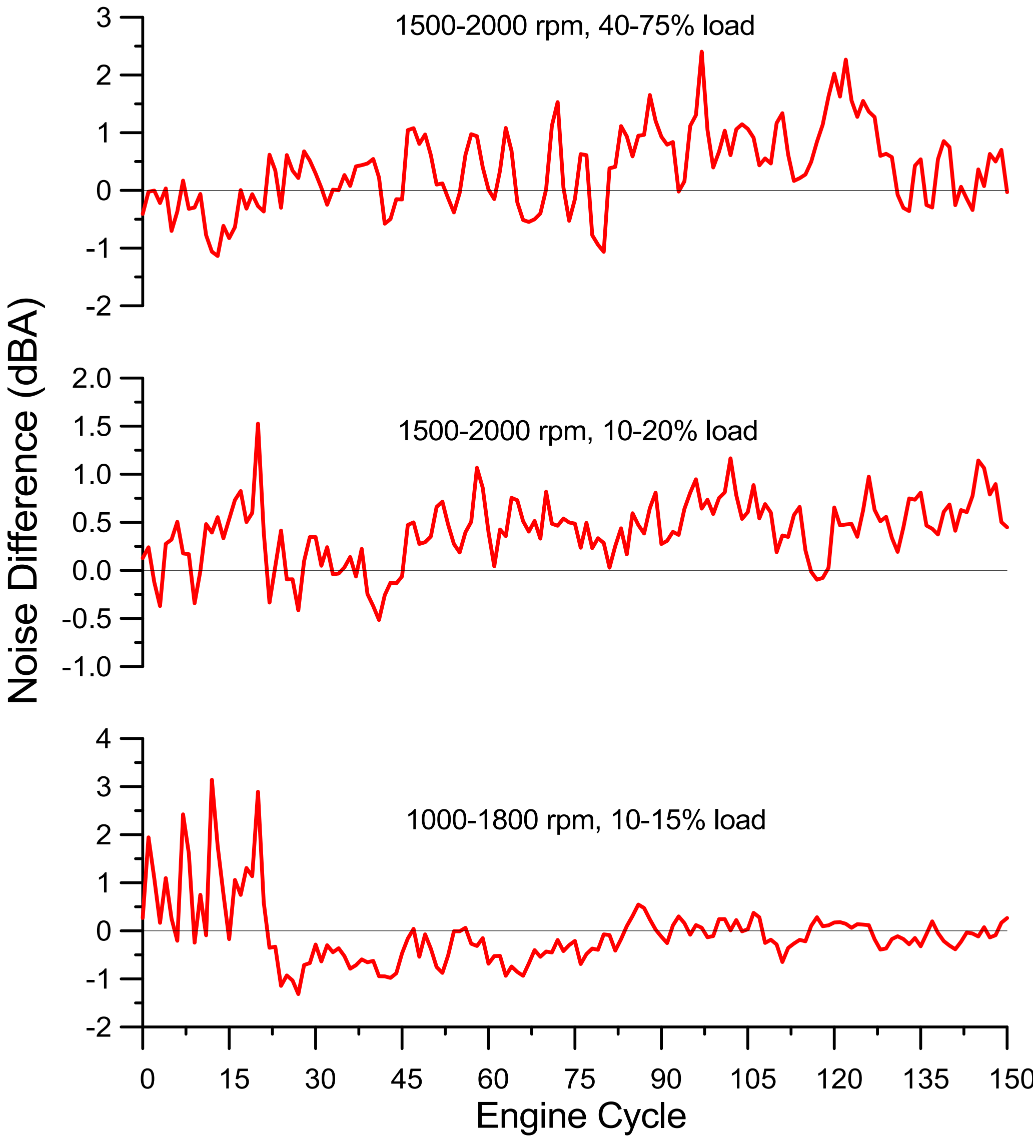

Fig. 19. Difference in the combustion noise between diesel fuel and a B30 blend throughout three acceleration tests [103]

Appendix - Details of the papers dealing with transient exhaust emissions from biodiesel-diesel blends

Table A

Details of the studies dealing with transient exhaust emissions of biodiesel-diesel blends in chronological order (up to the end of 2011).

	Research Group	Ref.	Year	Publication	Engine type	Engine MY or Emission Level	Biodiesel Percentage	Originating Oil	Transient Schedule	Emissions	Notes / Other Fuels Tested
1	Liotta and Montalvo	[26]	1993	SAE	heavy-duty	1991	5	soybean	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	3 glycol ethers, aromatic and aliphatic alcohols, polyether polyol / aldehydes, ketones
2	Callahan	[99]	1993	Report	heavy-duty	1991	10	soybean	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	
3	Peterson and Reece	[27]	1994	ASABE	medium-duty	1994	20, 50, 100	rapeseed	Transient Cycle (UDDS, arterial)	PM, NO_x, CO, CO_2, HC	
4	Sharp	[100]	1994	Report	heavy-duty	1991	20	soybean	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	additives
5	Peterson and Reece	[28]	1996	SAE	medium-duty	1994, 1995	20, 50, 100	rapeseed	Transient Cycle (UDDS, arterial)	PM, NO_x, CO, CO_2, HC	
6	Graboski et al.	[29]	1996	SAE	heavy-duty	1991	20, 35, 65, 100	soybean	Transient Cycle (FTP)	PM, NO_x, CO, CO_2, HC	
7	Purcell et al.	[30]	1996	Am Oil Chem Soc	light-duty	-	30, 100	soybean	Transient Cycles (heavy-duty, light-duty dynamometer)	PM, NO_x, CO, HC, particle size	indirect injection, naturally aspirated
8	Schumacher et al.	[92]	1996	SAE	heavy-duty	1991	100	soybean	Transient Cycle (FTP)	PM, NO_x, CO, HC	
9	Sharp	[97]	1996	Report	heavy-duty	1995	20, 50, 100	rapeseed	Transient Cycle (FTP)	PM, NO_x, CO, HC	

	Research Group	Ref.	Year	Publication	Engine type	Engine MY or Emission Level	Biodiesel Percentage	Originating Oil	Transient Schedule	Emissions	Notes / Other Fuels Tested
10	Starr	[31]	1997	SAE	heavy-duty	1991	20	soybean	Transient Cycle (hot start FTP)	PM, NO_x, CO, CO_2, HC	ignition retard effects, non-regulated
11	McCormick et al.	[32]	1997	Environ Sci Technol	heavy-duty	1989	8.9, 17.7	soybean	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	octanol, ethanol
12	Clark and Lyons	[33]	1998	ASABE	heavy-duty	1989–1994	35	soybean	Transient Cycle (West Virginia University)	PM, NO_x, CO, HC	8 vehicles
13	Smith et al.	[94]	1998	Report	heavy-duty	1997	20, 100	soybean	Transient Cycle (FTP)	PM, NO_x, CO, CO_2, HC	
14	Clark et al.	[34]	1999	SAE	heavy-duty	1994	20, 50, 100	soybean	Transient Cycle (hot start FTP)	PM, NO_x, CO, CO_2, HC	Fischer-Tropsch, iso-butanol
15	Wang et al.	[35]	2000	Environ Sci Technol	heavy-duty	1987–1994	35	soybean	Transient Cycle (West Virginia University)	PM, NO_x, CO, HC	various engines and cycles
16	Peterson et al.	[36]	2000	ASABE	medium-duty	1994	20, 100	rapeseed, soybean, mustard, cocunut, safflower	Transient Cycle (UDDS)	PM, NO_x, CO, CO_2, HC	unsaturation effects
17	Sharp et al.	[37]	2000	SAE	heavy-duty	1995–1997	20, 100	soybean	Transient Cycle (FTP)	PM, NO_x, CO, HC	PM characterization, 3 engines

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18	Durbin et al.	[38]	2000	Environ Sci Technol	light-duty	1988–1996	20, 100	-	Transient Cycle (UDDS)	PM, NO_x, CO, HC, PAHs	synthetic diesel
19	Haas et al.	[39]	2001	Energy Fuels	heavy-duty	1991	20, 100	soybean, soapstock	Transient Cycle (FTP)	PM, NO_x, CO, HC	
20	McCormick et al.	[40]	2001	Environ Sci Technol	heavy-duty	1991	20, 100	soybean, yellow grease, canola, tallow, lard	Transient Cycle (FTP)	PM, NO_x	unsaturation, cetane number and density effects
21	Schumacher et al.	[41]	2001	ASABE	heavy-duty	1992	20, 30	soybean	Transient Cycle (FTP), FTP smoke test	PM, NO_x, CO, HC, opacity	
22	Schumacher et al.	[42]	2001	ASABE	heavy-duty	1991	20, 35, 65, 100	-	Transient Cycle (FTP)	PM, NO_x, CO, HC, opacity	
23	McCormick et al.	[43]	2002	SAE	heavy-duty	1991	20, 100	soybean, yellow grease	Transient Cycle (FTP)	PM, NO_x, CO, HC	ignition improvers
24	McGill et al.	[44]	2003	SAE	passenger car	-	30	soybean, rapeseed, used vegetable	Transient Cycle (FTP75)	PM, NO_x, CO, HC	non-regulated emissions
25	Zou and Atkinson	[45]	2003	Environ Sci Technol	passenger car, light duty		20, 40, 60, 80, 100	canola	Transient Cycle (ECE)	PM, NO_x, CO, CO_2, HC	PAHs

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26	Frank et al.	[46]	2004	SAE	heavy-duty	2001	20	soybean	Transient Cycle (FTP)	PM, NO_x, CO, CO_2, HC	ethanol
27	Souligny et al.	[47]	2004	SAE	heavy-duty	1998, 2000	5, 20	vegetable, waste grease, animal fat	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	
28	McCormick et al.	[48]	2005	SAE	heavy-duty	2002, 2003	10, 20, 50, 100	soybean, canola, yellow grease, beef tallow	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	unsaturation, cetane number and intake air humidity effects
29	Frey and Kim	[98]	2005	Report	heavy-duty	1998–2004	20	-	Real working conditions	PM, NO, CO, CO_2, HC	5 dump trucks
30	Environment Canada	[95]	2005	Report	heavy-duty	1998	20	canola	Transient Cycle (hot FTP)	PM, NO_x, CO, CO_2, HC	
31	Li et al.	[49]	2006	Canadian Biosyst Eng	non-road	-	20, 50, 100	soybean	Real working conditions	NO_x	
32	Armas et al.	[50]	2006	Fuel	passenger car	-	30, 70, 100	sunflower	Cold starting, Load increase, Acceleration	Smoke opacity	
33	Knothe et al.	[51]	2006	Energy Fuels	heavy-duty	2003	100	soybean	Transient Cycle (hot FTP)	PM, NO_x, CO, HC	hexadecane, dodecane

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34	McCormick et al.	[91]	2006	Report	heavy-duty	2002–2006	20	soybean	Transient Cycles (5 chassis dynamometer cycles)	PM, NO_x, CO, CO_2, HC	8 HD vehicles
35	Karavalakis et al.	[52]	2007	SAE	passenger car	1998	5, 10, 20	soybean	Transient Cycles (NEDC, Athens DC)	PM, NO_x, CO, CO_2, HC	non-regulated emissions
36	Durbin et al.	[53]	2007	Atmos Environ	medium-duty	1999, 2004	20, 50, 70, 100	soybean, yellow grease	Transient Cycles (FTP75, US06)	PM, NO_x, CO, HC	JP8
37	Sze et al.	[54]	2007	SAE	medium-duty	2006	20, 50	soybean	Transient Cycles (FTP, UDDS, NRTC, WHTC, Highway)	PM, NO_x, CO, HC	comparative study
38	Arapaki et al.	[55]	2007	SAE	passenger car	Euro III	5, 10, 20	used frying	Transient Cycle (NEDC)	PM, NO_x, CO, HC	non-regulated emissions
39	Tzirakis et al.	[56]	2007	SAE	passenger car	EURO IV	5, 20, 50	used frying	Real working conditions	smoke opacity, NO_x, CO, HC, CO_2	
40	Nuszkowski et al.	[57]	2008	SAE	heavy-duty	1999, 2004	20	soybean, tallow, cottonseed	Transient Cycle (FTP)	PM, NO_x	cetane improvers

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41	Bielaczyc and Szczotka	[58]	2008	SAE	light-duty	Euro 4, Euro 5	5, 20, 30	rapeseed	Transient Cycle (NEDC)	PM, NO_x, CO, CO_2, HC	
42	Kawano et al.	[59]	2008	SAE	light-duty	2005	5, 20, 80, 100	rapeseed	Transient Cycle (JE05)	PM, NO_x, CO, HC	
43	Muncrief et al.	[60]	2008	Energy Fuels	heavy-duty	1999	20, 50, 100	cottonseed, soybean	Transient Cycle (WVU refuse truck cycle)	PM, NO_x, HC, CO, CO_2	DPF and EGR effects
44	Tatur et al.	[102]	2008	SAE	passenger car	-	5, 20	soybean	Transient Cycles (FTP75, US06, HWFET, UDDS)	PM, NO_x, HC, CO,	DPF, SCR, NAC, aging results
45	Bielaczyc et al.	[61]	2009	SAE	light-duty	Euro 4	30, 50, 100	rapeseed	Transient Cycle (NEDC)	PM, NO_x, CO, CO_2, HC	
46	Karavalakis et al.	[62]	2009	SAE	passenger car	Euro 4	10, 30	soybean	Transient Cycle (NEDC, Artemis)	PM, NO_x, CO, CO2, HC	non-regulated emissions
47	Armas et al.	[63]	2009	Energy Fuels	passenger car	Euro 2, 3	30, 70, 100	sunflower	Load increase, Deceleration	smoke opacity, NO_x, HC	
48	Fontaras et al.	[64]	2009	Fuel	passenger car	Euro 2	50, 100	soybean	Transient Cycle (NEDC, Artemis), Acceleration	PM, NO_x, CO, CO_2, HC, particle number and size distribution	carbonyl compounds

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49	Lujan et al.	[65]	2009	Biomass Bioenergy	passenger car	Euro 4	30, 50 100	-	Transient Cycle (NEDC)	PM, NO_x, CO, HC	
50	Lance et al.	[66]	2009	SAE	passenger car	Euro 4	10, 20, 30, 50, 100	rapeseed, soybean, jatropha	Transient Cycle (NEDC)	NO_x, CO, CO_2, HC	
51	Kousoulidou et al.	[67]	2009	SAE	passenger car	Euro 3	10	palm, rapeseed	Transient Cycle (NEDC)	PM, NO_x, CO, HC	
52	Chien et al.	[68]	2009	Aerosol Air Quality Res	passenger car	-	20, 60, 80	waste cooking	Transient Cycle (FTP)	PM, particle size distribution	PAHs
53	Frey and Kim	[69]	2009	Transport Res	heavy-duty	2006	20	soybean	Real working conditions	PM, NO, CO, CO_2, HC	8 vehicles
54	Karavalakis et al.	[70]	2009	Sci Total Environ	passenger car	Euro 2	5, 10, 20	palm, rapeseed	Transient Cycle (NEDC, Athens)	PM, NO_x, CO, CO_2, HC	non-regulated emissions
55	Lopez et al.	[71]	2009	Transport Res	heavy-duty	Euro IV	20, 100	-	Bus Cycle	PM, NO_x, CO, CO_2, HC	DPF, SCR
56	Moser et al.	[72]	2009	Fuel Process Technol	medium-duty	2002	20	soybean, hydrogenat. soybean	Custom Cycle	PM, NO_x, CO, HC	
57	Durbin et al.	[93]	2009	Report	heavy-duty	2006	5, 20, 50, 100	soybean, tallow	Transient Cycles (UDDS, FTP)	PM, NO_x, CO, CO_2, HC	
58	Nikanjam et al.	[96]	2009	SAE	heavy-duty	2006	20	soybean	Transient Cycles (UDDS)	NO_x, CO, HC	

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59	Nuszkowski et al.	[101]	2009	IMechE (Part D)	heavy-duty	1992, 1999, 2004	20	soybean	hot FTP	NO_x	additives
60	Löfvenberg	[89]	2009	Report	heavy-duty	Euro III	5	rapeseed	Transient Cycle (ETC)	PM, NO_x, CO, CO_2, HC	ethanol
61	Rakopoulos et al.	[73]	2010	Energy	medium-duty	Euro II	30	cottonseed/sunflower	Acceleration	smoke opacity, NO	n-butanol
62	Fontaras et al.	[74]	2010	Environ Pollution	passenger car	Euro 3	10	palm, rapeseed, soybean, used frying, sunflower	Transient Cycle (NEDC, Artemis)	PM, NO_x, CO, CO_2, HC, particle number and size distribution	
63	Lindgren et al.	[75]	2010	Biosyst Eng	non-road	-	5	rapeseed	Acceleration, Load increase	PM, NO_x, CO, CO_2, HC	
64	Bannister et al.	[76]	2010	IMechE (Part D)	light-duty	Euro 3	5, 10, 20, 30, 50	rapeseed	Transient Cycle (NEDC)	PM, NO_x, CO, HC	ambient temperature effects
65	Clark et al.	[77]	2010	SAE	heavy-duty	2002–2008	20	-	Transient Cycles (OCTA, UDDS)	PM, NO_x	
66	Tinsdale et al.	[78]	2010	SAE	passenger car	Euro 5	30	-	Transient Cycle (NEDC)	PM, particle number	
67	Rose et al.	[79]	2010	SAE	light-duty	Euro 4	10, 30, 50	rapeseed	Transient Cycle (NEDC)	PM, NO_x, CO, CO_2, HC	3 vehicles

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68	Thompson and Nuszkowski	[80]	2010	Engine Res	heavy-duty	1992	10, 20	soybean	Transient Cycle (FTP)	PM, NO_x, CO, HC	3 different base fuels
69	Bakeas et al.	[81]	2011	Sci Total Environ	passenger car	Euro 4	10, 20, 30	animal fat, soybean, used frying, olive	Transient Cycle (NEDC, Artemis)	PM, NO_x, CO, CO_2, HC	
70	Lin et al.	[82]	2011	Energy	heavy-duty	1994	5, 10, 20, 30	waste cooking	Transient Cycle (FTP)	PM, NO_x, CO, CO_2, HC	PAHs
71	Kooter et al.	[83]	2011	Atmos Environ	heavy-duty	Euro III	5, 10, 20, 100	-	Transient Cycle (ETC)	PM, NO_x	pure plant oil, PAHs
72	Rakopoulos et al.	[84]	2011	Appl Energy	medium-duty	Euro II	30	cottonseed/sunflower	Hot starting	smoke opacity, NO, combustion noise	n-butanol
73	Pelkmans et al.	[85]	2011	IMechE (Part D)	passenger car/heavy-duty	Euro 3 (bus), Euro 4	5, 10, 30, 100	rapeseed	Transient Cycles (hot NEDC, ETC)	PM, NO_x, CO, CO_2, HC	pure plant oil
74	Macor et al.	[86]	2011	Appl Energy	light-duty	Euro 3	30	rapeseed	Transient Cycle (NEDC)	PM, NO_x, CO, HC, particle number	non-regulated emissions

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75	Karavalakis et al.	[87]	2011	Energy	passenger car	2007	10, 20, 30	soybean, palm, rapeseed	Transient Cycle (NEDC, Artemis)	PM, NO_x, CO, HC	PAHs
76	Bakeas et al.	[88]	2011	Fuel	light-duty	Euro 4	30, 50, 80	soybean, palm, used frying	Transient Cycle (NEDC, Artemis)	PM, NO_x, CO, CO_2, HC	PAHs, unsaturation effects
78	Bermudez et al.	[90]	2011	Biomass Bioenergy	passenger car	Euro 4	100	soybean, rapeseed, palm	Transient Cycle (NEDC)	NO_x, CO, CO_2, HC	Fischer-Tropsch / non-regulated emissions
77	Giakoumis et al.	[103]	2012	IMechE (Part D)	medium-duty	Euro II	30	cottonseed/sunflower	Acceleration	combustion noise	n-butanol