# Dependence of oxidation reactivity on optical textures of cokes and solid carbons and oxygen functionalities on carbon surfaces

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## Introduction

Properties of cokes and carbon materials depend on structure at three different scales, atomic (bonding), nanostructure (aggregation of crystallites), and microstructure (optical texture)[1]. Polarized-light microscopy (PLM) has been used to characterize the optical texture of cokes and carbons to assess the extent of their microstructural anisotropy. Oxidation reactivity can be measured as a function of temperature, using a Temperature-Programmed Oxidation analysis (TPO). TPO has been used in a range of studies from understanding the mechanisms of carbon deposition on metal surfaces in engine fuel systems to assessing the degree of graphitization in heat treated carbons[2,3]. For the applications of activated carbons, surface functional groups affect the performance in adsorption processes or as catalyst supports in chemical reactions[4]. Temperature-Programmed Desorption (TPD) can be used to characterize surface functional groups[5]. This work presents findings on the relationships between optical texture and oxidation reactivity of anisotropic carbons and the effects of surface groups on the oxidation reactivity of adsorbent carbons.

## Materials and Methods

PLM examinations were performed on polished pellets of coke samples with a Zeiss Universal polarized-light microscope. TPO analyses were carried out in a LECO Multi-phase Carbon Analyzer RC612. The samples (50 mg) were oxidized under continuous flow of $O_2$ (1-3 L/min) up to 700-1000 °C at 10-30 °C/min. The evolved $CO_2$ (including the evolved CO that was oxidized to $CO_2$ on a copper oxide catalyst) was quantified with an IR spectrophotometer. TPD-MS analyses were carried out in a Micromeritics TPD/TPR 2910 equipment, on 120 mg of samples. After 30 minutes at 120 °C in Ar flow, the samples were heated at 10 °C/min to 900-950 °C and kept at final temperature for 15 minutes. The amounts of evolving CO and $CO_2$ were measured by an on-line quadrupole mass spectrometer (Ametek Dycor Bench Top, USA).

## Results and Discussion

**Figure 1a** presents TPO profiles and PLM micrographs of three petroleum cokes. The PLM micrographs show the overall texture consists of small domains and mosaics for shot coke, domains and curved flow domains for sponge coke, and acicular flow domains for needle coke. One property of cokes that can be related to optical texture is their reactivity. Indeed, TPO profiles display a higher reactivity, or lower oxidation temperature for shot coke, followed by sponge coke and needle coke which has the lowest reactivity and the highest degree of anisotropy. This strong relationship between optical texture and reactivity can be used as a basis for a quick inference on optical texture using an inventory of TPO profiles, if samples have negligible volatile matter in the absence of inorganic elements that can catalyse carbon oxidation.

To study the effect of surface oxygen groups on reactivity, three adsorbent carbons having different pH (3, 6.5 and 10.5) as examples, were analysed by TPO and TPD. **Figure 1b** shows a plot of CO and $CO_2$ evolving from the decomposition of O-surface groups measured by TPD-MS analysis versus TPO temperature at which maximum rate of $CO_2$ evolution was observed. The acidic carbon which has a higher concentration of O-surface groups displayed a higher reactivity, or lower oxidation temperature, followed by the carbons with the increasing pH, respectively.

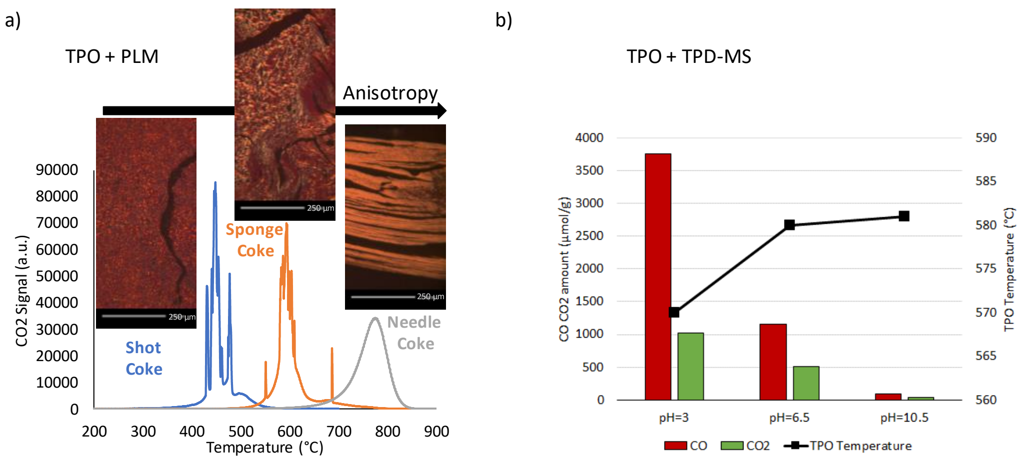


**Figure 1. a) TPO profiles and PLM micrographs for three petroleum cokes; b) CO and $CO_2$ amounts from TPD-MS analysis and oxidation temperature from TPO analysis for adsorbent carbons with pH in 3-10.5 range.**

## Conclusions

Using a catalogue of TPO profiles for coke and carbon samples, a simple TPO analysis may help provide preliminary information on optical texture of anisotropic carbons, higher the reactivity, lower the degree of anisotropy. Similarly, for adsorbent carbons with isotropic texture, TPO results may relate to the nature and concentration of oxygen functional groups on carbon surfaces.

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