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Effect of biodiesel fuels on diesel engine emissions

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Abstract

The call for the use of biofuels which is being made by most governments following international energy policies is presently finding some resistance from car and components manufacturing companies, private users and local administrations. This opposition makes it more difficult to reach the targets of increased shares of use of biofuels in internal combustion engines. One of the reasons for this resistance is a certain lack of knowledge about the effect of biofuels on engine emissions. This paper collects and analyzes the body of work written mainly in scientific journals about diesel engine emissions when using biodiesel fuels as opposed to conventional diesel fuels. Since the basis for comparison is to maintain engine performance, the first section is dedicated to the effect of biodiesel fuel on engine power, fuel consumption and thermal efficiency. The highest consensus lies in an increase in fuel consumption in approximate proportion to the loss of heating value. In the subsequent sections, the engine emissions from biodiesel and diesel fuels are compared, paying special attention to the most concerning emissions: nitric oxides and particulate matter, the latter not only in mass and composition but also in size distributions. In this case the highest consensus was found in the sharp reduction in particulate emissions.

Keywords: Diesel engines; Emissions; Biodiesel; Particulate matter; Fuel consumption

Contents

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1. Introduction

The fuels used in road transportation are subject to increasingly stringent regulations (EN-590 in Europe [1], ASTM D 975 in USA [2]). In recent years, the reduction in sulfur content is the most notable restriction (50 ppm currently, 10 ppm by 2009 in Europe), and it has had economic consequences on oil company investments and on the final fuel price. This, together with the oscillating increase in the oil price per barrel and with the total or partial detaxation of biofuels, depending on the country, has opened the way for the commercialization of biodiesel and bioethanol and has provided a useful tool to fight against the impact of transportation (considered as a diffuse source of emissions) on climate change. In the case of biodiesel, such an impact could be even higher in European countries where the "dieselization" process has sharply increased in the last decade, leading to an unbalanced fuel production in oil refineries.

The term biodiesel commonly refers to fatty acid methyl or ethyl esters made from vegetable oils or animal fats, whose properties are good enough to be used in diesel engines. The regulations limiting such properties are EN-14214 in Europe [3] and ASTM D-6751-03 in USA [4], although ethyl esters are not yet acknowledged as biodiesel in Europe [5]. Research papers presenting results of diesel engine emissions from biodiesel often ignore some of the basic properties of the biodiesel used [6], which makes it difficult to determine whether its quality has some effect or not.

The call for the use of biofuels, and particularly of biodiesel, which is being made by many governments following international energy policies is presently finding some resistance from car and components manufacturing companies, private users and local administrations. This opposition makes it more difficult to reach the targets of increased use of biofuels in internal combustion engines. One of the reasons for this resistance is a certain lack of knowledge about the effect of biodiesel on diesel engines. There are four issues related to biodiesel where public knowledge is still low:

- Automotive fuels are delivered in petrol stations by volume, and their price is correspondingly established per unit volume. However, it is not the volume but the energy which moves vehicles. Both volume and energy are related through fuel density and its heating value, or in summary, through the heating value in energy basis (MJ/l). It should be kept in mind that biodiesel has around 9% less heating value in volume than conventional diesel fuel. Thus, if engine efficiency is the same, engine fuel consumption should be proportionally higher, and consequently vehicle autonomy proportionally lower, when using biodiesel. However, differences in efficiency have occasionally been found in the literature comparing diesel and biodiesel fuels, along with claims of increases in consumption different to those expected, as shown below.
- Biodiesel fuels have higher lubricity than conventional fuels, but they can contribute to the formation of deposits, the degradation of materials or the plugging of filters, depending mainly on their degradability, their glycerol (and other impurities) content, their cold flow properties, and on other quality specifications [7]. The long-term effects of biodiesel are currently one of the least explored issues and a very small number of experimental studies have been published about this.
- Biodiesel is 100% renewable only when the alcohol used in the transesterification process is also renewable, but this proportion is reduced to around 90% (if the balance is made in mass) or 95% (if the balance is made in carbon mass) when fossil alcohol (usually methanol) is used. This high renewable proportion justifies the nil consideration of CO_2 emissions from biodiesel combustion in European directives. However, life-cycle analyses of CO_2 emissions should be accounted for in order to evaluate the impact of biodiesel on the global greenhouse effect. Results of well-to-wheel CO_2 emissions are very variable [8–12], locally dependent and often unreliable, but a saving of between 50% and 80% (and even more in the case of waste-oil biodiesel [9–11]) with respect to petroleum diesel emissions could be accepted as a high confidence range. In any case, this makes biodiesel a powerful tool to reduce CO_2 emissions from transportation, which is considered responsible for 23% of greenhouse emissions in the Annex I countries of the Kyoto Protocol, as published by the United Nations Framework Convention for Climate Change [13].

- Biodiesel fuels also have an interesting potential to reduce chemical emissions. However, the effect of biodiesel is specific for each of the different pollutant species, and depends on the type of engine, on the engine speed and load conditions, on the ambient conditions, on the origin and quality of biodiesel, etc.

The main objective of this paper is to analyze the latter issue by means of a literature review. Although a previous review was published by Graboski and McCormick [14] in 1998, the increasing interest in the use of biodiesel calls for a new revision of the state-of-the-art, since many experiments have been carried out in the last years to clarify some of the effects of biodiesel on diesel emissions. Out of all emissions, oxides of nitrogen and particulate matter (PM) are the most significant in diesel engines due to the high flame temperature and diffusive combustion in the combustion chamber. Since nitric oxides (NO_x) and PM emissions from current diesel technologies are close to the limits permitted by regulations and both limits will be even more stringent in the near future, these two emissions will be critical factors in the development of new diesel engines. For example, Euro 5 will reduce NO_x and PM emission limits for passenger cars from 0.25 and 0.025 g/km to 0.18 and 0.005 g/km, respectively (emissions tested over the NEDC chassis dynamometer procedure [15]). Moreover, Euro 5 will consider both mass and number based PM emission limits, although the measurement method for particle number must previously be established [16]. For the other regulated emissions, carbon monoxide (CO) and total hydrocarbon (THC), no further development in engines seems to be necessary to meet future limits.

An improved knowledge of the potential to reduce these types of emissions could help (a) engine manufacturers to adapt their engines to the use of biodiesel and to optimize them, readjusting the compromise between efficiency, costs (mainly due to aftertreatment systems) and emissions within the regulation limits, (b) national administrations to design their energy policies and to define measures to externalize environmental costs, (c) local administrations to promote its use in urban areas, especially in countries with extreme dieselization, where particle concentrations in the air are reaching alarming levels, and (d) private users, to encourage them to use biodiesel, attesting to their environmental concern.

The literature reviewed was selective and critical. Highly rated journals in scientific indexes were the preferred choice, although other non-indexed publications, such as SAE technical papers or some internal reports from highly reputed organizations (National Renewable Energy Laboratory, National Biodiesel Board, Environmental Protection Agency) have also been cited. Some papers have been excluded as they do not mention the instrumentation or methodology used. Finally a bibliometric study showed (Fig. 1) that the number of publications related to both biodiesel and biodiesel emissions has increased exponentially in the last 15 years, which reveals the increasing interest of this alternative and of its environmental benefits.

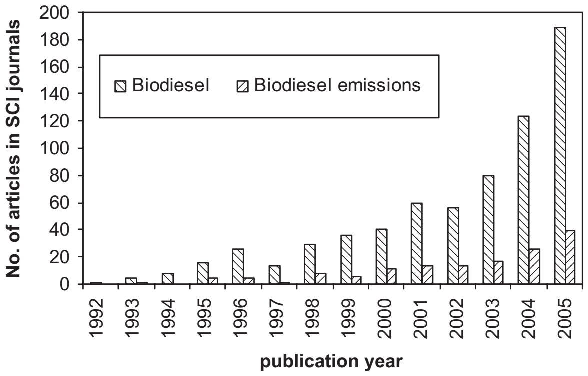

Fig. 1. Chronogram of published papers related to biodiesel and to biodiesel emissions (ISI Web of knowledge).

Table 1
Ranges of the specifications of the fuels used in the reviewed studies

Specifications	Biodiesel	Diesel
Density (15 °C) (kg/m^3)	870–895	810–860
Viscosity (40 °C) (cSt)	3.5–5.5	2–3.5
Cetane number	45–65	40–55
Cold filter plugging point (°C)	−5 to 10	−25 to 0
Cloud point (°C)	−5 to 10	−20 to 0
Pour point (°C)	−15 to 10	−35 to 0
Lower heating value (MJ/kg)	36.5–38	42.5–44
Water content (mg/kg)	0–500	
Acid number (mg KOH/g)	0–0.60	
Ester content (% w/w)	>96	
Glycerin content (% w/w)	0–0.25	
Sulfur content (mg/kg)		15–500

A wide range of diesel engine sizes and types was tested in the reviewed literature. The most frequently used engines were direct injection, turbocharged, and 4-cylinder diesel engines. Since engine characteristics might have some influence on the effects of biodiesel, this information has been considered useful to this study. However, in order to avoid awkward reading, this information is only specified in the following sections if the tested engine was different to the above mentioned type. To the same end, the biodiesel fuels used in the reviewed studies were composed of methyl esters produced from different oils, unless otherwise specified. However, although the original vegetable oils are usually mentioned in the reviewed studies, many of the quality specifications (i.e. glycerin content, ester content, etc.) of biodiesel fuels are often missing, which makes it difficult to discuss the results provided. When indicated, the specifications belong to the ranges shown in Table 1, unless otherwise specified. For example, the following sections only specify the cases where the sulfur content of the diesel fuel used for comparisons is ultra low (below 15 ppm, ULS hereinafter) or high (above 500 ppm).

2. Engine performance

2.1. Brake effective power

Nowadays automotive engines are usually oversized and the power output when using biodiesel fuels is usually the same as with diesel fuel, as the accelerator is not fully pressed down in most cases. Drivers unconsciously over-press the accelerator with respect to how they used to drive with diesel fuel, in order to compensate for the reduced heating value of biodiesel. When testing an engine in a test bench, equivalent performance requires attaining the same engine speed and torque, regardless the fuel used. A meaningful comparison of emissions and fuel consumption is only possible if tests are carried out under the same operation mode. Puhan et al. [17] tested petroleum diesel fuel and ethylic biodiesel fuel (with viscosity of 6.2 cSt) in a naturally aspirated D.I. diesel engine in four steady operation modes, defined by their engine speed and brake mean effective pressure (*bmep*), the latter being proportional to the effective torque. Tsolakis [18] defined three operation modes in a single-cylinder naturally aspirated D.I. engine by setting engine speed and *bmep* in the tests in which they compared ULS diesel and rapeseed biodiesel fuels. Armas et al. [19] and Lapuerta et al. [20,21] selected five steady operating modes by setting engine speed and torque in both direct and indirect injection engines. Senatore et al. [22] selected six operating modes, defined by engine speed and equivalence ratio when testing rapeseed biodiesel in their 1.9 l engine. The equivalence ratio is also closely related to the torque because the loss of heating value of biodiesel is more or less compensated by the higher mass of fuel needed by a given mass of air for a stoichiometric reaction. In all cases the set effective power was easily reached.

In all the studies mentioned, the operation modes selected tried to simulate representative engine conditions, often taking as reference certification cycles, which in the case of heavy-duty engines [17,18] cover the whole load range (concentrating mainly on 25%, 50%, 75% and 100% of maximum torque) at various speeds and, in the case of vehicle engines, are concentrated around the low–medium load [19–22].

Only at full-load conditions, with the accelerator fully pressed down, or at partial load but with equal fuel consumption or equal accelerator position, the power output delivered with biodiesel is reduced with respect to that delivered with diesel fuel. Although reductions around 8% (the loss of heating value in volume basis) would be expected, the reported results show some variations. Many authors found that the loss of power is lower than expected. Kaplan et al. [23] compared sunflower-oil biodiesel and diesel fuels at full and partial loads (the latter defined by constant fuel mass delivery) and at different engine speeds in a 2.5 l 53 kW engine. The loss of torque and power ranged between 5% and 10%, and particularly at full load, the loss of power was closer to 5% at low speed and to 10% at high speed. Çetinkaya et al. [24] compared pure waste-oil biodiesel and diesel fuels in a 75 kW 4-cylinder common rail engine in full-load conditions. The shape of the torque-speed curve was similar and the loss of torque was only between 3% and 5% with biodiesel. Although the authors just pointed out the reduced heating value as responsible for this reduction, some power recovery can be supposed. A similar result was obtained by Lin et al. [25] in a naturally aspirated 2.84 l engine. They operated with ULS diesel, pure palm-oil biodiesel (with a pour point of 15 °C) and a 20% palm biodiesel blend. The loss of power at full load was only 3.5% with pure biodiesel and 1% with the blend. Other experiences showing similar power recoveries have been reported [26,27].

There are also some publications reporting surprising increases in rated power or torque when using biodiesel. Altiparmak et al. [28] measured a 6.1% increase in maximum torque when they used a blend with 70% tall-oil biodiesel, with respect to that measured with diesel fuel. Although they explained this increase with the increased cetane number, unusually high values of density and viscosity of the biodiesel tested (922 kg/m^3 and 7.1 cSt at 40 °C, respectively) could also partially explain such a result. Similarly, Usta [29] observed an increase in torque and power when using biodiesel from tobacco seed oil (with a lower heating value of 39.8 MJ/kg) in different blends with diesel fuel in an indirect injection diesel engine at 1500 and 3000 rpm. The highest values of torque and power were obtained with a 17.5% blend, despite the reduced heating value of biodiesel. They used the increase in density, viscosity and an improved combustion to explain this.

Other authors report power losses in the same range as the reduction in heating value. For example, Yücesu and Ilkiliç [30] measured reductions in torque and power when they used pure cottonseed biodiesel of 3–8%, while they declared a heating value for biodiesel of only 5% below that of diesel fuel. They did not use the loss of heating value to justify the power loss, but difficulties in the fuel atomization, instead. Murillo et al. [31] tested diesel fuel and biodiesel from used cooking oil in a marine outboard 3-cylinder naturally aspirated engine. At full load, the biodiesel resulted in a power loss of 7.14% as compared with diesel fuel, very close to the difference in heating values. Results from the Southwest Research Institute (collected in Ref. [32]) show 1.5–2% reductions in rated power when using 20% blends and 8% reductions when using pure biodiesel. In a combined test bench/on-road program for biodiesel promotion carried out in Australia with waste-oil biodiesel [33] a loss of rated power of 17% was found in the bench, this loss being slightly higher than expected. The low methyl ester content (below 90% in average) or the high acid value (0.9 mg KOH/g) could have led to a lower than usual heating value. However, drivers declared not noticing any power loss, probably as a consequence of the infrequent demand for full-load power.

Finally, a small number of papers reported no significant differences on the engine rated power with diesel and biodiesel. These are the cases of Romig and Spataru [34], who tested six blends with different concentrations of rapeseed and soybean oil-biodiesel at 1200 and 2000 rpm in a 6-cylinder DDC engine, and of Shaheed and Swain [35], who tested cottonseed oil biodiesel at different engine speeds in a single-cylinder 2.75 kW engine.

Various reasons, most of them related to viscosity, have been given in the literature to explain the torque and power recovery (with respect to the loss of heating value) at full load with respect to that obtained with diesel fuel:

- The higher viscosity of biodiesel, which may affect the engine brake effective power, especially in full-load conditions. Tat [36] compared pure soybean-oil biodiesel with conventional diesel in a turbocharged engine at 1400 rpm and full load (accelerator fully pressed down) equipped with two different injection pumps. He found that not only the mass of fuel but also the volume injected was higher (1.2–3.2%) in the case of biodiesel. The higher viscosity, which reduces the back flow across the piston clearance of the injection pump, was used as an explanation. Moreover, the difference in fuel delivery was reduced as the injection temperature was increased, in accordance with the corresponding decrease in viscosity. By contrast, when injection temperatures for diesel and biodiesel were adjusted to provide similar viscosities, then diesel fuel delivery in volume was slightly higher as a consequence of its lower density, which enhances the flow rate through orifices. Usta [29] also explained the increased injected volume in the case of biodiesel by means of an increase in viscosity.
- The higher bulk modulus and sound velocity of biodiesel [37–39], together with its higher viscosity [36,40,41], lead to an advanced start of injection. This, jointly with any cetane number increase, may slightly advance the start of combustion. Current diesel engines need to have delayed combustion in order to reduce pressure and temperature peaks in the combustion chamber, and thereby nitric oxide formation. Such a delay involves a loss of thermal efficiency and consequently of brake effective power. If the start of injection, and thus that of combustion, is advanced, the combustion process is then re-centered and the power output increases [28].
- The higher lubricity of biodiesel could also reduce friction loss leading to an increased brake effective power. Only Ramadhas et al. [42] use this argument to explain the increased thermal efficiency or the rated power recovery, although they did not explain how such an improvement could happen (reduction of mechanical losses in the injection pump, the cylinder walls, etc.). In any case, it is very unlikely that lubricity could contribute to the torque and power recovery.

Table 2
Estimated share of literature (in percentage of number of publications) reporting decreases, similarities or increases in engine performance and emissions using biodiesel and diesel fuels

	Increases	Same[a]	Decreases	Synergies
Effective power (full load)	–	2	96	2
Brake-specific fuel consumption	98	2	–	–
Thermal efficiency	8	80	4	8
NO_x emissions	85	10	5	–
PM emissions	3	2	95	–
THC emissions	1	3	95	1
CO emissions	2	7	90	1

[a] Many references included in this category have reported both increases and decreases depending on engine load conditions, engine type, engine operation temperature, etc.

Some other authors found differences in the shape of the full-load torque vs. engine speed curve. Carraretto et al. [26] tested a 6-cylinder engine at full load with ULS diesel fuel, pure biodiesel from mixed soybean, rapeseed and sunflower oils and different biodiesel blends. Besides the observed 3–5% power losses with pure biodiesel, they found a displacement of the torque peak towards higher engine speed values. They explained this effect by an increase in the flame velocity with biodiesel. On the contrary, other studies collected by the National Biodiesel Board [43], showed that the full-load torque curve was flatter and with the peak at lower engine speeds when different biodiesel fuels (obtained with both methanol and ethanol) were used. Finally, a few authors found synergic effects with low biodiesel content blends. Silva et al. [27] tested a 9.6 l 6-cylinder engine with high sulfur diesel (1700 ppm) and 5% and 30% blends with biodiesel from sunflower oil (with a water content of 618 ppm). While a 30% blend led to the expected torque and power loss, the 5% blend presented a slight increase in torque, especially at high engine speed.

Summarizing this subsection, two general conclusions can be derived: firstly, biodiesel does not cause any loss of power unless the maximum power is demanded. A surplus in fuel consumption would, in any case, compensate the lower heating value of biodiesel as compared with diesel fuel. Secondly, most of the published literature reports some decrease in rated power (see Table 2), this decrease being lower than the reduction in heating value in volume basis as compared to diesel. The lower fuel leakages in the injection pumping system, the advance of the combustion process and the higher lubricity of biodiesel have been pointed out as contributing to the mentioned power recovery.

2.2. *Brake-specific fuel consumption*

Brake-specific fuel consumption (*bsfc*) is the ratio between mass fuel consumption and brake effective power, and for a given fuel, it is inversely proportional to thermal efficiency. If the latter is unchanged for a fixed engine operation mode, the specific fuel consumption when using a biodiesel fuel is expected to increase by around 14% in relation to the consumption with diesel fuel, corresponding to the increase in heating value in mass basis. In other words, the loss of heating value of biodiesel must be compensated with higher fuel consumption. An indicator of the loss of heating value, and thus of the expected fuel consumption is the oxygen content in the fuel. Graboski et al. [44] tested biodiesel from soybean oil in 20%, 35%, 65% as well as pure, and found a good correlation between *bsfc* and oxygen content. The small standard error of this correlation (0.8%) was explained because the C/H ratio (another indicator for heating value) is very similar in diesel and biodiesel fuels. As Rakopoulos et al. [45] showed in a short literature review, the increase in *bsfc* is only observed when the oxygen enrichment comes from the fuel, but not from the intake air.

The United States Environmental Protection Agency (EPA) [46] collected 39 papers up to 2001, reporting on pure and blended biodiesel laboratory tests. They restricted their study to heavy-duty engines without exhaust gas recirculation (EGR) and without any aftertreatment system. From the *bsfc* results they obtained the following equation with a confidence level of 95%. An almost linear increase and a maximum increase of 9% for pure biodiesel ($\%B = 100$) can be obtained from the equation, as shown in Fig. 2. Since this maximum increase is lower than the loss in heating value, this result implies a certain improvement of the thermal efficiency with biodiesel fuel:

$$bsfc/bsfc_D = \mathrm{e}^{0.0008189\%B}. \tag{1}$$

Most of the studies found in the literature confirm that fuel consumption is on average similar to the loss of heating value, whether heavy-duty or light-duty engines were tested. Some studies performed at the Southwest Research Institute (USA) and described in [32] showed that fuel consumption with pure soybean biodiesel increased from 13% to 18% with respect to that with diesel fuel, while with 20% blends *bsfc* increases presented more variability, ranging from −3% (*bsfc* decreased) to 9%. This variability could be due to the different engines and operation modes used in each study, although this information is not fully reported in [32]. Turrio-Baldassarri et al. [47] tested a 6-cylinder 7.8 l engine following the ECE R49 test cycle with 20% blends of rapeseed-oil biodiesel (with a glycerin content of 1.15%) in diesel fuel. They measured a mean *bsfc* increase of 2.95% with 95% statistical confidence. A similarly sized engine (6 cylinders and 170 kW of rated power) was tested by Hansen and Jensen [48] with pure rapeseed-oil biodiesel in five selected modes among those of the ECE R49 test cycle. They measured a 14% increase in *bsfc*. Last et al. [49] tested another heavy-duty engine in the same cycle, showing a linear increase in *bsfc* as the biodiesel content in the blend was higher, up to a 12.4% increase with pure soybean-oil biodiesel (with a lower heating value of 41.8 MJ/kg). Also Alam et al. [37] found *bsfc* increases from their heavy-duty engine tests with 20% soybean-oil biodiesel blends in an eight-mode cycle, although they did not quantify such increases.

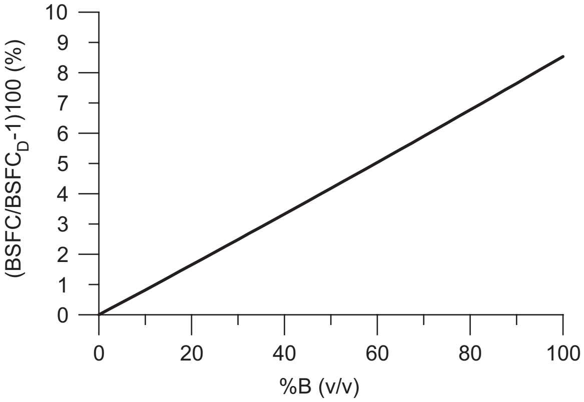

Fig. 2. Mean increase in *bsfc* as the biodiesel content increases (trend obtained from Ref. [46] for heavy-duty engines with no EGR or aftertreatmen system).

In the vehicle engine size range, there are also many reported experiences with similar results. Canakci and Van Gerpen [50] and Canakci [51] obtained about 2.5% increases in *bsfc* from their tests with 20% blends and about 14% from those with pure biodiesel. They compared waste-oil and soybean-oil biodiesel fuels in a 57 kW engine, and proved that the original oil did not have any influence. Senatore et al. [22] tested a 1.9 l engine in six steady modes with diesel and pure rapeseed-oil biodiesel fuels. The increase in *bsfc* with biodiesel was again very similar to the loss of lower heating value (36 MJ/kg for the biodiesel fuel). The same proportionality was found by Tsolakis [18] in a single-cylinder research engine tested in three steady modes with rapeseed-oil biodiesel. Other authors looked for differences between the nature or properties of biodiesel. For example, Lapuerta et al. [52] tested a 2.2 l engine in five modes with biodiesel fuels made from differently stressed waste oils. In all cases the increase in *bsfc* was similar to the loss of heating value. Monyem and Van Gerpen [53] tested a 4.5 l engine with differently oxidized soybean-oil biodiesel fuels. The increase in *bsfc* with pure biodiesel was 15.1% in the case of oxidized biodiesel (with a peroxide index of 340 meq/kg) and 13.8% in the case of non-oxidized biodiesel. They attributed this difference to the different heating value of both biodiesel fuels. Most of the authors have explained these increases by the loss of heating value, although some others [17] attributed them to the different density of biodiesel and diesel fuels. This explanation cannot be correct, since the set operating modes were defined by their engine speed and *bmep*, not by the accelerator position.

A few studies have reported results which differ from this general trend. Lin et al. [25] observed 3.3% and 16.7% increases in *bsfc* when palm-oil biodiesel was used in 20% blends and pure respectively with respect to that obtained with ULS diesel fuel. Similarly, Haas et al. [54] found 18% increases when they used pure biodiesel from soybean oil and soapstock. These increases are supposedly higher than the loss of heating value, unless the ester content of biodiesel was unusually low. Conversely, a few other studies found only small increases in fuel consumption or even found no differences at all between diesel and biodiesel. Yücesu and Ilkiliç [30] used a diesel fuel and a biodiesel fuel from cottonseed oil at full load, and found an increase of just 3–8% in mass basis in the case of pure biodiesel. Silva et al. [27], observed no significant changes in *bsfc* when they tested their 6-cylinder 9.6 l engine following the ECE R49 test cycle with 5% and 30% sunflower-oil biodiesel blends. Similarly, Dorado et al. [55] tested a 3-cylinder 2.5 l engine in eight steady modes with pure biodiesel from waste olive oil biodiesel and did not find significant differences in *bsfc* with diesel fuel. Finally, Kaplan et al. [23] stated that the fuel consumption was better with biodiesel, causing a reduction in smoke opacity, although they could have meant thermal efficiency instead.

In summary, with respect to consumption of diesel fuel, a large majority of authors found increases in biodiesel fuel consumption in proportion to the biodiesel content in the blends and to the loss of heating value (around 14% in mass basis for most pure biodiesel fuels) (see Table 2). In those cases where different trends were found, some deficiencies either in biodiesel quality or in measurement accuracy can be supposed.

2.3. Thermal efficiency

Thermal efficiency is the ratio between the power output and the energy introduced through fuel injection, the latter being the product of the injected fuel mass flow rate and the lower heating value. Thus, the inverse of thermal efficiency is often referred to as brake-specific energy consumption. Since it is usual to use the brake power for determining thermal efficiency in experimental engine studies, the efficiency obtained is really a brake-specific efficiency. This parameter is more appropriate than fuel consumption to compare the performance of different fuels, besides their heating value. From the section dedicated to fuel consumption (2.2) it can be derived that most researchers would have observed no significant change in thermal efficiency when using biodiesel. However, only those providing explicit results of efficiency are cited in this section.

Among the studies already cited, Tsolakis [18], Senatore et al. [22], Shaheed and Swain [35], Graboski et al. [44], Canakci and Van Gerpen [50], Canakci [51], Lapuerta et al. [52], and Monyem and Van Gerpen [53] acknowledged no variations in thermal efficiency when using different types of biodiesel fuels. Apart from these studies, Graboski et al. [56] tested a large number of methyl esters from different feedstocks and even pure esters in a 11.1 l 254 kW engine following the transient cycle for heavy-duty engines 40 CFR Part 86 subpart N. From the results obtained they showed that neither the oil origin, nor the length of the carbon chain, nor the number of double bonds provided significant differences in thermal efficiency. Hamasaki et al. [57] tested a single-cylinder 1 l 11.77 kW engine at different loads and constant engine speed using three biodiesel fuels obtained from waste oil but with different acid values (0.33, 0.58 and 0.90 mg KOH/g). The thermal efficiency was similar in all cases.

A few authors stated having observed some improvement in thermal efficiency, although this is not confirmed by the data provided. Sahoo et al. [58] tested different blends with polanga-oil biodiesel in a single-cylinder engine. They concluded that no variations in thermal efficiency were obtained at full load, but noted slight increases at low loads. However, the high dispersion of the results presented makes the significance of such an improvement doubtful. Puhan et al. [17] stated measuring increases in efficiency when using ethyl ester from mahua oil as compared with that obtained with diesel fuel (and explained using composition and density differences), but the results provided were 26.42% against 26.36%, respectively.

A minor number of experiments have also been found to report some improvement or some decrease in thermal efficiency when using biodiesel fuels. Kaplan et al. [23] explained their observed increase in efficiency by means of an improved combustion, giving no further reasoning. In the Handbook of Biodiesel [32], it is asserted that an improvement in thermal efficiency occurs when 20% blends are used, thereby compensating for the loss of heating value. However, no references are cited to support this statement. Agarwal and Das [59] tested linseed-oil biodiesel differently blended with high sulfur diesel fuel in a single-cylinder 4 kW portable engine widely used in the agricultural sector and showed increases in thermal efficiency, especially at low load. Conversely, Lin et al. [25] found a decrease in efficiency (they reported increases in energy consumption) when using palm-oil biodiesel, pure and in 20% blends, in a 2.8 l indirect injection engine, although the small differences (below 2.3% in all cases) can hardly be considered significant.

Finally some authors have found positive and negative synergies when blending biodiesel. Labeckas and Slavinskas [60] tested a 4.75 l engine under different steady modes using 5%, 10%, 20%, 35% blends and pure rapeseed-oil biodiesel. The thermal efficiency appeared to reach a maximum for 5–10% blends. Ramadhas et al. [42] tested a 5.5 kW single-cylinder engine with 10%, 20%, 50%, 75% blends and pure biodiesel from Indian rubber seed oil. They obtained maximum efficiencies for 10% and 20% blends. This improved efficiency was explained by the increased lubricity of these blends as compared to their pure components. However, the reported 25% efficiency increase in the case of the 10% blend lessens credibility to this study. To the contrary, Murillo et al. [31] found negative synergies. These authors tested different blends of conventional diesel fuel and biodiesel from used cooking oil, at full load, in a marine outboard 3-cylinder naturally aspirated engine. With blends of 10%, 30% and 50% of biodiesel, efficiency was lower than that obtained with diesel fuel, but the highest efficiency was found with pure biodiesel.

The summary of this subsection is that most authors find similar thermal efficiency to diesel fuel when using biodiesel or even with blends (see Table 2). Thus, the above mentioned increase in fuel consumption is not caused by any loss in efficiency but rather by the reduced heating value of biodiesel. A minor number of studies report small improvements in efficiency with biodiesel, or even synergic blending effects, which could be caused by reductions in friction loss associated with higher lubricity.

3. Nitric oxides

3.1. *Effect of biodiesel*

Although most of the literature reviewed shows a slight increase in NO_x emissions when using biodiesel fuel (these works will be classified as Group I hereinafter), some works showing different effects have been found. Some of them found NO_x increases only in certain operating conditions (Group II), some others did not find differences between diesel and biodiesel fuels (III), and others still found decreases in NO_x emissions when using biodiesel (IV).

I. An experimental work carried out in a 7.3 l Navistar engine running the 13-mode US Heavy-Duty test cycle using different soybean-oil biodiesel blends is described in the report [61]. The increases in NO_x emissions obtained were in proportion to the concentration in biodiesel. An 8% increase was reached in the case of pure biodiesel. Schumacher et al. [62] tested a 200 kW 6-cylinder at 1200 and 2100 rpm and 50% and 100% load with 10%, 20%, 30% and 40% soybean-oil biodiesel blends. The NO_x emissions increased up to 15% in the case of the 40% blend. Marshall et al. [63] tested a Cummins L10E engine under transient conditions with diesel fuel and 20% and 30% biodiesel blends. They observed an increase in NO_x emissions of 3.7% with the 20% blend while only a 1.2% with the 30% blend. They also tested the engine with pure biodiesel under steady conditions (work collected in [14]) reaching a 16% increase with respect to diesel fuel NO_x emissions. Other experiments measuring increases in NO_x emissions were also collected by Graboski and McCormick [14]. For example, Police et al. measured increases around 20%, while Rantanen et al. found 4–10% increases, in both cases operating heavy-duty engines under the ECE R49 test cycle with pure rapeseed-oil biodiesel.

There are even combustion models simulating the increase on NO_x emissions when using biodiesel fuels. Yuan et al. [64] and Choi and Reitz [65] each presented one model. Both models were quite similar and provided results on auto-ignition delay times, and temperature distributions in the combustion chamber using biodiesel from soybean and waste oils as well as diesel fuel. They both obtained reduced auto-ignition times and higher extension of the high-temperature areas when using biodiesel fuels. They used these results to explain the typically observed increase in NO_x emissions.

II. Other authors concluded that the effect of biodiesel on NO_x emissions depends on the type of engine and its operating conditions. Serdari et al. [66] measured on-road emissions from three different vehicles using high sulfur diesel fuel (1800 ppm) and 10% sunflower-oil biodiesel blends. They found both increases and decreases in NO_x emissions, and attributed such differences to the different engine technology and maintenance conditions. Hamasaki et al. [57] tested a single-cylinder engine at 2000 rpm and different loads with three waste-oil biodiesel fuels. They measured slight decreases in NO_x emissions at low loads but increases at high loads. Staat and Gateau [67] tested a 6-cylinder engine following the ECE R49 test cycle and an urban transient cycle named AQA F21 established by the French Agency of Air Quality. They observed a 9.5% increase in NO_x emissions in the ECE R49 test cycle, while a 6.5% reduction in the transient urban cycle. Krahl et al. [68] collected different European experiments with rapeseed-oil biodiesel and obtained an average increase of 15% in NO_x emissions. However, they recorded some cases, mainly those testing indirect injection diesel engines under transient cycles, where the NO_x emissions were similar with diesel and biodiesel fuels. Tat [36] concluded from his literature review that NO_x emissions with biodiesel fuels are usually higher than those from diesel fuel when they are measured in an engine test bench but not when they are measured from vehicles. The reason pointed out was that engine loads are usually lower in vehicles than those imposed in experimental test rigs. This conclusion is consistent with the results obtained by Staat and Gateau [67], mentioned above, and also with those obtained by McCormick [69,70], who measured NO_x emission reductions around 5% when using 20% soybean-oil biodiesel blends.

The higher cetane number of biodiesel fuel as compared to diesel fuel could explain the above mentioned different effect of biodiesel on NO_x emissions depending on the engine load. As pointed out by Li and Gülder [71] the sensitivity of NO_x to changes in cetane number is higher at low load than at high load. In fact, they observed that NO_x emissions were reduced at low load with enhanced cetane number. This effect could compensate any increase caused by the chemical composition of biodiesel. Tat [36] proposed an additional reason: the injection pump tended to advance the injection process at low load, but he observed that this advance was higher with diesel than with biodiesel fuel in a certain load range, leading to increased NO_x emissions with diesel fuel at these load conditions.

III. Durbin et al. [72] tested four different engines with diesel, pure biodiesel and a 20% biodiesel blend. The engines were chosen to represent a wide variety of heavy-duty engines: turbocharged and naturally aspirated, direct and indirect injection. Small differences in NO_x emissions were found and the authors concluded they were not significant. The same conclusion was reached by these authors [73] when they used these fuels in seven different vehicles. Nabi et al. [74] tested a single-cylinder 9.8 kW engine at a single operating mode with different EGR rates. Although they measured increased NO_x emissions without EGR, no significant differences between diesel and neem-oil biodiesel fuels were measured for EGR rates between 5% and 30%. Wang et al. [75] tested nine vehicles with diesel and 35% soybean-oil biodiesel blends. They also concluded that differences in NO_x emissions were not significant. Among the cited studies, only in the case of Nabi et al. [74] the similar NO_x emissions obtained with diesel and biodiesel fuels might be attributed to the low unsaturation level of neem oil, in correspondence with the effect of unsaturation commented below.

IV. A minor number of papers have reported decreases in NO_x emissions when using biodiesel fuels. Peterson and Reece [76] used several blends of diesel fuels with both ethyl and methyl esters from rapeseed oil in vehicles equipped with similar 5.9 l engines. They measured reductions in NO_x emissions of around 10% both with ethyl and methyl ester blends. McDonald et al. (as collected in [14]) obtained NO_x decreases of 5–10% from their transient tests with pure soybean-oil biodiesel in a Caterpillar engine. Dorado et al. [55] recorded reductions above 20% from testing biodiesel from waste olive oil in an eight-mode cycle. Lapuerta et al. [77] observed a small decrease in NO_x emissions from an indirect injection 1.9 l engine operating in five selected steady modes with pure and blended biodiesel from sunflower and cardoon oils.

In the above cited literature review by the US EPA [46] laboratory experiments with different heavy-duty engines (without EGR or an aftertreatment system) were collected and the resulting NO_x emissions were used to adjust the following equation, which was considered statistically significant with a confidence level of 95%:

$$NO_x/NO_{xD} = e^{0.0009794\%B}. \tag{2}$$

This equation provides an almost linear increase in NO_x emissions as the biodiesel content is increased, as shown in Fig. 3. This diagram has been widely used [69,70,78,79] to describe the effect of biodiesel on NO_x emissions.

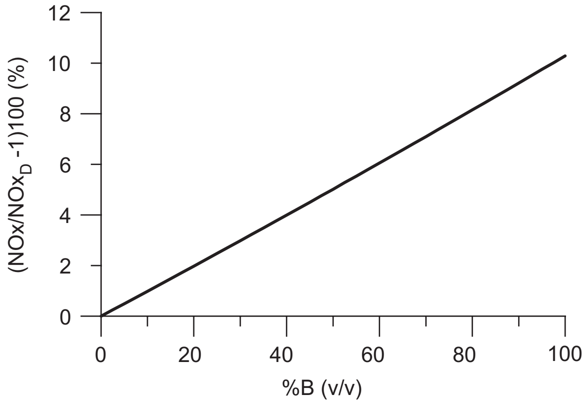

Fig. 3. Mean increase in NO_x emissions as the biodiesel content increases (trend obtained from Ref. [46] for heavy-duty engines with no EGR or aftertreatmen system).

In summary, a light increase in NO_x emissions is the most common observation in the research literature, although no unanimity has been found (see Table 2).

3.2. Reasons for the increase in NO_x emissions with biodiesel

Various arguments have been used in literature to explain the observed increase in NO_x emissions when using biodiesel fuels. Most researchers propose that the combustion process is advanced as a consequence of the advanced injection derived from the physical properties of biodiesel (viscosity, density, compressibility, sound velocity) [80]. More recently, an electronic advance in the injection pump when biodiesel is used instead of diesel fuel has been suggested [36] as an additional reason. Thus, it seems that the main reasons for the increase of NO_x emissions with biodiesel are injection-related. For example, Cardone et al. [80] observed a higher increase in NO_x emissions at high load, and they showed, by means of a diagnostic single-zone model which provided the heat release curve from the in-cylinder pressure signal, that the start of combustion was more advanced with biodiesel, leading to a higher mean temperature peak. The observed shift in the start of combustion increased with increasing loads. The authors attributed this advance to the injection advance, and suggested that it could be corrected from the electronic control unit to re-establish the original NO_x emission level.

The effect of the physical properties of biodiesel on the injection advance (with respect to the start of injection with diesel fuel) has been widely proved in engines without common rail injection system, but with pump-line-nozzle systems. When biodiesel is injected, the pressure rise produced by the pump is quicker as a consequence of its lower compressibility (higher bulk modulus) and also propagates more quickly towards the injectors as a consequence of its higher sound velocity. In addition, the higher viscosity reduces leakages in the pump leading to an increase in the injection line pressure. Therefore, a quicker and earlier needle opening is observed with respect to the case of diesel fuel. This reasoning has been used by different authors [41,53,80,81] to explain the resulting higher temperature peaks and NO formation rates. However, the electronic control unit also often contributes to this advanced injection when using biodiesel, as a consequence of the accelerator overpressing needed to compensate the reduced heating value [36].

Some other authors are in agreement with the role of advanced injection in NO_x emissions increases [22]. Monyem and Van Gerpen [53] even found a good correlation between the start of injection and the NO_x emissions, independently of the fuel used, which suggests that this is really the only reason for the NO_x increase. On the contrary, when they plotted the start of combustion versus NO_x emissions, the biodiesel tests provided lower

NO_x emissions (for a given start of combustion), as a consequence of the reduction of premixed combustion, as discussed below. Also Szybist et al. [82] found a good correlation between the start of injection and the NO_x emissions, but they found an even better correlation when using the angle where the temperature peaks were reached, again independently of the fuel used. Only the results presented by Boehman et al. [83] indicate that biodiesel fuels do not always lead to injection advances as compared to diesel fuels, since they observed some injection delays with biodiesel as compared to a very low sulfur content diesel fuel. The authors attributed this result to other effects related to the electronic control unit of the engine.

However, some results from experiments held by keeping the injection start unchanged have recently shown increased NO_x emissions with biodiesel. Thus, other arguments than advanced injection timing should be considered. The one which has received more attention recently is the increased flame temperature with biodiesel, caused either by an increase in the adiabatic flame temperature or by a reduction in the heat dissipation by radiation, as a consequence of the lower amount of soot emitted:

- Regarding the adiabatic flame temperature, some authors state that it is slightly higher for biodiesel [21,84,85]. However, no unanimity is found, since others maintain that it is higher for diesel fuels [40,74].
- Regarding the reduction in soot formation with biodiesel (see Section 4.1), Cheng et al. [86] carried out their tests with soybean-oil biodiesel and a reference diesel fuel, maintaining both the start of combustion and the rate of premixed combustion unchanged. Even in these conditions, they measured increased NO_x in the case of biodiesel, which they partly attributed to the reduced soot radiative heat transfer and the subsequent increase in flame temperature. In common-rail engines, where the physical properties of the fuels do not lead to any injection advance, the lower heat dissipation by the soot emitted from the use of biodiesel could explain the increased NO_x emissions.

Two other arguments frequently discussed to explain the higher NO_x emissions when biodiesel is used, although to a lesser extent than those mentioned above, are (1) the increased cetane number of biodiesel, which leads to an advanced combustion by shortening the ignition delay [53] and (2) the higher oxygen availability in the combustion chamber when using biodiesel, which could promote the NO formation reactions [87,88]. Schmidt and Van Gerpen [87] observed similar NO_x increases when using oxygen-enriched intake air as when using biodiesel but standard air, with the same additional oxygen content in both cases. Iida et al. [88] observed that enriching air with oxygen from 21% to 29% led to an exponential increase in NO_x emissions. Song et al. [89] showed that both the intake oxygen enrichment and the use of oxygenated fuels increase NO_x emissions. This increase was higher when oxygen enrichment was used rather than when using oxygenated fuels.

However, these two arguments are questionable. Higher cetane numbers may cause not only a combustion advance but a decrease in premixed combustion, the latter leading to softer pressure and temperature gradients, and thus to lower NO formation [87]. In fact, at least in the cases where premixed combustion is significant, most authors have shown decreases in NO_x emissions with higher cetane number fuels. Chang and Van Gerpen [90] observed that the more saturated the esters, the lower the NO_x emissions, and they attributed this effect to the increased cetane number of saturated esters. Also Graboski and McCormick [14] found NO_x decreases with increasing cetane numbers, although one of the co-authors of this work, McCormick, concluded in a subsequent study (McCormick et al. [91]) that cetane number has no effect on NO_x emissions in modern common-rail engines. The US EPA [92], in a different literature review from the one mentioned above, studied the effect of cetane enhancers on the combustion of conventional diesel fuels, and proved that, on average, NO_x emissions decrease with increasing cetane number.

Other authors provide arguments against that of oxygen availability. Lapuerta et al. [21,77] concluded that the oxygen content of biodiesel could not cause any increase in NO formation because diffusion combustion occurs mainly in regions with oxygen-fuel ratio around the stoichiometric one, which is 2.81 for biodiesel and 3.58 for a standard diesel fuel. The internal oxygen in the fuel molecule is not enough to compensate such a difference. Canakci [51] agreed to discard the oxygen content of biodiesel as a reason for the increase in NO_x emissions and pointed out the injection advance as a reason. Yuan et al. [64] did not find any correlation between NO_x emissions and oxygen content from their tests blending a conventional diesel fuel with different biodiesel fuels and with ethanol. Moreover, they did not find any correlation with combustion temperature either, thereby suggesting that thermal NO could be questioned as dominating path in NO formation.

Although less frequently, other hypotheses have been proposed to explain the increase in NO_x with biodiesel fuels. Some of them were proposed by Parker, collected and discussed by Graboski and McCormick [14]:

- The characteristics of the injected fuel. The fuel spray characteristics, such as droplet size distribution, droplet moment of inertia, air entrainment, penetration, fuel evaporation, and heat dissipation are all affected by the fuel properties: viscosity, surface tensio, and boiling temperature. All these physical phenomena may have some influence on the delay time, on the premixed/diffusion combustion ratio and, in consequence, on the NO formation.
- Nitric oxide formation through the prompt mechanism. The reactions governing the prompt mechanism are

sensitive to the concentration of radicals, which could be higher during the combustion of biodiesel.

- The reduced soot formation, which could eliminate the reactions between carbon and nitric oxide. However, very little knowledge about these reactions has been developed as yet.

To sum up, among all the reasons given to explain the increase in NO_x emissions, only the advance of injection start when compared to diesel fuel appears to be a solid argument, specially in the case of a pump-line-nozzle injection system, where apart from being advanced as a function of the accelerator position, the injection is affected by the pressure transmission speed through the injection line.

3.3. Effect of biodiesel characteristics

Some authors have reported differences in NO_x emissions from engines using different types of biodiesel fuel. Graboski et al. [56] tested a 11.1 l engine under a transient cycle with different pure methyl and ethyl esters and with biodiesel from different oils. Their results show that NO_x emissions increased as the mean carbon chain length decreased and as the unsaturation increased. The latter effect led to a linear relationship with the iodine number (which accounts for the number of double bonds in the ester molecule). Both effects can be shown in Fig. 4. They concluded that no increases in NO_x emissions should be expected in cases where the mean number of double bonds is below 0.5 or the iodine number is below 38. Otherwise, they did not observe significant differences between NO_x emissions from methyl and ethyl esters. Also Peterson et al. [93] observed increases in NO_x emissions with increasing values of the iodine number.

Graboski et al. [56] explained that iodine number is closely related to density, compressibility and cetane number, and suggested that the observed increase in NO_x could be caused by the above discussed effects on the injection or combustion timing rather than by the molecular unsaturation. In a literature review [46], the EPA confirmed the direct relationship between NO_x emissions and molecular unsaturation. They observed that on average, soybean-oil biodiesel provided a 15% increase in NO_x emissions as compared to those with diesel fuel, rapeseed provided a 12% increase, while biodiesel made from animal fats led to only a 3% increase. Wyatt et al. [94] found the same trend when observing that 20% blends of soybean-oil biodiesel provided a 3–6% increase in NO_x emissions as compared to those from similar blends of three animal fat-derived biodiesel fuels, and Tat [36] also observed increased NO_x emissions from soybean with respect to those measured from a more saturated waste-oil biodiesel.

Knothe et al. [95] compared conventional diesel fuel with oleic methyl ester (C18:1), palmitic methyl ester (C16:0) and lauric methyl ester (C12:0) in a 6-cylinder engine under transient conditions, and observed a 4% and 5% reduction in NO_x emissions for the saturated palmitic and lauric esters respectively, whereas a 6% increase for the oleic ester. The authors pointed out that the adiabatic flame temperature and the different intermediate combustion products were responsible for such differences. Finally, McCormick et al. [91] tested different pure biodiesel fuels and 20% blends with ULS diesel fuel with two high injection pressure engines, one of them equipped with common rail. They concluded that the effect of biodiesel unsaturation on NO_x reductions was less significant with the common-rail injection engines than with the older ones.

3.4. Measures to compensate the effect of biodiesel on NO_x emissions

Two types of measures have been proposed to eliminate the increase in NO_x emissions when diesel fuel is substituted by biodiesel. On the one hand, those involving a re-adjustment of the engine tuning, and on the other, those related to the selection or modification of the fuels to be used.

The injection cartographies are optimized by engine designers as a function of the NO_x-soot trade-off. Delaying injection has often been proposed to return the NO_x emissions level back to that observed with diesel fuel, although the advantage of lower soot or PM emissions is

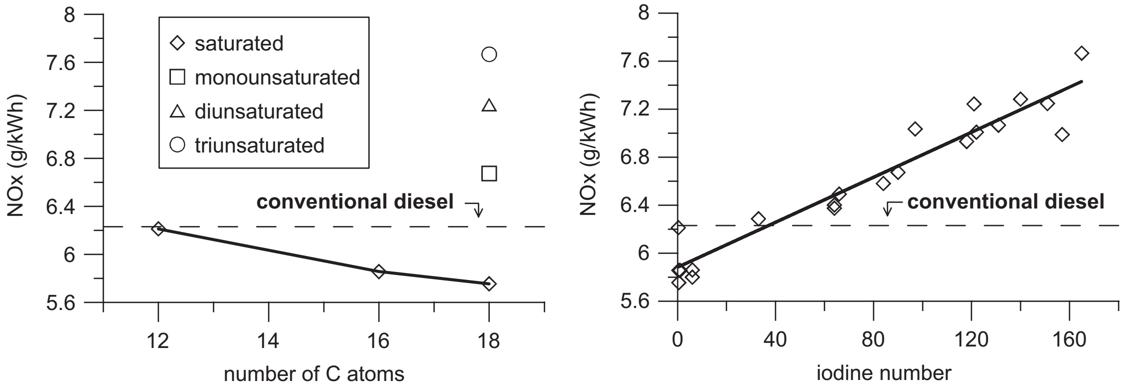

Fig. 4. Effect of the carbon chain length and the iodine number on the NO_x emissions, from different biodiesel fuels. Data obtained from [56].

then reduced [14,63,70,96]. For example, Graboski and McCormick [14] collected results from other papers and noted that NO_x and PM emissions varied $+10\%$ and -65%, respectively, in Detroit Diesel Corporation engines when using pure biodiesel instead of diesel fuel, while in Cummins engines these variations turned to 0% (NO_x emissions) and -25% (PM emissions). These differences were explained by the different engine optimization chosen by manufacturers. Leung et al. [97] proposed that other injection parameters, in combination with injection timing, should be modified in order to eliminate the expected NO_x emissions increase without any penalty in PM reductions. They proposed increases in the injection pressure or even changes in the size of some injection pump components. Last et al. [49] proposed a joint optimization of the injection process and the EGR. By just delaying injection until PM emissions are back to the same level as with diesel fuel, they observed that NO_x emissions could decrease to 20% when running their Navistar engine with 20% biodiesel blends. Furthermore, when they combined this with an increase in EGR they were able to decrease NO_x emissions to 30%, without incurring penalties in either other emissions or fuel consumption. To implement the corrections in injection timing, Tat and Van Gerpen [98,99] proposed a sensor whose response was proportional to the fuel dielectric constant, similar to those used in alcohol/gasoline flexible fuel vehicles (FFVs). They confirmed that, although this sensor was insensitive to the biodiesel characteristics, it provided a linear response with respect to the biodiesel content in the blends.

With regard to the selection of the biodiesel fuels, most of the proposals agree to select more saturated biodiesel fuels in order to reduce NO_x emissions. Chapman et al. [100] proposed to blend soybean-oil biodiesel with short-chain methyl esters such as caprilic (C8:0) or capric (C10:0) ones, in a proportion of 15% of short-chain esters. The short chain was required to avoid worsening the cold flow properties. They measured 2.8% decreases in NO_x emissions with 20% blends of biodiesel including short-chain esters as compared to those with 20% blends of unmodified biodiesel. They also achieved 1.5% reductions by hydrogenating the soybean-oil biodiesel. In a later work [101] these authors also hydrogenated the original soybean oil prior to transesterification. They obtained iodine numbers of 90 by turning linoleic (C18:2) and linolenic (C18:3) acids into oleic acid (C18:1). They measured reductions in NO_x emissions mainly at low engine speed. Szybist et al. [38] reached similar emissions as with ULS diesel fuel when they used 20% blends of modified soybean-oil biodiesel with increased oleic ester at the expense of linoleic ester, while NO_x emissions had previously been around 4% higher when blends were made with unmodified biodiesel. Other authors [102] propose to select a low aromatic content diesel fuel as a measure to compensate the increases in NO_x emissions when blending with biodiesel. McCormick et al. [102] estimated that reducing the aromatic content from 32% to 26% would be enough to avoid NO_x increases in the case of 20% blends, while others [103] did not find any effect. Additization has also been proposed in the literature for reducing NO_x emissions. Cetane enhancers as di-tert-butyl peroxide (DTBP) or ethyl hexyl nitrate (EHN) have been proposed [102] to decrease premixed combustion, but they were more effective with 20% biodiesel blends than with pure biodiesel, as they mainly enhance the diesel fuel cetane number rather than that of biodiesel fuel. Anti-oxidant additives have also been proposed to reduce NO_x emissions. McCormick et al. [102] observed reductions when using tert-butyl hydroquinone (TBHQ), while Hess et al. [104] found that butylated hydroxyanisole (BHA) was the most efficient in a selection of different anti-oxidant additives. Finally, Lin and Lin [105] proposed to use water-biodiesel emulsions to reduce NO_x emissions although they did not provide experimental confirmation.

4. Particulate matter and smoke opacity

4.1. Effect of biodiesel on PM and soot emissions and on smoke opacity

Although some authors have occasionally reported some increases in PM emissions when substituting diesel fuel by biodiesel [72,106,107], a noticeable decrease in PM emissions with the biodiesel content can be considered as an almost unanimous trend [14,21,53,67,75,80].

PM emissions data collected from a number of laboratory studies were used by EPA [46] to adjust the following equation, statistically significant with a 95% confidence level:

$$PM/PM_D = e^{-0.006384\%B}. \quad (3)$$

This equation provides a maximum reduction of PM emissions of close to 50% for pure biodiesel, as shown in Fig. 5. The share of the reviewed literature on this effect is presented in Table 2.

Krahl et al. [68] confirmed this general trend from their already cited collection of studies with rapeseed-oil

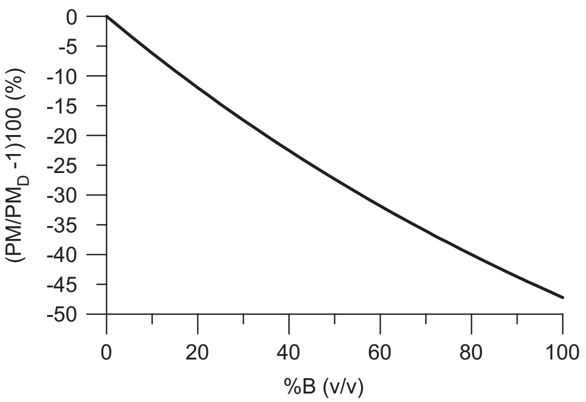

Fig. 5. Mean reduction in PM emissions as the biodiesel content increases (trend obtained from Ref. [46] for heavy-duty engines with no EGR or aftertreatmen system).

biodiesel. However, they noticed that PM emissions reductions were lower (or there were no significant reductions) in heavy-duty engines than in light-duty engines (20–40% reductions), and maximum reductions (around 40%) were reached in the case of indirect injection engines. Many studies reported reductions of the same order, either from PM emissions measurements [21,108] or from smoke opacity measurements [48,57]. Other authors found even higher PM emissions reductions with biodiesel. Among the studies collected in [32] reductions of up to 70% can be found with pure biodiesel and up to 45% with 20% biodiesel blends. Canakci and Van Gerpen [50] obtained 65% reductions from their above described tests with both soybean-oil and waste-oil biodiesel fuels, coincidentally with Schumacher et al. [109] with soybean-oil biodiesel. Extreme PM emissions reductions of 75% [110] and 91% [33] have also been reported.

A very small number of authors did not find significant reductions in PM emissions with biodiesel as compared with those with diesel fuel [47] or even found increases [48,76,106]. In these cases it is generally explained because the reduction in the insoluble fraction (ISF) of the PM (mainly composed of soot) was compensated by a sharp increase in the soluble organic fraction (SOF), which is widely accepted to be increased when using biodiesel [14,21,48,56,109]. Such an increase is probably caused by the lower volatility of the unburned hydrocarbons, which favours their condensation and adsorption on the particles surface. Yamane et al. [81] observed, by means of optical visualization of the fuel jet from the combustion chamber, that evaporation and air mixing were slower with biodiesel and used this to explain the typical increase obtained in SOF. Synergic effects can also be found in literature. Tinaut et al. [111] tested two vehicles under the New European Driving Cycle (NEDC) with pure and blended sunflower-oil biodiesel. Although pure biodiesel showed poor benefit (no decrease or only a slight decrease) in PM emissions, 5% and 10% biodiesel blends led to increases in PM emissions in both vehicles.

The reductions in PM emissions have been shown, in general, as being more effective with lower biodiesel concentrations in the blends, in agreement with Eq. (3) [46]. Haas et al. [54] obtained 20% reductions with 20% blends, while only 50% reductions with pure biodiesel. Lapuerta et al. [112] measured higher relative reductions (with respect to the biodiesel content) for 25% blends than for 50%, 75% and 100%. Not only under steady conditions but under transient ones, higher effectiveness has been reported with partial blends conditions, as in the study by Armas et al. [113], who measured the highest relative reductions in the smoke opacity peaks for 30% blends. Even Last et al. [49] reached the surprising conclusion that the reductions in PM emissions were around 30% when diesel was blended independently of the biodiesel proportion. On the contrary, other authors found linear reductions with the biodiesel content [14,56].

Other authors have studied the effect of biodiesel on PM emissions together with other parameters, such as the load conditions, the quality of diesel fuel used for blending, the type of engine or even the operation temperature. Most researchers found larger decreases in particle emissions at high load operation conditions [49,57,73,97]. Leung et al. [97] tested their single-cylinder engine with a diesel fuel and a pure biodiesel from rapeseed oil at different load conditions, and found larger decreases for biodiesel at high load operation modes. The authors explained this trend because particles are mainly formed during diffusion combustion, and at high load most of the combustion process is diffusive, meaning that the oxygen content of biodiesel may end up being more effective in reducing PM. Durbin and Norbeck [73] also found larger decreases at high load, but their explanation was the sharp increase in SOF at low load when biodiesel from yellow grease and soybean oil was used. On the contrary, Lapuerta et al. [112] measured larger decreases at low load conditions in their tests under a collection of low-middle load operation modes. Both Krahl et al. [114], with a 125 kW engine, and EPA [46], in their review already mentioned, found smaller PM decreases [46] or even no differences [114] when the biodiesel fuel was compared to a high-cetane ULS diesel fuel rather than to a conventional low sulfur one. Also the type of engine may have some effect, since EPA [46] found in their review that biodiesel further reduced PM emissions in 1991–1993 engines, by up to 60% with respect to the diesel fuel, but only by 35% in more modern or older engines. Coincidentally, the period 1991–1993 was the time at which new and more stringent regulations for PM and NO_x emissions came into force with the US Federal Test Procedure cycle. Finally, some other authors concluded that the general advantage of biodiesel in opacity may be reduced or even reversed when a cold temperature test is performed. Armas et al. [113] carried out several load, speed and start-up transient tests in a direct injection engine with two biodiesel fuels from waste oil and sunflower oil, pure and differently blended with a diesel fuel. All the transient tests, except the start-up one, showed noticeable decreases in smoke opacity when biodiesel content was increased. The reason given by the authors was that the higher viscosity and lower volatility of biodiesel make especially difficult the fuel atomization and evaporation in the cold conditions of the start-up period. Martini et al. [115] performed their test using the NEDC using three biodiesel fuels from different origins. During the urban part of the cycle, where the temperature was cold, the biodiesel increased PM by 40%. The slight decrease or even no decrease in PM emissions when substituting diesel by biodiesel (results obtained by Tinaut et al. [111] and commented above) could be a consequence of the cold engine temperature when starting the test cycle.

In any case, the reductions in PM emissions with biodiesel provide an interesting opportunity to re-optimize the engine emissions trade-off NO_x/PM together with the injection setting (injection timing combined with split

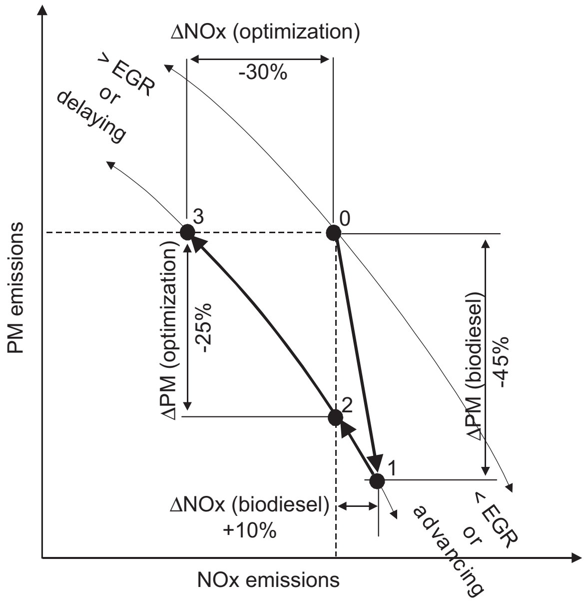

Fig. 6. Schematic diagram of the trade-off between NO_x and PM emissions, when combining the use of biodiesel fuels and engine optimization through injection setting and exhaust gas recirculation. Numbers are indicative values inferred from different literature studies.

injection and other injection parameters) and the EGR, by following the path 0-1-2 and lasting anywhere between points 2 and 3 (Fig. 6), depending on the aftertreatment system chosen. The numbers given in this figure are just indicative, and have been inferred from the data provided in the literature studies cited in Sections 3.1, 3.4 and 4.1.

4.2. Reasons for the reduction of PM emissions with biodiesel

Various reasons have been used to explain the reductions of PM emissions when using biodiesel or biodiesel blends:

- The oxygen content of the biodiesel molecule, which enables more complete combustion even in regions of the combustion chamber with fuel-rich diffusion flames [14,21,75,87,90,116,117], and promotes the oxidation of the already formed soot. Frijters and Baert [118] tested various biodiesel fuels among other oxygenates and found a good correlation between PM emissions and the oxygen content in the fuel. Schmidt and Van Gerpen [87] observed that the need for additional oxygen to get a certain reduction in PM emissions was lower when using oxygenates than when using oxygen-enriched air as combustion reagent. This experiment proved the advantage of fuel-oxygen as a consequence of its higher accessibility to the flame. In a heavy-duty single-cylinder research engine, Choi et al. [116] blended a conventional diesel fuel with 20% of octadecene ($C_{18}H_{36}$) and compared PM emissions with those provided by similar blends with soybean-oil biodiesel. Both components have the same saturation level (a single double bond per molecule) and atomic structure, but only the latter has oxygen in the molecule. They concluded that the effect of the composition and structure on PM emissions is negligible as compared to the oxygen content, which was acknowledged as the main factor causing PM emission reductions. Sison et al. [119] observed lower soot formation in the combustion chamber of a single-cylinder engine with optical access when using different oxygenates, including biodiesel, than with diesel fuel. Flynn et al. [120] developed a combustion kinetic model based on the Dec's conceptual model of diesel combustion [121]. They used mixtures of *n*-heptane and methanol or dimethyl ether as fuel. Their results showed sharp decreases in the formation of soot precursors when increasing the oxygen content in the fuel. As the oxygen content was increased, larger fractions of the fuel carbon were converted to CO in the rich premixed region, rather than to soot precursors. Another important issue is whether all the oxygenated fuels are equally effective in reducing particulate emissions. Mueller et al. [122] tested tri-propylene glycol methyl ether and di-butyl maleate (an ester), the former being more effective. The authors explained that the decarboxylation of the ester group (directly leading to CO_2 formation) only removed one carbon atom from the soot precursors, while the oxidation through CO (dominant in the case of the ether) removed two. In a subsequent study (Buchholz et al. [123]), the same authors confirmed the mechanism of decarboxylation of the ester groups when using di-butyl maleate as fuel, by applying a carbon-14 labeling technique. Recently, Szybist et al. [124] tested several fuels including methyl decanoate in a rapid compression machine, and again confirmed that largest amounts of CO_2 were formed in the case of esters through decarboxylation.
- The lower stoichiometric need of air in the case of biodiesel combustion [19,21], which reduces the probability of fuel-rich regions in the non-uniform fuel/air mixture.
- Absence of aromatics in biodiesel fuels, those being considered soot precursors [21,75,87,90]. The decrease in aromatic content obtained by Schmidt and Van Gerpen [87] by blending diesel fuel with octadecane ($C_{18}H_{38}$) provided a significant reduction in PM emissions, which was even more significant if soybean-oil biodiesel was also added in the blend. Knothe et al. [95] tested a 6-cylinder 14-l engine and obtained 45–50% reductions in PM emissions when using dodecane and hexadecane, and even higher reductions (73–83%) when using three pure methyl esters with respect to the PM emissions obtained with a diesel fuel with typical aromatic content. Despite the above mentioned conclusion obtained by Choi et al. [116], a detailed observation of their results reveal that PM emissions were reduced down to 25% in some operation modes when 20% octadecene blends were used, showing that the oxygen content was not in fact the only significant factor in the reduction of PM emissions.

- The combustion advance derived from the use of biodiesel. This effect, already discussed in Section 3.2, enlarges the residence time of soot particles in a high-temperature atmosphere, which in the presence of oxygen promotes further oxidation [80,87,90]. Choi et al. [116] observed that the sensitivity of this effect was higher as the injection was more advanced. Although differences in cetane number between diesel and biodiesel fuels are usually very small, the increased cetane number of biodiesel might also contribute to the combustion advance. However, most authors agree that this effect is minor [116,118,125].
- The different structure of soot particles between biodiesel and diesel fuels, which may also favor the oxidation of soot from biodiesel. Boehman et al. [39] used thermogravimetry to analyze soot particles obtained from diesel combustion (with both low and ULS diesel fuels) and from the combustion of 20% blends with soybean-oil biodiesel. After devolatilization by heating under inert atmosphere, the samples were again heated under oxidizing atmosphere, and the authors observed lower oxidation temperature in the case of biodiesel blends. From transmission electron microscopy (TEM) images they also found more amorphous and disordered arrangement of graphene segments for biodiesel soot as opposed to diesel soot. They concluded that the reactivity of biodiesel soot was higher. The same authors (Song et al. [126]) extended the work to pure soybean-oil biodiesel and from TEM images confirmed faster oxidation in the case of soot from pure biodiesel. They observed that the internal structure of primary particles tended to create hollow cavities probably caused by the internal oxygen of biodiesel molecules, and they suggested that this could favor faster oxidation. Jung et al. [127], measuring with differential mobility analyzers in a soot furnace, showed that the oxidation velocity of biodiesel soot was up to six times higher than that of diesel soot.
- The nil sulfur content of most biodiesel fuels, which prevents sulfate formation, this being a significant component of typical diesel PM [21,75,116], and the scrubbing effect, by which sulfur becomes an active center for hydrocarbon adsorption on the soot surface [128]. However, the importance of this argument is currently fading as the standards of sulfur content in diesel fuels are also being sharply reduced.
- The usually lower final boiling point of biodiesel, despite its higher average distillation temperature, provides lower probability of soot or tar being formed from heavy hydrocarbon fractions unable to vaporize [21].

Some of the above mentioned factors were comparatively studied by Ullman et al. [125] under a transient driving cycle. They used fuels with different sulfur, oxygen and aromatic content, and different cetane numbers. They concluded that neither cetane number nor aromatic content significantly affected PM emissions but that both oxygen and sulfur content did: 1% increases in oxygen content led to 6–7% reductions in PM emissions while 100 ppm decreases in sulfur content provided 3–5% reductions.

4.3. *Effect of biodiesel characteristics*

It is not clear from the literature reviewed whether or not PM emissions depend on origin of the biodiesel fuel. Some authors have reported results which suggest that biodiesel PM emissions depend somewhat on the feedstock. EPA [46], in their review, and Kado and Kuzmicky [110], in a 6-cylinder engine, found lower particulate emissions with biodiesel from animal fats than with biodiesel from vegetable oils, although no explanation was provided. Knothe et al. [95] tested their 6-cylinder 14 l engine with lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl esters, resulting in slightly higher PM emissions when the oleic ester was used. According to the authors, this was caused by its slightly lower oxygen content. Schmidt and Van Gerpen [87] found increases in SOF as the saturation level was increased, because of the lower volatility of saturated esters. Graboski et al. [56], in their previously mentioned study, tested different ethyl and methyl pure esters and conventional biodiesel fuels under a transient cycle for heavy-duty engines. Their results did not show any correlation either with the chain length or with the unsaturation level. They argued that PM emissions depend on the oxygen content, which is almost constant for every biodiesel or pure ester. However, there was some dependence on the density and cetane number. When the biodiesel density was higher than 895 kg/m^3 or the cetane number lower than 45 the PM emissions increased considerably. However, density should not be considered as intrinsically responsible for such PM emissions increases, although it could lead to indirect increases as the smoke correction systems limit the fuel volume injected during transient operation. Finally, other authors found no dependence on the biodiesel feedstock. Both Tat [36] and Canakci and Van Gerpen [50] tested a conventional diesel fuel and two biodiesel fuels from used cooking oil and soybean oil in similar engines. Both biodiesel fuels provided reductions in PM emissions as compared to the diesel fuel, but there was no difference between them. Haas et al. [54] tested diesel and biodiesel fuels with a different saturation level in a 6-cylinder direct injection engine. All biodiesel fuels provided 50% reductions in PM emissions, regardless of their saturation level. Similarly to Graboski et al. [56], Haas et al. [54] concluded that the main factor affecting PM formation is the oxygen content in the fuel.

It is also unclear if the alcohol used in the transesterification process has any effect on these emissions. While results reported by Graboski et al. [56], who tested several ethyl and methyl esters, showed apparently no dependence on this factor, results collected in [14] showed higher PM emissions when ethyl rapeseed biodiesel was used as opposed to methyl rapeseed biodiesel. This is consistent with the slightly higher oxygen content of the methyl ester.

4.4. Effect of biodiesel on particle size distributions (PSDs)

PSDs provide important information about the harmful effect of particulate emissions. It is widely accepted that such an effect is higher for smaller particles for various reasons: (a) longer residence time in atmospheric suspension [129], and thus higher probability of inhalation, (b) higher specific surface and thus higher capability to adsorb organic compounds, some of which are potentially carcinogenic [130–132], (c) higher capability to penetrate into the respiratory system, to be retained in the interstitial tissue of the lung or even to penetrate into the cardiovascular system [129–131], thus causing pulmonary or vascular diseases, and (d) lower filtrability in traps and filter, thus reducing the efficiency of aftertreatment systems [127,129]. It is difficult to evaluate the effect of biodiesel on the PSD because these are very sensitive to the dilution needed prior to the sampling and to the engine operating conditions [130,133]. This may cause wide disparities in the measurements. For example, Hansen and Jensen [48] found an almost 10-fold difference in mean diameter when they compared biodiesel and diesel fuels.

There are reasons which could explain both increases and decreases in the number of small particles emitted. On the one hand, the nil or very low sulfur content of biodiesel fuels could contribute to reduce the smallest particles, as sulfur has often been associated to the formation of the nucleation mode (consisting of particles below 50 nm) [129,134]. On the other hand, the increased viscosity of biodiesel and the electronic control system may lead to some increase in the injection pressure and to some injection advance, both changes being associated in the literature to an increased number of small particles [18,135].

However, the majority of authors have reported increases in the number of small particles with biodiesel. Krahl et al. [114,136] tested their engine under the ECE R49 test cycle with pure rapeseed biodiesel and two different (low and ultra-low sulfur) diesel fuels. They observed an increased number of particles in the 10–40 nm range, but reduced numbers of emitted particles above 40 nm, when the biodiesel was compared to the low sulfur diesel. Surprisingly, the number of particles emitted with the ULS diesel was larger than with biodiesel over the whole diameter range. These authors extended their study to additional pure soybean-, rapeseed- and palm-oil biodiesel fuels and their blends [137]. They again observed increases in particle number below 30 or 40 nm when measuring both with a scanning mobility particle sizer (SMPS) and with an electrical low-pressure impactor (ELPI). Jung et al. [127] tested an engine with pure rapeseed-oil biodiesel and diesel fuels and observed a 38% reduction in the number of particles with biodiesel and a decrease in the mean diameter of the PSD from 80 nm (with diesel) to 62 nm (with biodiesel). The reduction in particle concentration was especially sharp for particles above 50 nm, while the concentration of very small particles (below 10 nm) was observed to increase. Tsolakis [18] also used rapeseed-oil biodiesel and ULS diesel in three steady operation modes in a single-cylinder engine. They measured decreases in mean particle size and increases in particle number, when using biodiesel, by means of an ELPI. They also translated these results to obtain decreases in the mass of the emitted particles, although they used a questionable density of 1 g/cm^3 for the whole PSD. Munack et al. [106] tested rapeseed-oil biodiesel in an agricultural engine and observed an increased number of particles in the 10–180 nm range, but in a later work [131] they contracted such a range down to 10–20 nm.

Some other authors are in agreement with the global decrease in particle number and mean size, but did not observe significant increases in the number of small particles. For example, Lapuerta et al. [52] tested two biodiesel fuels from differently stressed waste oils under five selected steady modes and obtained a decrease in the mean diameter with respect to that obtained from a conventional diesel fuel. They proved that this was caused by a sharp decrease in the emission of large particles rather than by an increased emission of smaller ones. A similar result was found by Bagley et al. [108] in terms of particle volume. They found decreases in the submicron range up to 65% when using soybean-oil biodiesel in an indirect injection diesel engine.

A single study has been found reporting a decrease in the number of the smallest particles. Aakko et al. [134] tested a bus engine fuelled by rapeseed-oil biodiesel, pure and blended with diesel fuel and observed such a decrease from Berner low-pressure impactor (BLPI) measurements (in the 50 nm–10 μm range), ELPI measurements (40 nm–1 μm) and SMPS (10–400 nm). They attributed the decrease in the number of nucleation particles to the lower sulfur content of biodiesel (80 ppm) as compared to that of diesel fuel (400 ppm). In fact, the nucleation mode disappeared when they repeated some tests with a 10 ppm sulfur diesel fuel.

Finally, some other authors did not find any significant effect of biodiesel on the particle sizes. Turrio-Baldassarri et al. [47] tested rapeseed-oil biodiesel in 20% blends with diesel fuel in a 6-cylinder engine, and concluded from their TEM analysis that both particle size and morphology remained within the same range for all fuels. Chen and Wu [138] tested a single-cylinder engine under three steady modes and found no significant differences in the mean diameters of the PSD obtained with SMPS between diesel and soybean-oil biodiesel fuels, although they did find decreases in the mass (24–42%) and number (40–49%) of emitted particles. Lapuerta et al. [21] could only observe a sharp decrease in the number of particles but not in their size when they analyzed particulate filters by Scanning Electro Microscopy (SEM). Particularly unusual are the results presented by Bünger et al. [139], who used rapeseed-oil biodiesel and conventional diesel and measured with SMPS and BLPI. They did not find significant differences in the PSD obtained from SMPS, but their BLPI measurements allowed them to observe increased particle mass with biodiesel throughout the whole diameter range.

The dilution ratios used in the cited studies ranged from very low dilution (with dilution air/exhaust gas ratios below 12 [18,134,138]) to very high ones (above 200 [108,127]). Although similar dilution ratios were used to compare PSDs from biodiesel and diesel fuels in all cases, the conclusions reached could be affected by the increased contribution of nucleation mode (often associated with hydrocarbon condensation) as the dilution ratio was smaller.

5. Total hydrocarbons

5.1. Effect of biodiesel on THC emissions

Most authors' results show a sharp decrease in THC emissions when substituting conventional diesel fuel with biodiesel fuels [53,67,87,140–142]. The EPA review [46], already mentioned, shows a 70% mean reduction with pure biodiesel with respect to conventional diesel, according to Eq. (4) and Fig. 7:

$$THC/THC_D = e^{-0.011195\%B}. \tag{4}$$

However, a few studies may be found in the literature showing no significant differences [47,60,66,134] or increases [57] in THC emissions when fuelling diesel engines with biodiesel instead of diesel. Even decreases with high biodiesel percentages but increases at low percentages (synergic effects) have been reported [111]. Anyway, these surprising trends may be due either to the small content of biodiesel in the fuel [47,134] or to the very low THC emissions [60,66], close to the lower detection limit of the detectors, as is typical in diesel engines.

Rather similar reductions to the one supported by EPA (70%) were reported by other researchers. Nwafor [143] tested a research single-cylinder indirect injection engine with diesel and several blends of rapeseed-derived biodiesel. THC emissions with pure biodiesel were 60% lower than those with diesel fuel. Last et al. [49] tested biodiesel from soybean oil, finding 75% THC reductions with respect to a diesel fuel. Peterson and Reece [76] and Krahl et al. [136], both testing biodiesel from rapeseed oil, found higher than 50% THC reductions with their biodiesel. Other authors reported lower [68] or even higher [32] reductions. Finally, Alam et al. [144] found a 60% reduction when substituting ULS diesel fuel by biodiesel in a 6-cylinder engine.

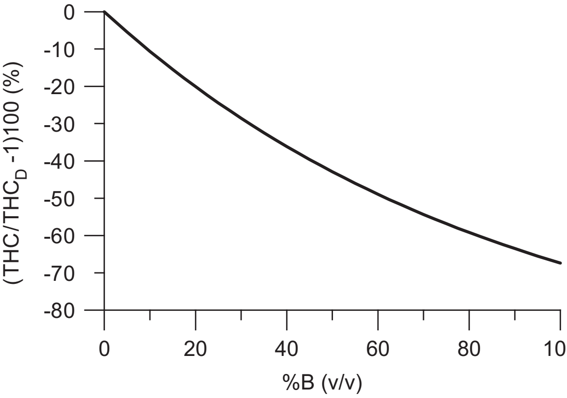

Fig. 7. Mean reduction in THC emissions as the biodiesel content increases (trend obtained from Ref. [46] for heavy-duty engines with no EGR or aftertreatment system).

An interesting issue is whether lower biodiesel concentrations are, relatively speaking, more effective than larger ones or not. According to Fig. 7 (data reported by EPA [46]), lower biodiesel concentrations are more effective. Results presented by Last et al. [49] also show the same trend. They tested 10%, 20%, 30%, 50% and 100% biodiesel from soybean oil in a heavy-duty engine. THC reductions with 10%, 20% and 100% biodiesel were 28%, 32% and 75%, respectively, so relatively larger reductions were reached with lower biodiesel contents. On the contrary, other works reported linear THC reductions. Results collected in [32] testing 100% biodiesel and 20% blends provided an approximately linear reduction with increasing biodiesel concentration. Peterson and Reece [76] carried out their experiments with several blends of methylic and ethylic biodiesel in a diesel fuel, resulting in a linear decrease of up to 50% with pure biodiesel.

As in Section 4, the influence of the biodiesel content together with some other parameters has been also analyzed. These parameters are the load conditions [21,77,145], the presence of an oxidative catalytic converter [106,134], the injection pressure [97] and the quality of the reference diesel fuel used for comparison [46,137]. Operation load does not seem to be a decisive factor since Charlet et al. [145], who tested biodiesel from rapeseed oil in a direct injection engine, and Lapuerta et al. [21,77], who fuelled an indirect injection engine with biodiesel from cardoon and sunflower oil, found approximately the same THC reduction ratios in all the modes tested. However, Muñoz et al. [146] found THC reductions when substituting conventional diesel fuel with biodiesel from sunflower oil only in low load operation modes. It is clearer how the oxidative catalytic converter affects THC emissions. Aakko et al. [134] tested a heavy-duty engine on the ECE R49 test cycle with diesel fuel and three biodiesel fuels from rapeseed, soybean and used cooking oil. THC emissions were reduced when biodiesel fuels were used, but this decrease was sharper when the engine was not equipped with a catalytic converter. The same conclusion was reached by Munack et al. [106] when testing rapeseed-oil biodiesel in an agricultural engine. The effect of injection pressure was studied by Leung et al. [97], but their results showed increases with increasing injection pressure with both diesel and biodiesel fuels. Finally, EPA [46] and Krahl et al. [137] studied the effect of diesel quality. EPA [46] found large THC reductions using pure biodiesel, but such reductions ranged from 70% when comparing with conventional diesel fuel to 50% when comparing with a high-cetane, low-density diesel fuel. Similarly, Krahl et al.

[137] reported 30–40% reductions if comparing biodiesel from rapeseed, soybean and palm oils with conventional diesel, and 20% when the reference fuel was a high-cetane, low aromatic content and ULS one.

An estimated share of the literature reporting decreases in THC emissions is presented in Table 2.

5.2. Reasons for the reduction of THC emissions with biodiesel

Several reasons have been proposed to explain the decrease in THC emissions when substituting conventional diesel for biodiesel:

- The oxygen content in the biodiesel molecule, which leads to a more complete and cleaner combustion [32,140]. Rakopoulos et al. [45] concluded in to their review that THC emissions decreased as the oxygen in the combustion chamber increased, either with oxygenated fuels or oxygen-enriched air.
- The higher cetane number of biodiesel [48,140,147] reduces the combustion delay, and such a reduction has been related to decreases in THC emissions [40,148].
- Although biodiesel is less volatile than diesel fuel, higher final distillation points have been reported for diesel fuel [31,47]. This final fraction of the diesel may not be completely vaporized and burnt, thereby increasing THC emissions.
- The advanced injection and combustion timing when using biodiesel. It is widely accepted that injection advance may contribute to slightly increased NO_x emissions with biodiesel, as explained in Section 3, but Storey et al. [149] also observed that the more advanced the injection, the lower the THC emissions.
- The flame ionization detectors (FIDs) conventionally used for measuring these emissions may have a lower sensitivity detecting oxygenated compounds, such as the ones that might be present in the exhaust gas when using an oxygenated fuel like biodiesel [48,117].
- The sampling line conducting part of the exhaust gas from the exhaust pipe to the measuring instrument is usually heated up to 190 °C to avoid hydrocarbon condensation in the line. Since biodiesel is a less volatile fuel, hydrocarbons with high molecular weights and high boiling points could remain in the exhaust gas. In this case, 190 °C may not be high enough to avoid their condensation [48,87,141], so these hydrocarbons could condense and not reach the FID.

Regarding the last reason, Chang and Van Gerpen [150] modeled the hydrocarbon condensation and adsorption on the PM, which is trapped in the filters not reaching the FID, in order to determine the effect of the sampling line temperature on those phenomena. They contrasted the results obtained from these models to those obtained from experimental tests carried out in a 59 kW engine fuelled with diesel fuel and 20%, 50% and 100% soybean-oil biodiesel. Their experimental results showed that THC emissions were 50% lower with pure biodiesel than with conventional diesel, and these emissions decreased with decreasing sampling line temperature regardless of the fuel used. The condensation model did not predict significant hydrocarbon losses by condensation, but the adsorption model predicted that 13–29% of the THC was adsorbed on the particle when using biodiesel, and only 1% with diesel fuel. Since the experimental reduction in THC emissions was 50% in this work and even greater in others, the adsorption of hydrocarbons could only partly explain the total THC reduction with biodiesel.

5.3. Effect of biodiesel characteristics

Most authors concluded in their works that the biodiesel origin is not a factor affecting THC emissions [36,46,50], unless pure esters were used [56,95]. Both Canakci and Van Gerpen [50] and Tat [36] tested diesel and two biodiesel fuels (from cooking and soybean oil) in their turbocharged, direct injection engines. They obtained 50% THC reductions when using pure biodiesel instead of diesel fuel, regardless of the origin of the biodiesel. Also EPA [46], in their review, found the same THC reductions (approximately 70%) both with saturated and unsaturated biodiesel. Results reported by Graboski et al. [56] when testing pure esters showed that THC emissions depend somewhat on their characteristics. They tested several pure methyl esters in an 11.1 l engine, resulting in higher reductions as the chain length or the saturation level of the esters was increased. Similarly, Knothe et al. [95] reported reductions in THC emissions with the increased biodiesel chain length when they fuelled a 6-cylinder engine with lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl ester, but they could not reach any conclusion about the saturation level.

The alcohol used in the production process showed no or little effect on these emissions. Graboski et al. [56], mentioned above, carried out some tests with methyl and ethyl pure esters and conventional biodiesel fuels, but a trend with the type of alcohol was not found. Peterson and Reece [76] reported 9% lower emissions when using ethylic biodiesel from rapeseed oil as opposed to the corresponding methylic biodiesel, which could be explained by the lower heat of vaporization of ethyl esters.

The presence of peroxides as a consequence of the biodiesel oxidation process may result in lower THC emissions. Monyem et al. [40] tested biodiesel before and after oxidizing it (after oxidation, the peroxide value was up to ten times more). THC emissions were lower with oxidized biodiesel and this was explained by the increased cetane number.

6. Carbon monoxide

6.1. Effect of biodiesel on CO emissions

With regard to most of the literature reviewed, a decrease in CO emissions when substituting diesel fuel with biodiesel can be considered as the general trend [32,46,48,140,147]. Nevertheless, a few authors found no differences between diesel and biodiesel [66], and even noticeable increases when using biodiesel [57]. After revising several works, EPA [46] proposed Eq. (5) for the general trend, leading to mean CO reductions of almost 50% with biodiesel with respect to conventional diesel fuel, as shown in Fig. 8:

$$\mathrm{CO}/\mathrm{CO}_D = \mathrm{e}^{-0.006561\cdot\%B}. \tag{5}$$

Other authors also found similar CO reductions values. Krahl et al. [136], after testing biodiesel from rapeseed oil, obtained approximately a 50% decrease with respect to both low and ultra-low sulfur diesel fuels. Peterson and Reece [76] fuelled a turbocharged engine with diesel and several biodiesel fuels, pure and differently blended. They concluded that the decrease in CO emissions with biodiesel was almost 50%. It is however possible to find lower reductions in other sources [32,49,68]. The report of a research project [32] showed 28–37% reductions in CO emissions when using pure biodiesel. Last et al. [49] tested a heavy-duty engine with biodiesel from soybean oil, and reported a slight decrease (14%) with respect to the reference diesel fuel. Krahl et al. [68] reviewed some studies and reported a mean 15% reduction when using biodiesel instead of diesel fuel. Tinaut et al. [111] tested two vehicles under the NEDC and reported an average reduction of 22% in CO emissions when comparing pure sunflower-oil biodiesel with a high sulfur diesel fuel. However, they measured CO increases when fuelling their vehicles with 5% and 10% biodiesel blends.

As in the case of THC emissions, linear [46,125] and non-linear [49,76] trends in CO emissions as biodiesel content is increased have been reported. Ullman et al. [125] fitted a linear correlation ($R^2 = 0.82$) between CO emissions and oxygen content in the fuel (not necessarily biodiesel). As already observed in Fig. 8, Eq. (5), adjusted by EPA [46], presents an almost linear trend. Graboski et al. (collected in [14]) tested pure biodiesel from soybean oil and 20%, 35% and 65% blends. A linear CO reduction resulted. On the contrary, Peterson and Reece [76] tested several biodiesel fuels, pure and blended with a diesel fuel, and reported a decrease in CO emissions of up to 50% in the case of pure biodiesel. This decrease was not linear, since 90% of the total CO reduction was reached in the blend range 0–50%. Last et al. [49] fuelled a heavy-duty engine with 10%, 20%, 30%, 50% and 100% soybean-oil biodiesel. All the blends reduced CO emissions with respect to the diesel fuel, but such decreases did not depend on the biodiesel percentage (10%, 8%, 18%, 6% and 14% reductions, respectively).

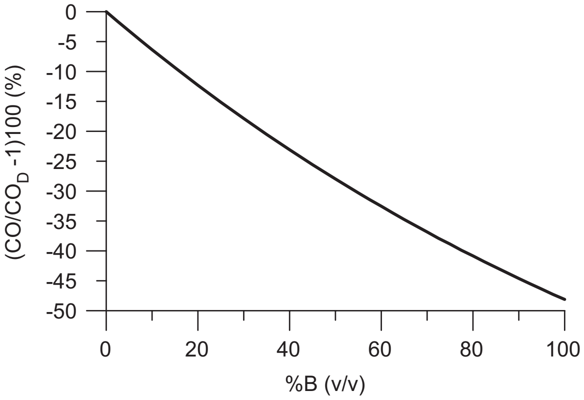

Fig. 8. Mean reduction in CO emissions as the biodiesel content increases (trend obtained from Ref. [46] for heavy-duty engines with no EGR or aftertreatment system).

Once again the effect of biodiesel content in the fuel together with the load conditions, the quality of diesel fuel and the use of an oxidative catalyst has been studied. Load conditions have been proved to have a remarkable effect on CO emissions. Most authors report CO decreases when using biodiesel except at low-load conditions. Choi et al. [116] tested their single-cylinder research engine with biodiesel from soybean oil. They reported no differences in CO emissions at low load and decreases with biodiesel at high load. Charlet et al. [145] performed the ECE R49 test cycle in a heavy-duty engine. Although biodiesel decreased CO emissions in most of the modes, this trend was reversed at idle, where biodiesel increased CO up to 60%. The same trend was found by Silva et al. [27] when testing the ECE R49 test cycle. In contrast, Alam et al. [37] reported a higher decrease in CO emissions when using biodiesel at low load. Other studies focused on the effect of the quality of the diesel fuel used as reference [37,46,137]. In their review, EPA [46] showed 45% CO mean reductions when biodiesel was compared to conventional diesel and 35% when it was compared to a clean diesel (high-cetane number, low density). Alam et al. [37] tested a 20% blend (from soybean-oil biodiesel), which reduced CO emissions with respect to two diesel fuels (low and ultra-low sulfur). Such reductions were lower when comparing with low sulfur diesel. Also Krahl et al. [137] found lower CO reductions when pure biodiesel fuels were compared to those obtained with high-cetane low sulfur diesel fuels (one of them from gas-to-liquid production) rather than a conventional one, although in another study [114] the same authors did not find this trend. The use of an oxidation converter has been found to have some importance, since Aakko et al. [134] and Munack et al. [106] showed in their works that biodiesel fuels reduced CO emissions when the engines were not equipped with the converter, but increases were found when they were.

An estimated share of the literature reporting decreases in CO emissions is presented in Table 2.

6.2. *Reasons for the reduction of CO emissions with biodiesel*

Several reasons have been reported to explain the general CO decrease when substituting conventional diesel for biodiesel:

- The additional oxygen content in the fuel, which enhances a complete combustion of the fuel, thus reducing CO emissions [32,125,140]. For example, Rakopoulos et al. [45] reported lower CO concentration in the exhaust line when oxygen in the combustion chamber was increased either with oxygenated fuels or oxygen-enriched air.

- The increased biodiesel cetane number [48,125,140,147]. The higher the cetane number, the lower the probability of fuel-rich zones formation, usually related to CO emissions [151]. Sharp, as collected in [14], presented tests with diesel fuel and two 20% blends (with and without a cetane enhancer). He reported a higher CO reduction with the additivated blend.
- As commented in other sections, the advanced injection and combustion when using biodiesel may also justify the CO reduction with this fuel. Storey et al. [149] adjusted the injection timing when fuelling their 1.7 l engine with a diesel fuel. They reported reductions in CO emissions when the injection timing was advanced.

Regarding the first two reasons, Ullman et al. [125] made an interesting study. They tested a set of fuels designed to assess the effect of several parameters (aromatic content, oxygen content, cetane number) on CO emissions. They fitted their measurements to a linear equation ($R^2 = 0.82$) that showed CO reductions as both the cetane number and the oxygen content in the fuel were increased.

6.3. *Effect of biodiesel characteristics*

The effect of the biodiesel feedstock on CO emissions has also been studied. EPA [46] concluded, based on their review, that CO reductions were higher if biodiesel from animal fat was used instead of biodiesel from rapeseed or soybean oil (rapeseed oil provided higher reductions than soybean oil). This result seems to indicate that CO emissions decrease as the saturation level is increased. The same was found by Graboski et al. [56] when they tested conventional biodiesel fuels (from vegetable oils, cooking oil, etc.) but not when testing pure methyl esters. Canakci and Van Gerpen [50] and Tat [36] found CO reductions when comparing biodiesel (from both cooking oil and soybean oil) with diesel fuel, but there was no difference between the types of biodiesel fuels. Knothe et al. [95] fuelled their engine with lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl esters, and reported lower CO emissions as the chain length was increased.

Other authors studied the effect of biodiesel acidity and oxidation on CO emissions. Hamasaki et al. [57] tested their single-cylinder engine with diesel fuel and three biodiesel fuels from cooking oil. The acid values of the biodiesel were different, from 0.33 to 0.90 mg KOH/g. CO emissions were increased as the acid value was increased. The authors explained that this trend could be caused by a higher hydroperoxide concentration as the acid value was higher, since they participate in CHO, HCHO and CO formation reactions. Monyem et al. [40] tested oxidized and unoxidized biodiesel (see Section 5) and found lower CO emissions in the case of the oxidized biodiesel, which had a higher cetane number.

7. Other non-regulated emissions

7.1. *Introduction*

Some hydrocarbons and oxygenates emitted by diesel engines are hazardous for human beings or environmentally dangerous, although they are not generally limited by regulations. This is the case of polyaromatic hydrocarbons (PAHs) and aldehydes. The information given in literature about the effect of biodiesel on the emission of these compounds is scarce, has low repeatability [14,46] and is often questioned by the authors themselves. EPA concluded from its above mentioned review [46] that the emissions of toxic compounds was lower with biodiesel than with diesel fuel by about 16% in the case of pure biodiesel. This reduction is lower than that of THC (see Fig. 7), which means that the concentration of toxics in the emitted hydrocarbons is higher for biodiesel. EPA identified eleven compounds as toxics: acetaldehyde, acrolein, benzene, 1,3-butadiene, ethyl-benzene, formaldehyde, *n*-hexane, naphthalene, styrene, toluene and xylene. Among the PAH, naphthalene and phenanthrene are those with typically highest concentration in diesel exhaust gas.

7.2. *Aromatic and polyaromatic compounds*

Aromatic compounds and derivatives are toxic, mutagenic and carcinogenic, especially benzene, and they contribute to the formation of tropospheric ozone [68]. The intensity of these effects depends on their structure and on how they mix with each other. These synergies make it very difficult to predict the carcinogenic or mutagenic effects of the mixtures.

Most authors have observed some decrease in the aromatic and polyaromatic emissions when using biodiesel [14,80,140], although a noticeable dependency on engine operation conditions (load, driving cycle, etc.) is usually acknowledged [14,114]. The National Biodiesel Board (NBB) [79] estimated reductions in PAH and nitro-PAH of about 80% and 90% respectively. Although some authors state that these compounds can be formed during combustion [48], the observed reductions are mainly a consequence of the absence of PAH in biodiesel fuels [140]. From a literature review, Krahl et al. [68] concluded that PAH emissions decreased when rapeseed-oil biodiesel was used for all engine types and operation conditions. However, no such clear conclusions were obtained about total aromatic emissions, since benzene and benzene-related compounds showed occasionally some increases with biodiesel. The Handbook of Biodiesel [32] presented reductions in the PAH emissions of 12% an 29% as compared to those from diesel fuel, when tests were carried out with 20% biodiesel blends in a Cummins and a DDC engine respectively. These reductions reached up to 74%

and 68%, respectively, when pure biodiesel was used. Some authors [47,140,152] explained that the observed reductions in PAH emissions are caused by an enhanced adsorption of these compounds in the PM. Among these authors, Kado et al. [152] tested different blends of rapeseed ethyl ester and diesel fuel in a 5.9 l engine under the heavy-duty transient EPA cycle, and proved that PAH emissions were reduced in most cases, but were highly affected by the initial test conditions and by the presence of an oxidizing catalyst. In fact, they observed some increases in non-volatile PAH emissions when the cycle was started in hot conditions and the engine was equipped with an oxydizing catalyst. No effect on the volatile PAH emissions could be observed at these conditions as they were below the detection limit. A similar conclusion was obtained by Bagley et al. [108], who could only observe reductions in PAH emissions when no oxidizing catalyst was mounted in their naturally aspirated indirect injection engine. Lin et al. [25] tested palm-oil biodiesel, pure and 20% blended with ULS diesel fuel, in a naturally aspirated 2.84 l engine. They observed reductions in PAH emissions of 43% with the blend and of 90% with pure biodiesel. All the PAH groups (heavy, medium and light) were proved to contribute to these reductions. In their literature review, EPA [46] concluded that some aromatic emissions, such as those of ethylbenzene, naphtalene and xylene showed consistent reductions with biodiesel, while others, such as those of styrene, benzene and toluene presented very variable results, which did not allow them to reach any conclusion. Hansen and Jensen [48] analyzed 15 PAH in the engine emissions from diesel and rapeseed-oil biodiesel fuels. The only PAH detected when biodiesel was used was phenanthrene and it was eight times lower than with diesel fuel. Staat and Gateau [67] found reductions in the emissions of naphtalene and methyl-2-naphtalene which were proportional to the rapeseed-oil biodiesel content in the blends used. Tritthart and Zelenka [153] analyzed ten different PAH, and observed reductions in their overall emissions, but did not observe significant reductions in four which had specific biological activity: chrysene, benzo(a)fluoranthene, benzo(b)fluoranthene and indene. Wörgetter [154] compared 13 PAH emissions from diesel and rapeseed-oil biodiesel fuels. All of them were reduced with biodiesel by more than 50%, and some of them, such as phenanthrene and anthracene were reduced by 90%. Sharp et al. [155] found reductions between 50% and 75% in the PAH and nitro-PAH emissions when using biodiesel fuels in their tests with three different engines.

A minor number of authors did not observe significant differences in PAH emissions between diesel and biodiesel fuels. This is the case of Mittelbach and Tritthart [156], who analyzed the same ten compounds as Tritthart and Zelenka [153]. Turrio-Baldassarri et al. [47] only found significant reductions in toluene emissions but not in any of the analyzed PAH or nitro-PAH. Munack et al. [106] proved, from their tests in a single-cylinder 4.2 kW engine, that increasing proportions of blended rapeseed-oil biodiesel provided increasing benzene emissions. They also tested a 52 kW engine and observed a slight increase in aromatic emissions. They concluded that there is no relationship between the fuel aromatic content and the aromatic content in exhaust emissions. Also Ballesteros et al. [157] found increased benzene, toluene and xylene emissions from waste-oil biodiesel when they tested their 2.2 l engine under an operating mode with high THC emissions. Pedersen et al. [158] measured higher benzene emissions from a combustor at 550 °C fuelled with rapeseed-oil biodiesel as compared to ULS diesel fuel. They proposed that these emissions were related to the content of linolenic ester (C18:3) in the biodiesel fuel. In order to investigate whether such effect could be extended to diesel engines or not, Krahl et al. [114,136] tested a 125 kW engine under the ECE R49 test cycle and observed that aromatic emissions, including benzene, were lower when biodiesel fuel was used.

7.3. *Oxygenated compounds*

The oxygenated compounds more frequently studied in diesel exhaust are aldehydes and ketones, which appear in intermediate phases of the combustion process. These compounds are precursors of ozone formation (and other oxidative species) in the troposphere (photochemical smog). It is widely believed that biodiesel could increase emissions of these oxygenated compounds as a consequence of the oxygen content in the molecule. In fact, some papers report increases when using pure or blended biodiesel as fuel [67,140,153,157]. However, from the literature reviewed it is not clear whether or not biodiesel really increases these emissions, since many other studies find some decreases or insignificant differences [46,47,106,155]. In any case, arguments can be found to explain that, despite their higher oxygen content, the decomposition of esters via decarboxylation [123,124] could decrease the probability of forming oxygenated combustion intermediates with respect to conventional diesel combustion.

Staat and Gateau [67] tested conventional diesel, and 30% and 50% blends (from rapeseed oil) in a 6-cylinder engine. Aldehyde emissions with 30% biodiesel did not significantly differ from those with diesel fuel, but an increase of approximately 9% was measured when testing a 50% blend. Tritthart and Zelenka [153] and Hansen and Jensen [48] found 25% increases in different collections of oxygenated compounds (formaldehyde, acrolein, etc.) when substituting diesel by pure rapeseed biodiesel. Costa Neto's results, collected by Pinto et al. [140], showed a 20% increase in formaldehyde and acetaldehyde emissions when testing pure biodiesel from cooking oil instead of diesel fuel. Ballesteros et al. [157] fuelled their engine with diesel, and biodiesel from pure cooking oil and a 70% blend. Although oxygenated emissions did not differ when comparing diesel and the 70% biodiesel blend, pure biodiesel considerably increased ketone and aldehyde emissions.

Other authors presented inconclusive results or insignificant differences between diesel and biodiesel. Munack et al. [106] tested two different engines in five operation modes from an agricultural cycle. In one engine they only tested pure diesel and rapeseed biodiesel, resulting in higher aldehyde emissions in the case of biodiesel. In the other engine, the authors also tested a 40% blend. Pure biodiesel emissions were now lower than those from diesel, but the 40% blend emissions were the highest. Turrio-Baldassarri et al. [47] reported a statistically significant increase in formaldehyde but no significant differences in acrolein, acetaldehyde and propionaldehyde when testing a 20% biodiesel (from rapeseed oil) blend in a 6-cylinder engine. Several studies revised by Graboski and McCormick [14] in their review showed no differences in oxygenated emissions between diesel fuel and pure and blended biodiesel.

Other studies have been found showing decreases in these emissions when testing biodiesel fuels. The review of EPA [46] reported slight decreases, of around 10%, in formaldehyde and acetaldehyde emissions when using pure biodiesel. Krahl et al. [114] measured the concentration of 13 specific oxygenated compounds when using pure rapeseed-oil biodiesel and both low and ultra-low sulfur diesel fuels. The concentration of almost every compound was decreased by around 30% with biodiesel. Sharp et al. [155] carried out their test in three engines (119, 205 and 276 kW) with diesel and pure biodiesel from soybean oil. They concluded that aldehydes and ketones were reduced in the range of 0–30% when using biodiesel. Also absolute reductions in three specific aldehyde emissions were found in [33], although the relative reductions with respect to conventional diesel were not reported by the authors.

Finally, the quality of biodiesel (regarding the content in mono, di and triglycerides, glycerin) used as fuel has shown some effect on oxygenated emissions. Some authors propose that acrolein concentration in the exhaust is related to the glycerin content in the biodiesel fuel used [14,57,67]. Different biodiesel fuels were tested by Graboski et al. [56], one of them resulting in a sharp increase in aldehyde emissions. Authors explained that this trend was caused by the high glycerin content of that biodiesel.

8. Conclusion

A wide disparity of results has been found in general concerning emissions from biodiesel. Although a dominant trend has been found in most cases, there have always been opposing trends proposed elsewhere by contrast. One reason for this is the large number of different engine technologies tested, the varying operating conditions or driving cycles followed, the different biodiesel fuels used (from different feedstocks and with different qualities), and the various measurement techniques and procedures applied. Especially with regard to the instrumentation or the methodology used for measurements, several studies have been found wanting in fulfilling the expected quality requirements. The following general conclusions could however be proposed from the present literature review:

- At partial load operation, no differences in power output should be expected, since an increase in fuel consumption in the case of biodiesel would compensate its reduced heating value. At full-load conditions, a certain decrease in power has been found with biodiesel, but such a decrease is lower than that corresponding to the decrease in heating value, which means that a small power recovery is often observed.
- An increase in *bsfc* has been found when using biodiesel in most of the reviewed studies. Such an increase is generally in proportion to the reduction in heating value (9% in volume basis, 14% in mass basis). Consequently, the thermal efficiency of diesel engines is not appreciably affected when substituting diesel by biodiesel fuel either pure or blended.
- Most of studies report slight increases in NO_x emissions when using biodiesel fuels. The reason most frequently pointed out is that the injection process is slightly advanced with biodiesel. The physical properties of biodiesel or the response of the electronic unit could cause such an advance. Some authors propose delaying injection as a mean to eliminate the increase in NO_x emissions, with a minor penalty in particulate emissions.
- The majority of studies have found sharp reductions in particulate emissions with biodiesel as compared to diesel fuel. This reduction is mainly caused by reduced soot formation and enhanced soot oxidation. The oxygen content and the absence of aromatic content in biodiesel have been pointed out as the main reasons. Under cold-start conditions the mentioned reduction could be eliminated or even reversed to result in a certain increase.
- The majority of authors have reported decreases in the mean diameter of the PSDs obtained when biodiesel fuels are used. Although such a shift is mainly caused by a sharp decrease in the number of large particles, some studies have also found a certain increase in the number of the smallest ones.
- Other regulated emissions such as those of THCs and CO are usually found to significantly decrease with biodiesel. A more complete combustion caused by the increased oxygen content in the flame coming from the biodiesel molecules has been pointed out as the main reason in both cases.
- The emission of aromatic and polyaromatic compounds, as well as their toxic and mutagenic effect, has been generally considered to be reduced with biodiesel. However, no conclusive trend has been found regarding the emissions of oxygenated compounds such as aldehydes and ketones. Further studies should be performed in this field in the future.

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