Fuel Processing Technology 144 (2016) 248–254

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Structural evaluation of Xiaolongtan lignite by direct characterization and pyrolytic analysis

Yu-Gao Wang [a,b], Xian-Yong Wei [a,*], Sheng-Kang Wang [a], Zhan-Ku Li [a], Peng Li [a,c], Fang-Jing Liu [a], Zhi-Min Zong [a]

[a] Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China
[b] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China
[c] Research Center of Heterogeneous Catalysis and Engineering Science, School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, Henan, China

ARTICLE INFO

Article history:
Received 29 October 2015
Received in revised form 23 December 2015
Accepted 31 December 2015
Available online 15 January 2016

Keywords:
Lignite
Organic matter
Direct characterization
Pyrolytic analysis

ABSTRACT

Organic matter in Xiaolongtan lignite (XL) from Southwest China was analyzed by direct characterization instruments (including solid-state ^{13}C nuclear magnetic resonance spectrometer, X-ray photoelectron spectrometer, and Fourier transform infrared spectrometer) and pyrolytic tools (including thermogravimetric analyzer and Curie-point pyrolyzer-gas chromatograph/mass spectrometer). Organic carbons in XL mainly consist of aliphatic and aromatic carbons. Specifically, methylene dominates in the aliphatic carbons and average carbon number in the methylene chains is ca. 5. Each aromatic cluster contains 2 rings and each aromatic ring has 4 substituents on average. XL is rich in oxygen-functional moieties (OFMs), including C_{al}–O, C_{ar}–O, >C=O, and –COOH, among which C_{al}–O and C_{ar}–O are predominant and thereby cleaving C_{al}–O and C_{ar}–O bonds facilitates the devolatilization of organic matter in XL. Phenols are the richest components in the volatiles from flash pyrolysis of XL, which may result from the cleavage of C_{ar}–O in the organic matter. The pyrolytic analyses imply that selectively cracking these bonds would greatly facilitate converting XL into liquid fuels or fine chemicals.

1. Introduction

The reserve of lignites is significantly huge over the world [1]. However, the low calorific value and high water content seriously hinder the direct fuel use of lignites [2]. Besides combustion, lignites are usually subjected to gasification, liquefaction, and pyrolysis to afford gaseous, liquid, and solid products [3–5]. The yield and quality of these resulting products not only depend on the various processing parameters of the conversion technologies, but also mainly rely on the intrinsic structures of lignites. Moreover, the abundant oxygen-functional moieties (OFMs) in lignites have an inherent advantage in manufacturing the oxygen-containing organic chemicals [6–8]. Therefore, an insight into the organic structures of lignites is not only greatly important for understanding the basic chemistry involved in lignite liquefaction, gasification, and pyrolysis, but also especially for cultivating a novel and potential method to efficiently use lignites [9].

The direct characterization tools can directly and conveniently analyze the whole, unaltered, and solid coals. The solid-state (SS) ^{13}C nuclear magnetic resonance (NMR) spectrometer has been successfully used to determine the carbon skeletal structure as well as OFMs in coals [10–12]. Organic functional groups in coals could be revealed by Fourier transform infrared (FTIR) spectrometer [13–15]. For elemental analysis, X-ray photoelectron spectrometer (XPS) is a powerful tool to investigate the forms of organic heteroatoms, such as oxygen, sulfur, and nitrogen in coals [11,16–18].

Most of current coal utilization processes involve in thermal reactions. Hence, thermogravimetric analysis (TGA) of coals is usually conducted to understand coal pyrolysis behavior [19,20]. Liu et al. proposed a new method to study coal structures and pyrolysis reactions by correlating mass loss during TGA of coals and cleavage of covalent bonds in coals [19]. Because flash pyrolysis could effectively reduce secondary reactions [21,22], the resulting compounds in the volatiles could represent some original structural features of macromolecular portions (MMPs) in coals [23,24]. Curie-point pyrolyzer (CPP) is a qualified flash pyrolysis device because of its rapid heating rates (up to 5000 °C·s^{-1}) and precise control of temperature as determined by the Curie-point temperature of the used ferromagnetic alloy [25–27]. Gas chromatograph/mass spectrometer (GC/MS) succeeds in quantitatively and qualitatively analyzing complex organic mixtures [28]. Therefore, CPP combined with GC/MS (CPP-GC/MS) is an important tool to deduce original organic structure information on coals at the molecular level [25,29].

In the paper, Xiaolongtan lignite (XL), a typical lignite in Southwest China, was subjected to direct characterization by SS ^{13}C NMR, XPS, and FTIR and pyrolytic analyses with TGA and CPP-GC/MS to explore the organic structures of XL.

---

[*] Corresponding author.
E-mail address: wei_xianyong@163.com (X.-Y. Wei).

http://dx.doi.org/10.1016/j.fuproc.2015.12.034
0378-3820/

Nomenclature

CPP	Curie-point pyrolyzer
CPP–GC/MS	Curie-point pyrolyzer–gas chromatograph/mass spectrometer
DTG	differential thermal gravity
FTIR	Fourier transform infrared
GC/MS	gas chromatograph/mass spectrometer
MMPs	macromolecular portions
MSPs	methoxy-substituted phenols
NMR	nuclear magnetic resonance
OFMs	oxygen-functional moieties
OSs	other species
PAPs	phenol and alkylphenols
SS	solid-state
TGA	thermogravimetric analysis
XL	Xiaolongtan lignite
XPS	X-ray photoelectron spectrometer

2. Experimental

2.1. Materials

XL was collected from Xiaolongtan Coal Mine in Yunnan Province of China. It was pulverized to pass through a 200 mesh sieve (particle size of <74 μm) followed by desiccation in a vacuum oven at 80 °C for 24 h prior to use. Table 1 lists its proximate and ultimate analyses.

2.2. Analyses of XL with SS ^{13}C NMR, XPS, and FTIR

A Bruker Avance III NMR spectrometer was used to record SS ^{13}C NMR spectrum of XL. It is equipped with a 4 mm cross-polarization magic angle spinning double-resonance probe and operating at a ^{13}C frequency of 100.63 MHz at room temperature. About 0.2 g XL was packed into a 5 mm diameter zirconia rotor with a spin rate at 14 kHz. The contact time, recycle delay time, and spectral width were set to 1 ms, 0.5 s, and 10 kHz, respectively. Organic functional groups in XL were analyzed with a Nicolet Magna IR-560 FTIR spectrometer using KBr pellet technique by collecting 50 scans at a resolution of 4 cm^{-1} in reflectance mode with measuring region of 4000–400 cm^{-1}. The elemental analysis of XL was performed with a Thermo Fisher ESCALAB 250Xi XPS equipped with a monochromatized Al Kα X-ray source and operated at 150 W. The spectra of XPS were demonstrated in a fixed analyzer transmission mode and corrected by a reference to the C1s peak at 284.8 eV.

2.3. Analyses of XL with TGA and CPP-GC/MS

TGA of XL was conducted on a Mettler Toledo TGA/SDTA851^{e} thermogravimetric analyzer. XL (ca. 15 mg) was put into a ceramic crucible, which was heated at 10 °C·min^{-1} with a constant argon flow of 60 mL·min^{-1} from room temperature to 110 °C and held at the temperature for 0.5 h to remove moisture, then from 110 to 900 °C to release volatiles.

Table 1
Proximate and ultimate analyses of XL (wt.%).

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$
M_{ad}	A_d	VM_{daf}	C	H	N	O^{a}	
21.40	7.55	38.50	59.94	5.24	1.82	>30.73	2.27

daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, i.e., moisture-free base); VM_{daf}: volatile matter (dry and ash-free base); $S_{t,d}$: total sulfur (dry base); α: by difference.

About 1 mg XL was collected in a metal crucible with 500 °C of Curie-point temperature and pyrolysed for 5 s using a JHP-5 CPP with a constant helium flow of 1.0 mL·min^{-1}. The resulting volatiles were online analyzed using an Agilent 7890/5975 GC/MS equipped with a HP-5MS capillary column (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness).

2.4. Data processing

The result of differential thermal gravity (DTG) analysis was obtained by the first derivative of the thermogravimetric curve with respect to temperature. PeakFit software was used for curve fitting of the SS ^{13}C NMR spectrum and DTG curve to afford the distributions of different carbon types and chemical bonds, respectively. XPS PeakFit software was adopted for peak fitting and semi-quantitation of the XPS spectra. Chemstation software for Agilent GC/MS was used for the qualitative and semi-quantitative analyses of the compounds in the resulting volatiles during Curie-point pyrolysis of XL.

3. Results and discussion

3.1. Direct characterization of XL

As Fig. 1 shows, the aliphatic (0–90 ppm) and aromatic (90–170 ppm) carbon bands are predominant, while carbonyl carbon band (170–220 ppm) is weak in the SS ^{13}C NMR spectrum of XL, suggesting that the carbon skeletal structure of XL mainly consists of aliphatic and aromatic carbons with small amounts of carbonyl carbons. Referring to previous studies [30,31], the spectrum could be further fitted into 16 individual sub-curves, representing 16 different types of aliphatic, aromatic, and carbonyl carbon types (Fig. 1 and Table 2). Methylene (f_{al}^{3}) centered at 31.6 ppm is the most abundant aliphatic carbon, some of which may exist as methylene in alicyclic moieties, while protonated aromatic (f_{a}^{H}) and aromatic bridgehead (f_{a}^{B}) carbons dominate in the aromatic carbon region followed by alkylated *ortho*-oxyaromatic carbon (f_{a}^{O2}). Noteworthily, OFMs exist as various forms in XL, such as C_{al}–O (f_{al}^{O1}, f_{al}^{O2} and f_{al}^{O3}), C_{ar}–O (f_{a}^{O1}/f_{a}^{O3} and f_{a}^{O2}), –COOH (f_{a}^{CC1}), and >C=O (f_{a}^{CC2}), which is related to the high oxygen content of XL. Among these OFMs, C_{ar}–O is predominant followed by C_{al}–O, suggesting that the abundant ethers, alcohols, and phenols exist in XL.

Carbon structural parameters were summarized in Table 3 on the basis of data in Table 2 for better elaborating carbon skeleton of XL. The aromaticity (f_a) and aliphaticity (f_{al}) indexes imply that there are ca. 47 aromatic and 46 aliphatic carbons in 100 carbon atoms, while the rest exist as carbonyl carbons in XL. The molar fraction of aromatic bridgehead carbon (x_b) is a key parameter for estimating the aromatic cluster rings [10]. The x_b of XL is 0.19, which is nearly equal to the x_b (0.20) of naphthalene, indicating that each cluster has 2 aromatic rings on average in XL. The average carbon number (C_n) in methylene

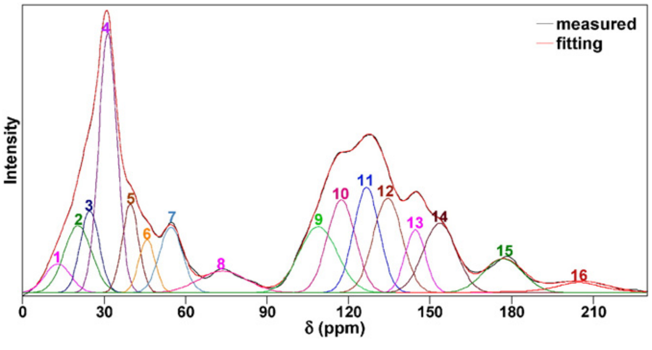

Fig. 1. SS ^{13}C NMR spectrum and its fitting curves of XL.