Demineralisation of semi-anthracite char with molten salts/HCl Effects on the porous texture and reactivity in air

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Abstract

The effects of chemical heat treatments of a semi-anthracite char (AC) on textural properties and reactivity in air of the material are investigated. The starting char was first treated with a mixture of LiCl/KCl or LiCl/KCl/CaO at 743, 873 or 1173 K and the products obtained were then washed thoroughly with distilled water. A small fraction of these samples were treated with 10^{-3} M HCl solution. Valuable information on textural modifications produced in the material was derived from the adsorption isotherms for CO_2 at 273 K. The reactivity tests were carried out at 808, 823 and 823 K. The microporosity developed and the reactivity in air increased in the partially demineralised products. The former effect was stronger for the LiCl/KCl/CaO-treated samples and the latter for a larger number of the LiCl/KCl-treated samples.
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1. Introduction

The continuing use of coal is influenced by the environmental concern, as carbon dioxide emissions cause global warming, and by the decline of oil and natural gas reserves. As a result, the way in which coal is used in the future is expected to change. Perhaps, the demand of clean coal will rise. This coal is likely to be better feedstock than coal for the production of carbon-based fuels, chemicals and materials, which are currently produced from oil. In addition, the carbon content of coal is much higher than that of oil, and is largely present as aromatic structures. Coal may be a better feedstock than oil for the production of aromatic chemicals and products such as engineering plastics, high temperature heat-resistant polymers and carbon fibres [1,2].

Coal with a high mineral matter content, in particular, certainly requires special beneficiation treatments to remove enough mineral matter for the material to be utilisable. On a small laboratory scale, most chemical methods of coal demineralisation consist of leaching the material with an aqueous solution at temperatures below the boiling point of water. With such an aim, HCl and HF at 313 K are frequently used [3]. However, the techniques of significant industrial importance involve the treatment of coal with alkali at temperatures as high as between 423 and 623 K, at atmospheric pressure or at higher pressures ranging between 25 and 172 atm [4–6].

By the alkali method, clean coal with an ash content of less than 0.5 wt.% is obtained [7]. However, in spite of this success, the chemical cleaning is not commercially available at the present moment due to the high reagent cost and a high operating cost. As an alternative, the use of calcium oxide (lime) as the leaching agent instead of sodium hydroxide has been attempted. Lime is a cheaper and much more available reagent than sodium hydroxide. There other salient advantages of using lime instead of sodium hydroxide: (1) there is less extensive extraction of coal organic matter into the leaching solution; (2) it is less corrosive to the reactor and equipment materials; (3) there is a lesser fouling effect of the residue if chemically treated coal is employed in combustion or gasification applications. As a result, the chemistry of

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hydrothermal reactions of $Ca(OH)_2$ with pure quartz and pure kaolinite, both of which are the major constituents in coal mineral matter, has been investigated previously [7].

Chemical reactions in molten state have found application in metallurgical slagging processes. Owing to their properties, molten salts are suitable media for a great variety of chemical reactions to occur. Thus, molten salts are able to dissolve a large number of substances with very different properties (metals, oxides, salts, etc.). In chemical reactions, molten salts can take part as a reactant, solvent or catalyst [1].

In connection with the use of molten salts in demineralisation treatments of coal, firstly, a LiCl/KCl mixture containing a metal oxide (i.e., CaO, MgO, FeO, CoO, NiO, Cu_2O or ZnO) was employed for a semi-anthracite char at 873 K [8]. Results obtained then revealed that CaO (a basic oxide, which is further soluble in alkali metal chloride melts [9]) was able to react with SiO_2 (an acid oxide) to give γ-calcium orthosilicate [8,10]. Subsequently, the same coal char was reacted with LiCl/KCl and LiCl/KCl/CaO mixtures at 743, 873 or 1173 K, and the effects of these treatments on mass and composition, textural properties and reactivity in air were investigated [11]. Lately, the LiCl/KCl and LiCl/KCl/CaO-treated products have been washed with HCl solution, and the associated effects on the porous texture and reactivity in air are reported here.

2. Experimental

A semi-anthracite from Peñarroya (Córdoba, Spain) was used. Its ash content was somewhat higher than 42 wt.%, dry basis [12]. The as-received coal was oven-dried, ground, and sized, the particle size between 0.15 and 0.20 mm being chosen. After these operations, the material was first carbonised at 1273 K for 2 h in N_2 (purity > 99.998 vol.%, flow rate = 100 - cm^3 min^{-1}). Subsequently, around 5 g of the carbonised product (AC, hereafter) were treated with 5 g of either LiCl/KCl (60/40 mol%, mp = 723 K) or LiCl/KCl/CaO (4 g Cl^-/1 g CaO) at 743, 873 or 1173 K for 5 h in N_2. After that, the product obtained was thoroughly washed with distilled water until the absence of Cl^- ions from the residual liquid and oven-dried at 383 K for 24 h. A small fraction of these products (≈1 g) in successive steps was treated with 10^{-3} M HCl solution (100 mL), washed again with distilled water, and oven-dried. The samples are noted as AC–LiCl–KCl–T–HCl and AC–CaO–T–HCl (T = maximum heat treatment temperature).

A Micromeritics ASAP 2010 surface area analyser was used to measure the adsorption isotherms for CO_2 at 273 K. Prior to effecting adsorption measurements, the samples were out-gassed at 393 K for 12 h, up to a residual pressure of 5– 10×10^{-3} Torr.

The gasification tests were carried out using a Seiko 320 thermogravimetric system. Samples of ≈10 mg were first heated from room temperature to 1173 K in N_2 (purity > 99.998 vol.%, flow rate = 75 cm^3 min^{-1}) to determine the volatile matter content. Then, in the same N_2 atmosphere, the system was cooled down to the reaction temperature, i.e., 808, 823 or 838 K. After replacing the N_2 atmosphere with an air stream (flow rate = 75 cm^3 min^{-1}), the heat treatment was extended isothermally for 1 h. In parallel tests, the ash content of the samples was also determined by heating at 1023 K for 20 min in air (flow rate = 75 cm^3 min^{-1}).

3. Results and discussion

As shown in Table 1 [12], the moisture content is relatively high for the semi-anthracite used in the present study as for coals of high rank it is usually lower. The low fixed carbon content in this coal can be accounted for on the basis of its high mineral matter content. For most coals the nitrogen content ranges between 1.4 and 2.0 wt.% [13], for the semi-anthracite being 1.0 wt.%. The presence of sulphur is not wished in coal, owing to detrimental effects on coal utilisation processes and on the environment. In the case of this semi-anthracite, the content of this heteroatom is low as for other coals it lies commonly between 0.2 and 10 wt.%, although only rarely the sulphur content exceeds 5 wt.% [13]. For commercial coal the sulphur content is below 1 wt.% [13]. Of the oxides analysed in semi-anthracite ashes, SiO_2 ranks first as the most abundant component. Then, although much less, it is found Al_2O_3. According to their content, the oxides vary by the sequence $SiO_2 > Al_2O_3 > Fe_2O_3 > K_2O > CaO > MgO > Na_2O \approx S$-$SO_3 > TiO_2$.

The CO_2 adsorption isotherms have been analysed by applying the Dubinin–Radushkevich equation [14]:

$$\log W = \log W_0 - D \log^2 \left(\frac{p^0}{p} \right) \tag{1}$$

$$D = B \left(\frac{T}{\beta} \right)^2 \tag{2}$$

where p/p^0 is the equilibrium relative pressure, W the micropore volume filled with the adsorbate as liquid at a given p/p^0 value, W_0 the total micropore volume, D or B a constant related to the porous structure of the adsorbent, β a scale factor and T is the absolute temperature.

From the B value, the characteristic energy of adsorption (E_0) can be calculated by expression:

$$E_0 \, (\text{kcal mol}^{-1}) = \frac{8.3144 \times 10^{-3}}{B^{0.5}} \tag{3}$$

Table 1
Chemical analyses of semi-anthracite and its ashes

Proximate analysis	
Moisture	9.09
Ash[a]	42.89
Volatile matter	8.01
Elemental analysis	
Fixed carbon	40.01
C	49.02
H	2.1
N	1.0
S	0.55

[a] Ashes (wt.%): SiO_2 (55.4), CaO (2.5), MgO (2.0), Fe_2O_3 (5.7), Al_2O_3 (27.9), Na_2O (0.6), K_2O (3.8), TiO_2 (0.5) and SO_3 (0.6).