

AN ASSESSMENT OF CARBON OXIDATION MECHANISM BY DYNAMIC OXIDATION/DESORPTION IN A LOOPING REACTOR

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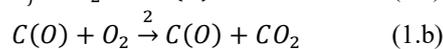
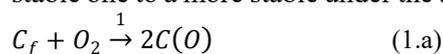
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Abstract

The mechanism of carbon oxidation by oxygen has been scrutinized by means of dynamic experiments consisting of cyclic oxidation of solid carbon at low-moderate temperature (200-300°C) followed by desorption of surface oxides at high temperature (700-800°C). The rapid shift between oxidation and desorption conditions is accomplished thanks to a purposely designed reactor consisting of a dual fluidized bed configuration equipped with a rapid transfer line that enables fast pneumatic conveying of the solid sample from one reactor to the other while keeping distinct reaction conditions in the two reactors. Results are analysed with a specific focus on the role and nature of surface oxides as intermediates in carbon gasification. The existence of surface oxides of different chemical nature and stability provides the starting point to elaborate a tentative mechanistic frame of the experiment. The key features of the phenomenology, namely the oxidation rate and the CO/CO₂ ratio in the evolved gasification products, are interpreted in the light of the relative abundance and stability of “edge” oxides and epoxy moieties generated by carbon oxidation.

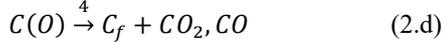
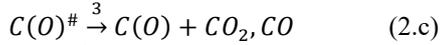
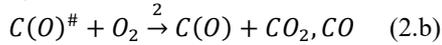
1. Introduction

Modelling the kinetics and mechanisms of carbon combustion has been accomplished with lumped and semi-lumped models of increasing complexity. The three-step mechanism proposed by Hurt and Calo [1] (eq.1) introduces the so called “switch over reaction” which describes the evolution of C-O complex from a less stable one to a more stable under the action of molecular oxygen with release of CO₂:



The three steps mechanism of Hurt and Calo has been included in the CBK model and was able to fit a large set of experimental data of coal combustion mainly in EFR.

Haynes and co-workers [2] further extended the model into a four-step kinetic mechanism (eq.2):



which, based on experimental evidence, considered the formation of a “metastable” ($C(O)^\#$) surface oxide which can undergo complex switch-over in the presence of oxygen, as already described in the previous three step scheme, but can also be rearranged into more energetically favourable forms. Other two differences between the semi-lumped schemes of Hurt and Calo [1] and Haynes et al. [2] deserve mention. The first difference lies in the mechanism of chemisorption, which is dissociative for Hurt and Calo and non-dissociative for Haynes and coworkers. Radovic [3] and Larciprete et al. [4-5] showed, thanks to ab initio quantum chemistry calculations of graphene oxidation, that both paths of formation of carbon-oxygen complexes are possible. On carbene-type edge sites, O_2 chemisorption is non-dissociative and leads to direct CO_2 formation [3]. Alternatively, O atoms bond in bridge position over the C–C bonds, forming epoxy groups [4-5]. This species, which can be roughly identified with the metastable carbon-oxygen complexes, may undergo surface diffusion and unzipping steps and finally CO_2 formation. In Haynes and coworkers’ scheme all the reaction steps produce CO and CO_2 , whereas in Hurt and Calo’s model CO_2 mainly comes from the switch over reaction, and CO from the desorption step, accordingly the CO/ CO_2 ratio in the combustion products would derive from the relative rate of the second and third reaction steps.

In the present study the mechanism of carbon-oxygen interaction is scrutinized by performing dynamic oxidation in a purposely designed reactor that enables periodic exposure of a solid fuel sample to different reaction environments and temperatures with minimum transfer and heat up/cooling time. This technique may offer a valuable tool for the assessment of the mechanism of interaction of solid carbon with oxygen. Studies in this field are helpful not only in view of applications to innovative technologies of stationary combustion or gasification [6], but also to shed light on the dynamical patterns of carbon chemisorption/desorption under alternating oxidizing conditions, relevant to “looping combustion” of carbon [7-8].

2. Experimental description

In order to investigate the carbon-oxygen mechanisms under fast dynamic conditions the experimental campaign has been carried out in a novel lab-scale apparatus, named Twin Beds (TB), consisting of two identical fluidized beds which can be operated separately in batch mode. The main feature of TB is that the two reactors are connected to each other by a duct which is partially immersed in both beds. The duct, equipped with valves, enables the fast pneumatic conveying of the char sample

from one reactor to the other and vice-versa. The Twin Beds apparatus is depicted in Fig.1. A detailed description of the TB system can be found elsewhere [9].

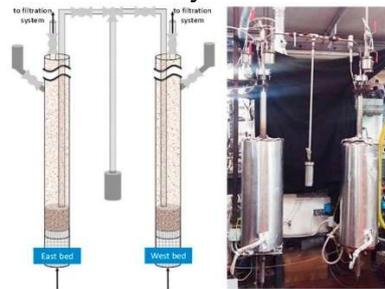


Figure 1. Twin fluidized bed apparatus.

Tests have been carried out with samples of a South African char (400-1000 μ m) obtained by devolatilization in a fluidized bed at 850 $^{\circ}$ C for 5 min of mm-sized coal particles. Char properties are given in the Table 1. Silica sand (900-1000 μ m) in both reactors was used as a ballast in order to avoid significant bed temperature variations due to chemical reactions and solid conveying. For our purposes, the two reactors were employed as an Oxidizer and a Desorber respectively. Several oxidation/desorption cycles were carried out varying the oxidation temperature values between 200 and 300 $^{\circ}$ C and the desorption temperature values between 700 and 800 $^{\circ}$ C. Each test is labeled with the acronym O_x - D_y where the O_x and D_y indicate the oxidation and the desorption steps with their relative operating temperatures in $^{\circ}$ C, respectively.

Table 1. Proximate and ultimate analysis of the coal char

Moisture raw wt%	Volatiles wt%	Fixed Carbon wt%	C dry, wt%	H dry, wt%	N dry, wt%	S dry, wt%	O dry, wt%	Ash dry, wt%
3.34	7.04	69.17	71.92	1.37	0.52	0.02	4.26	20.45

For each test (O_x - D_y), three oxidation-desorption cycles were carried out and the concentration of CO and CO₂ in the exhaust was monitored by means of NDIR analyzer throughout.

3. Results

Fig. 2 reports the typical outcome of a dynamic oxidation experiment, namely the time-series of CO and CO₂ concentration measured at the exhaust of the TB reactor during 3 oxidation/desorption cycles. Profiles in Fig. 2 correspond to O_{200} - D_{700} test conditions. During the desorption step a large amount of CO₂ was released, and several peaks appear in CO and CO₂ profiles in the early stages of desorption, which suggest the presence of different superficial -C(O) complexes. As soon as air is fed to the oxidizer an abrupt release of CO and CO₂ occurs. The origin of these very high

peaks under dynamic conditions is not clear. A possible explanation may be the formation of reactive sites (C_f and/or $-C(O)$) during dynamic desorption at 700°C , that are stable enough not to be desorbed during the desorption step, but reactive enough to undergo switch-over in the subsequent oxidation stage, in the presence of oxygen, despite the fairly low temperature of the oxidation step.

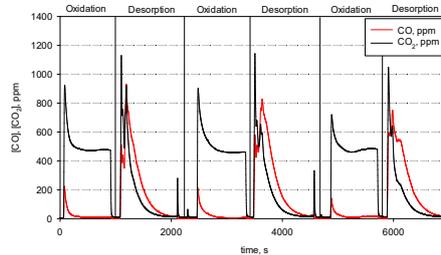


Figure 2. Time series of CO and CO₂ concentrations at the exhaust during the oxidation/desorption cycles.

Table 2 reports the CO/CO₂ ratios obtained during oxidation and desorption steps in different experiments.

Table 2. Average moles of CO and CO₂ released per Kmole of carbon loaded and CO/CO₂ molar ratio during the oxidation/desorption cycles.

	CO/C	CO ₂ /C	CO/CO ₂
O₂₀₀-D₇₀₀	0.0047	0.0130	0.3602
	0.0314	0.0219	1.4344
O₂₅₀-D₇₀₀	0.0136	0.0374	0.3640
	0.0547	0.0318	1.7198
O₃₀₀-D₇₀₀	0.0269	0.0863	0.3120
	0.1037	0.0439	2.3633
O₂₀₀-D₈₀₀	0.0037	0.0069	0.5312
	0.0368	0.0246	1.4928

It is interesting to note that, despite the fact that the amount of CO+CO₂ increases with the oxidation temperature, the CO/CO₂ ratio remains almost unchanged. On the contrary, in the desorption stage the CO/CO₂ ratio increases from the value of 1.4 of O₂₀₀-D₇₀₀ to the value of 2.4 for O₃₀₀-D₇₀₀. This suggests that the nature and/or amount of surface oxides which are formed during the oxidation stages have a strong influence on the subsequent desorption steps. Moreover, when the temperature of the desorption step is increased, while keeping the oxidation temperature fixed at 200°C , the release of CO and CO₂ during the subsequent oxidation steps appears to be enhanced. Data of CO and CO₂ produced during each cycle of Oxidation/Desorption have been further worked out to calculate the moles of oxygen uptaken during the

oxidation steps. A rough indication on the rate of oxygen uptake is obtained by dividing the total amount of oxygen uptaken during the oxidation step by the duration of the oxidation stage (20 min). A linear trend is obtained accounting for an activation energy in the order of $E=30$ kJ/mol. The value is comparable with the value of $E=25$ kJ/mol suggested for the chemisorption reaction by Hurt and Calo [1].

4. Discussion and Conclusion

In this study a novel Twin Beds reactor has been used to perform dynamic oxidation of carbon, consisting of periodic oxidation/desorption cycles on a bituminous coal char. The key findings of the present experimental campaign can be summarized in the following statements:

- a) the extent (and rate) of oxygen uptake during the oxidation step increases with oxidation temperature, and is well correlated by an Arrhenius-like law with an activation energy of the chemisorption step ($E=30$ kJ/mol). This activation energy is fairly smaller than typical activation energies found when the combustion rate of similar carbons is correlated according to single-step kinetic models ($E=120$ kJ/mol);
- b) the CO/CO₂ ratio during a given oxidation or desorption step is not constant;
- c) the CO/CO₂ ratio in the products of the oxidation step is barely influenced by the oxidation temperature, whereas it is affected by changes in the temperature of the desorption step;
- d) the CO/CO₂ ratio in the desorption step is heavily affected by the temperature of the oxidation step, but barely affected by the desorption temperature.

Understanding these features requires consideration of the nature of the different surface carbon-oxygen groups that are formed in the oxidation processes and their possible interaction with the adjacent carbon sites. In particular, the CO/CO₂ ratio provides an indication of the alternative paths along which carbon gasification occurs, and may be helpful to track the prevailing path to carbon conversion.

The following tentative mechanism can be offered to explain the recorded phenomenology. Oxidation at mild temperature yields surface oxides to an extent and rate that depend on oxidation temperature according to an Arrhenius-type law. The moderate activation energy suggests that the prevailing moiety of surface oxide formed during early oxidation is the “metastable” epoxy, which may eventually act as oxygen “donor”. The rate of oxygen uptake might be at least partly controlled by surface diffusion (spill over) of mobile epoxy over the polyaromatic basal domains. Results of previous studies [10-11] suggest that increasing oxidation temperature (from 200 to 300 °C) should result in a larger fractional content of “edge” oxides (ether, carbonyl, lactone) as compared to the epoxy. As reaction conditions are switched to the desorption stage, the much higher temperature promotes the formation of further stable edge oxides at the expenses of epoxy. Edge oxides eventually undergo decomposition either as CO or, by interaction with neighboring mobile epoxy and unzipping, as CO₂.

It may be inferred that the CO/CO₂ ratio observed during the desorption step reflects

the relative abundance of edge versus epoxy sites established during the previous oxidation stage: the higher the oxidation temperature (from 200 to 300°C), the larger the edge vs epoxy fractional content, the larger the CO/CO₂ ratio (from 1.43 to 2.36). The release of CO₂ and, to a lesser extent, of CO during the early oxidation stages might instead be related to decomposition of surface oxides that have survived the previous desorption step, as their stability is undermined by direct interaction with molecular oxygen (complex switch-over) or with newly formed neighbouring surface oxides. Further investigation is in progress to fully assess the dynamics of epoxy and different types of edge oxides and to provide a quantitative mechanistic frame for carbon oxidation and combustion.

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