Fuel Processing Technology 169 (2018) 269–279

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Textural characterization of chars using fractal analysis of N_2 and CO_2 adsorption

Manuel María Mahamud*, Verónica García

University of Oviedo, Department of Chemical and Environmental Engineering, Faculty of Chemistry, Campus de El Cristo, 33071 Oviedo, Spain

ARTICLE INFO

Keywords:
Gas adsorption
Fractal analysis
Char texture
Coal oxidation

ABSTRACT

The application of fractal analysis to nitrogen and carbon dioxide adsorption isotherms is used together with other textural analysis techniques with the aim of obtaining a better knowledge of the phenomena leading to char formation. This is an important point since chars are key intermediate materials during the manufacturing process of active carbons. The materials under study were series of chars obtained from a high-volatile A bituminous coal oxidized in air at 543 and 473 K for different periods of time extending up to 42 days. The fractal characteristics of the chars were obtained from the nitrogen and carbon dioxide adsorption isotherms by using the methods proposed by Neimark, Wang and Li, and the fractal version of the Frenkel-Halsey-Hill method. The latter approach was found suitable for the high pressure interval of N_2 isotherms. Evolution of the fractal properties in the series of chars is compared with that corresponding to the series of precursor coals. Changes in pore network during carbonization depend on the severity of the air preoxidation of the coal. This happens since preoxidation conditions other properties and processes such as the texture of the precursor coals, the release of the volatile matter as well as the plastic behaviour of coals. These three points were found to be the key factors that determine the fractal characteristics of char. The role of the pore characteristics of the coal on the textural features of the obtained chars is boosted if coal preoxidation is carried out at the more elevated temperature, 543 K. The role that the phenomena occurring throughout the carbonization of oxidized coals have on the textural characteristics of the chars obtained is explained considering fractal features together with other textural properties. The results of this work are compared with previous fractal studies based on mercury porosimetry data and conventional textural techniques.

1. Introduction

The manufacture of active carbons from bituminous coals generally includes three main steps: the oxidation of coal particles; the carbonization of the oxidized coals, leading to a char with a more developed pore network and a very low volatile matter content; and at the end, the activation that creates a highly porous material from the char by means of a chemical reaction with an oxidant [1,2,3,4]. Coal preoxidation has a three-fold purpose. First, the oxygen functional groups introduced by oxidation and the simultaneous decrease in the C—H linkages play a key role in the elimination of the plastic behaviour during carbonization [5]. This results in an increase in the surface areas of the chars [1,2,3] as the collapse of the micro and macroporous network created by the preoxidation steps is reduced [6]. Otherwise, carbonization of bituminous coals that passes through a plastic phase will lead to a coke with a very poor pore structure (mainly macropores) not suitable for obtaining good active carbons [6]. Second, the oxidation also contributes to a development of the pre-existent pore network in the coal (mainly micropores) due to the opening of initially non-accessible porosity and to the widening of the existent pores [7,8] leading to a more extended and interconnected pore network [9]. This fact will play an important role in the pore network growth when devolatilization takes place in the carbonization step, allowing an easier release of the volatile matter. Third, the oxidation produces an increase in the volatile matter of the coal [5] and additionally, the release of the volatile matter occurs in a broader temperature interval [1,2]. Consequently, the release of this increasing amount of volatile matter, together with the more developed pore network in the coal and the absence of plastic behaviour, leads to the development of a larger pore network in the resultant char from the oxidized coal, increasing the percentage of micropores [1,6,10]. Preoxidation of other carbonaceous raw materials prior to activation is also an important step for obtaining adsorbent materials with high surface area [4,10]. It was previously shown how the application of fractal analysis to data obtained from mercury porosimetry tests is a useful tool to understand the phenomena lying behind each step in the manufacture of granular active carbons [9,11,12]. Mercury porosimetry and

* Corresponding author.
E-mail address: mahamud@uniovi.es (M.M. Mahamud).

http://dx.doi.org/10.1016/j.fuproc.2017.10.013
Received 1 July 2017; Received in revised form 14 October 2017; Accepted 16 October 2017
0378-3820/ © 2017 Elsevier B.V. All rights reserved.

fractal analysis together with more classical textural studies also proved to be very useful to understand the pore evolution of coals with oxidation time [7] as well as to establish correlations with technological properties of coals and other porous materials [13,14,15,16]. The fractal characteristics of a surface depends on its own features, independently of the particle size or the pore region where the surface is found. Fractal properties are intrinsic characteristics of surfaces and are apparently independent of surface size or macroscopic shape. The fractal surface characteristics of a porous solid may change from one region to another and then it is possible to obtain a fractal profile also termed the fractal fingerprint of the material. There is also an evolution of fractal characteristics when porous materials undergo changes due to their processing. These changes are conditioned by the properties of the raw material (including textural properties) and the changes induced in the surface and pore network by the process itself. The abovementioned papers showed how the application of fractal analysis to data obtained from mercury porosimetric analysis grants extra textural information that complements the results of traditional determinations such as pore volume, surface area or densities.

The present paper shows how the fractal approach based on the adsorption isotherms by using models developed by different authors [17,18,19] can be employed to analyze several series of chars. These results will be considered together with previous findings from fractal analysis of mercury porosimetrical determinations and from classical textural studies, helping to assess the role of certain operation variables and coal properties in the textural development of chars obtained in the carbonization step.

2. Methods for the determination of the fractal dimension and other textural properties from gas adsorption isotherms

Physical adsorption of gases is a technique widely used for textural characterization of porous solids [20,21,22] that allows the obtaining of parameters such as surface area, pore volume and its distribution. The use of N_2 and CO_2 adsorption leads to a good pore characterization for coals [23] and is also very useful when estimating adsorption possibilities for technological applications [24].

In the same way that fractal analysis was developed for application to the data from mercury porosimetry analysis [25,26,17,27,28,12], there exist several models that are employed to analyze gas adsorption data from a fractal point of view.

The genuine method for checking the fractal characteristics of the pore surface of an adsorbent can be to measure its surface area by means of the adsorption of gases with different molecular sizes. They act as real “yardsticks” that can fit the surface irregularities according to their effective sizes. For a fractal object, the relationship between the size of the yardstick, α, and the number of yardsticks needed to cover the object, N, is the following

$$\mathrm{N}(\alpha) \propto \alpha^{-D} \tag{1}$$

The method will be laborious as determinations with several adsorbates will be needed and the range of sizes will also be limited [29,30,31].

The thermodynamic method proposed by Neimark [17] relies on three basic relationships: First, the fractal relationship between the surface area, S, and the size of the yardstick employed for measuring it –that in our case is the radius of curvature of the meniscus, r– is derived directly from Eq. (1).

$$S(r) \propto r^{2-D} \tag{2}$$

Second, the Kelvin equation, that relates the radius of curvature of the meniscus $r(\mu)$ with the relative pressure, $\mu = P/P_0$, as follows

$$r = \frac{2\sigma\nu}{\mathrm{RT}(-\ln\mu)} \tag{3}$$

where σ is the surface tension, ν the molar volume, R the universal gas constant and T the absolute temperature. Third, the surface area, $S(\mu)$, of the adsorbed gas film that can be expressed according to the following equation

$$S(\mu) = \frac{\mathrm{RT}}{\sigma}\int_{N}^{N_{\max}} (-\ln\mu)\,dN \tag{4}$$

being N the amount adsorbed at a relative pressure μ, and N_{max} the amount adsorbed when $\mu \to 1$.

Linearizing Eq. (2) and taking into account Eqs. (3) and (4), the following expression is obtained:

$$D_N = 2 + \frac{d[\ln S(\mu)]}{d[\ln(-\ln\mu)]} \tag{5}$$

i.e., the Neimark fractal dimension, D_N, is obtained from the slope of the graph $\ln S(\mu)$ as a function of $\ln(-\ln\mu)$. Eq. (5) can also be expressed in function of the average pore radius, r, by using the Kelvin relationship of Eq. (3) [18]. The alternative expression is

$$D_N = 2 - \frac{d[\ln S(\mu)]}{d[\ln r]} \tag{6}$$

The method of Wang and Li [18] applied basic fractal relationships between volumes and fractal surfaces together with Eq. (4), to obtain

$$\ln A(\mu) = constant + D_W \ln B(\mu) \tag{7}$$

where $A(\mu) = \frac{-\int_{N(\mu)}^{N\max} \ln\mu\, dN(\mu)}{r(\mu)^2}$ and $B(\mu) = \frac{[N_{\max} - N(\mu)]^{1/3}}{r(\mu)}$, allowing the calculation of the fractal dimension, D_W, as the slope of the plot $\ln(A)$ vs. $\ln(B)$.

The fractal version of the Frenkel-Halsey-Hill (FHH) method [32] was developed by Pfeifer et al. [33,19] leading to two expressions for calculating the fractal dimension. When capillary condensation takes place the following equation can be used

$$\ln N = constant + (D_{FHH} - 3)\ln(-\ln\mu) \tag{8}$$

and when the solid-gas interactions are dominant, the isotherm may be written as follows

$$\ln N = constant + \frac{(D_{FHH} - 3)}{3}\ln(-\ln\mu) \tag{9}$$

where $N(\mu)$ is the amount of gas adsorbed at the relative pressure μ and D_{FHH} is the fractal dimension estimated by this method.

The determination of the pore size distributions was carried out by applying the procedure of Medek and Weishauptova [34]. The volume of the pores with radius smaller than r_i can be estimated transforming the Dubinin-Astakhov equation into the following expression

$$w_i = w_0 \exp\left[-\left(\frac{k}{E_0}\right)^n r_1^{-3n}\right] \tag{9}$$

where w_0, the limiting volume filling the micropores, E_0, the characteristic energy, and n are the parameters of the Dubinin-Astakhov equation. The constant k, the interaction factor, depends on the nature of the adsorbate and the adsorbent, having a value of 3.145 kJ mol^{-1} nm^3 for the CO_2 and a carbonaceous material. By differentiating Eq. (9), the expression for the pore volume distribution is obtained

$$\frac{dw}{dr} = 3nw_0\left(\frac{k}{E_0}\right)^n r^{-(3n+1)} \exp\left[-\left(\frac{k}{E_0}\right)^n r^{-3n}\right] \tag{10}$$

The fractal dimensions of surfaces obtained from different procedures are intended to be in the interval 2–3 according to the degree of complexity of the pore walls. Nevertheless, values exceeding the limits of that interval can be obtained. Values of D over 3 can be for example due to pore filling, and not necessarily be related to the surface unevenness. According to some authors [35], values of D as high as 3.5 may be treated as fractals.

Download English Version:

https://daneshyari.com/en/article/6656552

Download Persian Version:

https://daneshyari.com/article/6656552

Daneshyari.com