

NO_x EMISSIONS FROM A DIESEL ENGINE FUELLED WITH FATTY ACID METHYLESTERS MIXTURES

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ABSTRACT

One of the most challenging barriers to biodiesel utilization is the widely reported slight increase in NO_x emissions when compression-ignition engines are fuelled with neat or blended biodiesel fuels instead of neat conventional diesel fuels. To gain further insight into the effect of biodiesel chemical structure, specifically its degree of unsaturation, on the NO_x emissions of automotive diesel engines, an experimental investigation was conducted on a high speed direct injection diesel engine fuelled with three mixtures of fatty acid methyl esters, covering a wide range of concentrations of the most common molecules contained in commercial biodiesel fuels. Results indicate that engine performance and injection timing are not significantly affected by the degree of unsaturation of the biodiesel fuel. A lower degree of unsaturation leads to higher cetane numbers, shorter ignition delays and consequently more advanced combustion timings. Although these conditions could favor the formation of NO_x inside the combustion chamber due to a possible increase of the residence time of the combustion products at high temperatures, the higher cetane number of the less unsaturated biodiesel fuels also leads to less premixed burning and so lower combustion rates, which finally results in lower in-cylinder bulk-gas-averaged temperatures during the closed valves period. Comparing biodiesel fuels, it is found that as the degree of unsaturation decreases, the cetane number increases leading to a net reduction in NO_x emissions.

Key words: biodiesel, NO_x emissions, diesel combustion

1. Introduction

It has been widely demonstrated that biodiesel fuels are suitable for fuelling compression-ignition engines. Numerous experimental and theoretical research works have been carried out in order to compare engine performance, combustion characteristics and emissions, when neat or blended biodiesel fuels are used instead of conventional petroleum diesel fuels. Comprehensive reviews analyzing the results of most representative works have been presented by Grabosky and McCormick in 1998 [1] and Lapuerta et al in 2008 [2]. Regarding engine emissions, there is a wide consensus that biodiesel fuelling tends to decrease significantly exhaust levels of regulated emissions including particulate matter (PM), total hydrocarbons (THCs) and carbon monoxide (CO). In the case of nitrogen oxides (NO_x), although the highest consensus lies in a slight increase of those emissions with biodiesel fuelling, some contradictory trends have been reported. It has been argued, that much of the disparity reported in measured exhaust NO_x emissions may be partly a consequence of the variability in the experiments [2-4]. Experimental tests may differ in engine technology, engine speed and load, ambient conditions, principle and resolution of the measurement apparatuses and sensors, and so on. A simple systematic issue, often not sufficiently weighted, is the nature of the tested fuels: the specific biodiesel fuel used and the diesel fuel either used as comparison base or for blends preparation.

The term biodiesel fuels is intentionally used in this manuscript to highlight that biodiesel is not a unique compound. From a chemical standpoint, a biodiesel fuel is a mixture of monoalkyl esters of fatty acids. An essential feature of a biodiesel fuel is that its fatty acid profile corresponds to that of its parent oil or fat. Thus, biodiesel fuels derived from different feedstocks may have significantly varying compositions and properties.

The main structural features that influence the physicochemical properties of a fatty acid alkyl ester molecule are the chain length and branching of the alkyl group, and the length, branching and number of double bonds of the fatty acid chain. Most commercial biodiesel fuels are mainly composed of natural medium to long-chain (C₁₆-C₁₈) fatty acid methyl esters for which the main structural difference is consequently the number of double bonds. As the interest for widening the possible raw materials for biodiesel production has increased worldwide and the research community has realized the significance of the effect of molecular structure on biodiesel fuel properties, it has grown the number of research

works trying to explain the consequent effect of the structural features of the fatty acid alkyl esters, mainly chain length and unsaturation degree, on engine performance, combustion characteristics and emissions. Results are not conclusive yet and in some cases are contradictory.

Tat et al [5] compared the NO_x emissions of a John Deere 4045T direct-injection diesel engine fuelled with regular soybean oil biodiesel (high content of poly-unsaturated fatty acid methyl esters) and with a high-oleic soybean biodiesel (high content of monounsaturated fatty acid methyl esters) produced from a genetically modified oil. Results showed a significant reduction in NO_x emissions using the high-oleic soybean biodiesel.

Lapuerta et al [6] carried out an experimental work in order to determine the effect of the degree of unsaturation of biodiesel fuels on NO_x and particulate emissions from a direct injection diesel engine typical of those used in European cars. Four biodiesel fuels produced from different feedstock and having iodine values ranging from 90 to 125 were tested. Results showed that the degree of unsaturation of biodiesel fuels had significant effects on the NO_x emissions. As the biodiesel fuel became more unsaturated, NO_x emissions increased.

Puhan et al [7] tested three types of biodiesel fuels with different molecular weight and degree of unsaturation in order to study the effect of molecular structure on the combustion characteristics and emissions of a single-cylinder direct injection diesel engine. Biodiesel fuels were prepared from linseed, jatropha and coconut oils. More unsaturated biodiesel fuels exhibited higher heat release rates, ignition delays, advancements in fuel injection timing; maximum gas pressures and exhausts gas temperatures. Emissions of NO_x also increased with the degree of unsaturation.

Schönborn et al [8] conducted a series of experiments on a single-cylinder research engine investigating the influence of molecular structure on the combustion behavior of fatty acid alkyl ester molecules under diesel engine conditions. The tested fuels comprised eight samples of pure individual fatty acid alkyl esters molecules of different structure, as well as four biodiesel fuels produced by the transesterification of rapeseed oil, palm oil, jatropha oil and tallow. It was observed that the structure of the fuel significantly influenced the formation of NO_x and particulate matter and their respective concentration in the exhaust

gas. The influence on the formation of NO_x in particular, appeared to be exerted first through the effect which the molecular structure had on the auto-ignition delay, and second through the flame temperature at which the various molecules burned.

The aim of the present work is to contribute to the understanding of the effect of the degree of unsaturation of biodiesel fuels on the NO_x emissions of automotive diesel engines. Therefore, an experimental work was conducted on a high speed direct injection diesel engine fuelled with three mixtures of fatty acid methyl esters covering a wide range of concentrations of the most common molecules contained in commercial biodiesel fuels (methyl esters of palmitic acid C16:0, oleic acid C18:1, linoleic acid C18:2 and linolenic acid C18:3).

2. Experimental conditions

Test fuels

Three fuel samples called BFL (biodiesel fuel-low unsaturation), BFM (biodiesel fuel-medium unsaturation) and BFH (biodiesel fuel-high unsaturation) were prepared by mixing methyl esters produced by the basic transesterification of palm and linseed oils. As can be seen in table I, test fuels are mixtures of the most common methyl esters found in commercial biodiesel fuels covering a representative range of unsaturation degree.

Table I. Chemical composition of test fuels (% mass)

Type of methyl ester		BFL	BFM	BFH
Lauric	12:0	0.31	0.17	0.00
Miristic	14:0	1.03	0.60	0.00
Palmitic	16:0	43.3	25.9	5.30
Stearic	18:0	4.20	4.10	3.90
Palmitoleic	16:1	0.15	0.12	0.07
Oleic	18:1	41.8	32.1	20.5
Linoleic	18:2	9.10	12.8	17.1
Linolenic	18:3	0.15	24.3	53.1
Total unsaturated		51.1	69.2	90.8

The physicochemical properties of the test fuels were determined according to recommended standard methods or by means of simple mixing rules or empirical correlations.

The iodine value (IV) of pure methyl esters was calculated as a function of their molecular weight and number of double bonds. For the test fuels, the IV was estimated by multiplying the mass percentage of the unsaturated methyl esters by their respective IV.

Cetane numbers of the test fuels were estimated as a function of the reported cetane numbers of the individual methyl esters by a weighted mass average.

Experimental equipment

Tests were carried out in an instrumented automotive diesel engine whose specifications are given in Table II. The engine was coupled to a 230 kW Eddy current dynamometer (Schenck W230). Air and fuel consumptions were measured with a hot-wire sensor (Magnetrol TA2) and an electronic balanced mass flow sensor, respectively. NO_x emissions were measured by a Horiba EXA 240CL chemiluminescence analyzer. In-cylinder combustion diagnosis was carried out using a two species (air and combustion products), single-zone model, based on the approach proposed by Lapuerta et al [9]. Atmospheric pressure was taken into account in the pressure signal processing. For recording the instantaneous in-cylinder pressure, a Kistler 6056A piezoelectric pressure transducer installed in the glow plug and a Kistler 5011B charge amplifier were used. One hundred pressure curves were registered in each engine operation mode in order to guarantee confidence in the combustion diagnosis. The instantaneous piston position was determined using an angular encoder with a resolution of 1024 pulses/revolution (Heidennhain ROD 426) coupled to the crankshaft at the opposite extreme of the fly-wheel. The angle of start of injection was measured with a clamp-on transducer connected to an AVL DICOM 4000 analyzer. High speed data were acquired using *Tone*[®] LabView based software and National Instruments[™] data acquisition system (Model PCI-MIO-16E-4 board).

Test conditions

All tests were conducted under a single operating mode characterized by an engine load and an engine speed of 95 Nm and 2420 rpm, respectively. That operating mode yielded the

minimum air-fuel ratio and maximum smoke opacity among the collection of steady operating modes that reproduce the Federal test procedure (FTP-75) homologation cycle. Before starting experiments with a new fuel, lines were drained, fuel was then added and the engine operated at least for one hour in order to purge any fuel remaining from previous experiments. Runs with the different fuels were conducted without any modification of the engine or fuel injection system. The experiments were carried out at 1500 m above sea level (atmospheric pressure of 640 mmHg).

Table II. Test engine characteristics

Reference	ISUZU 4JA1
Type	Turbocharged, direct injection, rotating pump
Swept volume	2499 cm ³
Configuration	4 in-line cylinders
Diameter x stroke	93 mm x 92 mm
Compression ratio	18.4
Rated power	59 kW (80 hp) at 4100 rpm
Maximum torque	170 Nm at 2300 rpm

3. Results and discussion

Fuel properties comparison

Table III presents the chemical formula, molecular weight, oxygen content and iodine value of the test fuels and pure unsaturated methyl esters. Table IV lists the main physicochemical properties of the test fuels. As can be seen in table III, the average chain length of the biodiesel fuels varied within a narrow range (from 18.04 to 18.88) indicating that the main structural difference among them was their degree of unsaturation. For pure methyl esters, the oxygen content increases slightly with unsaturation degree due to the decrease in molecular weight associated with the displacement of two hydrogen atoms by each double bond. In the case of the test fuels, the more unsaturated biodiesel fuel had the lowest oxygen content as a consequence of the higher sensitivity of molecular weight to chain length.

Table III. Chemical characteristics and iodine value of test fuels

Compound	Chemical formula	Molecular weight	Oxygen content (% mass)	IV g I ₂ /100g
Methyl oleate	C ₁₉ H ₃₆ O ₂	296.50	10.79	85.6
Methyl linoleate	C ₁₉ H ₃₄ O ₂	294.49	10.87	172.4
Methyl linolenate	C ₁₉ H ₃₂ O ₂	292.47	10.94	260.4
BFL	C _{18.04} H _{34.92} O ₂	283.96	11.27	52.0
BFM	C _{18.40} H _{34.25} O ₂	287.58	11.13	112.7
BFH	C _{18.88} H _{33.49} O ₂	292.53	10.93	185.4

Table IV. Physicochemical properties of test fuels

Property	Method	BFL	BFM	BFH
Density at 15 °C (kg/m ³)	ASTMD1298	871.6	885.2	893.5
Kinematic viscosity at 40°C (mm ² /s)	ASTM D445	4.6	4.4	4.2
Higher heating value (MJ/kg)	ASTM D240	39.86	39.75	39.63
Lower heating value (MJ/kg)	-	37.14	37.13	37.12
Lower heating value (MJ/m ³)	-	32444	32866	33169
T10: Temperature at 10% recovered (°C)	ASTM D86	322	327	327
T50: Temperature at 50% recovered (°C)	ASTM D86	328	334	338
T90: Temperature at 90% recovered (°C)	ASTM D86	336	347	361
Rancimat oxidation stability (hours)	EN14112	12.83	0.51	0.1
Stoichiometric fuel/air ratio	-	12.57	12.50	12.43
Cetane number (mass weighted average)	-	63.7	51.3	36.5
Average reported cetane number	-	62.7	-	30.0

Consequently with its high content of polyunsaturated methyl esters, BFH had an IV (185.4 g I₂/100g) significantly higher than that of BFL (52 g I₂/100g) and the maximum limit specified in the European standard EN 14214 (120 g I₂/100g).

Density, viscosity, heating value, volatility and cetane number are the main physical properties of the fuel that affect the diesel combustion process. As can be inferred from table IV, these properties are affected in different extent by unsaturation degree.

The density of the test fuels increased with the degree of unsaturation. Other important fuel properties which are more difficult to measure have been correlated with density. Tat et al calculated the isentropic bulk modulus of pure methyl esters and several biodiesel fuels as a function of density and speed of sound at elevated pressures [10-11]. They found that the speed of sound and the isentropic bulk modulus of biodiesel fuels also tend to increase as the degree of unsaturation increases.

The higher heating value (HHV) of the test fuels underwent a slight decrease with unsaturation degree. Since the values of the HHV of the most common saturated and unsaturated long-chain methyl esters vary within a narrow range [12], the test fuels as well as commercial biodiesel fuels must have similar values of this property.

The distillation profile of the test fuels showed some differences which became more noticeable at the medium (T50) and high-temperature (T90) points. The T50 and T90 points were higher for the more unsaturated fuels. However, that increase in distillation temperatures may be due partly to the slight differences in chain length and density among fuels.

The cetane number is a key fuel property very sensitive to the degree of unsaturation. The values of the estimated cetane numbers were in agreement with average measured reported values for palm oil [13] and linseed oil [7] biodiesel fuels. The cetane number of BFH is significantly lower than the minimum specifications stipulated in the European standard EN 14214 (51) and in the ASTM standard D6751 (47).

Engine performance

Table V compares the average values resulting from three measurements of the engine performance parameters for the test fuels at the fixed operating mode. Results indicate that engine performance was not significantly affected by the type of biodiesel fuel or its degree of unsaturation. This was expected since the heating value, stoichiometric fuel/air ratio and oxygen content, which are the properties of the biodiesel fuels that affect in great extent engine performance, were very similar.

The similarity in break power guarantees that tests were carried out maintaining the same energy output, regardless the fuel tested. This was possible without significant changes in the brake specific fuel consumption (*bsfc*) due to the slight differences in the lower heating value of the test fuels. Additionally, the thermal efficiencies were almost the same. This indicates that the engine converted the chemical energy of the test fuels to mechanical energy with a similar efficiency. Since the stoichiometric fuel/air ratios of the test fuels and the engine *bsfc* were very similar, the global equivalence ratios were practically the same.

Table V. Average engine performance parameters

Fuel	Break power (kW)	<i>bsfc</i> (g/kWh)	Thermal efficiency (%)	Equivalence ratio
BFL	23,9 ± 0,15	283,5 ± 0,95	0,342 ± 0,001	0,42 ± 0,005
BFM	24,3 ± 0,08	280,7 ± 2,34	0,345 ± 0,003	0,41 ± 0,004
BFH	24,07 ± 0,21	281,3 ± 2,07	0,345 ± 0,003	0,41 ± 0,005

The attainment of a nearly equivalent engine performance for all test fuels allows a meaningful analysis of the effect of fuel nature on combustion characteristics and engine emissions.

Combustion characteristics

Table VI presents the main parameters that characterize the in-cylinder combustion process and figure 1 shows the apparent heat release rate (AHRR) for the test fuels at the fixed operating mode, respectively.

Table VI. Combustion characteristics

Fuel	Start of injection angle SOI (deg)	Ignition delay ID (ms)	Maximum dp/dα (kPa/deg)	Peak in-cylinder averaged temp. (°C)
BFL	23,5 ± 0,15	0,90 ± 0,05	463,54 ± 1,4	1717 ± 4,2
BFM	23,7 ± 0,10	0,96 ± 0,01	528,87 ± 1,2	1731 ± 5,2
BFH	23,6 ± 0,28	0,98 ± 0,008	621,66 ± 1,3	1780 ± 3,1

The angle of start of injection (SOI) was almost the same for all test fuels. The small differences found in this parameter were probably caused by the experimental error and measurement instruments accuracy rather than to any effect of biodiesel type or unsaturation degree. This result indicates that the differences in density, viscosity, velocity

of sound and bulk modulus, which are the main fuel properties that affect the start of injection in engines equipped with conventional pump-line-nozzle fuel injection systems, were not high enough to cause any artificial advance or retard in injection timing. Additionally, since the differences in the heating value among the test fuels were not significant, the injection pump did not have to compensate the energy input by starting the injection earlier in order to increase the amount of fuel injected to the cylinders.

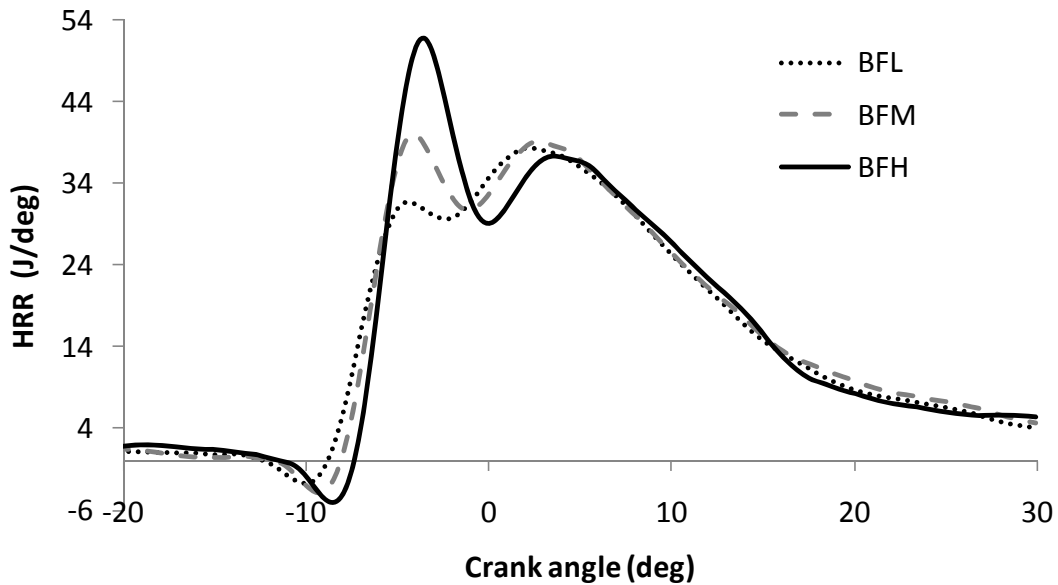


Figure 1. Heat release rate

Since the injection timing was practically constant for all test fuels, the differences in the angle of start of combustion (SOC) or combustion timing, which can be noticed in figure 1, did not depend on induced responses of the fuel injection system but on the inherent properties of biodiesel fuels. Therefore, combustion timing was mainly determined by the ignition delay, which in turn was mainly affected by the fuel's cetane number. As the cetane number of the biodiesel fuels increased, the ignition delay was shortened and so the combustion timing was advanced.

In-cylinder pressure is shown in figure 2. The peak pressure of more unsaturated biodiesel fuel (BFH) is slightly higher than the BFL. The maximum gradient pressure was higher for the more unsaturated biodiesel, which explains its higher premixed combustion rate; nevertheless, the smoothest pressure rise was obtained with the less unsaturated biodiesel.

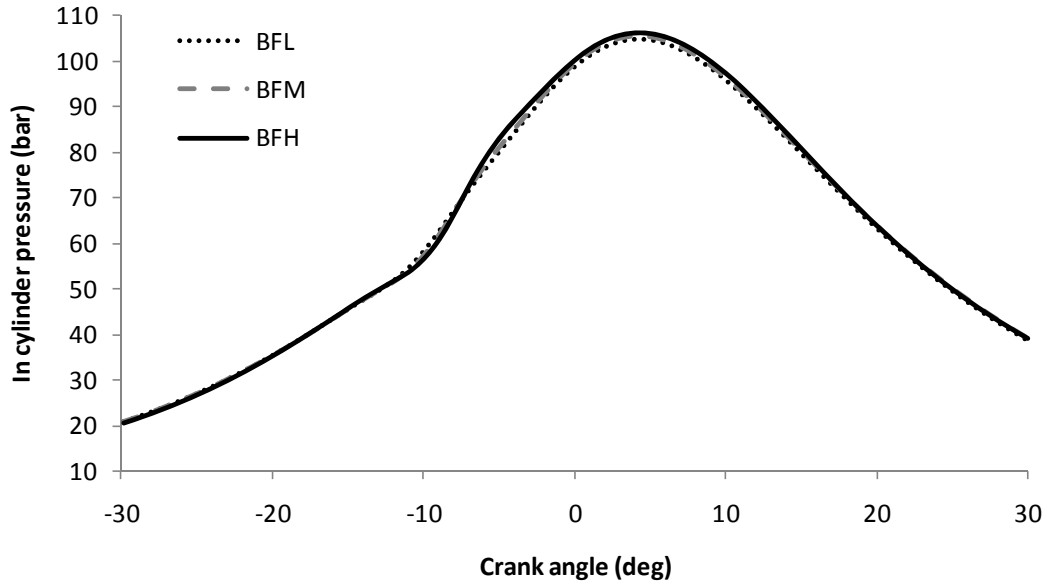


Figure 2. In-cylinder pressure

The ignition delay (ID), which can be defined for measurement purposes as the time corresponding to the angular interval occurring between the SOI and the 5% of the cumulative heat release, increased with unsaturation degree (see table VI). Combustion timing and ignition delay had a significant influence on the global heat release patterns. As can be seen in figure 1, the typical phenomenology of conventional diesel combustion, a “two stage” heat release with premixed burn followed by diffusion burn, was undergone by all test fuels. As the degree of unsaturation of the test fuels increased, the premixed portion of combustion, the peak heat release rate, the maximum pressure gradient ($dp/d\alpha$) and the peak in-cylinder bulk-gas-averaged temperature also increased (see table VI).

Figure 3 shows an increase in maximum in-cylinder bulk average gas temperature as the degree of unsaturation of the biodiesel fuel increased, which corresponds with the higher premixed combustion observed in figure 1.

Premixed combustion corresponds to the fuel that is mixed with air and prepared to burn during the ignition delay period. Unsaturated fuels with longer ignition delay allow more fuel/air mixing to take place before ignition. Since this flammable mixture usually burns very quickly, the heat release rate for premixed combustion is substantially higher than that of diffusion combustion. Accordingly, an increase in the premixed fraction results in more energy being released over a short time scale close to top dead center (TDC) with a nearly

constant combustion chamber volume, resulting in higher pressure gradients and gas temperatures.

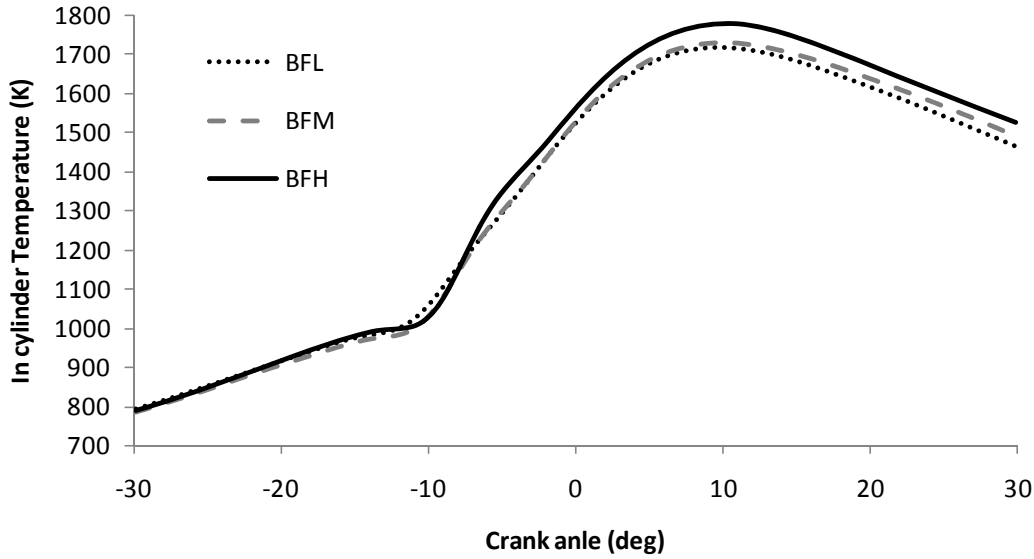


Figure 3. In-cylinder bulk-gas-averaged temperatures

Exhaust NO_x emissions

NO_x formation in diesel engines is a very complex phenomenon, because it is not quantitatively determined by a change in a single fuel property, but rather is the result of a number of coupled mechanisms whose effects may tend to reinforce or cancel one another under different conditions, depending on specific combustion and fuel characteristics [14].

The thermal or Zeldovich mechanism has been widely considered as the dominant mechanism of NO formation in diesel combustion [15]. Thus, the in-cylinder temperature, the residence time of the in-cylinder mixture at high temperatures and the local oxygen and molecular nitrogen concentrations are major factors affecting NO_x formation.

Figure 4 shows an increasing trend in specific exhaust NO_x emissions as the unsaturation degree of the biodiesel fuel, quantified as iodine value, increased.

As discussed earlier, a lower degree of unsaturation led to a shorter ignition delay (higher cetane number) and consequently to a more advanced combustion timing. These conditions could favor the formation of NO_x inside the combustion chamber due to a possible increase of the residence time of the combustion products at high temperatures. However, the higher cetane number of the less unsaturated biodiesel fuels also led to less premixed burning and

so lower combustion rates, which finally led to lower in-cylinder bulk-gas-averaged temperatures during the closed valves period (see figure 3). Comparing biodiesel fuels, it can be said that as the degree of unsaturation decreases the cetane number increases and its net effect is to decrease NO_x emissions.

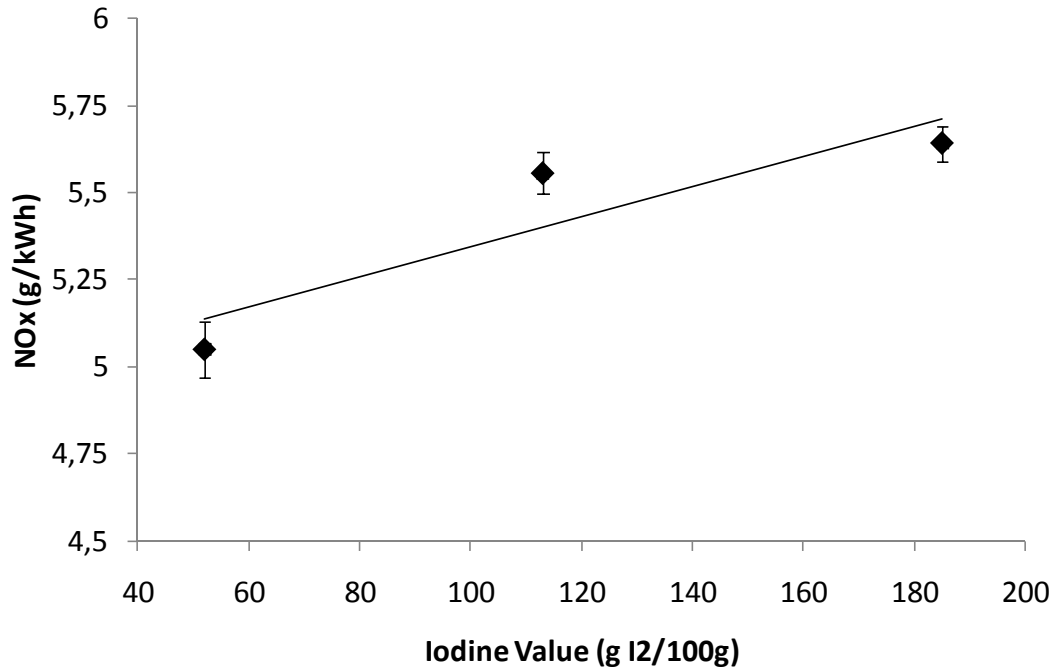


Figure.4 Specific NO_x emissions

However, it is necessary to bear in mind that NO_x emissions are very sensitive to local temperatures and species concentrations, and that actual flame temperatures are also affected by other factors which can be related with unsaturation degree. For instance, it has been suggested that more unsaturated biodiesel fuels tend to produce more NO_x because they have higher adiabatic temperatures [8, 14, 16]. On the other hand, it has been reported that less unsaturated biodiesel fuels tend to produce less soot. Since soot radiation is the primary means of heat loss from an in-cylinder flame, radiative heat losses will be lower for less unsaturated biodiesel fuels and so they should produce higher actual flame temperatures and more thermal NO_x [14].

It has also been argued that the NO_x increase for more unsaturated biodiesel fuels could possibly be caused by the increased NO formation via the prompt NO mechanism instead

of being driven by the Zeldovich mechanism. It has been suggested that the double bonds could contribute to the formation of higher levels of certain hydrocarbon radicals in the premixed fuel-rich mixture, which could result in more prompt NO formation during the subsequent combustion [17].

4. Conclusions

From the experimental work carried out in order to investigate the effect of the degree of unsaturation of biodiesel fuels on NO_x emissions, the following conclusions can be drawn:

1. The degree of unsaturation of biodiesel fuels does not affect significantly engine performance and injection timing.
2. A higher degree of unsaturation leads to lower cetane numbers, longer ignition delays and consequently more retarded combustion timings.
3. The exhaust NO_x emissions are mainly controlled by the fuel's cetane number or the ignition delay, and so by the relative amount of heat released during the premixed combustion phase. The higher cetane number of the less unsaturated biodiesel fuels leads to less premixed burning and lower combustion rates, which finally results in lower in-cylinder bulk-gas-averaged temperatures during the closed valves period, and therefore less thermal NO_x formation.

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