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Study of the uncatalyzed and catalyzed combustion of diesel and biodiesel soot

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ABSTRACT

The effect of the type of fuel (diesel or biodiesel) on the characteristics of the soot produced, affecting the non-catalytic and catalytic combustion, has been studied. For this comparison, two copper-based catalysts (5%Cu/Al_2O_3 and $Sr_{0.8}K_{0.2}Ti_{0.9}Cu_{0.1}O_3$) have been selected. The results of soot characterization by DRIFTS, XRD, Raman spectroscopy and TEM do not reveal significant differences between both soot samples, which present the expected features for this type of carbon materials. It has been observed that the use of biodiesel fuel has a double positive effect because, in addition to the expected reduction in the soot production rate, the reactivity of biodiesel soot is higher than that observed for diesel soot. The higher reactivity of biodiesel soot is mainly attributed to both, metals with catalytic activity (mainly Mg, Cu, K and Cr) which come from the raw materials and from the synthesis process and, to the higher oxygen content of the biodiesel soot. For biodiesel soot, the soot production rate and the uncatalyzed combustion rate at 515 °C are equal, and the copper catalysts tested lower this temperature to around 450 °C. For conventional diesel soot, much higher temperatures are required to balance the production and combustion rates.

1. Introduction

Biofuels are attracting much attention as renewable, biodegradable and non toxic fuels. In 2003, the European Directive (2003/30/EC) established that, by 2010, a 5.75% of conventional fuel for road transport has to be replaced by biofuels, because they are recognized as an important pillar in reducing greenhouse gas emissions [1]. The most widely employed option for diesel substitution is biodiesel. Biodiesel is a processed fuel derived from the esterification and transesterification of free fatty acids and triglycerides, respectively, which occur naturally in renewable biological sources such as plant oils and animal fats. Biodiesel presents some similar characteristics to conventional diesel but with beneficial impacts on engine exhaust emissions as it reduces particulate matter (soot), carbon monoxide, unburned hydrocarbons and, also, the overall lifecycle carbon dioxide emissions. On the contrary, nitrogen oxides (NO_x) emissions are generally increased, as consequence of fuel properties (higher viscosity, density, cetane number and oxygen content), but also to the specific operation conditions for the biodiesel use which implies a higher oxygen availability in the combustion chamber and a higher combustion temperature [2–4].

To accomplish the upcoming diesel emissions standards, even when biodiesel is replacing diesel fuel [5,6], the incorporation of pollutants control systems is still mandatory. Nowadays, the most effective after-treatment technique for soot removal is the use of diesel particulate filters (DPF) [7], where the soot particles are retained and subsequently eliminated by oxidation. Usually, the temperature required for soot combustion is higher than the exhaust gas temperature, and hence the process has to be catalyzed. In this context, the challenge is to design active, stable and low-cost catalysts able to meet the requirement of diesel engines manufacturers. Oxidation catalysts based on platinum are highly effective but expensive [8], so, alternative catalysts are needed. Among non-noble catalysts studied for soot combustion [7–22], potassium and copper catalysts have been proposed as interesting options.

This paper compares the effect of diesel and biodiesel fuels on the characteristics of soot produced in a diesel engine affecting the non catalytic and catalytic oxidation. To achieve this purpose, both uncatalyzed and catalyzed soot oxidation experiments have been performed using two copper-based catalysts (5%Cu/Al_2O_3 and $Sr_{0.8}K_{0.2}Ti_{0.9}Cu_{0.1}O_3$).

2. Experimental

A direct injection turbodiesel engine (NISSAN-2000), working in idle conditions at 880 rpm, was used to produce soot from commercial fuels: biodiesel (B100) from sunflower, provided by a

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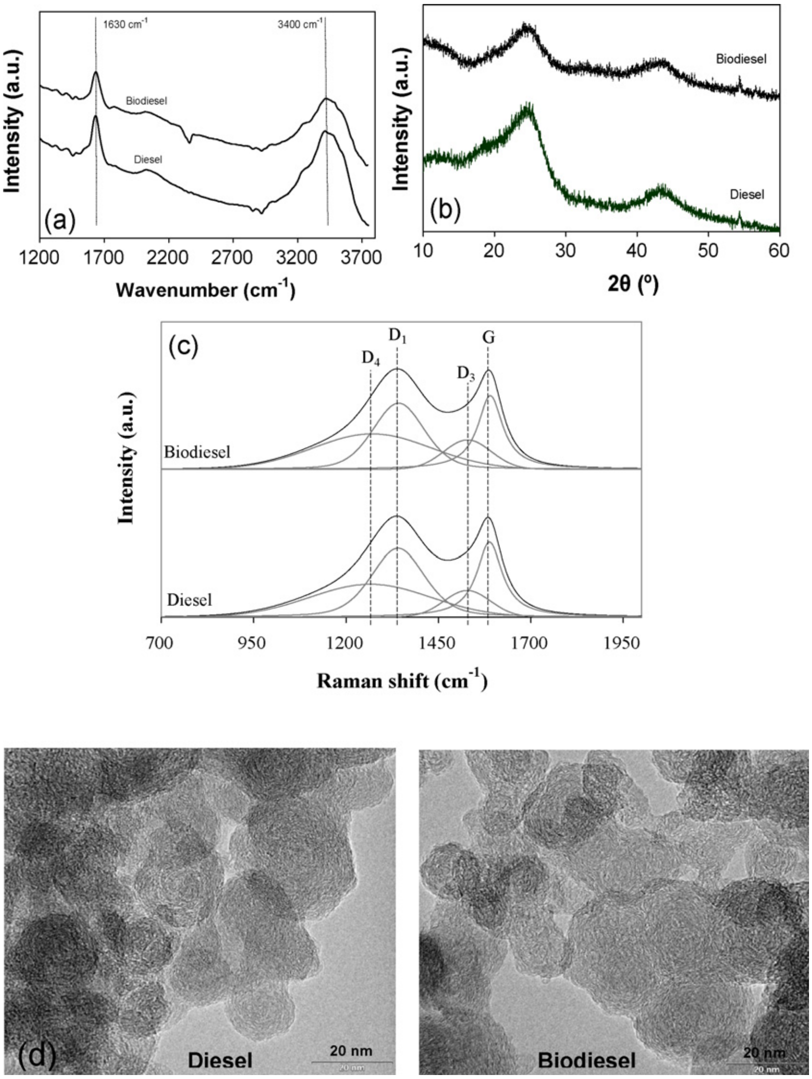

Fig. 1. Soot samples characterization by: (a) DRIFTS, (b) XRD, (c) Raman and (d) TEM.

local authorized biodiesel producer, and conventional (petroleum) diesel. The soot samples, referred to as "diesel" and "biodiesel" soot, were collected using a filter paper located in the exhaust pipe. The soot production rate is determined gravimetrically after 3 h collecting soot. For soot samples characterization the following techniques were used: elemental and immediate analysis, N_2 adsorption at −196 °C, XRF, DRIFTS, XRD, Raman spectroscopy and TEM.

The catalysts preparation has been detailed elsewhere [10,11]. In brief, for 5%Cu/Al_2O_3 catalyst preparation, γ-Al_2O_3 was impregnated with a $Cu(NO_3)_2 \cdot 3H_2O$ water solution; the solvent was removed by air bubbling, dried at 110 °C in static air for 12 h and, finally calcined at 700 °C in air for 5 h. The catalyst $Sr_{0.8}K_{0.2}Ti_{0.9}Cu_{0.1}O_3$ ($SrKTiCuO_3$) was prepared by the sol–gel method using H_2O_2, citric acid, titanium(IV) isopropoxide and nitrates of Sr, Cu and K and calcined in static air at 850 °C for 6 h. The full characterization of these catalysts was reported elsewhere [10,11].

Soot oxidation tests (uncatalyzed and catalyzed) were performed in a fixed-bed reactor at atmospheric pressure under NO_x/O_2 (500 ppm/5% in N_2), consisting of heating the soot – catalysts mixtures (80 mg of catalyst + 20 mg of soot + 300 mg of SiC, 1:4 soot catalysts ratio and loose contact) from 25 to 800 °C at 10 °C/min (Temperature Programmed Reaction, TPR) or keeping the temperature constant (isothermal reactions at selected temperatures). The gas composition was continuously monitored on-line by specific NDIR-UV gas analyzers for NO, NO_2, CO, CO_2 and O_2. The soot conversion was calculated from CO and CO_2 evolved.

3. Results and discussion

Table 1 shows the elemental analysis, the BET surface area, and the ash content (in dry basis) of both soot samples. The elemental composition reveals that, as observed by other authors [4,6,23], biodiesel soot presents a higher oxygen content. The percentage of volatile matter (adsorbed hydrocarbons) is 34.5% for diesel soot and 30.4% for biodiesel soot, which is consistent with the lower hydrogen percentage in biodiesel soot. The BET surface area is very similar for both soot samples; meanwhile the ash content is higher for biodiesel soot than for diesel soot. The chemical analysis (obtained by XRF) of soot samples reveals the presence of some metallic elements coming from the engine, the lubricant oil or, in the case of biodiesel fuel, from the raw vegetal material and/or from the synthesis process [3,4]. It is remarkable the presence of Mg (2.9%), Cu (1.8%), Cr (1.4%), K (0.5%) and, in lower extent Ni (0.2%) in biodiesel soot, as these elements could act as catalysts for the soot oxidation reaction [8–22]. The results of soot characterization by DRIFTS spectra (Fig. 1a), show two bands at around 1630 and

Table 1
Biodiesel and diesel soot characteristics.

Soot	C (%)	H (%)	N (%)	S (%)	O (%)[a]	S_{BET} (m^2/g)	Ash (wt%)[b]	Volatile matter (%)[b]
Biodiesel	82.15	2.70	0.69	0.25	14.21	91	4.3	30.4
Diesel	86.08	3.73	0.63	0.14	9.42	86	1.2	34.5

[a] Calculated by difference.
[b] Dry basis.

3400 cm^{-1} corresponding, the former, to oxygenated groups with quinone structure and to stretching of the aromatics C=C bonds and, the later, to OH groups, carboxylic acids and to stretching of the C–H bonds, are observed. The X-ray diffractograms (Fig. 1b) present two wide bands at 24.9° and 43.6°, assigned to the (0 0 2) and (1 0 0) planes, respectively, of a graphite-like crystalline structure. The band at 24.9° shows a slightly higher intensity for diesel soot, which seems to indicate a slightly larger crystallite size for this soot sample. In Fig. 1c the Raman spectra are drawn along with the deconvoluted bands G, D_1, D_3 and D_4 [24], whose position and intensity provide information about the crystallinity of a carbon material. TEM (Fig. 1d) indicates that the two soot samples have the expected structure composed by chain-like agglomerate of spherical particles, but significant differences are not observed [4]. Concluding, XRD, Raman spectroscopy and TEM evidences, as referred by other authors [6,25], that both soot samples present a quite similar crystalline structure.

Fig. 2a and b shows the soot conversion profiles obtained for uncatalyzed and catalyzed soot combustion during TPR experiments for both soot samples. The uncatalyzed combustion of diesel (Fig. 2a) and biodiesel soot (Fig. 2b) occurs in a similar range of temperature ($250\,^{\circ}C < T < 600\,^{\circ}C$, approximately), but biodiesel soot presents a higher reactivity than diesel soot. Since the nanostructure of both soot samples is quite similar, the higher reactivity of biodiesel soot seems to be mainly related to both the catalytic effect of some metallic components and to the higher oxygen content of the biodiesel soot. This conclusion is in line with that proposed by other authors [23,25,26]. Note that the use of catalysts increases the soot combustion rate and, as consequence, the $T50\%$ parameter (temperature required for 50% soot combustion) is lowered. For biodiesel soot the $T50\%$ value shifts from 540 °C (no catalyst) to 469 °C and 462 °C with 5%Cu/Al_2O_3 and $SrKTiCuO_3$ catalysts, respectively, and for diesel soot, from 561 °C (no catalyst) to 518 °C and to 468 °C with the same catalysts. The use of catalysts also affects the CO_2 selectivity ($100 \times (CO_2/CO + CO_2)$) which is increased from 75% and 64% for biodiesel and diesel soot, respectively, to more than 90% for both catalysts and both soot samples. Other important feature observed in the soot conversion curves of Fig. 2 is that the 5%Cu/Al_2O_3 catalyst is the most effective below 425 °C, meanwhile at higher temperature, the catalyst $SrKTiCuO_3$ becomes the most active. This behaviour is related to the higher activity of 5%Cu/Al_2O_3 catalyst for the oxidation of the hydrocarbons adsorbed on the soot surface. Note that the percentage of adsorbed hydrocarbons is higher for diesel soot than for biodiesel soot and, as consequence, the effect of the 5%Cu/Al_2O_3 catalyst is higher for the former. Thus, it can be concluded that the biodiesel soot can be eliminated by uncatalyzed and catalyzed oxidation at lower temperature than diesel soot.

On the other hand, it is interesting to follow the NO_x conversion because, as it was previously indicated, the use of biodiesel fuel increases the NO_x level in the diesel engine exhaust. Fig. 2c shows the NO_x conversion profile during TPR experiments for uncatalyzed and $SrKTiCuO_3$-catalyzed biodiesel soot. For uncatalyzed combustion, it is observed that the NO_x conversion takes place in the same range of temperature than the soot oxidation, which means that a fraction of NO_x is being reduced by soot. For the catalyzed reaction, a decrease of the temperature required for NO_x reduction by

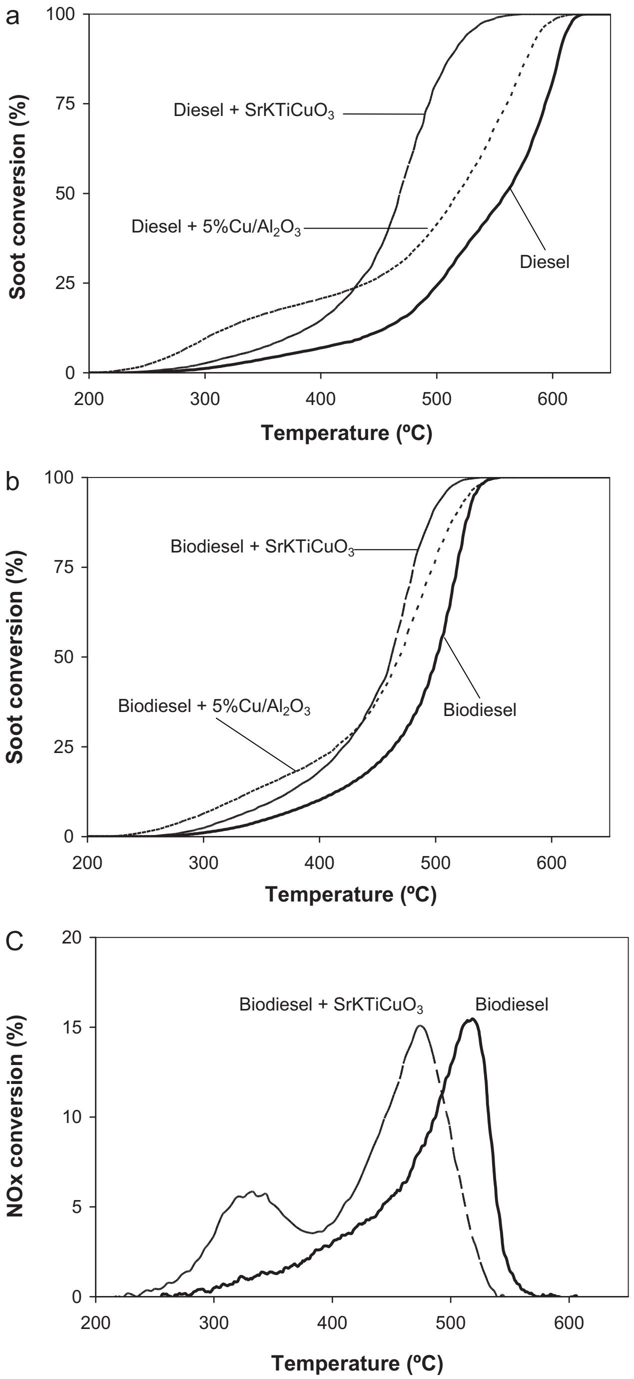

Fig. 2. Conversion profiles in TPR experiments: (a) soot conversion for diesel soot, (b) soot conversion for biodiesel soot and (c) NO_x conversion with biodiesel soot.

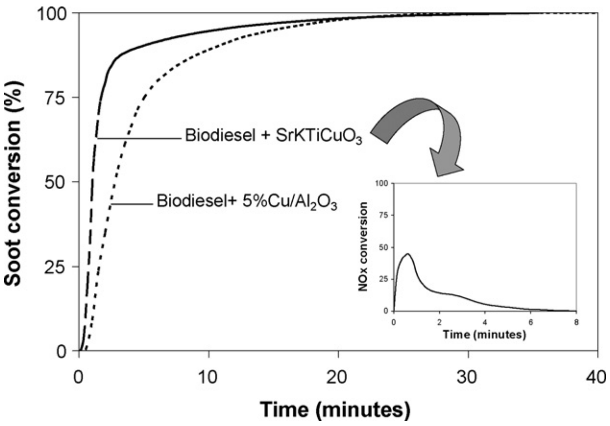

Fig. 3. Soot and NO$_x$ conversion profiles during reaction at 480 °C.

soot is observed, and the profile shows two maxima at 350 °C and 480 °C. The maximum at 350 °C corresponds to NO$_x$ chemisorption on the catalyst [11] and the maximum at 480 °C to the NO$_x$ reduction by soot. Concluding, during biodiesel soot combustion, a simultaneous NO$_x$ reduction takes place for both uncatalyzed and SrKTiCuO$_3$-catalyzed reaction.

In order to obtain additional information about soot oxidation process, experiments in isothermal conditions have been carried out. The range of temperature selected, considering the TPR soot combustion profiles of Fig. 2, is 450–530 °C and both uncatalyzed and catalyzed soot combustion reactions were performed. Fig. 3 shows, as an example, the soot and NO$_x$ conversion profiles obtained for catalyzed biodiesel soot combustion at 480 °C. In agreement with TPR results, the SrKTiCuO$_3$ catalyst is more active than 5%Cu/Al$_2$O$_3$ and, a concomitant NO$_x$ conversion is taking place during the first 10 min of reaction, where the highest soot consumption is observed. From the soot conversion profile obtained at different temperatures, the soot combustion rate at 90% conversion level was calculated and, in Fig. 4, these values are compared with the diesel and biodiesel soot production rates (dotted lines), measured in the experimental conditions used for soot collection (Section 2).

First at all, the use of biodiesel fuel decreases the soot production rate in a 32% approximately, being this reduction percentage similar to that determined by other authors in loaded conditions [5,27]. For example, Päivi et al. [27], using a Volvo bus engine, showed a reduction of soot emission close to 40% for a biodiesel (from rapeseed and soybean) respect to the standard European diesel. Additionally, it is confirmed that the biodiesel soot is more reactive than diesel soot, even in the absence of catalysts. Thus, Fig. 4 shows that biodiesel soot could be eliminated by uncatalyzed combustion at 515 °C, because the uncatalyzed combustion rate achieves the biodiesel soot production rate. On the contrary, the combustion rate of the least reactive diesel soot does not achieve the diesel soot production rate in the range of temperature tested. In the presence of catalysts, the soot oxidation rate increases for both diesel and biodiesel soot, the SrKTiCuO$_3$ catalyst being the most active one. Using this catalyst, the biodiesel soot can be eliminated at around 450 °C meanwhile, for the least reactive diesel soot a temperature of 512 °C is needed.

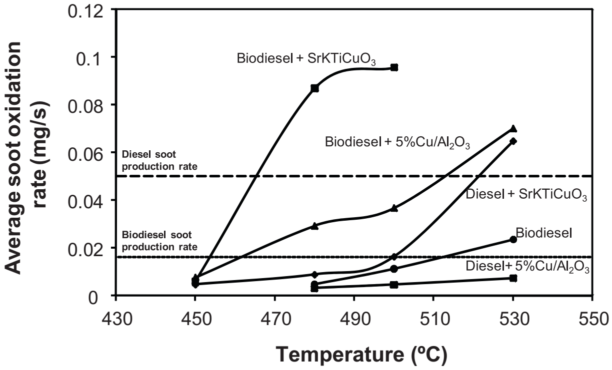

Fig. 4. Soot oxidation rate during isothermal reaction.

4. Conclusions

From the study of the effect of fuel nature (diesel or biodiesel) in the characteristic of soot concerning its removal by oxidation, the following conclusions can be drawn:

- The use of biodiesel fuel has a double beneficial effect because, in addition to the expected reduction in the soot production rate, the reactivity of biodiesel soot is higher than that observed for diesel soot. This seems to be mainly related to both, the higher oxygen content of the biodiesel soot and to the incorporation into the biodiesel soot particles of metallic elements (mainly Mg, Cu, K and Cr), with catalytic activity, coming from the biodiesel raw material and/or from the synthesis process.
- For biodiesel soot, the uncatalyzed combustion rate achieves the soot production rate at 515 °C, and, as consequence, a DPF could be regenerated at that temperature. In the presence of copper-based catalysts (5%Cu/Al$_2$O$_3$ and SrKTiCuO$_3$), the DPF regeneration could be done at around 450 °C. In addition for catalyzed reaction, the CO$_2$ selectivity is increased and the NO$_x$ reduction by soot is improved.

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