



Research Paper

Effect of heat reflux extraction on the structure and composition of a high-volatile bituminous coal

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HIGHLIGHTS

- A novel HRE process with CYC is proposed to dissolve coal.
- Most of the aliphatic compounds in coal are extracted during HRE process.
- The carbon crystallite structure of coal changes after HRE process with CYC.
- The thermal degradation behavior of ER is significantly different from that of the SFHB.

ARTICLE INFO

Article history:

Received 24 May 2016

Revised 25 July 2016

Accepted 18 August 2016

Available online 20 August 2016

Keywords:

High-volatile bituminous coal

Heat reflux extraction

Structure evolution

Functional groups

TG-FTIR

ABSTRACT

Heat reflux extraction (HRE) process with cyclohexanone (CYC) in a high-performance mass transfer extractor was applied to dissolve Shenmu-Fugu high-volatile bituminous (SFHB) coal for the first time to afford extract (*E*) and extract residue (ER) from the extraction. SFHB, *E*, and ER were characterized by elemental analysis, solid-state ¹³C NMR spectrometry, FTIR spectrometry, XRD, SEM, and TG-FTIR to elucidate the effect of HRE on the evolution of functional groups and macromolecular structure of coal during extraction. The soluble portion in SFHB was 24.37% in the course of HRE with CYC. The aromaticity of SFHB derived from both curve-fitting of ¹³C NMR and FTIR spectra was obviously increased after extraction suggesting that most of the aliphatic fractions were extracted during HRE process. It was clarified that the substituted degree of aromatic ring in SFHB became low but the substituents on aromatics were larger after extraction. Due to irreversibly swelling crystal structure of SFHB, its interlayer spacing became larger and the stacking height of crystallite decreased after extraction. Moreover, significant amounts of volatile matters were extracted, which caused relatively lower mass loss rate and contents of gaseous products (CO₂, aliphatic moieties, CH₄, and CO) of ER than SFHB during main pyrolysis stage.

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1. Introduction

Coal is a biological sedimentary rock created from the remains of plant debris that lived and died around 100–400 million years ago when parts of the earth were covered with huge swampy forests [1]. The nature of carbonaceous-enrichment macerals in coal in addition to inorganic minerals makes this abundant resource widely apply in electricity generation, steel production, cement manufacturing, and chemical engineering [2–4]. An accurate and deep understanding the organic structures of coals are crucial for

optimizing the above processes and efficient utilization of coals, especially for obtaining value-added chemicals from coals. Solvent extraction of coal under mild conditions is an essential approach for studying chemical composition, distribution of functional groups, and molecular skeleton structures of coals as well as their extracts and residues [5,6]. Solvent extraction methods mainly include low-temperature extraction, thermal dissolution, and ionic liquids extraction, among which low-temperature extraction is believed to be an effective approach for preliminarily separating organic portion from coals and is also the most commonly used method [7,8]. This extraction procedure is usually performed in a container reactor (Bunsen beaker and Erlenmeyer flask) or a Soxhlet extractor with single or mixed organic solvents such as alkanes, alkanols (e.g., methanol, ethanol, and isopropanol),

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Nomenclature

A	ash	R_{\max}	maximum decomposition rate
ad	air dry base	R_1	mass loss rate for DTG peak 1
CYC	cyclohexanone	R_2	mass loss rate for DTG peak 2
d	dry base	SEM	scanning electron microscope
daf	dry and ash-free base	SFHB	shenmu-fugu high-volatile bituminous coal
D_i	devolatilization index	SS ^{13}C NMR	solid-state ^{13}C nuclear magnetic resonance
d_{002}	interlayer spacing of aromatic layers	T_f	terminated decomposition temperature
DTG	derivative mass loss	TGA	thermogravimetric analysis
E	extract	THF	tetrahydrofuran
EBF	extraction bag filter	T_{in}	initial devolatilisation temperature
EOM	extractable organic matter	T_{\max}	maximum mass loss temperature
ER	extract residue	T_1	temperature for DTG peak 1
FTIR	fourier transform infrared	T_2	temperature for DTG peak 2
FWHM	full width at half maximum	V	volatile matter
HRE	heat reflux extraction	XRD	X-ray diffraction
L_c	mean height of crystallite in c-direction	θ	diffraction angle
M	moisture		
NMP	N-methyl-2-pyrrolidone		
PAHs	polycyclic aromatic hydrocarbons		

amines, benzene, chloroform, CS_2 , dichloromethane, ketones, N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide, pyridine, quinoline, tetrahydrofuran (THF), tetralin, toluene, CS_2 /NMP mixture, and CS_2 /pyridine mixture [9]. Maceral fractions derived from six coals were extracted using CS_2 /NMP mixed solvent in stainless centrifuge tube by Dyrkacz and Bloomquist [10] and they found that vitrinites showed higher extract yields than both liptinites and inertinites. In another example, Xue et al. [11] detected the polycyclic aromatic hydrocarbons (PAHs) in extracts obtained from CS_2 and CH_2Cl_2 extractions of coals both in Soxhlet and ultrasonic-assisted extractors. They concluded that 24 h was suitable for extraction of PAHs from coals by Soxhlet extraction method and both Soxhlet and ultrasonic-assisted extraction methods showed similar PAHs concentration patterns. Three extraction solvents involving CS_2 , CH_2Cl_2 , and supercritical carbon dioxide were utilized to dissolve three high volatile bituminous coals, Kolak and Burruss [12] found that Soxhlet- CH_2Cl_2 and Soxhlet- CS_2 extractions yielded similar amounts of extractable organic matter (EOM) and distributions of individual hydrocarbons, whereas supercritical CO_2 extractions (40 °C, 100 bar) yielded approximately an order of magnitude less EOM. In addition, a recent work by Zou et al. [13] has tried to use THF for dissolving the mobile phase of a lignite in a 1000 mL conical flask and the obtained 5.1% percentage of mobile phase was further pyrolyzed in a new in-situ pyrolysis-time of flight mass spectrometry to evaluate the initial products species. Although a high extraction performance can be achieved by low-temperature extraction of coal in the container and Soxhlet reactors with single or mixed solvents, there are defects in further enhancement of the extraction yields when the two reactors are involved. As we known, sample is often immersed into the solvent and forms reaction mixture together with extract and solvent during extraction process in the container reactors. This limits the release of soluble portions from the pores of inner coal matrix to the external solvent phase and results in a poor diffusion effect during extraction. For Soxhlet extraction process, sample is placed inside a glass microfiber thimble and further loaded into the main chamber of the Soxhlet extractor. The solvent vapor rises from the distillation flask to the condenser through a distillation arm and then droplets of the solvent drip down to the chamber as long as the temperature reaches to its boiling point. After several minutes of soaking, solvent dissolving the extract will be led into the distillation flask again under the action of siphon

mechanism when the chamber is full enough. It is worthwhile to note that the solvent is not heated (normally slightly higher than room temperature) as it extracts the organic portion in the sample during Soxhlet extraction. This greatly limits the solvent extraction efficiency because the effect of temperature-induced mass transfer disappears under the ambient temperature [14]. However, heat reflux extraction (HRE) process using reflux extractor as reactor will not only enhance the contact efficiency but also promote the effect of temperature-induced mass transfer between solvent and coal on account of the fact that hot fresh solvent vapor generated from the solvent container directly passes through sample via a vapor hole and then flows down continuously from the condenser, which minimizes the secondary interaction between extract and coal sample [15]. In addition, cyclohexanone (CYC) is known as an important industrial solvent possessing characteristics of electron donor and condensed plane molecular structure, which was proved to have excellent performance during extraction such as, good compatibility with coals, high swelling power, and easily penetrating into the inner region of coal matrix [16]. Therefore, extraction of coal using CYC in a heat reflux extractor may further maximize the extraction yields compared with other low-temperature extractor such as container reactor or Soxhlet extractor. Generally, the amounts of solvent insoluble portions in coals are higher than that of the soluble portions and the insoluble portions can more accurately reflect the structural characteristics of the macromolecular skeleton of coals. Furthermore, identical structures (e.g., functional groups and aromatic skeletons) are normally distributed in both extract and residue during extraction. Hence, a deep insight into changes of chemical structures between raw coal and its solvent insoluble portions is of significant importance for efficient use of coals as well as directly revealing of solvent extraction mechanism during extraction. However, so far, there are few related studies on the structural changes of coals during HRE process with CYC and some essential issues such as the extraction performance of the solvent and the evolution of functional groups and macromolecular structure have not yet been fully understood [17].

Recently, numerous efforts have been focused on the identification of composition and structure of coal and its extract and residue from low-temperature extraction by several direct characterization technologies including solid-state ^{13}C nuclear magnetic resonance (SS ^{13}C NMR) spectrometry [18–20] elemental

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