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Determination of aldehydes and ketones with high atmospheric reactivity on diesel exhaust using a biofuel from animal fats

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ABSTRACT

Biodiesel from animal fats appears as an alternative for conventional diesel in automotive consumption. Animal fats are classified into three categories, although only one of them can be used for biodiesel production, according to regulation. Due to its novelty, researchers testing animal-fat biodiesel on diesel engines focus only on regulated emissions. In this paper, the experiments carried out analyze carbonyl compounds emissions, due to its highly atmospheric reactivity, to complete the characterization of the total emissions in this kind of biofuel. Two fuels, a reference petro-diesel and a pure animal-fat biodiesel, were tested in a 4-cylinder, direct injection, diesel engine Nissan Euro 5 M1D-Bk. Samples were collected in 4 different operating modes and 3 points along the exhaust line. The analyses of samples were made in a high performance liquid chromatography, following the method recommended by the CARB to analyze air quality. Results show, on the one hand, a significant rise in carbonyl emissions, almost three times at the mode with highest hydrocarbon emissions, when biodiesel is used. On the other hand, on average, a reduction of 90% of carbonyl emissions when exhaust gases go through the different post-treatment systems installed. Despite this reduction, specific reactivity does not decrease substantially.

1. Introduction

Governments throughout Europe have reduced the limits of nitrogen oxides (NO_X) and particulate material (PM) emissions, in response to the increase in the number of light vehicles on circulation in the last years and the higher preoccupation of the population about environment and atmospheric contamination. One possible strategy for attaining the more and more restrictive regulations is to employ new types of fuels, obtained from vegetable oils or animal fats, via transesterification reaction. Also, this strategy supposes a decrease of the dependency on fossil fuels.

The most common feedstock for biodiesel production is vegetable oils, mainly soybean oil, because of its low price in the oils market. However, in some regions the cultivation of these plants becomes in conflict with those fields dedicated to human feeding, increasing their prices. A solution for that is to employ waste or non-edible feedstocks, such as wasted vegetable oil and wastes from animal ranching and fats, to produce biodiesel.

The animal subproducts are classified into three categories attending to their risk level, as it is said in the Regulation (EC) Number 1774/2002 by the European Parliament and the Council (http://eur-lex.europa.eu/LexUriServ/site/en/consleg/2002/R/02002R1774-20070724-en.pdf). In category 1, they are included those which present TSE (Transmissible Spongiform Encephalopathy) risks, unknown risks or risks related to illegal substances or environmental contaminants. In category 2, they are included those which present other risks related to animal diseases or other wastes of veterinarian medicaments. Finally, in category 3, they are included those which come from healthy animals with *ante-* and *post-mortem*. Among these three categories, only category 3 is used to biofuel production. The other two categories are excluded due to their relation with diseases. In category 3, it can be found, for example, slaughtered animal parts considered suitable for human consumption, but not destined for this purpose for commercial reasons, or skins, hooves, horns, bristles and feathers from animals sacrificed in slaughterhouses and without any transmissible disease.

Despite animal fats are a low-cost raw materials, the use of these fats in biodiesel production is quite limited. This can be explained by the high contents in free fatty acids (FFA), which cannot be treated by the conventional ways used in biodiesel production from vegetable oils, principally with regard to alkaline catalysts (Canakci

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and Van Gerpen, 2001a; Oner and Altun, 2009). This increases the global cost of the generation of biodiesel, leaving this type of biodiesel practically in the same level of costs than ordinary biodiesels. However, studies with biodiesel from animal fats report some advantages when using this fuel, as an improvement in cetane number and the reduction in NO_X emissions (Lapuerta et al., 2009).

Among the non-regulated diesel emissions, the study of carbonyl compounds has had a major boost in fuel and environment fields, being really abundant the number of papers that include the analysis of these emissions. However, most of the fuels tested by these researches were made from vegetable oils or were blends of these biodiesel fuels with petro-diesel fuel (Corrêa and Arbilla, 2008; Guarieiro and Pereira, 2008; Pang et al., 2008; He et al., 2009; Shah et al., 2009). Moreover, those papers presenting emissions results from biodiesel derived from animal fats were focused on regulated emissions (Wyatt et al., 2005; Guru et al., 2010).

Besides, because there are no regulations specifying the sampling method, the methods described are somewhat different between them, although it seems to be common to collect the exhaust gas diluted in ambient air. Nevertheless, in this paper, the samples are collected directly from the exhaust gas line, without any dilution ratio. This method has been chosen with the purpose of knowing the real concentration of carbonyl compounds emitted, not the concentration after the possible reactions that these compounds can generate when they are in contact with air.

Carbonyl compounds, in general, have a very high atmospheric reactivity. This reactivity is parameterized through the Maximum Incremental Reactivity (*MIR*), not only for carbonyl compounds, but all species that can be found in the atmosphere. *MIR* values are continuously being updated due to the improvement of the technology of measurement and analysis (Carter, 1994, 2010). Nevertheless, this parameter becomes insufficient if the global emission reactivity of a specific engine is studied. For that, the Specific Reactivity (*SR*) (Shah et al., 2009), parameter that weights each *MIR* value with its corresponding carbonyl compound emission, according to the following formula, can be used. In this formula, HCO_i means each carbonyl compound emission and MIR_i the corresponding value of maximum incremental reactivity.

$$SR = \frac{\sum_i (HCO_i \times MIR_i)}{\sum_i HCO_i} \quad (1)$$

In this paper, the effect that two post-treatment systems have in carbonyl emissions is also analyzed. The presence of these equipments, a diesel oxidation catalyst (DOC) and a diesel particle filter (DPF), is necessary since Euro 5 legislation entered into force (www.dieselnet.com).

2. Experimental equipment and procedures

2.1. Engine and operation conditions

A diesel engine Nissan Euro 5 M1D-Bk was employed during the testing, equipped with intercooler, diesel oxidation catalyst and diesel particle filter. This engine has been chosen because it is representative of what can be found in the currently Spanish fleet of vehicles. Tests were conducted in the Fuels and Engines Group at University of Castilla-La Mancha (UCLM). The engine was mounted and operated on a Schenk Pegasus (model Dynas Ll250) dynamometer functioning as the present load at real operating conditions. The main specifications of the engine are given in Table 1. In addition, the test engine was equipped with the necessary instrumentation for measurement and monitoring temperature and pressure levels (intake air, fuel, exhaust gases, lube oil, etc.).

Table 1
Diesel engine specifications.

Fuel injection system	DI, common-rail
Cylinders	4
Valves	16
Bore [mm]	84
Stroke [mm]	90
Compression ratio	16:1
Displacement [cm^3]	1994
Maximum power [kW]	111 @ 4000 rpm
Maximum torque [Nm]	323.5 @ 2000 rpm
Weight [kg]	215

The operating modes were selected among the collection of steady stages which reproduce the transient cycle that the vehicles with this type of engine must follow according to the European Emission Directive 70/220. The selection was based on two criteria. In the first one, it was chosen an urban mode (U) with high HC emissions (U10) and an extra-urban mode (EU) with similar velocity than previous mode but with high torque (EU16). In the second criterion, other urban and extra-urban modes were chosen, in this case, due to their relationship with the diesel particle filter charge (U9) and regenerative stages (EU8). All these four modes were common for all tested fuels. Details of the operating modes representing the transient European cycle are showed in Table 2.

Samples were taken in three points along the exhaust line, before the diesel oxidation catalyst, after the diesel oxidation catalyst (that is also before the diesel particle filter) and after the diesel particle filter (see Fig. 1). Nomenclature for these points from now on is *b DOC*, *a DPF* and *b DPF*, respectively.

2.2. Test fuels

Two different fuels were tested during the procedure, a pure diesel fuel (GO) used as reference fuel, supplied by Repsol, and a biodiesel fuel (AF) derived from animal fats via transesterification reaction, supplied by Stock del Vallés, S.A. (Barcelona, Spain). Properties of both fuels are showed in Table 3.

As it can be seen in the table of properties of biodiesel, this fuel has a problem with the cold-filter plugging point (CFPP), which exceeds the limit establish in the European standard EN 14214. Because of that, this fuel could not be used directly in cold climates. However, cold-flow depressant additives or blends with other biofuels could reduce its CFPP value below the limits.

2.3. Regulated emissions

Gaseous emissions were measured to establish any possible correlation with carbonyl emissions. The measurement point was, in this case, only after the diesel oxidation catalyst, due to the impossibility, at the moment of the experiments, to measure as carbonyl emissions as gaseous emissions at the same time at the other two points.

Total hydrocarbon (THC) emissions were measured with a flame ionization detector Graphite 52M-D (minimum detectable = 0.05 ppm).

A smoke meter AVL 439 (0.1% resolution) was used to determine the smoke opacity (expressed here in percentage of the light absorbed or dispersed with respect to the intensity of the emitted beam).