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Full Length Article

Effects of pyrolysis conditions on the structure of chars prepared from an Argentine asphaltite

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HIGHLIGHTS

- Effect of pyrolysis conditions on an Argentine asphaltite char structure was studied.
- Experimental conditions investigated were temperature, heating rate and holding time.
- A significant reordering of the carbonaceous matrix was observed above 600 °C.
- Char aromaticity and crystalline carbon fraction were the most sensitive parameters.
- Appearance of a liquid phase during heating affected the char particle morphology.

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ABSTRACT

As gasification reactivity of carbonaceous solid material chars is known to be strongly dependent on their formation conditions, a comprehensive study was carried out on the effects of pyrolysis conditions on structure of chars prepared from an Argentine asphaltite. The study comprised qualitative and quantitative analyses of char structures by X-ray diffraction, complemented with the characterization of physical morphology of char particles by scanning electronic microscopy and high-resolution transmission electronic microscopy. Effects of pyrolysis temperature, heating rate and holding time at the peak temperature were investigated separately in a fixed bed tubular reactor. Additionally, the overall effect of variations in time-temperature history of individual char particles was evaluated using a drop tube furnace reactor. Experimental results have shown that pyrolysis conditions have a strong influence on the asphaltite-derived char structure, producing a significant reordering of the carbonaceous matrix at high heat treatment temperatures that is evidenced by increments in aromaticity and crystalline carbon fraction. The resulting physical morphology of asphaltite-derived char particles was found to be profoundly influenced by the heating rate at which the volatile matter is released, due to the appearance of a liquid phase during the heating process.

1. Introduction

Coal and other carbonaceous solid materials have been historically used for power generation through direct combustion which is a highly inefficient and pollutant way of extracting the chemical energy stored in these natural resources. Improvements of the overall efficiency and cleanliness of the energy production systems are currently an urgent demand since the global population growth and energy consume are steadily increasing while environmental protection standards become more and more stringent.

In this challenging framework, a renewed interest on gasification technologies has recently emerged worldwide since they offer the potential of a clean and efficient energy. One attractive characteristic of gasification technologies is the possibility of co-production of electricity, hydrogen, liquid fuels, and high-value chemicals that contribute to the improvement of power generation efficiency compared with conventional pulverized coal fired plants [1]. Gasification has also the additional advantage of accommodating a wide range of feed stocks, including low-cost fuels like petroleum coke, biomass, and municipal wastes [2].

Abbreviations: XRD, X-ray diffraction; SEM, scanning electronic microscopy; HRTEM, high resolution transmission electronic microscopy; T_d, active thermal decomposition temperature; f_a, aromaticity; L_{002}, average crystallite height; d_{002}, interlayer spacing; X_C, crystalline fraction of carbonaceous matrix; X_A, amorphous fraction of carbonaceous matrix; FB, fixed bed; DTF, drop tube furnace.

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Gasification process involves a set of exothermic and endothermic chemical reactions of feed solid particles with air or O_2, steam, CO_2, or a mixture of these gases at a temperature exceeding 700 °C, to yield a gaseous product suitable for use either as a source of energy or as a raw material for the synthesis of chemicals, liquid fuels or hydrogen. It is well-known that gasification is a two-step process. In the first step, pyrolysis or devolatilization, the volatile components of the feed solid material are rapidly released at temperatures between 300 °C and 600 °C, leaving a residual solid fuel or char and mineral matter as by-products. The second step, char conversion, involves the gasification of the residual char and it is much slower than devolatilization step, becoming then the rate-limiting step of the overall process [3].

Earlier studies demonstrated that reactivity of chars to gasifying agents depends strongly on their formation conditions, since very complex physical and chemical transformations occur during the solid particle heating while yielding volatile matter and generating solid residues. A good understanding of the behavior of solid feed particles during heating, when chemical and physical structure of chars is formed is then essential to the development of gasification kinetic models [4,5].

In this paper, a study on the effects of pyrolysis conditions on chemical and physical structure of chars prepared from an Argentine asphaltite is presented. Asphaltites seem to be an excellent raw material for the production of synthesis gas through gasification processes due to their low content of ashes and high percentage of elemental carbon [6].

The study comprised qualitative and quantitative analyses of the char structure by XRD, complemented with the characterization of physical morphology of char particles by SEM and HRTEM. Pyrolysis conditions investigated were temperature, heating rate, holding time at the peak temperature, and the overall effect of variations in the time-temperature history of individual char particles.

2. Theoretical background

Pyrolysis or devolatilization of carbonaceous solid materials refers to the release of volatile matter by thermal decomposition. Much evidence supports the hypothesis that devolatilization is a chemical decomposition reaction. As a solid particle is heated, the cross bonds are severed, the weaker ones rupture at lower temperatures and the stronger ones at higher temperatures. The resulting products consisting of carbon oxides, pyrolysis water, hydrocarbons and hydrogen, which are collectively referred as volatile, escape through the solid carbon matrix to the surrounding environment. Some of volatile species like tar, that is very reactive, may also undergo secondary reactions, i.e. cracking and repolymerization, as they are evolving [7,8].

As temperature is the most important parameter affecting pyrolysis, it is useful to divide the overall pyrolysis process into three main temperature regions with reference to T_d, beyond which the massive weight loss takes place [4,9]:

(1) Temperatures below 300–400 °C, where limited thermal alterations of the original molecular structures occur, mostly by condensation reactions, prior to the massive release of volatile matter.
(2) Temperatures between 400 °C and 600 °C, where the so-called primary pyrolysis takes place. It consists of a primary degradation as a result of which the weakest bridges may break to generate molecular fragments. The fragments subtract the hydrogen from the hydroaromatics or aliphatics thus increasing the concentration of aromatic hydrogen. These fragments are released as tar if they are small enough to vaporize and be transported out of the solid particles. Functional groups also decompose to release gases, mainly CO_2, light aliphatics and H_2O.
(3) Temperatures higher than 600 °C, where reactions that take place involve mainly the condensation of the carbonaceous matrix and the release of CO and H_2. In this high-temperature range, a reordering of the char structure also takes place which results in a loss of the char reactivity toward further gasification or combustion. This char deactivation process is known in literature as thermal annealing [10].

Carbonaceous solid materials contain crystalline particles (crystallites) with diameters in the order of nanometers, which are composed by graphite-like layers arranged turbostratically. Heat treatments at high temperatures can enlarge these crystallites and make them more ordered, and this process can be characterized by XRD that is a well-developed technique for analyzing carbon matrices [11–13]. XRD is a non-destructive method that uses a relatively large amount of sample and collects most of the intensities scattered from the examined sample, yielding to average properties from the sample rather than local properties. This fact is very important for a material like coals and asphaltites which are inherently heterogeneous.

Fig. 1 shows a characteristic XRD pattern obtained from a carbonaceous char sample after subtracting the background intensity from the observed XRD diagram. Different structural parameters such as the amorphous and crystalline carbon fractions, aromaticity, crystallite height, interlayer spacing and other properties can be obtained from this XRD pattern.

Three two-dimensional bands are observed over the examined 2θ range. The band in the low angle region (2θ ≈ 25°) corresponds to the (0 0 2) peak of graphite which is generally accepted as the stacking of the graphitic basal plans of char crystallites. The other two bands in the higher angle region, which are indicated as (1 0) and (1 1), are attributed to hexagonal ring structure in char crystallites [11,12]. The asymmetric shape of the (0 0 2) diffuse peak suggests the existence of another band (γ) in its left hand side. This γ band that usually occurs in the angular range of 16–23° (2θ) has also been observed by many other authors and it is associated with packing of the saturated structures such as aliphatic side chains [13,14].

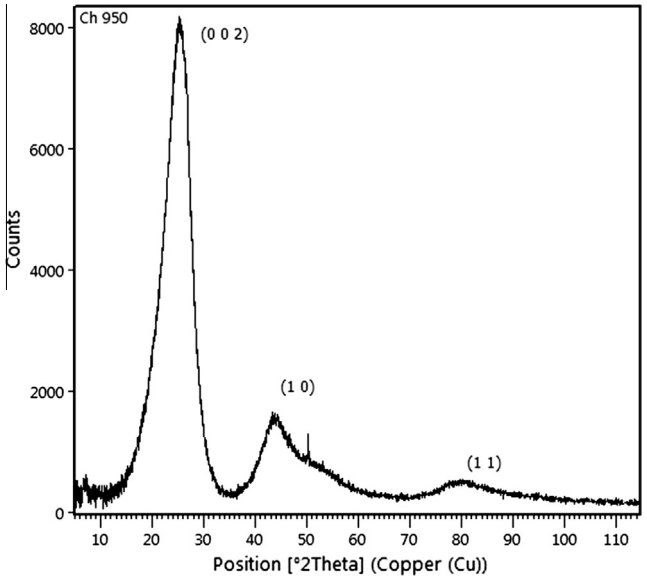

Fig. 1. Typical corrected XRD pattern of a carbonaceous material char sample.