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The influence of char surface oxidation on thermal annealing and loss of combustion reactivity

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Abstract

Thermal annealing associated with heat treatment of coal chars affects gasification reactivity and levels of unburned carbon in residual ash from coal-fired furnaces. The present study addresses the effect of char surface oxidation, occurring upon exposure to oxygen, on the course of thermal annealing, and related loss of combustion reactivity. This goal is pursued by comparing the extent of thermal annealing suffered by coal char upon heat treatment in a nitrogen atmosphere with that of chars that underwent oxidation prior to or during heat treatment. Oxidation of char was accomplished by supplying single or multiple pulses of air during the heat treatment, which were sufficient to oxidize the char surface but small enough to limit carbon gasification to less than 5%. The extent of thermal annealing was characterized both in terms of the loss of combustion reactivity and of the development of structural anisotropy of char samples, investigated by HRTEM. Results of the present study confirm that heat treatment reduces oxyreactivity of char samples, the effect being more pronounced at temperatures exceeding 1200 °C. Oxidation of samples mitigates the effects of heat treatment, as demonstrated by the smaller loss of gasification reactivity and by the more limited development of structural anisotropy of oxidized samples. Correspondingly, elemental analysis of samples indicates the formation of stable surface oxides upon oxidation, that are subsequently desorbed upon heat treatment. At temperatures exceeding 1200 °C, the effect of oxidation vanishes. Results are analysed and discussed in the light of the possible hindrance of thermal annealing due to the formation of stable surface oxides and of the parallel modifications occurring to the ash constituents.

Keywords: Coal; Thermal annealing; Oxidation; Reactivity

1. Introduction

The course of coal combustion is determined by the progress of purely thermally activated processes (coal pyrolysis, thermal annealing of its char, and physico-chemical modifications of ash constituents) and heterogeneous oxidative processes (coal and char combustion) in series and/or parallel to each other (Fig. 1). Among the others, thermal annealing of coal chars upon heat treatment has recently gained renewed interest [1–7], since it has been recognized as one key to the loss of gasification reactivity of chars and the level of unburned carbon at the exhaust of coal-fired furnaces.

Whereas a rich literature addresses pyrolysis and thermal annealing under inert conditions, the mutual interaction between purely thermally

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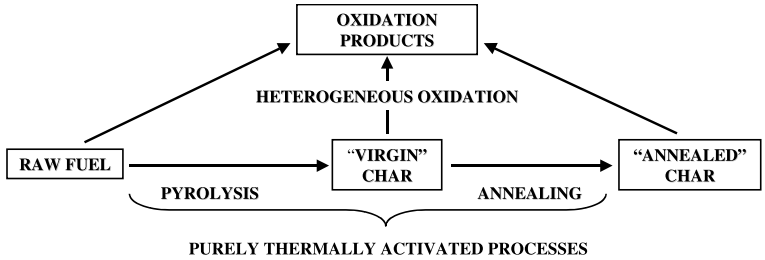

Fig. 1. Network of processes active during coal combustion.

activated processes and heterogeneous oxidation has received comparatively little attention. Studies on this subject have mostly addressed oxidative pyrolysis in the early stage of coal conversion. It has been observed that oxidative pyrolytic conditions enhance the release of volatile matter from coal [8,9]. This can be attributed to the introduction in the carbon structure of oxygenated compounds more labile than those present in the original coal structure [10,11]. The influence of the establishment of oxidizing versus inert atmosphere on the rate and extent of thermal annealing of a coal char has never been addressed in the literature.

Thermal annealing actually involves a broad spectrum of solid state transformations of the "turbostratic" carbon structure [12]: change of carbon hybridization and aromatization prevail at low temperatures, stacking, and reordering of graphene layers at moderate temperatures, and lateral growth of carbon crystallites at higher temperatures. On the other hand, it is recalled here that microporous carbons feature extensive formation of surface oxides upon exposure to oxygen-containing atmospheres at moderate to high temperatures [13]. The chemical nature of such complexes is still debated. Carbonyl/ether and anydride/lactone complexes are the main forms of oxygen complexes according to Kelemen and Freund [14], Tomita and coworkers [15], and Haynes [16]. Both types of complexes could contribute, along different chemical pathways, to carbon gasification. Intercalation of oxygen between basal planes of graphitized carbons is invoked by Yang and coworkers [17,18] to explain the formation of stable carbon surface oxides. This hypothesis, based on the results of molecular orbital calculations, receive some support from experimental studies regarding oxygen chemisorption on basal planes of graphite assessed by fast temperature programmed spectroscopy studies [19] and edge decoration studies [20,21]. The population of surface oxides displays a broad range of thermal stabilities, some being stable upon heat treatment, even at temperatures in excess of 1500 °C [14,17].

Altogether, the very chemical nature of transformations associated with thermal annealing and the possible formation of thermally stable surface oxides lead to the expectation that thermal annealing is affected by the inert versus oxidizing nature of the atmosphere. The present study addresses this issue. It aims at a preliminary assessment of the effect of exposure to oxygen on the rate and extent of thermal annealing of a coal char. To this end, the extent of annealing of heat treated char samples is compared with that of samples that were oxidized by exposure to a limited amount of oxygen during heat treatment. Char sample characterization included thermogravimetric analysis, elemental analysis, and quantitative HRTEM.

2. Experimental

2.1. Materials

Experiments have been carried out using a South African bituminous coal whose properties are given in Table 1. Coal samples were ground and sieved in the size range 75–125 μm.

Gases were nitrogen of chromatographic grade and air of technical grade.

2.2. Apparatus and procedures

2.2.1. Sample pre-treatment

Coal samples were subjected to different pre-treatments in a Rheometrics TG1000M/1500 thermobalance with heating rates of 1000 and 10,000 °C/min or in an electrically heated tubular furnace with a heating rate of 300 °C/min. For each test approximately 2 and 50 mg of coal were loaded in the TG and in the tubular furnace, respectively. Two different pre-treatment procedures have been followed:

(a) heatup in nitrogen to a temperature 900 °C $< T <$ 1350 °C, followed by isothermal heat treatment in nitrogen at temperature T for a time between 1 and 30 min;
(b) heatup in nitrogen to a temperature 900 °C $< T <$ 1350 °C followed by isothermal heat treatment in nitrogen at temperature T for a time between 1 and 30 min. During