

Diesel particulate emissions from biofuels derived from Spanish vegetable oils

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ABSTRACT

Methyl esters obtained from the most interesting Spanish oleaginous crops for energy use -sunflower and cynara cardunculus- were both used as diesel fuels in this work, pure and in 25% blends with a reference commercial fuel which was also used pure. A stationary engine test bed, together with the appropriate instrumentation for chemical and morphological analysis, allowed to evaluate the effect of these fuels on the engine emissions, particularly in the main particulate matter characteristics, such as soluble organic fraction, origin of adsorbed hydrocarbons, sulphate content, particle number per unit filter surface, and mean particle diameter. Both the consideration of the main thermochemical properties of the tested fuels and the computations of a chemical equilibrium model were helpful for the analysis of the experimental results. These results proved that the use of these vegetable esters provides a significant reduction on particulate emissions, mainly due to reduced soot and sulphate formation. On the contrary, no increases on NO_x emissions nor reductions on mean particle size were found.

INTRODUCTION

The production of biofuels for diesel applications from traditional laboring is an energy alternative of increasing interest, as it enables surplus agricultural production, reduction both the global and local environmental impact of diesel engines, and relief from energy dependency on imports. The recent increases of the petroleum barrel price and the development of industrial technologies for biodiesel production makes this biofuels option more competitive against conventional diesel fuel for the future.

The most interesting crops in Spain for seed oil production for fuel use are sunflower and an autochthonous cardoon named cynara cardunculus (1), both belonging to the same botanical family. The seed oil

content is around 25% in both cases. However, the production cost is still too high to compete with fossil diesel, unless the special taxes presently applied to petroleum-derived fuels were reduced or eliminated. Other experiences with rapeseed oil (2)(3), soybean oil (4)(5) and palm oil (6) have been successful in different countries, and have demonstrated advantages on particulate emissions.

Methyl esters from sunflower (SME) and cynara (CME) were both used as diesel fuels in this work, pure and in 25% blends with a reference fuel which was also used pure. The reference fuel is a typical diesel fuel available in Spanish petrol stations, attaining the present fuel quality requirements for diesel vehicles. It was supplied by Repsol-YPF. A stationary engine test bed, equipped with the appropriate instrumentation for chemical and morphological analysis, allowed evaluation of the effect of these fuels on the engine emissions, and particularly in the main particulate matter characteristics.

PRODUCTION AND CHARACTERIZATION OF VEGETABLE ESTERS AS DIESEL FUELS

CHARACTERISTICS OF VEGETABLE OILS

Table 1. Fatty acid oil content of vegetal oils.

Acid	Sunflower	Cynara
Myristic	0	0.11
Palmitic	6.38	10.62
Palmitoleic	0	0.14
Stearic	4.09	3.7
Oleic	23.68	24.95
Linoleic	63.79	59.87
Linolenic	0.36	0
Araquic	0.3	0.36
Gadoleico	0.27	0.15
Behenic	0.83	0
Lignoceric	0.3	0

The fatty acid oil content of each of the vegetable oils used in the engine tests is shown in Table 1. It can be noticed that there are only small differences between them. The proportion of unsaturates is 88.1% for sunflower oil and 85.1% for cynara oil.

OBTAINMENT OF VEGETABLE ESTERS

Both vegetable oils were subjected to a transesterification reaction with methanol, using NaOH as catalyst. The reaction conditions were similar in both cases. The transesterification procedure was developed and carried out in CIDAUT (Centro de Investigación y Desarrollo en Automoción) and reached 95% efficiency after 1 day decantation and double washing with water and acidified water. The reaction lasted 1 hour at a temperature between 60°C and 70°C. The obtained biofuels were sunflower methyl ester (SME) and cynara methyl ester (CME), and in both cases an acidity below 0.5 mg KOH was reached.

THERMOCHEMICAL PROPERTIES

In order to estimate the main thermochemical properties, the group contributions Joback method (7) was used for the calculation of the specific heat at constant pressure and the standard enthalpy of formation:

$$\frac{C_p}{R}(\text{SME}) = -1.26159 + 0.21362 \cdot T - 1.2484E - 4T^2 + 2.7534E - 8 \cdot T^3$$

$$\frac{C_p}{R}(\text{CME}) = -1.10152 + 0.21159 \cdot T - 1.2295E - 4T^2 + 2.6825E - 8 \cdot T^3$$

$$h_f^0(\text{SME}) = -68851.88 \text{ K}^{-1}$$

$$h_f^0(\text{CME}) = -69615.53 \text{ K}^{-1}$$

These data were used in a chemical equilibrium model (8) which considers 29 chemical species (N_2 , O_2 , CO_2 , H_2O , CO , H_2 , NO , OH , N , H , O , Ar , N_2O , NO_2 , HO_2 , NH_3 , NH_2 , NH , CN , HCN , NCO , S , S_2 , SO , SO_2 , SO_3 , HS , H_2S , COS) to calculate the adiabatic flame temperature at constant pressure. Initial conditions of 80 bar and 900 K were taken as typical diesel in-cylinder conditions at the start of combustion. Other chemical characteristics of the fuel molecules are listed in Table 2.

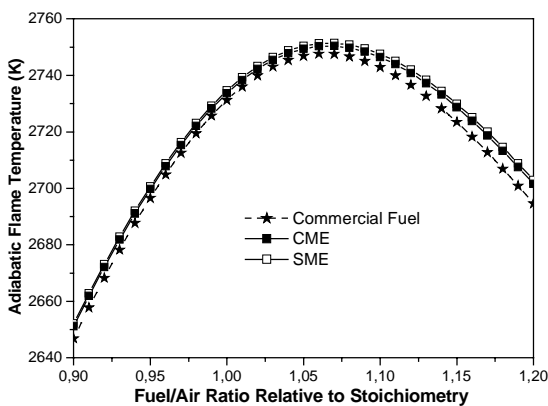


Figure 1. Adiabatic flame temperature vs fuel/air ratio at constant pressure (Initial conditions: $p=80$ bar and 900K)

Table 2. Chemical characteristics of sunflower ester and cynara ester, compared to commercial diesel fuel.

Fuel	Diesel	SME	CME
Summarized formula	$\text{C}_{15.27}\text{H}_{27.33}$	$\text{C}_{18.94}\text{H}_{34.82}\text{O}_2$	$\text{C}_{18.79}\text{H}_{34.68}\text{O}_2$
Molecular weight (g/mol)	210.7	294.58	292.64
Oxygen content (% w)	0	10.86	10.93
H/C ratio	1.807	1.838	1.846
Average No. double bonds	0	1.53	1.45
Aromatic content (% w)	37.23	0	0
Stoichiometric fuel/air ratio	1/15.5	1/12.423	1/12.421
Stoich. fuel/oxygen ratio	1/3.58	1/2.814	1/2.816

FUEL PROPERTIES

The obtained esters were tested as automotive fuels together with the commercial fuels, following the European standard methods, established in the European Norm EN590 (directive 98/70/CE). The main fuel specifications are listed in table 3. The lower heating values of esters are nearly compensated by their higher density in the volumetric injection system leading to heating values of the same order when expressed in MJ/l. Differences in viscosity and cetane number slightly affect the timing of injection (9) and combustion, respectively. As esters' composition are much more homogeneous than that of diesel fuel, their distillation curves are much more flat, leading to lower final point despite the higher general level of boiling temperature. Finally, higher sulphur content was found in CME than in SME, both being much lower than that of diesel fuel.

Table 3. Fuel properties of SME and CME, compared to commercial diesel fuel (* Cetane Index)

Fuel	Diesel	SME	CME
Density (kg/m^3)	830	885.4	887
Lower heating value (MJ/kg)	43.0	37.4	37.2
Lower heating value (MJ/l)	35.7	33.1	33.0
Cetane number	49.6	56.4	54.4*
Viscosity (cSt) (40°C)	3.16	4.13	4.88
Distillation T50 (°C)	277.7	340.0	-
Final Boiling Point (°C)	376.7	345.0	345.0
POFF (°C)	-15	-	-10
Sulphur content (ppm w)	312	40	160

EXPERIMENTAL SET-UP FOR TESTING AND ANALYSIS

ENGINE TEST BED AND INSTRUMENTATION

A turbocharged intercooler IDI diesel Renault engine, model F8Q, similar to those commonly used in European passenger car, was tested. The engine was coupled to a hydraulic brake and equipped with the instrumentation for its control and for the measurement of all the parameters affecting emissions (10). In all cases the engine was fully warmed up, which avoided the possible disadvantage of biodiesel blends in cold conditions due to their lower volatility at low temperature.

This engine was tested in five different operating conditions (see Table 4), selected among the collection

of steady stages (11) which reproduce the sequence of operating conditions that the vehicles equipped with this type of engines must follow during the transient cycle established in the European Emission Directive 70/220, amendment 2001/C 240 E/01. Tests with CME were carried out only in the extreme modes E and J, as the available quantity of cynara oil was limited. In all tests the lubricant oil was a SAE 15W40 supplied by Repsol-YPF.

Table 4. Engine operating conditions

Operation mode	Mean speed (km/h)	Engine speed (rpm)	Torque (N.m)
E	32	2087	11.2
E'	50	2311	20.7
F	70	2378	38.9
H	85	3139	70.0
J	120	3175	104.9

Particulate matter was collected in a partial dilution mini-tunnel (Nova Microtroll) through glass fiber filters covered by Teflon, as stated by regulations. The filters were conditioned in a climatic chamber (Minitest CCM-0/81), before and after the collection, in order to maintain constant temperature and humidity. An analytical balance was employed inside the chamber. The collection and conditioning procedure was optimised as described in reference (10).

Further insight into the exhaust composition was gained with the measurement of hydrocarbon and nitrogen oxides, which were detected, respectively, by flame ionisation (Amluk 2010uP) and gas-phase chemiluminescence (Beckman 951A). The smoke opacity of the exhaust gas was measured by a smokemeter (AVL 415).

INSTRUMENTATION AND SOFTWARE FOR CHEMICAL AND MORPHOLOGICAL ANALYSIS

After weighing, the filters with particles were subjected to an optimised Soxhlet extraction method (12). In this process, two particulate fractions were obtained: the soluble organic fraction (SOF), analysed by gas chromatography (Hewlett Packard 6890), and the insoluble fraction (ISF), which was measured by high performance liquid chromatography (Gibson 802C with a ionic conductivity detector 732 Ω Methrom). The SOF chromatograms allowed distinguishing the origin of SOF hydrocarbons by comparison with those from lubricant oil and fuel (13).

Filters similar to those used in the chemical analysis were imaged by Scanning Electron Microscope (SEM). Although these glass fiber filters have a rough surface, such support was selected over a flat glass surface in order to easily integrate the size characterisation method into the particulate certification procedure. The images obtained by SEM (500 magnification) were subjected to a digital treatment developed in Matlab. This program modifies the contrast in order to make the texture more uniform (14), detracts the fibers, and finally, binarizes into black/white images. The nanoparticles, smaller than

the pixel size, were subjected to a similar procedure from SEM images with 8000 magnification. The last step consist of a weighted counting. The final outputs are the particle size distribution, the standard deviation and several characteristic mean diameters, such as arithmetic or Sauter mean ones.

EFFECT OF BIOFUELS ON ENGINE EMISSIONS

Particulate emissions were reduced for every mode as the concentration of any of the tested biodiesel fuels were increased in the blend (Figure 2), despite the higher fuel/air ratio required in each mode necessary to compensate the lower heating value. These reductions are explained by the increase in oxygen content in the fuel which contributes to complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guaranties a complete evaporation of the liquid fuel. This effect can also be observed in the hydrocarbons emissions and the smoke opacity (Figures 3 and 4) which, unlike the particulate matter, were measured in hot and undiluted conditions. The particulate emission reduction is more significant at low load, because the cylinder temperature is relatively low, which in the case of a multi-component fuel such as the reference, could lead to some difficulties in evaporation and burning of heaviest hydrocarbons. The relative reductions in particulate emissions are more drastic from 0% biodiesel to 25 % than from this concentration to pure biodiesel.

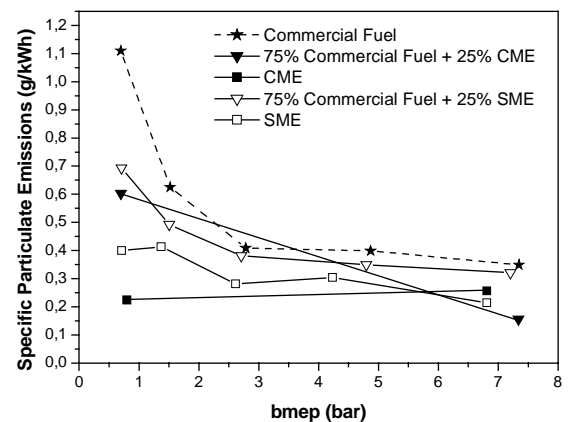


Figure 2. Specific particulate emissions vs bmep for different tested fuels

The comparison between particulate emissions with SME and CME could lead to the conclusion that CME provide slightly higher reductions than SME. Such differences might be due to the lower carbon concentration of CME, and consequently its higher oxygen concentration, although these differences are within the range of accuracy of the measurements. At least it is proved that CME is no worse than SME as a particulate-reducing fuel.

Another significant diesel engine emissions are nitric oxides. Figure 5 shows that the presence of oxygen on the ester molecule does not lead to increases on NOx formation. In fact, a certain decrease is observed at high load for all the tested fuels. Increases on NOx emissions

have often been attributed to the oxygen content of the fuel molecule (15)(16). However, a simple balance on oxygen availability, assuming local stoichiometric combustion, reveals (Table 2) that, even by including the oxygen of the ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel (2.92 in front of 3.58 in the case of sunflower ester). The extremely similar values obtained for the adiabatic flame temperature of the tested fuels (Figure 1) preclude difference in combustion temperature causing NOx formation differences.

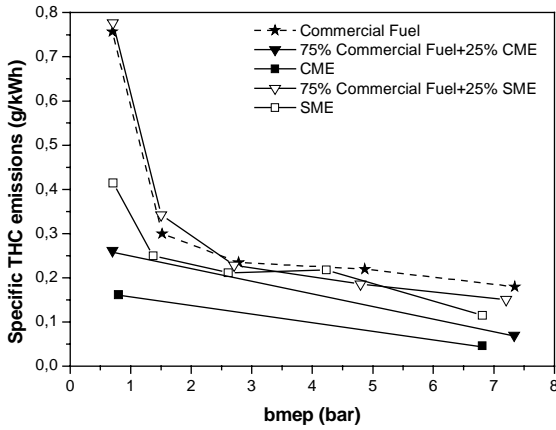


Figure 3. Specific hydrocarbons emissions vs bmep for different tested fuels

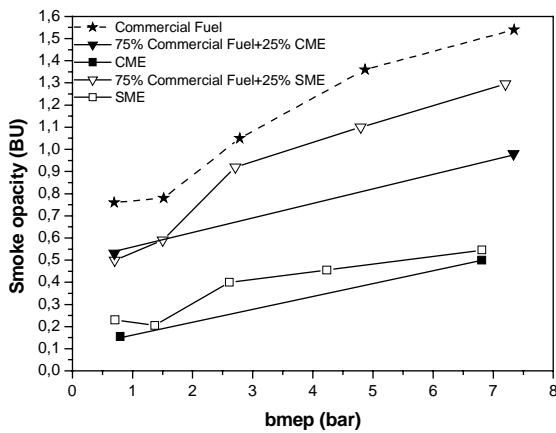


Figure 4. Smoke opacity vs bmep for different tested fuels

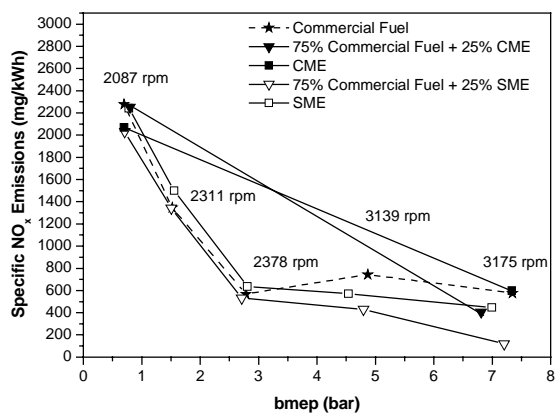


Figure 5. NOx emissions vs bmep for different tested fuels

EFFECT OF BIOFUELS ON PARTICULATE COMPOSITION AND ORIGIN

Although the total mass of hydrocarbons adsorbed on the surface of the carbon nuclei increased with load, its proportion with respect the total particulate mass (SOF) decreased as a consequence of the more sudden increase of soot formation. With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased SOF at any engine load (Figure 6).

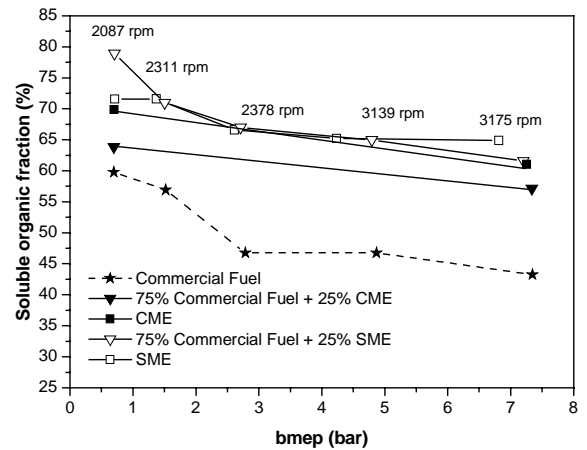


Figure 6. Soluble organic fraction of the collected particulate filters

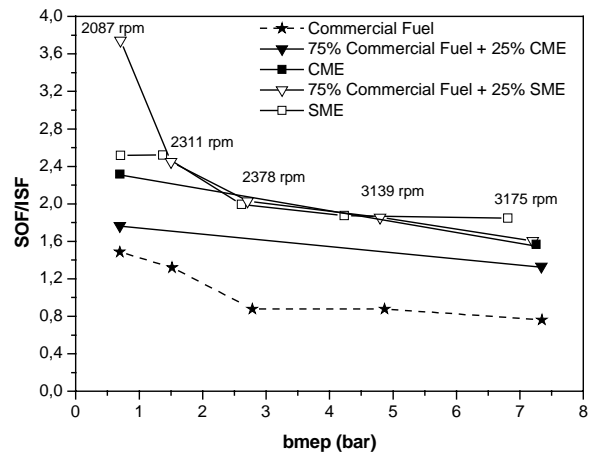


Figure 7. Relative adsorption of the collected particulate matter

In order to interpret this trend, the ratio between the soluble and the insoluble fractions (SOF/ISF) was plotted against bmep for all the tested fuels (Figure 7). This parameter is named here as relative adsorption. In case that the surface of the soot particles was saturated, the relative adsorption would be limited by the adsorption capacity of the soot particles, which depends on the particle size distribution and on the particle porosity. Figure 7 shows that the relative adsorption decreases with load and increases with the biodiesel concentration. As such trends are not accompanied by any increase of

particle mean diameter with load nor by any decrease of particle mean diameter with ester composition (Figure 14 presented below), it can be concluded that particles remain unsaturated, and consequently, a decrease on the soot formation does not lead to any restriction on hydrocarbon adsorption.

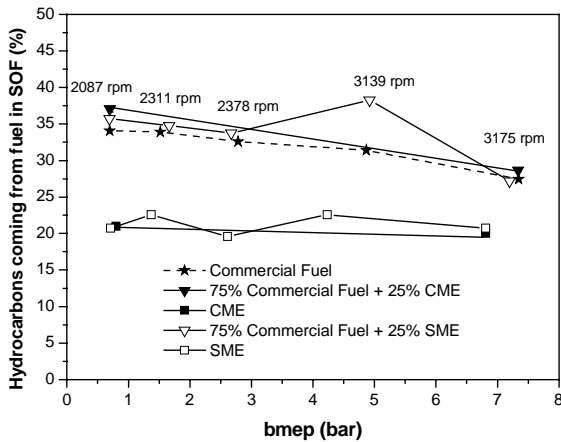


Figure 8. Origin of the adsorbed hydrocarbons in the particulate matter

The effect of fuel on the particulate matter composition is minimized because not all the adsorbed hydrocarbons come from fuel. Many others come from lube oil, which in this work remained the same. Figure 8 shows that the major contribution to SOF came from lube oil for all the tested modes and fuels, and that this proportion became even higher as the biodiesel concentration was increased, in accordance with the mentioned effect of oxygenated fuels to reduce not only soot but also hydrocarbons emissions.

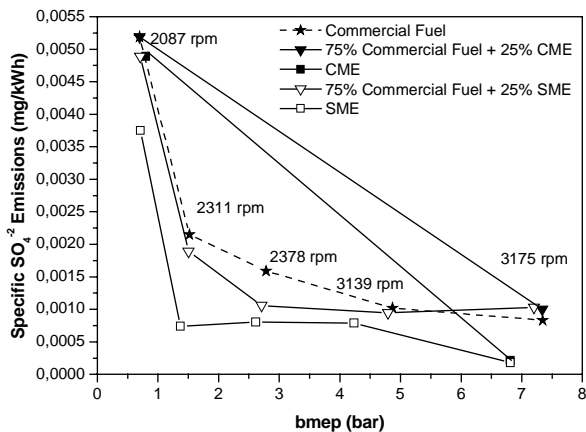


Figure 9. Sulphate content of particulate matter

The sulphate content in the particulate matter (Figure 9) was also reduced as the biodiesel concentration was increased, consistently with the sulphur reduction in the fuel (Figure 10). Note that the residual sulphur content detected in CME was much higher than in SME (Table 3). However, the mentioned reduction was lower than proportional, which could be justified by two reasons: The absence of oxidizing catalyser which did not guaranty a complete sulphur oxidation (17), and the possibility that

some of sulphates come from the lubricant oil sulphur content (around 6000 ppm).

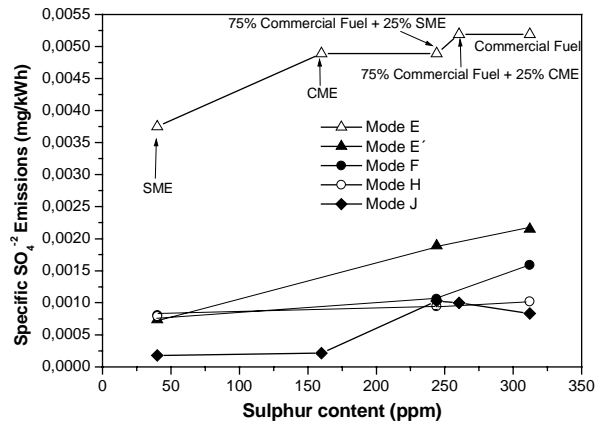


Figure 10. Sulphate content of particulate matter vs sulphur content of fuels

EFFECT OF BIOFUELS ON PARTICULATE MORPHOLOGY

Figures 11 and 12 are SEM images taken from filters obtained at high load mode from tests with commercial fuel and with pure esters. Although these images show visible differences, the particulate morphology was quantified through the number of particles per filter surface unit and the Sauter mean particle diameter. Both parameters resulted from the digital analysis of SEM images, as above described.

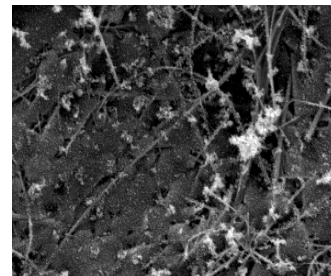


Figure 11. SEM image of particulate filter (500x) from engine operating mode J with commercial diesel fuel.

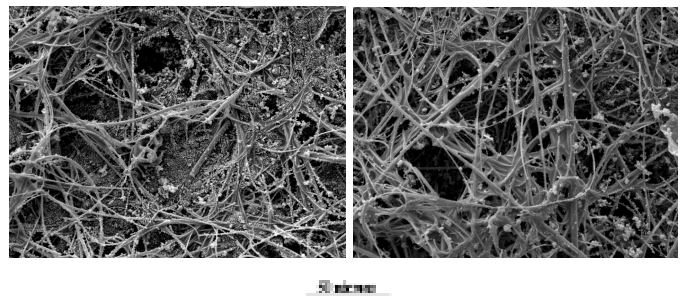


Figure 12. SEM images of particulate filters (500x) from mode J, with pure SME (left) and pure CME (right)

As Figures 13 and 14 show, the number of particles strongly increased with load while the mean size remained around a constant value. The presence of vegetable esters in the fuel led to dramatic decreases on

the number of particles, accordingly with the reduction in emitted particulate mass, and to slight increases in particle size. The last observation, which could constitute an important additional benefit of biodiesel fuels can hardly be considered significant because the reliability of the averaging process is reduced when the particle population becomes too small.

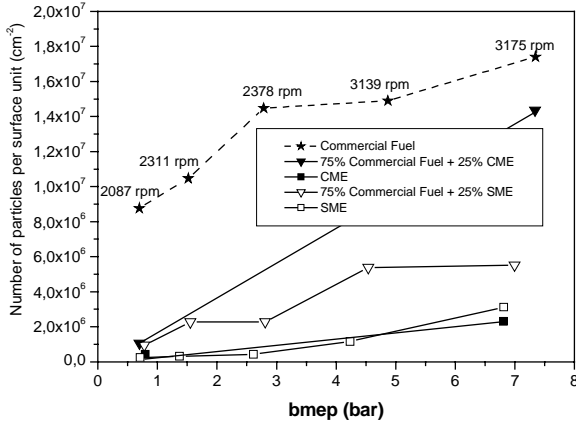


Figure 13. Number of particles per unit filter surface vs bmep for different tested fuels

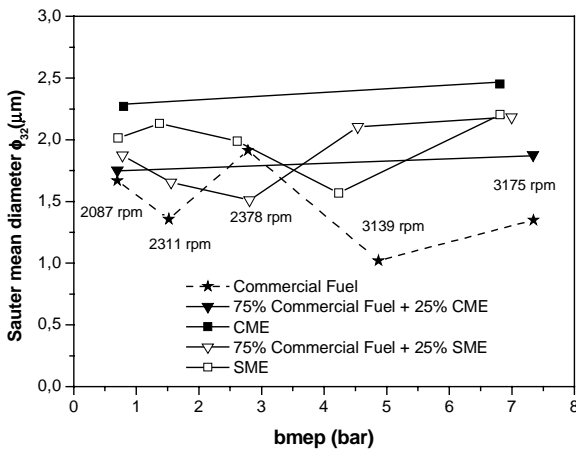


Figure 14. Particle Sauter mean diameter vs bmep for different tested fuels

CONCLUSIONS

- Particulate emissions were reduced for every mode tested as the concentration of any of the tested biodiesel fuels were increased in the blend. These reductions are justified by the increase in oxygen content in the fuel which contributes to a complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guarantees complete evaporation of the liquid fuel.
- The presence of oxygen on the ester molecules did not lead to increases in NO_x formation. On the contrary a certain decrease was observed at high load. Although increases on NO_x emissions have often been attributed to the oxygen content of the fuel molecule, a balance on oxygen availability, reveals that, even by including the oxygen of the

ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel.

- With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased soluble organic fraction (SOF) at any engine load.
- The relative adsorption (SOF/ISF) increased with the biodiesel concentration. As such trends are not accompanied by any decrease of particle mean diameter with ester composition, it was concluded that particles remain unsaturated, and consequently, a decrease in the soot formation does not lead to any restriction on hydrocarbon adsorption.
- The major contribution to SOF came from lube oil for all the tested modes and fuels, and this proportion became even higher as the biodiesel concentration was increased, in accordance with the effect of oxygenated fuels to reduce not only soot but also unburned hydrocarbons.
- The sulphate content in the particulate matter was also reduced, consistently with the sulphur reduction in the fuel. Highest reductions were found with sunflower methyl ester.
- The presence of vegetable esters in the fuel led to dramatic decreases in the number of particles, along with the reduction on emitted particulate mass, and to slight increases on the mean particle size.

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REFERENCES

1. Fernández, J.; Hidalgo, M.; Sánchez, G.; Curt, M.D. Towards a varietal screening of *Cynara Cardunculus* for oil production. Biomass for Energy and Industry. Proceedings of the 10th European Biomass Conference (C.A.R.M.E.N.), pp. 849-852. 1998.
2. Staat, F.; Gateau, P. "The effects of rapeseed oil methyl ester on Diesel engine performance, exhaust emissions and long-term behaviour – A summary of three years of experimentation". SAE paper 950053. 1995.
3. Hansen, K.L.; Jensen, M.G. Chemical and biological characteristics of exhaust emissions from a DI Diesel engine fuelled with rapeseed oil methyl-ester (RME). SAE paper 971689. 1997.
4. Chang, D.Y.; Van Gerpen, J.H. Fuel properties and engine performance for biodiesel prepared from modified feedstocks. SAE paper 971684. 1997.

5. Tritthart, P.; Zelenka, P. Vegetable oils and alcohols additive fuels for Diesel engines. SAE paper 905112. 1990.
6. Sapuan, S.M.; Masjuki, H.H.; Azlan, A. The use of palm oil as Diesel fuel substitute. IMechE. Vol. 210. pp 47-53. 1995.
7. Reid, R.C.; Praustnitz, J.H.; Poling, B.E. The properties of gases and liquids. 4th edition. Mc GrawHill. 1987.
8. Lapuerta, M.; J.J. Hernández, Armas, O. Kinetic modelling of gaseous emissions in a Diesel engine. SAE paper 2000-01-2939. 2000.
9. Lapuerta, M.; Armas, O.; Ballesteros, R.; Carmona, M. Fuel effects on automotive Diesel engine emissions. 3rd International Colloquium Fuels 2001. Technische Akademie Esslingen, pp. 225-232. 2001
10. Lapuerta, M.; Armas, O.; Ballesteros, R.; Durán, A. Influence of mini-tunnel operating parameters and ambient conditions on Diesel particulate measurement and analysis. SAE paper 1999-01-3531. 1999.
11. Lapuerta, M.; Armas, O.; Ballesteros, R.; Carmona, M. Fuel formulation effects on passenger car Diesel engine particulate emissions and composition. SAE paper 2000-01-1850. 2000.
12. De Lucas, A. Durán, A.; Carmona, M.; Lapuerta, M. Characterization of soluble organic fraction in DPM: optimization of extraction method. SAE paper 1999-01-3532. 1999.
13. IP PM BZ/96. Analysis of fuel- and oil-derived hydrocarbons in Diesel particulates on filters-Gas chromatography method. 1996.
14. González, R.C.; Wintz, P. Digital image processing. 2nd edition. Addison Wesley. 1987.
15. Sharp, C.A.; Howell, S.A.; Jobe, J. The effect of biodiesel fuels on transient emissions from modern Diesel engines. Part I. Regulated emissions and performance. SAE paper 2000-01-1967.
16. Seradi, A.; Fragioudakis, K.; Teas, C.; Zannikos, F.; Stournas, S. ; Lois, E. Effect of biodiesel addition to Diesel fuel on engine performance and emissions. Journal of propulsion and power. Vol. 15. No. 2. pp 224-231. 1999.
17. Naber, D.; Lange, W.W.; Reglitzgly, A.A.; Schafer, A.; Gairing, M.; Le'Jeune, A. The influence of fuel properties on exhaust emissions from advanced Mercedes Benz Diesel engine. SAE paper 932685. 1993.