# OXIDATION KINETIC STUDY OF ACETYLENE SOOT AND TWO COMMERCIAL CARBON BLACKS

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## Abstract

Hydrocarbon soot was formed by acetylene pyrolysis of 50000 ppmv acetylene at 1100 ºC. The values of its C/H molar ratio, BET surface area and particle diameter were determined. Considering these chemical and structural properties of acetylene soot, two commercial carbon blacks (*SEVACARB MT* and *CABOT*) have been chosen. A study of the oxidation of the three carbonaceous materials is performed using different oxygen concentrations (100-1000 ppmv) and temperatures (850-1000 ºC). The *Shrinking Core Model* with chemical reaction control was applied to determine the reaction order with respect to oxygen and the oxidation activation energy in the temperature range considered. Results obtained for the three materials are compared.

## Introduction

In the combustion of carbonaceous fuels, soot is formed under reducing local conditions. Considering their origin, different kinds of soot can be distinguished, such as flame soot, diesel soot and soot resulting from pyrolysis of hydrocarbons.

The oxidation of soot is of great significance for pollution control. Diesel soot oxidation has been analyzed by several authors (Otto et al., 1980; Gilot et al., 1993; Neeft et al., 1997; Messerer et al., 2006). Many of the kinetic models employed in soot oxidation description are based on power kinetic equations. According to this, different reaction orders with respect to oxygen have been proposed. For diesel soot, Otto et al. (1980) and Miyamoto et al. (1988) determined a reaction order with respect to oxygen equal to unity. Nevertheless, other authors found fractional reaction order (Petersen, 1987; Ahlström and Odenbrand, 1989; Neeft et al., 1997; Yezerets et al., 2005).

Few studies can be found related to the oxidation of soot formed from hydrocarbon pyrolysis. In this study, acetylene has been chosen as reactant in soot production because it appears to be one of the most important precursor species in soot formation from different fuels (Stanmore et al., 2001).

The goal of this work is to perform an oxidation kinetic study for one soot obtained from acetylene pyrolysis and to compare the results with those obtained in the same oxidation conditions for commercial carbon black, since carbon black has been traditionally used as soot surrogate (Marcucilli et al., 1994; Neeft et al., 1997; Müller et al., 2005, 2006).

According to these considerations, a selection of two different commercial carbon blacks has been carried out regarding the main structural properties determined for the acetylene soot. The oxidation of the acetylene soot and the two selected carbon blacks is performed for different conditions of temperature and oxygen concentration. An oxidation kinetic study is performed to determine reaction order with respect to oxygen and oxidation activation energy of the process for the three materials.

## Experimental methodology

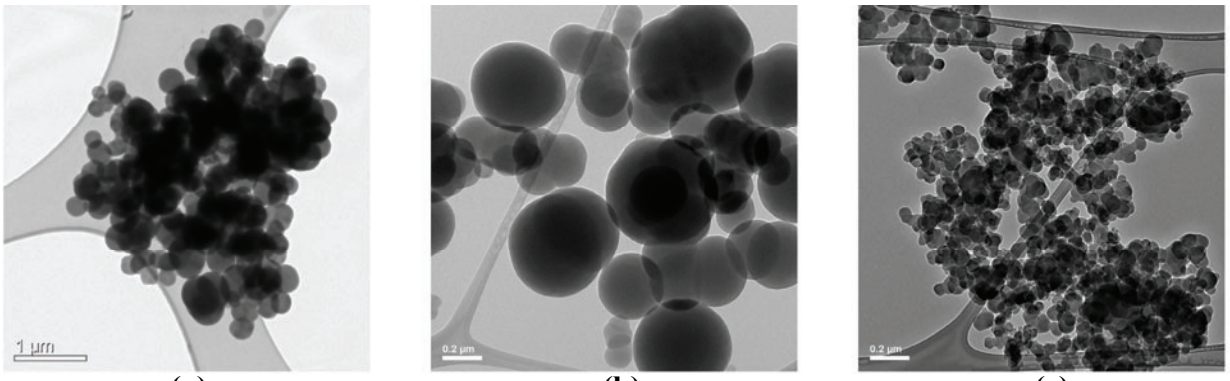
Acetylene soot was obtained from pyrolysis at 1100 ºC of 50000 ppmv acetylene diluted in nitrogen (Mendiara et al., 2005). Ultimate analysis gives a C/H molar ratio for acetylene soot of 13.5. BET area with

nitrogen at 77 K was also determined and resulted in 13.13 $m^2/g$. Particle diameter was obtained through TEM pictures showed in Figure 1. Taking into account these soot characterization results, two commercial carbon blacks with closer values of these structural properties have been chosen, namely, *SEVACARB MT* carbon black and *CABOT* carbon black. Table 1 gathers together the values of the molar C/H ratio, BET surface area and the particle diameter for the acetylene soot, *SEVACARB MT* carbon black and *CABOT* carbon black.

The values of C/H molar ratio are similar for the two carbon blacks but lower for acetylene soot. Acetylene soot and *SEVACARB MT* carbon black present closer values of BET surface area. *SEVACARB MT* carbon black presents a particle diameter distribution closer to the one of acetylene soot.

**Table 1.** BET surface area, molar C/H ratio and particle diameter for acetylene soot and *SEVACARB MT* carbon black and *CABOT* carbon black.

| | **Acetylene soot** | ***SEVACARB MT*** | ***CABOT*** |
|---|---|---|---|
| C/H (molar) | 13.5 | 20.6 | 20.2 |
| BET Surface area ($m^2/g$) | 13.13 | 7.00 | 30.00 |
| Particle diameter (nm) | 200-600 | 160-480 | 30-110 |




**(a)** **(b)** **(c)**

**Figure 1**. TEM pictures of (a) acetylene soot; (b) *SEVACARB MT* carbon black; (c) *CABOT* carbon black. Zoom of (a) 4000 times; (b) and (c) 10000 times.

Figure 2 shows the diagram of the experimental facility used in the study of the oxidation of the three carbonaceous materials. The reaction zone includes a quartz reactor of 15 mm of internal diameter. It is heated by an electrical furnace of 5 kW, which allows to reach temperatures up to 1600 º C.

The quartz reactor used in these experiments is designed including a bottleneck in its middle, where a quartz wool plug is placed. Soot or carbon black is mixed with silica sand particles (with a size less or equal to 150 µm), in solid/sand weight ratio of 1/30, to make it easier the introduction of the carbonaceous solid sample into the reactor and to prevent particles from agglomeration. The mixture is located over the plug, resulting in a thing layer. An amount of approximately 5 mg of carbonaceous solid sample was introduced in the reactor in oxidation experiments.

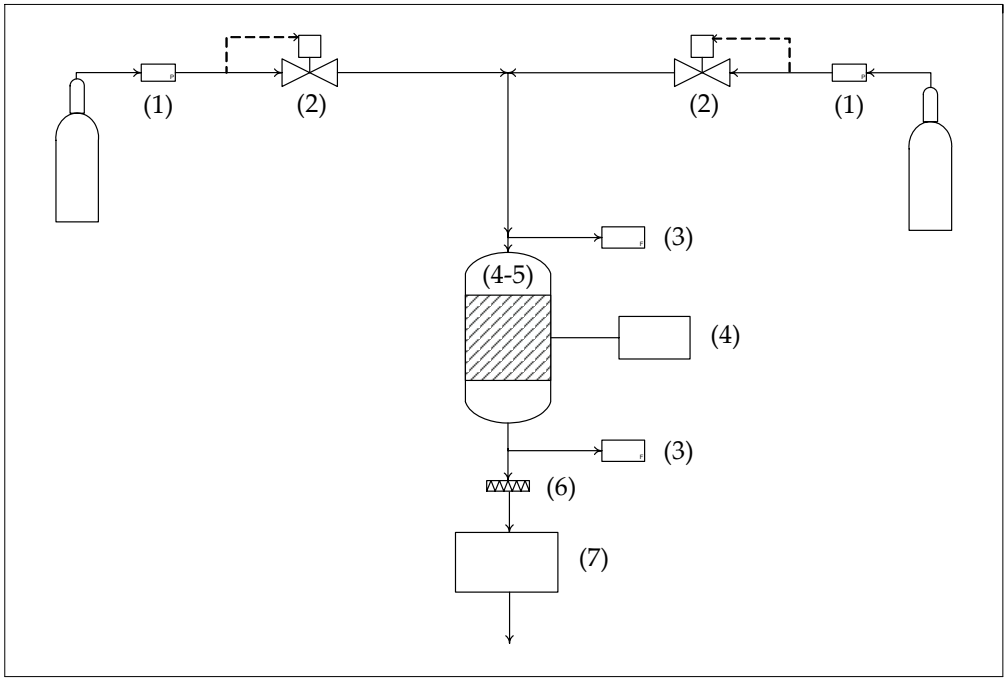



**Figure 2**. Experimental facility. 1: Reactant gases; 2: Mass flow meters and control unit; 3: Flow measurement; 4: Electrical furnace; 5: Reactor; 6: Particle filter; 7: $CO/CO_2$ analyser.

The sample is heated up to the reaction temperature in an inert flow of 1000 ml/min (STP) $N_2$, the same as the total gas flow rate that is used during the reaction. Once the desired temperature is reached, soot or carbon black is exposed to the oxygen/nitrogen mixture.

For acetylene soot and commercial carbon blacks, a study of their oxidation at 900 ºC, in the presence of different oxygen concentrations, is performed. Oxygen concentrations employed range from 100 to 1000 ppmv. Besides, experiments at 850ºC and 1100ºC, with oxygen concentration of 500 ppmv are also done to analyze the influence of temperature.

The outing gases are cooled down to room temperature. Prior to the analysing system, a particle filter is arranged in order to retain any solid particle that may escape away from the reactor. The main reaction carbon products are CO and $CO_2$ and are registered for different reaction times by using CO and $CO_2$ continuous infrared gas analyser. When CO and $CO_2$ values reach a value of approximately 10 ppmv, the experiment is considered to be finished.

The carbon weight percentage determined through ultimate analysis turned to be high (more than 96.0 %), for all the carbonaceous solids employed in this study. The reactivity to oxygen of acetylene soot and carbon blacks is quantified by the amount of carbon consumed.

The initial moles of carbon ( $N_{C_o}$ ) introduced into the reactor were calculated from the measured time evolution of CO and $CO_2$ concentrations in ppmv ( $C_{CO}$ and $C_{CO_2}$ respectively) of the exhaust gas by means of the following equation:

$$N_{C_0} = F \cdot 10^{-6} \cdot \int_0^{\infty} (C_{CO} + C_{CO_2}) \cdot dt \quad (1)$$

where $F$ is the outing molar flow.

The moles of carbon that remain at any time in the reactor, $N_C$ , can be calculated through the following equation:

$$N_C = N_{C_0} - F \cdot 10^{-6} \cdot \int_0^{t} (C_{CO} + C_{CO_2}) \cdot dt \quad (2)$$

The corresponding milligrams of carbon, $W_C$ , can be calculated as:

$$W_C = N_C \cdot M_C \quad (3)$$

where $M_C$ is the atomic weight of carbon.

## Oxidation kinetic study

The BET surface area values of acetylene soot and the two commercial carbon blacks showed in Table 1 can be considered corresponding to non-porous materials (Stanmore et al., 2001). Thus, to analyze the oxidation of acetylene soot, *SEVACARB MT* and *CABOT* carbon blacks, the model known as *Shrinking Core Model* for decreasing size particles with chemical reaction control (Levenspiel, 1999; Szekely, 1976) will be used in this work.

The global oxidation process can be represented by:

$$O_2(g) + bC(s) \rightarrow cCO(g) + dCO_2(g) \quad (4)$$

The value of the stoichiometric coefficient *b* can be calculated for each of the experiments of acetylene soot, *SEVACARB MT* carbon black and *CABOT* carbon black oxidation. According to the global reaction scheme represented by equation (4), *b* is calculated as:

$$b = \frac{\frac{CO}{CO_2} + 1}{\frac{1}{2} \cdot \frac{CO}{CO_2} + 1} \quad (5)$$

Regarding equation (5), the value of *b* depends on the value of the $CO/CO_2$ ratio for every experiment. As an example, Figure 3 shows the values of $CO/CO_2$ ratio versus carbon weight for oxidation experiments of the three materials performed with 500 ppmv oxygen at 850 ºC, 900ºC and 1000 ºC.

For acetylene soot oxidation experiments, the value of the ratio $CO/CO_2$ presents a maximum for all the oxygen concentrations tested. Nevertheless, for these experiments, the value of the $CO/CO_2$ is so high that its variation with carbon weight is not translated into an important variation of the stoichiometric coefficient *b* value calculated according to equation (5). In *SEVACARB MT* and *CABOT* carbon blacks oxidation, the ratio $CO/CO_2$ can be considered as roughly constant through the experiment. Therefore an average *b* value could be determined for each experiment, according to equation (5). For the oxidation experiments performed at 900 ºC and oxygen

concentrations in the range 100-1000 ppmv, similar evolution as the described before for the $CO/CO_2$ ratio is observed.

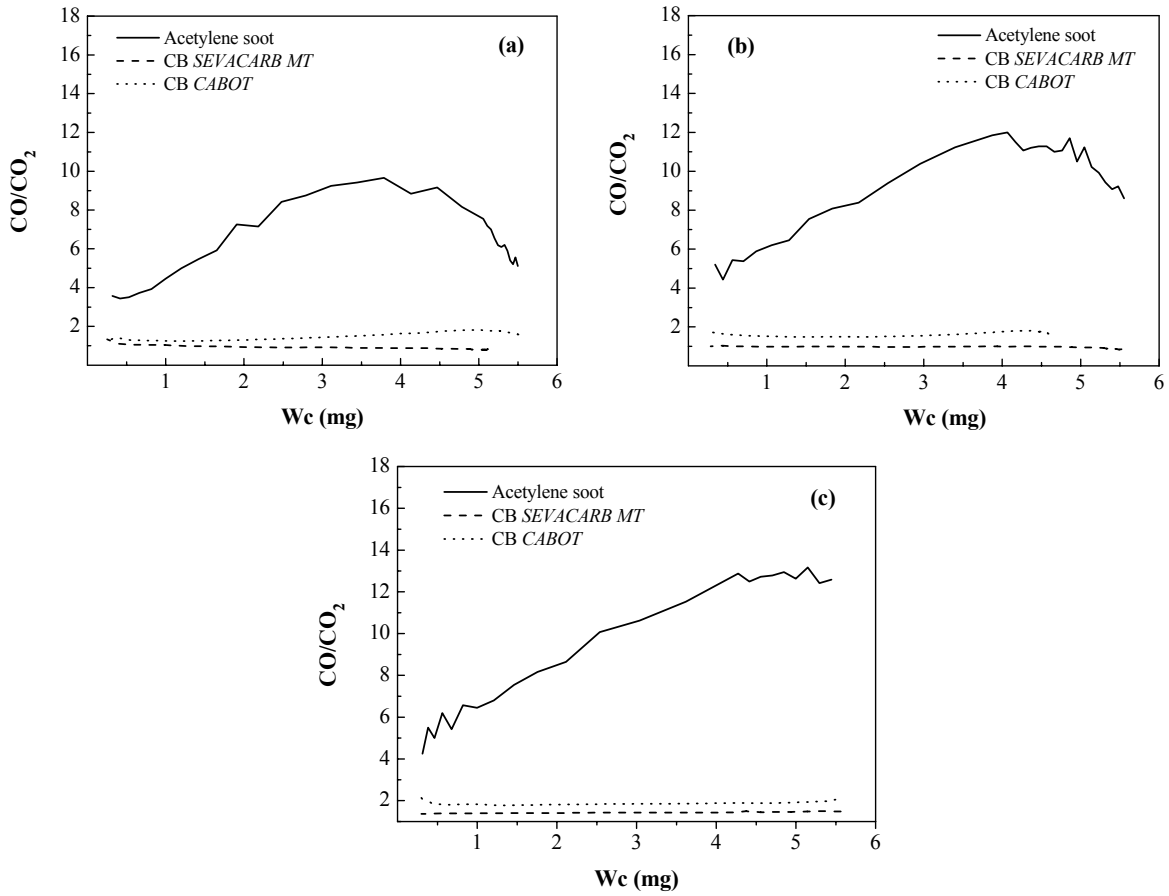



**Figure 3**. Evolution of the $CO/CO_2$ ratio versus carbon weight in the oxidation of acetylene soot, *SEVACARB MT* and *CABOT* carbon blacks with 500 ppmv $O_2$ at (a) 850 ºC; (b) 900 ºC; (c) 1000 ºC.

The application of the Shrinking Core Model for decreasing size particles with chemical reaction control implies the fitting of the acetylene soot, *SEVACARB MT* carbon black and *CABOT* carbon black oxidation data to the following equation connecting time and carbon conversion:

$$\frac{t}{\tau} = 1-(1-X_C)^{1/3} \tag{6}$$

where carbon conversion is defined as:

$$X_C = \frac{W_{C0} - W_C}{W_{C0}} \tag{7}$$

being $W_{C0}$ the initial carbon weight.

The parameter $\tau$ , which represents the time for the complete combustion of a particle, is defined as:

$$\tau = \frac{\rho_C \cdot R_0}{b k_s {C_{O_2}}^n} \tag{8}$$

where $\rho_C$ is the molar density of the carbonaceous material, $R_0$ is the initial radius of the particles, $k_s$ is the rate constant of the oxidation reaction, $C_{O_2}$ is the oxygen concentration and *n* is the reaction order with respect to oxygen.

Table 2 summarizes the values of $\tau$ , with the regression coefficient ($R^2$), obtained in the fitting of experimental data to equation (6) and the average values of *b* for the different experiments of acetylene soot, *SEVACARB MT* and *CABOT* carbon blacks oxidation with different oxygen concentrations and temperatures. At 900 ºC and for the three materials, the value of $\tau$ , decreases as oxygen concentration increases. For a similar oxygen concentration value, acetylene soot showed higher values of $\tau$ . In the experiments with 500 ppmv oxygen and different temperatures, a diminution of the $\tau$ values for the three materials was observed as temperature increased.

**Table 2**. Values of $\tau$ and average values of *b* for the experiments of acetylene soot, *SEVACARB MT* carbon black and *CABOT* carbon black oxidation with different oxygen concentrations (100-1000 ppmv) and temperatures (850–1000 ºC).

| | **T (ºC)** | **$O_2$ (ppmv)** | **$\tau$ (s)** | **$R^2$** | ***b*** |
|---|---|---|---|---|---|
| Acetylene soot | 850 | 500 | 8929 | 0.9985 | 1.74 |
| | 900 | 350 | 8850 | 0.9992 | 1.83 |
| | | 500 | 8130 | 0.9997 | 1.81 |
| | | 750 | 5587 | 0.9989 | 1.79 |
| | | 1000 | 4292 | 0.9901 | 1.76 |
| | 1000 | 500 | 7692 | 0.9957 | 1.45 |
| *SEVACARB MT* carbon black | 850 | 500 | 6369 | 0.9937 | 1.31 |
| | 900 | 100 | 24390 | 0.9979 | 1.38 |
| | | 150 | 15873 | 0.9972 | 1.33 |
| | | 250 | 10989 | 0.9984 | 1.38 |
| | | 350 | 9259 | 0.9988 | 1.32 |
| | | 500 | 5988 | 0.9910 | 1.32 |
| | | 1000 | 3717 | 0.9930 | 1.33 |
| | 1000 | 500 | 5405 | 0.9991 | 1.42 |
| *CABOT* carbon black | 850 | 500 | 4149 | 0.9967 | 1.44 |
| | 900 | 100 | 22222 | 0.9967 | 1.42 |
| | | 150 | 13333 | 0.9951 | 1.39 |
| | | 250 | 8474 | 0.9995 | 1.44 |
| | | 350 | 7752 | 0.9967 | 1.44 |
| | | 500 | 3344 | 0.9974 | 1.46 |
| | 1000 | 500 | 2475 | 0.9961 | 1.50 |

Considering the oxidation experiments carried out at 900 ºC for the three carbonaceous materials and based on equation (8), the following equation allows to determinate the reaction order with respect to oxygen.

$$log\left(\frac{1}{\tau \cdot b}\right) = log\left(\frac{k_s}{\rho_C \cdot R_0}\right) + n \cdot log\, C_{O_2} \tag{9}$$

Figure 4 shows in general a good fitting of the experimental data to equation (9). For acetylene soot an order with respect to oxygen of 1 is obtained. As it was previously mentioned, a reaction order of unity has been postulated for the study of soot oxidation by different authors. For *SEVACARB MT* carbon black, reaction order with respect to oxygen turned to be 0.78, close to 0.8 found by Ciambelli et al. (1994) in oxidation studies with carbon black. In the case of *CABOT* carbon black, again a reaction order of unity is obtained.

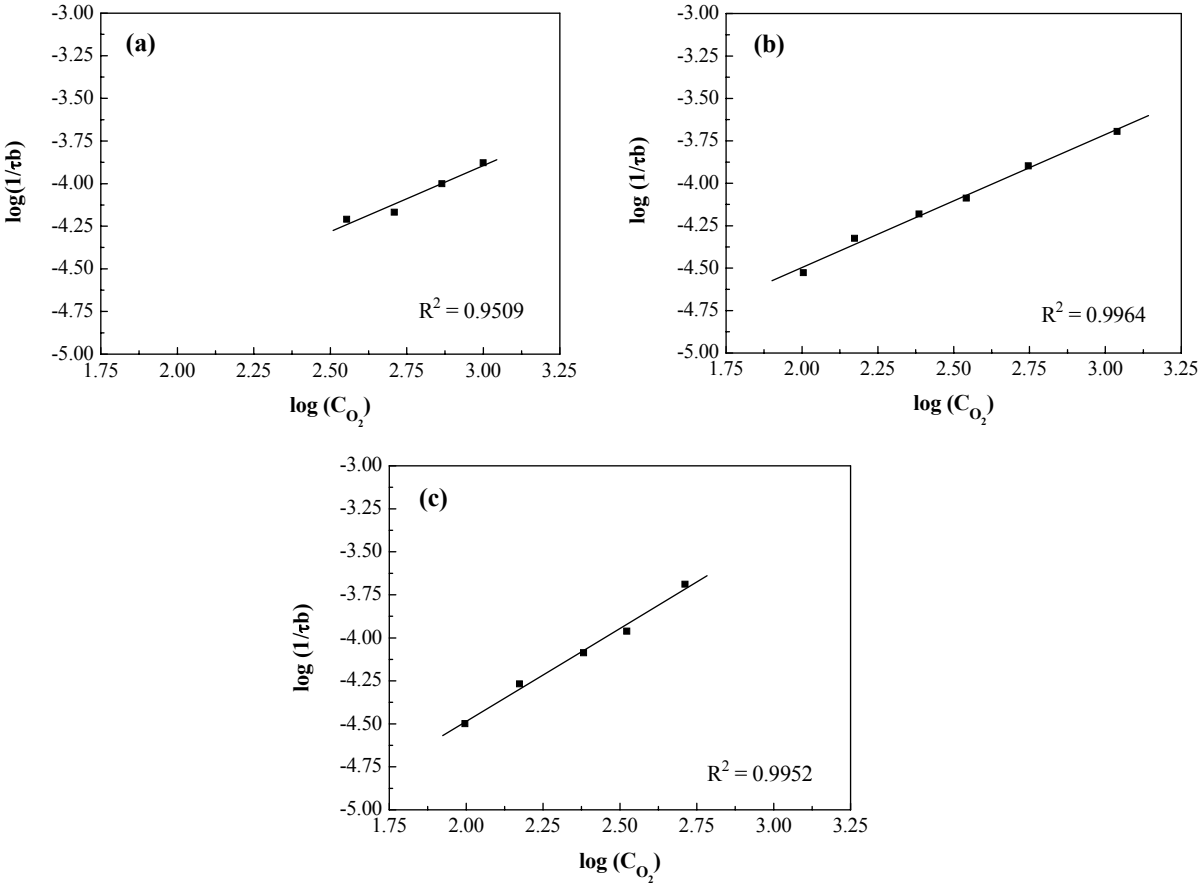



**Figure 4.** Determination of reaction order with respect to oxygen according to expression (9) in the oxidation at 900 ºC, with $O_2$ concentrations up to 1000 ppmv, of (a) acetylene soot; (b) *SEVACARB MT* carbon black; (c) *CABOT* carbon black.

Considering the experiments with 500 ppmv oxygen and at temperatures in the range 850-1000 ºC, the value of the activation energy for the oxidation process is determined. The values of $b$ and $\tau$ are obtained for every temperature using equation (5) and equation (6), respectively. According to equation (9) and considering the reaction order previously determined for each material, the $(k_s/\rho_C R_0)$ values are obtained at each temperature and treated by the Arrhenius plot shown in Figure 5. The resulting activation energies are 42.8 kJ/mol for acetylene soot, 23.5 kJ/mol for *SEVACARB MT* carbon black and 50.2 kJ/mol for *CABOT* carbon black.

To sum up, it can be said than the materials that present the most similar kinetic parameters, i. e. reaction order with respect to oxygen and activation energy, are acetylene soot and *CABOT* carbon black.

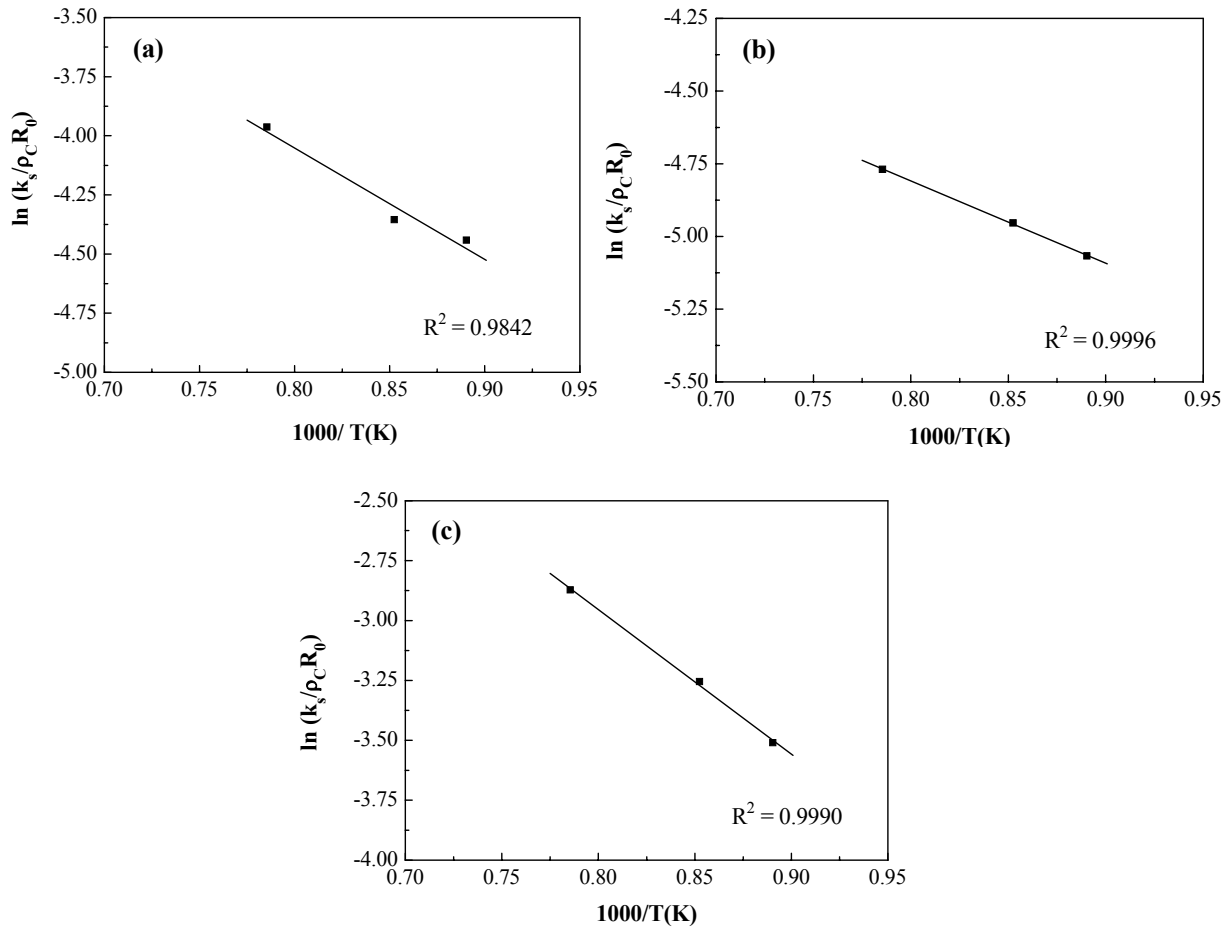



**Figure 5**. Arrhenius plot for oxidation in the 850-1000 ºC temperature range of (a) acetylene soot; (b) *SEVACARB MT* carbon black; (c) *CABOT* carbon black.
All data have been obtained with an oxygen concentration of 500 ppmv.

## Conclusions

A kinetic study of the oxidation of one acetylene soot and two structurally similar commercial carbon blacks (*SEVACARB MT* and *CABOT*) has been carried out. The oxidation the three materials has been performed in the range 850-1000 ºC and oxygen concentrations between 100-1000 ppmv.

The low BET area values of the materials made them to be considered as non-porous. The application of the *Shrinking Core Model* with chemical reaction control and decreasing particle size has allowed to characterize the oxidation of the acetylene soot and *CABOT* carbon black as a process of first order with respect to oxygen. For *SEVACARB MT* carbon black, a reaction order of 0.78 was determined. The activation energy values obtained for the oxidation in the 850-1000 ºC temperature range were 42.8 kJ/mol, 23.5 kJ/mol and 50.2 kJ/mol for acetylene soot, *SEVACARB MT* carbon black and *CABOT* carbon black, respectively. According to these results, the materials that present the most similar order with respect to oxygen and activation energy are acetylene soot and *CABOT* carbon black.

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