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# The evolution of the exhaust diesel soot adsorptive properties after $NO_2$ exposure and according to their SOF content

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## Abstract

Several samples of exhaust diesel soot are investigated by inverse gas chromatography and linear solvation energy relationship (LSER) modelling according to their soluble organic fraction content and their time of exposure in oxidative conditions. The results demonstrate the evolution of the adsorptive properties of the studied materials towards volatile compounds during the oxidation under $NO_2$.

*Keywords:* Soot; Catalytic oxidation; Surface properties; LSER modelling

## 1. Introduction

The emissions of exhaust diesel soot in the atmosphere are well known as hazardous particles for the human health. One of the challenges of the automotive constructors is to eliminate these emissions. For that, several methods are investigated such as filtration processes or catalytic combustion. In the present work, the degradation of soot is undertaken by catalytic oxidation with $NO_2$ as oxidative agent. In this case, the reactivity of different soot samples towards the oxidative conditions varies according to their chemical composition. In the aim to understand the reasons of such behavior several samples of soot (according to the time of exposure in oxidative conditions and the presence or absence of soluble organic fraction, SOF) are investigated by inverse gas chromatography and the linear solvation energy relationship (LSER) approach [1]. This method was already used in the characterization of the surface of carbonaceous materials and it is a complementary tool of the compositional methods in structure–behavior studies [2].

The soot samples are characterized quantitatively in terms of molecular interactions, and can be classified by five constants characterizing their hydrogen-bond acidity and basicity, the dipolar character, the n- and π-electron pairs interactions, and their hydrophobicity. For that purpose, soot samples are placed in a chromatographic column. Then, pure organic solutes of miscellaneous chemical nature are injected separately in the gas chromatograph. For each solute, the adsorption isotherm is established and the gas-sorbent partition coefficient ($K_c$) at zero concentration is determined by the elution by characteristic point (ECP) method of Conder et al. [3]. The free energy parameter $\log_{10}(K_c)$ is described for each known injected solute by the following LSER equation of Abraham et al. [1] as follows:

$$\log_{10}(K_c) = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l\log_{10}L^{16} \quad (1)$$

$R_2$ represents the ability of an injected solute to interact with the substrate through n- and π-electron pairs, $\pi_2^H$ is its dipolar/polarizable character, $\sum\alpha_2^H$ its hydrogen-bond acidity, $\sum\beta_2^H$ its hydrogen-bond basicity and $L^{16}$ its gas–liquid partition coefficient on *n*-hexadecane. All these parameters, also called descriptors, have been determined experimentally at room temperature and are available from a databank containing around 3000 organic compounds. Thus, for one studied sorbent material tested by injecting n pure organic solutes, n LSER equations can be established.

Then, five free energy coefficients (*r*, *s*, *a*, *b* and *l*) characterizing the sorbent material under study can be extracted from these *n* equations using a statistical procedure such as a multiple linear regression analysis. The *r*-coefficient describes

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the ability of the studied soot to interact through n- and π-electron pairs, the *s*-coefficient is its dipolar/polarizable character. The *a*- and *b*-coefficient represent the basicity and the acidity in terms of acceptor and of hydrogen-bond donors, respectively. The *l*-coefficient quantifies the non-polar or dispersive character of the soot. Thus for each material under study an LSER equation can be established. The solidity of such models are represented by several parameters such as: S.D. is the standard deviation, $\rho$ is the coefficient of correlation between observed and calculated $\log_{10}K_c$ values, $F$ is the Fischer-statistic and $n$ is the number of injected solutes.

## 2. Experimental

### 2.1. Chromatography

All the GC measurements were performed on a Shimadzu GC14 gas chromatograph equipped with a thermal conductivity detector (TCD). The carrier gas was helium (purity of 99.995%) with a flow-rate of 20 $\text{cm}^3\,\text{min}^{-1}$. The temperature of the column was 50 °C. The chromatographic columns were made of Teflon® and were 20 cm long.

The chromatogram data acquisitions were performed using Diamir software (Borwin Inc.) and an acquisition station Hercule 2000. All the statistical treatments were performed using Minitab software (Minitab Inc.).

All the injected solutes were supplied by Sigma–Aldrich Inc. and are at least 99% purity. *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *c*-hexane, hex-1-ene, hept-1-yne, oct-1-yne, benzene, toluene, thiophene, propan-1-ol, butan-1-ol, butan-2-ol, 2-methylbutan-1-ol, 1,1,1,3,3,3-hexafluoroisopropanol, 2,2,2-trifluoroethanol, propanone, pentan-2-one, dipropylether, 1,4-dioxane, propanoic acid, ethylacetate, triethylamine, pyridine, nitroethane, 1-nitropropane, chloroform, carbon tetrachloride.

The LSER calculations are performed using Minitab software (Minitab Inc.).

### 2.2. Materials

In this study six samples of soot were investigated by this way. VDS8, VDS25 and EDS are virgin diesel soots containing 8 and 25% of SOF (determined by weight), and a soxhlet extracted SOF-free material, respectively. These three materials were used to characterize the influence of SOF on their adsorptive properties. Then, HDS, HDS7 and HDS30 that are samples which had been exposed to $NO_2$ were investigated to study the influence of the oxidative conditions on the surface properties and thus on their adsorptive properties. HDS is the reference material simply heated. HDS7 and HDS30 correspond to increasing time of exposure in oxidative conditions that induced mass losses of 7 and 30% of material, respectively.

Soot samples were collected from the exhaust pipe of a test bench equipped with a F9Q diesel engine of 1900 $\text{cm}^3$ running at 2000 rpm. The samples were trapped on a SiC filter, using (soot VDS8) or not using an oxidation catalyst (soot VDS25).

The other samples of soot were prepared by treating VDS8 as starting material as follows: EDS was obtained by sequential soxhlet extraction using dichloromethane and toluene. HDS was obtained by heating VDS8 from ambient to 600 °C with a rate of 10 °C $\text{min}^{-1}$ under Helium and maintaining a plateau at 600 °C during 2 h. Then the sample was exposed to 1500 ppm $NO_2$ in helium from the room temperature until 350 °C with a rate of 10 °C $\text{min}^{-1}$. Two more samples were obtained with 7 and 30% of conversion depending on the time of exposure to $NO_2$ The percentage of conversion is calculated as follows: $\% = 100 \times (m_0 - m_1)/m_0$, where $m_0$ is the mass of the material without treatment and $m_1$ is the remaining mass after oxidative treatment.

## 3. Results and discussion

Some examples of LSER equations are given here-after (Eqs. (2)–(4)). The other results are presented in Table 1 and Fig. 1.

For the unextracted soot (VDS8) we found:

$$\log_{10}(K_c) = -1.61 - 0.52R_2 + 0.43\pi_2^{\mathrm{H}} + 1.02\sum\alpha_2^{\mathrm{H}} + 0.38 \times \sum\beta_2^{\mathrm{H}} + 0.717\log_{10}L^{16},$$
$$\text{S.D.} = 0.162,\quad \rho = 0.948,\quad F = 28.3,\quad n = 22 \tag{2}$$

For the extracted soot (EDS) the result is

$$\log_{10}(K_c) = 0.37\pi_2^{\mathrm{H}} + 0.81\sum\alpha_2^{\mathrm{H}} + 0.358\log_{10}L^{16},$$
$$\text{S.D.} = 0.102,\quad \rho = 0.915,\quad F = 995,\quad n = 20 \tag{3}$$

Table 1
LSER constants of the soot samples and other carbonaceous materials

| Soot | *r* | *s* | *a* | *b* | *l* |
|---|---|---|---|---|---|
| VDS25 | −0.41 (0.08) | 0.65 (0.08) | 0.96 (0.09) | 0.78 (0.07) | 0.407 (0.03) |
| VDS8 | −0.52 (0.19) | 0.43 (0.16) | 1.02 (0.22) | 0.38 (0.17) | 0.717 (0.063) |
| EDS | 0 | 0.37 (0.06) | 0.81 (0.16) | 0 | 0.358 (0.035) |
| HDS | 0 | 0.24 (0.06) | 0.51 (0.10) | 0 | 0.462 (0.011) |
| HDS7 | 0 | 0.26 (0.05) | 0.28 (0.09) | 0 | 0.315 (0.008) |
| HTA30 | −0.98 (0.11) | 0 | 0.36 (0.07) | 0 | 0.116 (0.031) |
| Graphite [4,7] | −0.26 | 0.99 | 1.11 | 0 | 0.59 |
| Fullerenes [5,7] | −0.24 | 0.72 | 1.04 | 0 | 0.48 |
| Carbon black [6,7] | −2.77 | 0 | 0 | 0 | 2.65 |

Standard deviations of the LSER constants are given in parenthesis.

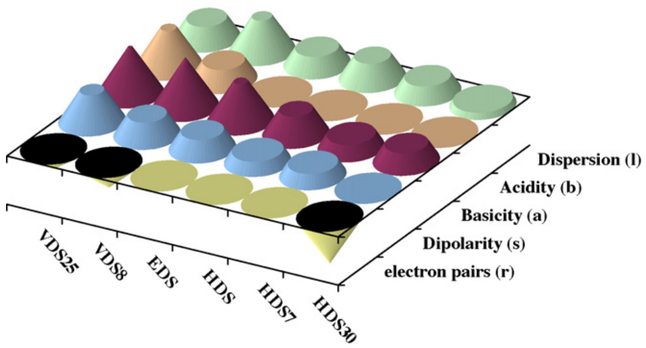

Fig. 1. Evolution of the strengths of the molecular interactions.

It can be noticed that the models are satisfactory from a statistical point of view with correlation coefficients between observed and calculated $\log_{10}(K_c)$ values of more than 0.900 for a number of around 20 injected solutes. Eq. (2) reveals that VDS8 can interact through different types of molecular interactions. Principally, this material is a basic material ($a = 1.02$) which can interact with organic compounds through dispersive ($l = 0.717$) and dipolarity/polarisability ($s = 0.43$) interactions. It presents also a weak acidic character ($b = 0.38$). The negative $r$-coefficient ($r = -0.52$) signifies that some lone pair–lone pair repulsive interactions occur between the hydrocarbon in the gas phase and the solid material.

Eq. (2) is different from Eq. (3). This means that both materials will behave differently towards gaseous organic compounds. Eq. (3) reveals that the SOF extracted soot (EDS) can only interact through basic, dispersive and dipolarity/polarisability interactions. In this case, when the SOF has been removed by extraction, no lone pair–lone pair repulsion and acidic interactions occur. In addition, the strength of the interactions is lower than those observed in Eq. (2). In the following section the results obtained in Eq. (3) are compared to those obtained by Abraham et al. [4–6] in the 1990s on graphite, fullerenes and carbon blacks at room temperature.

Considering the fact that the LSER coefficients are free energy parameters and that their values lead to zero when the temperature increases, by comparing our results obtained at 50 °C and those of Abraham et al. presented in Table 1, it can be concluded that the SOF extracted soot (EDS) behaves like graphite or fullerene [7]. Indeed, the graphite and fullerenes present a $r$-coefficient near to 0, $s$- and $a$- coefficients near to 1 and the $l$-coefficient near to 0.5. Considering a higher temperature such as 50 °C, the $r$-coefficient (will lead to 0), $s$- and $a$-coefficient will decrease as well as the $l$-coefficient. Then the $b$-coefficient will stay equal to zero. Thus, they will be never equal to the coefficient values of VDS8 and VDS25. Now, considering the carbon black, the $s$-, $a$- and $b$-coefficient are zero and, of course, will remain the same for an higher temperature such as 50 °C.

Now, it is obvious that the SOF modifies significantly the adsorptive properties of soot. As already discussed by Clague et al. [8] exhaust diesel soots have a polar surface and, in that respect, differ from carbon blacks which are often used as model materials for soot studies.

For VDS25 the established LSER equation is the following:

$$\log_{10}(K_c) = -1.56 - 0.41R_2 + 0.65\pi_2^{\mathrm{H}} + 0.96\sum\alpha_2^{\mathrm{H}} + 0.78 \times \sum\beta_2^{\mathrm{H}} + 0.407\log_{10}L^{16},$$
$$\mathrm{S.D.} = 0.065,\quad r = 0.978,\quad F = 71.9,\quad n = 22 \tag{4}$$

Like VDS8, VDS25 can interact through all types of molecular interactions. VDS25 is however a more acidic and dipolar material and less hydrophobic. This fact confirms the acidic and dipolar character of the SOF.

Now, considering heated and oxidised diesel soot samples, first of all, the results show differences between the studied materials. The starting soot VDS8 can interact through all types of molecular interactions, contrarily to the corresponding solvent extracted (EDS) and thermally treated samples. EDS and HDS are only basic materials able to interact through dipolar and dispersive interactions. These results show that the thermal treatment goes further in the removal of SOF leading to a more non-polar material than the extracted sample (EDS).

The HDS sample was oxidised by $NO_2$ at increasing burn-off levels. This study shows an evolution of the surface properties according to the time exposure at oxidative conditions. The polar character of the surface decreases for a longer time of exposure in $NO_2$. As summarised in Fig. 1, the $NO_2$ exposure wears out the surface of the soot.

## 4. Conclusion

These analyses showed that the adsorptive properties of soot towards organic compounds evolve according to the presence or not of SOF, their content and composition.

The SOF cleared soot (thermally or by solvent extraction) has adsorptive behaviour as fullerene or graphite and not as a carbon black. The adsorptive properties of soot depend on the composition and/or the quantity of soluble organic fraction. The removal of this fraction leads to a decrease of the surface energy of such materials because of, probably, the polar character of SOF (oxygenated derivatives from fatty acids for examples) that result of unburned fuel and lubricating oil. This, as well as the effect of oxidation by $NO_2$, can be followed by LSER approach. Extracted and thermally treated samples can interact through the same type of interactions confirming in both cases the loss of the SOF. Moreover, the exposure to $NO_2$ leads to the wear of the surface of soot and to a diminution of the strengths of the interactions and thus of its adsorptive properties.

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