



Coal pyrolysis: Comparative evaluation of the technical performance of two Southern Hemisphere demineralized bituminous coals



Andrew O. Odeh*, Samuel E. Ogbeide, Charity O. Okieimen

Department of Chemical Engineering, University of Benin, Benin City, Private Bag 1154, Benin City, Nigeria

ARTICLE INFO

Article history:

Received 14 December 2016

Received in revised form 17 May 2017

Accepted 18 May 2017

Keywords:

Reactivity

Coal

Char

Chemical properties

Physical properties

ABSTRACT

Differences in the physico-chemical properties of char can fundamentally affect the reactivity of the char during conversion processes and even the reaction pathway. Transformations from coal to char using a high heating rate have been thoroughly assessed; however, there is less information on the reactivity of this transition to chars. Two South African bituminous coals of $\leq 75 \mu\text{m}$ were acid washed, and subjected to a slow heating rate of $25 \text{ }^\circ\text{C}/\text{min}$ from 450 to $700 \text{ }^\circ\text{C}$ at atmospheric atmosphere. The chars were characterized by physical, chemical and petrographic evaluations. The effect of the heat treatment conditions on the reactivity of the chars towards oxygen under chemical kinetic controlled regime was assessed. The oxygen content of the resultant chars was also measured directly by scanning electron microscope (SEM) attached with element detector sensor (EDS) technique. The coals are medium rank C bituminous (Rov = 0.73 for high volatile and Rov = 0.78 for low volatile). Char properties determined revealed correlations of the chemical structural changes during the coal to char transition. The findings of this study would suggest that the loss of carbon combustion reactivity cannot be assessed on the basis of its time-temperature history only, but the extent of carbon interaction with oxygen also come into play. The synergy of reactions induced by modifications of the carbon structure, oxygen uptake and the reaction between oxygen and the resultant chars is presented and discussed.

© 2017 Published by Elsevier Ltd.

1. Introduction

Pyrolysis remains an important intermediate process for thermo-chemical coal conversion processes such as combustion, gasification and liquefaction. During fixed bed gasification, the coal passes through four distinct stages: drying, pyrolysis, reduction and combustion [1]. In the pyrolysis stage, volatiles are driven off and the properties of the formed char change significantly when compared to the original coal. The property of coal after pyrolysis is often affected by many factors which can be linked to coal properties and process conditions such as coal rank [1], particle size [2], porosity [3], surface area [4], mineral content [5], petrographic composition [6], process temperature [7], process pressure [8], catalyst and heating rate [3]. These properties have a strong impact on the char reactivity as a result of fracturing, shrinking, pore structure, swelling, agglomeration and the transformation of mineral matters which affects the physical [9] and chemical properties of the coal char [10]. The structural re-ordering of the carbon structure, as well as the transformations of the mineral matters, may contribute to heat treatment induced loss of reactivity of coal

during conversion processes [9]. Also, the heat treatment induced losses of reactivity of coal have been linked to the propensity of coal to chemisorption of oxygen which depends on the carbon matrix of the coal [11]. The presence of oxygen-containing functional groups in precursor coal is a key factor in char reactivity, related to the carbon active sites formed after decomposition of C(O) complexes during coal conversion processes such as pyrolysis [12]. Char reactivity has a major effect on the degree of carbon burnout, which is a crucial consequence from an environmental and economic point of view [13]. The reaction of char with oxygen has generally been described as being governed by the following controlling stages: (i) mass transfer (by diffusion) of oxygen to reaction sites; (ii) chemisorption of oxygen on the carbon surface, reaction of chemisorbed oxygen with carbon to form products, and desorption of products; and (iii) mass transport of the gaseous products from the reaction sites [12].

This study aims to investigate the chemical and structural changes that result from coal pyrolysis of two Southern Hemisphere bituminous coals from South Africa at various temperature intervals from 450 to $700 \text{ }^\circ\text{C}$ for an hour, a process time which is presumed to have allowed the volatile content of the coal to be driven off, thus making room for the carbonization of the coal at atmospheric pressure. The changes in the char structure were

* Corresponding author.

E-mail address: odehandy@yahoo.com (A.O. Odeh).

traced by establishing relationship between char formation process indices and coal/char properties. To achieve this, the selected coals were demineralized in order to study the effect of the organic part only.

2. Experimental

2.1. Sample preparation

Two South African coals of same rank but different petrographic composition were used in this study. The coal samples were pulverized to coal particle size of $\leq 75 \mu\text{m}$ by employing a mechanical size reduction jaw crusher (Samuel Osborne (SA) LTD, model: 66YROLL) and a Fritsch P-14 rotary mill containing ceramic balls (Model number: 46–126). The required particle size of $\sim 75 \mu\text{m}$ was finally obtained from screening the particles from the rotary mill using a 75 μm screen. All the samples were stored under argon in sealed bags.

The prepared coal samples were demineralized by sequential leaching with hydrofluoric acid (HF) and hydrochloric acid (HCl) as detailed in Strydom et al. [13]. The HF (48%) and HCl (32%) were obtained from Associated Chemical Enterprise (ACE), South Africa.

2.2. Apparatus and procedure

The char production sequence from the parent coal samples are as follows: The weighed coal samples (40 g) were placed in a ceramic boat and put in a horizontal tube furnace at atmospheric conditions (Fig. 1). Initially, the samples were left for fifteen minutes in the furnace and flushed with nitrogen (AFROX, ultra high purity grade) at atmospheric conditions, to remove oxygen from the oven. A flow rate of 1 L/min of Nitrogen was used. The furnace was then heated at 25 °C/min to the target temperature, and held isothermal for 60 min, then allowed to cool slowly back to ambient temperature. The target temperature ranged from 450 to 700 °C at 50 °C interval, while keeping the samples under a nitrogen atmosphere.

The conventional chemical analysis (both proximate and ultimate analyses) and calorific value of the untreated coal, demineralized and heat treated demineralized samples were performed

according to the ASTM 3172, ASTM 3176 and ISO 1928 standards respectively at Advanced Coal Technology (ACT), Pretoria, South Africa. The surface areas of the various samples were determined using the carbon dioxide adsorption CO_2 BET method on a Micromeritics ASAP2020 surface area analyser [14]. Prior to CO_2 adsorption, the samples (about 0.20 g) were degassed under vacuum (10.0 μmHg), at 25 and 380 °C for 48 h for the coals and chars respectively. The evacuated sample was analysed at 0 °C in an ice bath. The results were processed using the Accelerated Surface Area and Porosimetry System (ASAP) 2020 software linked to the Surface Area Analyzer. The spectra used in obtaining the structural properties of both the coal and char were obtained from the fourier-transform infrared spectrometer equipped with an attenuated total reflectance (FTIR-ATR), model Perkin-Elmer Spectrum 400. The procedure of FTIR-ATR as detailed by Odeh [14] was used. The coal morphology and that of the resultant char obtained in this study were observed using SEM (scanning electron microscopy) model FEI Quanta 250 with a field emission gun (FEG) emitter, equipped with an energy dispersive spectrometry (EDS) detector that does the elemental composition analysis; detailed procedure is reported by Odeh [15].

Aromaticity (f_a) was obtained from the ratio of aromatic bands in the 900–700 cm^{-1} region to the aliphatic and aromatic bands in the 3000–2815 cm^{-1} region [14]. The vitrinite reflectance of the parent coal indicating the coal rank was obtained following the procedure and equipment at the coal and carbon laboratory, University of Witwatersrand, South Africa detailed in Odeh [16].

Thermogravimetric analyses of the chars were carried in a Leco TGA701 thermogravimetric analyzer with pneumatic carousel assembly with capacity of being loaded with 19 samples per run. The analyses were done at coal and carbon laboratory, University of Pretoria, South Africa. The char combustion experiments were carried out isothermally at three different temperature ranging from 370 to 415 °C. The samples were heated under nitrogen from ambient temperature to the target temperature for an hour, after weight stabilization the nitrogen was replaced by oxygen atmosphere (10 vol%) [8] and held isothermal for six hours at a heating rate of 20 °C/min. Leco TGA701 has the capacity of being loaded with sample mass of 5 g. Sample masses of approximately 2 g, with



Fig. 1. Tube furnace used for char preparation.

Download English Version:

<https://daneshyari.com/en/article/8918866>

Download Persian Version:

<https://daneshyari.com/article/8918866>

[Daneshyari.com](https://daneshyari.com)