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Pollutants emissions from a light vehicle fuelled with unesterified new or waste vegetable oils: a pilot study

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Abstract
The emissions of regulated pollutants (CO, NOx, SO_2, particles) from a light vehicle fuelled with Diesel fuel, unused and waste vegetable oils, and blends of Diesel fuel and oils were measured, as a function of engine speed. Formaldehyde emissions were also quantified, as well as the smoke opacity. The emission levels when using pure or blended oil (25%, 50%, 75%) with diesel fuel are quite similar to the ones from diesel fuel alone, but patterns are found with a small overproduction of CO together with a decrease in NO emissions for the 50% blends. No significant effect of the nature or previous use of the oil has been found.

Keywords: Vegetable oil, Diesel fuel, alternative fuel, tailpipe emissions, regulated pollutants, carbonyls

1. Introduction
The possibility of replacing fuels derived from petroleum by biogenic fuels from renewable resources is of undeniable worldwide interest, because of uncertainties about the petroleum supplies and cost in the future, and because of the environmental benefits that such alternative fuels would provide, in particular the reduction of greenhouse gases. One of the alternatives is the use of fuels derived by esterification from vegetable oil, and in most European Union (EU) member states diesel contains up to 5 vol% biodiesel, i.e. fatty acid alkyl (usually methyl, but also sometimes ethyl) esters, with an EU proposed target at 10% by 2020.

The esterification of the vegetable oils presents the interest of obtaining a replacement fuel with physical characteristics, in particular its viscosity, close to those of conventional diesel fuel, and therefore compatible with most of the vehicles. The tailpipe emissions from these fuels are reasonably well documented [2-6], especially for the regulated emissions, though the non-regulated emissions such as carbonyls [7, 8] lack extensive research and are still under close scrutiny, both for their environmental effects and their health effects [1, 9, 10].

However, from an environmental point of view, the oil esterification also raises concerns, because of petroleum-derived reactants used in the process, of the reactants toxicity, methanol in particular, and because of the economic cost of transforming the oil [11]. This has triggered some work on the use of vegetable oil as fuel or additive with no prior chemical transformation. The viability to use vegetable oil as diesel fuel was first demonstrated in 1895 by Rudolph Diesel, who operated a diesel engine with peanut oil. Vegetable oils do not however present the same physical characteristics as Diesel fuel and can lead to damages to the engine, and modifications have be made to the tank and injection lines, in addition to the tuning of the engine settings.

A recent development is the investigation the use of waste material such as used cooking oil [12-17], as there is a growing concern about a possible considerable rise of food and water prices induced by the agricultural development needed to produce the oil specifically for fuel use. Waste cooking oil production is estimated to about 150000 tons per year in France, of which only 30000 tons are collected. Since waste cooking oils have to be recycled, their use as fuel therefore presents a double interest, on the economic and the ecologic levels. Waste oil consists basically of the same components (triglycerides) as unused oil, but they differ because of the presence of products resulting from thermal, oxidation and hydrolysis processes, as well as the presence of food residues [18].

Emissions from vehicles with unesterified oil are not as well documented, and lead to results widely diverging, in particular for CO and NOx. The only common observation is the emission of particles, which are reduced compared to vehicles fuelled with Diesel fuel.

In this paper, we report the analysis of the regulated pollutants and some unregulated pollutants emitted by a lightweight vehicle fuelled with used vegetable oil or blends of used vegetable oil and diesel fuel. This study was performed with the vehicle at rest, while maintaining a constant engine speed. The results from this pilot study will be used as reference data for a future large scale study of the emissions of vehicles fuelled with alternative fuels made from waste cooking oil, using standard and real-world driving cycles and chassis dynamometer facility with constant volume sampling equipment.

2. Experimental details

2.1. Fuels

The fuels used in this study are standard commercial gasoil, two unused sunflower oils, thereafter labelled PVO1 and PVO2, containing an antifoaming additive (E900, polydimethylsiloxane) in unspecified proportions, and four samples of used vegetable oils (UVO1 to UVO4) collected from restaurants in the Lille area. No chemical characterization of the oils has been performed. According to the restaurant owners indications, UVO1 to 4 each come from a single commercial oil, containing either pure sunflower, or sunflower mixed with palm, rapeseed or grapeseed. Additional experiments were performed on a mixture of oils collected from several restaurants, hereafter labelled UVO5. The origin of the constituents of UVO5 has not been traced, and it can therefore be considered as a generic waste oil. All the used oils may also contain the E900 additive. UVO1 to 4 have been used as collected (unfiltered), while UVO5 was centrifuged before use, and contains less than 0.3% water.

Emissions measurements were performed for pure Diesel fuel, pure oil, and for blends of oil and Diesel fuel (B25: 25 vol% vegetable oil, B50: 50 vol% vegetable oil, and B75: 75 vol% vegetable oil). Whatever the origin or previous use of the oil, the mixtures are immediately homogeneous and used without further treatment.

As the oil viscosity is the main problem encountered when using them as fuel, this parameter was measured for our fuels at ambient temperature (20°C) and at 50°C, which we consider to be the temperature of the fuel when it is injected in the fuelling line to the engine. Former studies recommended, on the basis of empirical results, to preheat the oil to about 70°C before injecting it to the engine. Pure oils viscosities, new or used, were found to be in the range 68 – 88 mPa.s at 20°C, decreasing to 47 – 52 mPa.s at 50°C, compared to diesel fuel viscosity of respectively 26 and 19 mPa.s at the same temperatures. Viscosity of blends varies almost linearly with the oil content between the values of pure diesel and pure oil.

2.2. Test vehicle

The test vehicle was a standard 1994 Renault Clio, with a 1.9 L engine. No specific attention was paid to the repair, servicing or modifications record of the vehicle since its first use, except for the change of the exhaust pipe prior to the experiments.

The only specific adaptation to prepare the vehicle for our study was the modification of the fuelling lines, with the addition of an external tank, in order to control the composition of the fuel, avoiding mixing the different fuels in the internal tank of the vehicle.

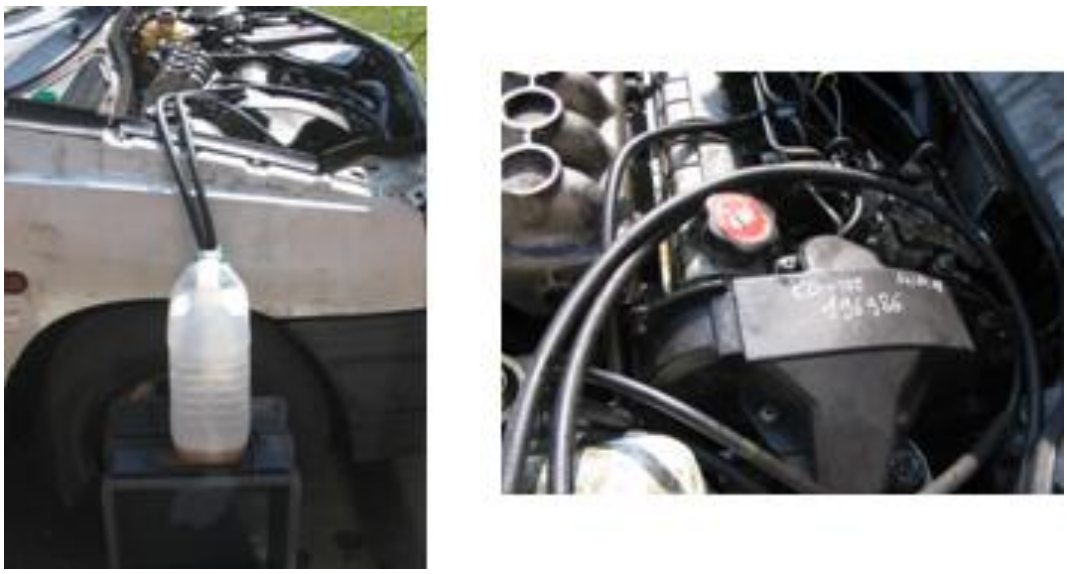


Figure 1: view of the external tank and of the fuelling lines

After each change of fuel in the tank, all lines were drained and then filled with the next fuel. The engine was first purged with the new fuel, while the excess fuel was discarded, before the emissions can be measured.

For each fuel, the emissions were measured with the vehicle at rest, while maintaining different engine speeds by inserting a metal block in the throttle: idling conditions (710 rpm) and 3 engine speeds (730, 1700, and 1930 rpm respectively). Each run lasted about 10 minutes.

2.3. Sampling and analysis

The general setup of the experiment is depicted on
Figure 2.

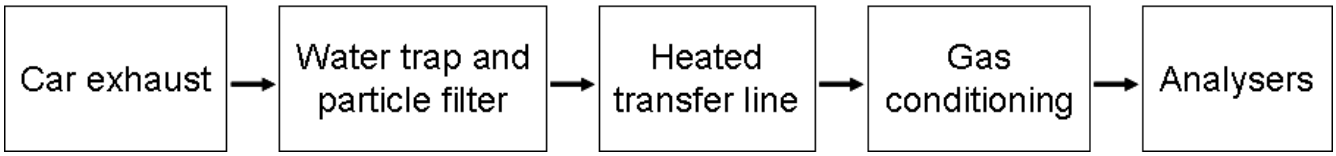


Figure 2: general setup of the experiment

The exhaust gas was sampled (about 400 $cc.min^{-1}$) in the centre of the exhaust pipe in order to avoid the capture of wall deposits. The exhaust gas was carried through a cellulose filter to remove larger particles and a water condenser filter before being diluted with nitrogen so as to bring the concentration of pollutants in the measuring range of the analyzers (dilution by a factor ~15 and ~200 for CO and NOx measurements respectively). Exhaust emissions were transferred from the exhaust pipe to the analysis equipment through a 120°C heated line.

Carbon monoxide (CO) was determined with a non-dispersive infrared (NDIR) gas analyzer (model CO11M, Environnement SA, France). Nitrogen oxides (NOx) were analyzed with a chemiluminescence gas analyzer (AC31M, Environnement SA, France). Sulfur dioxide (SO_2) is measured with a UV fluorescence analyzer (AF21M, Environnement SA, France). Carbonyl compounds are quantified by UV-HPLC after trapping on a DNPH coated cartridge. Additional measurements of formaldehyde were performed using tunable diode laser infrared absorption spectroscopy [19]. The opacity of the exhaust gases was measured in a separate set of experiments with a Diesel smoke meter chamber 495/01 for the Diesel fuel, oil PVO1, and the waste oil UV5, in idling conditions and the three accelerating engine speeds.

For each fuel and each engine speed, the measured regulated pollutants concentrations quickly reach a plateau, with additional periodic ~2-min oscillations. These oscillations are illustrated on Figure 3 in the case of Diesel fuel, and appear for each fuel and blend used in this study. This time-dependent component has been found to be concomitant with the onset of the cooling fan. Such a pattern in the emissions has already been observed in a previous study on trucks in idling conditions [20], though they were not explicitly linked to the cooling fan. Every pollutant concentration reported thereafter refers to the plateau, and does not include these oscillations.

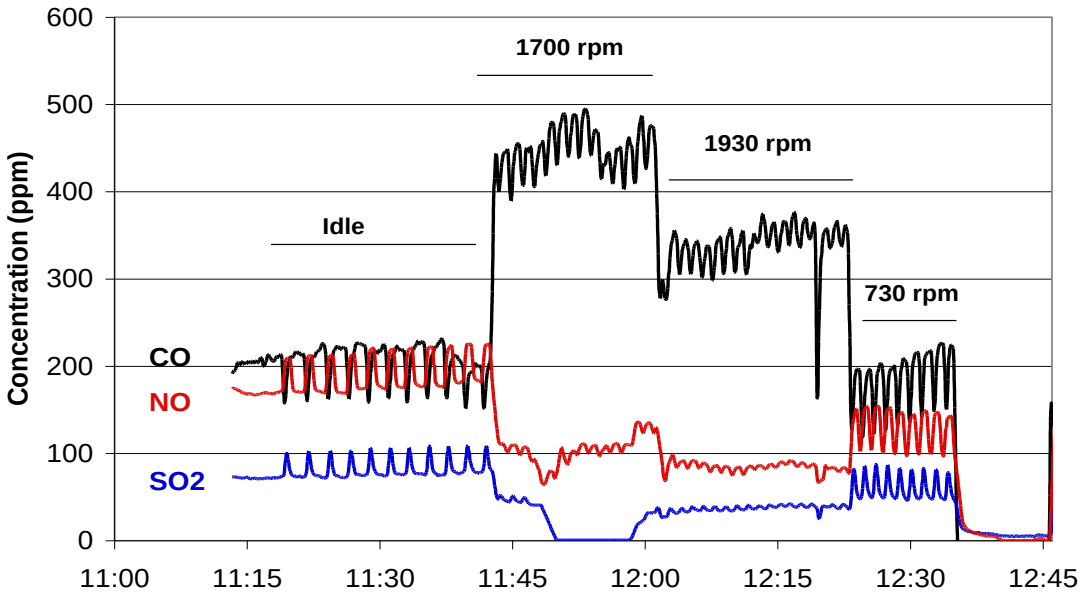


Figure 3: example of the emissions as a function of the engine speed (Diesel fuel)

3. Results and discussion

Experiments for each fuel and engine speed have been replicated several times to check for repeatability. From one run to the other, in the same conditions, variations in the concentrations of up to 25% have been observed, as is usually the case for vehicular emissions.

3.1. Regulated gaseous pollutants

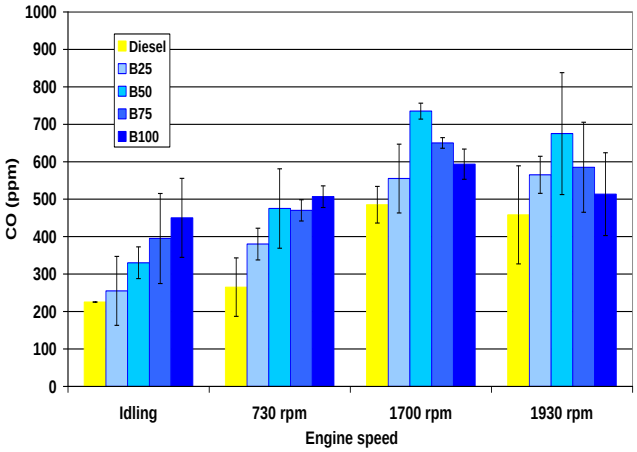
Gaseous emissions of CO, SO_2 and NO when the vehicle is fuelled with unused oils pure or in blends (25%, 50%, and 75%) are shown on

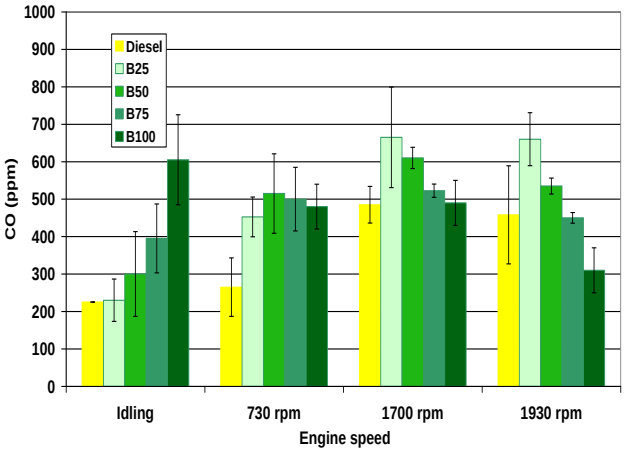
Figure 4, together with the emissions of Diesel fuel as reference. Emissions from all the used vegetable oils are shown on Figure 5, for pure oils and the 50% blends with Diesel. Except in a few runs with pure Diesel fuel, where concentrations of NO_2 of about 15 ppm have been measured, only NO has been found in the exhaust gases. This is in agreement with the results of Jimenez et al. [21], who have shown that NO_2 accounts for only 5 to 15 % of the total NOx emissions.

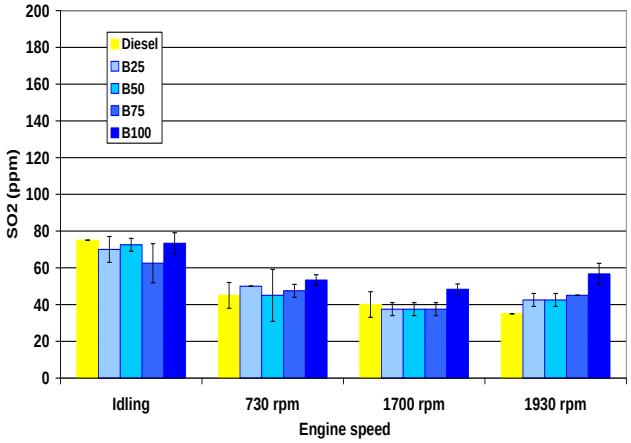
With Diesel fuel, CO emissions increase with the engine speed, from 200 to 450 ppm, whereas SO_2 and NO emissions decrease from 80 to 40 ppm and 150 to 80 ppm respectively.

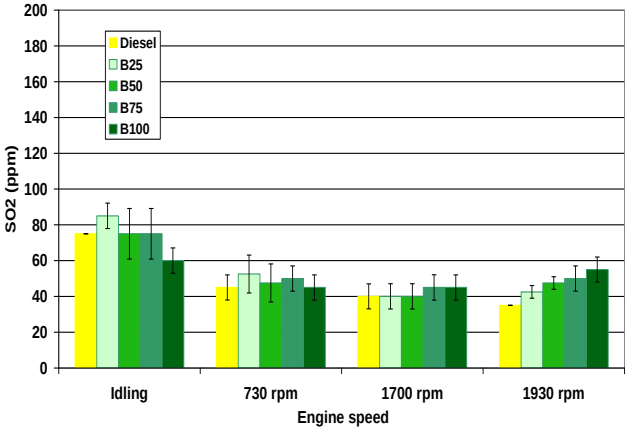
When using oil, pure or in blends, the observed pollutants levels do not vary much compared to Diesel fuel, the main differences being in CO concentrations in the exhaust gases. CO concentrations in that case range from 200 to 750 ppm, with differences between the oils appearing clearly from

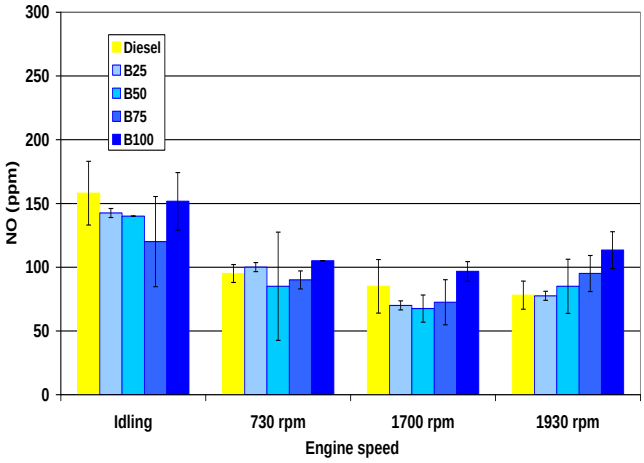
Figure 4 and Figure 5. At idling speed CO emissions increase clearly with the amount of oil, new or used, in the fuel. With unused oil, at high engine speed, CO emissions decrease with increasing oil proportion. This behaviour at higher engine speed is less marked with used vegetable oils (Figure 5). Maximal CO concentrations are obtained for intermediate (1700 rpm) engine speed. This behaviour may be linked to the injection timing, which was not modified in our experiments. It is indeed expected that the autoignition delay depends upon the composition of the fuel, with oil having a shorter ignition delay [22, 23].











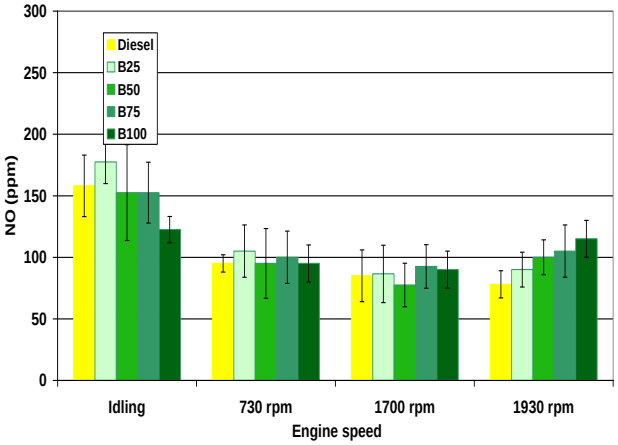
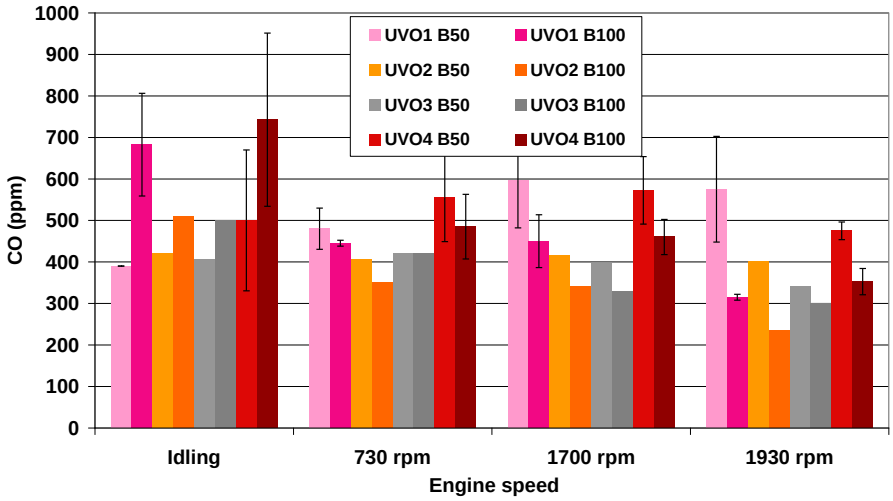
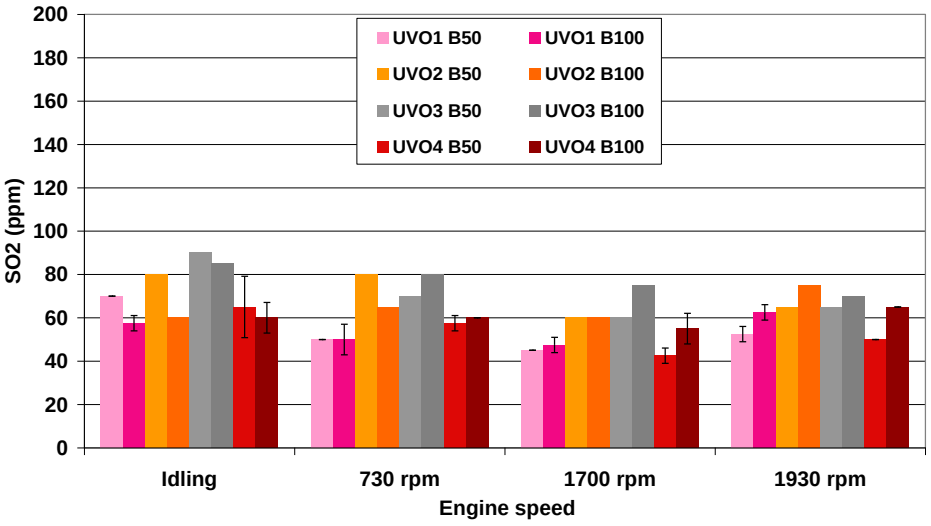


Figure 4 : Gaseous emissions with unused vegetable oils (left PVO1, right PVO2)





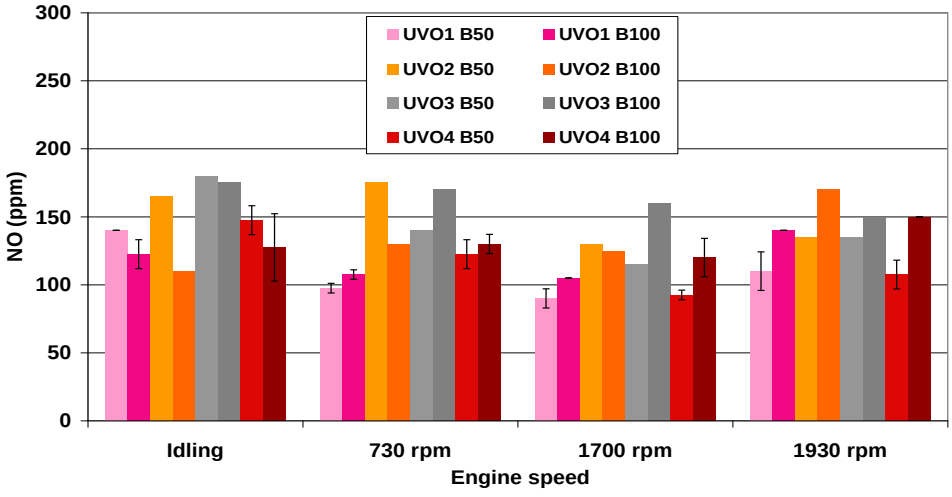


Figure 5 : gaseous emissions with used oils

NO emissions with oil are also in the same range (60 – 180 ppm) as Diesel emissions. All NO emissions curves with oil have the same profile, both as a function of the oil proportion in the fuel, and of the engine speed. Whereas for Diesel fuel there is a constant decrease when the engine speed increases, with oil we observe a minimum in the emissions at intermediate speeds. At the same time, at low engine speed, the NO emissions decrease slightly when the percentage of oil increases in the blend, but the trend is reversed at high engine speed where oil-rich blends give higher emissions. This behaviour pattern is anticorrelated with the CO emissions pattern, so it is likely that the injection timing is also the reason for it. Differences are noted between the oils, as some of them, PVO1, UVO3 and UVO4 in particular, induce higher emissions when used pure than when blended. No explanation, such as differences in the composition, has been found to account for this effect.

When using oil, SO_2 concentrations remain in the 40 – 80 ppm range whatever the engine speed, with a small but clear trend toward reduced emissions at high speed, and at the same time higher emissions when the oil content in the fuel increases, at least with the new oils. This is however not consistently the case with the used oils, where SO_2 emissions from B50 blends can be either higher or lower than emissions from B100 fuels. Still, the origin of these SO_2 emissions from the oils is quite unexpected, as the oils do not normally contain sulphur compounds, even though it may come from the foods that have been cooked in the oil. It is more likely that SO_2 comes from residues in the exhaust line, or from the engine lubricant, rather than from the fuel itself.

3.2. Carbonyl compounds

Formaldehyde content in the exhaust gases has been measured only for three unblended used vegetable. The results of these measurements, shown in

Table 1, illustrate the high variability of the emissions, where the formaldehyde concentrations at high engine speed can be lower, higher, or equivalent to the concentration at low engine speed. However, these concentrations are low compared to those reported when using ethanol/biodiesel/diesel blends [24], diesel fuel blended with biodiesel from waste cooking oil [25], or biodiesel and biodiesel/methanol blends [26]. In these three studies, the formaldehyde concentrations in the exhaust gases are in the range 1-100 $mg.m^{-3}$, much higher than in our study. We cannot however rule out experimental possible artefacts, in particular the solubilisation of formaldehyde inside the water in the water trap, because exhaust gases are diluted only after going through the trap.

Waste oil	Idling	1930 rpm
UVO2	423	197
UVO3	360	439
UVO4	220	228

Table 1: Formaldehyde concentration ($\mu g.m^{-3}$) in the exhaust gases

3.3. Fumes opacity

Opacity results are presented in

Table 2, for the four engine speed conditions, and three different fuels: Diesel fuel, pure unused oil, and one sample of used vegetable oil. Peak opacity of the exhaust gases under full acceleration conditions (norm NF R 10-025) is also given in the Table. Both new and used vegetable oils lead to lower opacity values than Diesel fuel at low engine speed. At high engine speed, there is

no noticeable difference between the three fuels. Peak value measurements however tend to show that in these conditions the oils produce fewer particles than the standard Diesel fuel.

Fuel	Idling	730 rpm	1700 rpm	1930 rpm	Peak value
Diesel	0.19	0.14	0.06	0.06	0.62 ± 0.06
PVO1	0.03	0.04	0.04	0.06	0.49 ± 0.10
UVO5	0.04	0.04	0.04	0.05	0.54 ± 0.17

Table 2: opacity measurements (m^{-1})

Conclusion

Literature data on the use of unesterified oil as fuel or additive to Diesel fuel are scarce, and henceforth also comparisons between the regulated and non regulated pollutants from diesel fuels, unused vegetable oil and used vegetable oil, pure or in blends with diesel fuel.

We performed tests on a vehicle fuelled with unesterified cooking oil, before or after use, performed at different engine speeds, spanning the typical driving conditions engine speed. These tests have shown the use of oil as fuel does not modify significantly the emissions of regulated pollutants. The previous use of the oil, i.e. the ingredients that have been cooked in it, the length of time it has been used, the temperature cycles it has undergone, seems to be irrelevant parameters for estimating the emissions. With oils, smoke opacity is reduced and NOx and SO_2 emissions are comparable to those of diesel fuel and only CO emissions are slightly increased. Formaldehyde emissions are also low, though because of the oxygen content of the oils, this compound should be investigated more closely.

Our measurements tend to show that in spite of differences in the individual emission profiles, depending upon the previous use and/or the composition of the oil, B50 blends seem to be the more appropriate fuels for use in urban driving conditions, because of the reduced CO emissions at low engine speed.

Since tests on a single vehicle were performed in our study, it is not possible yet to generalize these findings, and a full-scale measurement campaign must be initiated, encompassing more vehicles with different engine types, preferably on normalized driving cycles. The influence of the tuning of the injection timing, not considered so far, should also be investigated at the same time, as it could lead to an abatement of the emissions. It will also be necessary to add to the measurement of the regulated pollutants and of aldehydes the determination of odorous compounds, which are a source of nuisance when using oil in the fuel.

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