Fuel Processing Technology 170 (2018) 1–12

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Thin-layer drying characteristics and modeling of lignite under supercritical carbon dioxide extraction and the evolution of pore structure and reactivity

Hongjun Li, Qinghua Chang, Rui Gao, Zhenghua Dai, Xueli Chen, Guangsuo Yu, Fuchen Wang*

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, PR China
Engineering Research Center for Coal Gasification in Shanghai, PR China.

ARTICLE INFO

Keywords:
Lignite
Drying kinetics
$SCCO_2$
Apparent diffusion coefficient
Modeling for drying
Gasification reactivity

ABSTRACT

In this study, the drying characteristics and kinetics of two typical lignites were investigated by using supercritical carbon dioxide ($SCCO_2$) at mild temperature (62–102 °C). The drying characteristics results show that $SCCO_2$ extraction drying has advantages over conventional drying such as better heat transfer and faster diffusion rate. Seven previous thin-layer models and a new proposed model were applied to analyze the lignite drying kinetics, and the proposed model obtained the best fit to the lignite drying process in all of the models. Apparent diffusion coefficients of moisture in $SCCO_2$ drying are higher compared with conventional drying method. The activation energies for the diffusion process of two typical lignites are 10.5561 and 11.6218 kJ/mol, which are far lower in comparison to conventional drying process. The pore structure and gasification reactivity of drying lignite were analyzed and both of them have an obvious improvement after the $SCCO_2$ drying process.

1. Introduction

Lignite is abundant and accounts for 45% of total coal resources in the world [1,2] and 12.69% in China (approximately 130 billion tons) [3]. It constitutes a significant resource of both energy and chemical feedstocks. However, high moisture contents and oxygen-containing function group of lignite have led to low calorific value and tendency to combust spontaneously, which greatly limits its widely application [4–6]. Drying is the first and an essential step in most utilization process including pyrolysis, gasification and combustion, and upgrading lignite by dewatering is absolutely indispensable prior to further application [7].

To utilize lignite efficiently, cleanly and safely, various drying methods have been developed based on evaporative and non-evaporative drying. Evaporative drying methods include rotary drying, fixed/fluidized-bed drying and microwave drying. Non-evaporative drying methods include hydrothermal dewatering, mechanical thermal dewatering and solvent extraction [8]. Rotary drying and fixed bed drying are widely applied but suffered from high energy consumption [9,10]. Hot air or flue gas fluidized-bed drying causes great risk of self-ignition and oxidation [11]. Superheated steam fluidized bed drying technology has limited use in arid area because of high requirement of water amount [12,13]. Non-evaporative drying methods, such as mechanical thermal dewatering [14,15] and hydrothermal drying [16,17], are conducted at very high temperatures. Besides, among these drying methods, most of the discharged water is discarded without further utilization such as steam reforming of methane (SRM) [18]. Furthermore, to avoid the loss of volatile components which are required for effective lignite combustion/gasification, lignite is better to be dried at low temperatures. Hence, a new drying method which can meet these requirements is of significance to be developed. $SCCO_2$ extraction drying (classified into solvent extraction in non-evaporation methods) can be conducted below 100 °C and obtain the water separated from coal easily [19]. Meanwhile, self-ignition and oxidation of lignite in extraction process can be avoided because $SCCO_2$ is inert. Shrinkage and collapse of pore structure as well as chemical variations (such as cross-linking reactions) in lignite may be avoided through extracting water from lignite by $SCCO_2$ at mild temperatures [19]. Hence, the drying characteristics of lignite by $SCCO_2$ extraction and its effect on lignite physicochemical properties are of significance to explore in this study.

Many studies have investigated the drying kinetics of LRCs with different drying methods [20–31]. Saban Pusat et al. [10] found Wang and Singh model best described the drying behavior of coarse lignite particles in a hot air fixed bed at 70, 100, 130 °C. Li et al. [18] determined logarithmic model is the best one for predicting drying process of Huolinhe lignite in nitrogen and methane fixed bed. Arash tahmasebi et al. [32] reported that the Midilli–Kucuk model best

* Corresponding author at: No. 130, Meilong road, Shanghai, PR China.
E-mail address: wfch@ecust.edu.cn (F. Wang).

http://dx.doi.org/10.1016/j.fuproc.2017.09.010
Received 16 June 2017; Received in revised form 16 September 2017; Accepted 16 September 2017

described the drying kinetics of lignite in nitrogen fluidized-bed and superheated steam fluidized-bed, whereas Page model showed good fit to microwave drying. Zhao Pengfei et al. [33] investigated the drying characteristics and kinetics of Shengli lignite using four different drying methods at temperatures from 80 to 200 °C, and found the Midilli–Kucuk model best simulated the lignite dewatering processes in all of the drying methods. However, there are no studies about modeling the $SCCO_2$ extraction drying process on different materials were conducted, but the effects and advantages of $SCCO_2$ extraction drying on properties of different materials. Alessandro Zambon [34] et al. took advantage of $SCCO_2$ drying process and obtained a dry decellularized scaffold that could be used for the development of organ/tissue substitution. Natasa Jovanovic [35] et al. studied the influence of sucrose and trehalose during SCF drying on the protein stability and the physical powder characteristics of lysozyme and myoglobin formulations, and found that $SCCO_2$ dried formulations showed different physical properties compared with freeze-dried formulations. Robert A. Franich et al. [36] investigated the dewater process of green radiata pine sapwood by $SCCO_2$, and found the pine sapwood can be dewatered by CO_2 cycled between supercritical fluid and gas phase, and its dewatering curves is sigmoidal shapes, the dewatering mechanism was discussed. Yoshio Iwai et al. [19,37,38] conducted drying of three LRCs by using $SCCO_2$, and found that it is easy to extract water from LRCs. The surface areas of Berau and Taiheiyo coals dried with supercritical carbon dioxide were larger than thermally dried coals, and the swellability of low rank coals is enhanced by drying with supercritical carbon dioxide. The drying rate increased when methanol was added in supercritical carbon dioxide as an entrainer, and the tar yield was significantly larger and the char yield was smaller for the coal dried with supercritical carbon dioxide + methanol compared with those dried with supercritical carbon dioxide only and dried thermally.

Hence, two typical lignites in China were selected as samples and aimed to investigate the drying characteristics and kinetics of lignite by $SCCO_2$ extraction in this study. Seven previous thin-layer drying equations and a new proposed model were applied to model the drying kinetics. Based on these drying data, the apparent diffusion coefficient of moisture in lignite drying process and the activation energy of moisture removal in these processes were analyzed. At the same time, the effects of $SCCO_2$ dewatering process on pore structure and gasification reactivity of lignite were also provided.

Nomenclature

BET	Brunauer-Emmett-Teller method
HLBE, ZT	Hu Lun Bei Er lignite, Zhao Tong lignite
TGA	thermos-gravimetric analysis
X	moisture ratio
DR	drying rate
M_{inh}	inherent moisture content
TPV	total pore volume
k_{max}	maximum reactivity rates(min^{-1})
T_{max}	peak temperatures(°C)
RH	relative humidity
TG-DTG	thermo-gravimetric and differential curves
LRCs	low rank coals
D_{eff}	apparent diffusion coefficient
M_t	moisture content of lignite at any time
M_f	free moisture content
SSA	specific surface area
$SCCO_2$	supercritical carbon dioxide
k_{mean}	average reactivity rates(min^{-1})
APD	average pore diameter
SCF	supercritical fluid

Table 1
Ultimate and proximate analyses of HLBE lignites.

Terms	Values		Methodology for measures	Uncertainty(%)
	As-received (%)	Dry ash free basis (%)		
Free moisture	27.18	–	GB/T211-2007	0.1301
Inherent moisture	11.86	–	GB/T211-2007	0.1126
Proximate analysis				
Moisture	35.78	–	**GB/T 30732-2014**	–
Fixed carbon	32.02	55.07	**GB/T 30732-2014**	–
Ash	6.08	–	**GB/T 30732-2014**	–
Volatile matter	26.12	44.93	**GB/T 30732-2014**	–
Ultimate analysis				
C	36.79	63.28	**GB/T 31391-2015**	–
H	4.61	7.93	**GB/T 31391-2015**	–
Sulfur	0.48	0.82	**GB/T 31391-2015**	–
O	15.70	27	**GB/T 31391-2015**	–
N	0.56	0.97	**GB/T 31391-2015**	–

2. Experimental methodology

2.1. Raw materials

Two typical lignites were obtained from Hu Lun Bei Er (HLBE), Zhao Tong (ZT), China. The raw lignites were crushed and sieved, then screened to a size range between 100 and 600 μm. The lignite samples were sealed in plastic bags to minimize moisture changes. The proximate and ultimate analyses of two typical lignites were shown in Table 1 and Table 2.

2.2. Experimental setup

Fig. 1 shows the schematic of experimental system. A $SCCO_2$ extraction device (HA120-50-01-C) was used to extract water from lignite samples. From a gas cylinder, carbon dioxide was supplied and liquefied through a cooling unit. The liquefied carbon dioxide was compressed by a compression pump and sent to preheater. Then, the carbon dioxide reached the supercritical fluid state. An extraction kettle was made of stainless steel, and its external diameter, inner diameter and

Table 2
Ultimate and proximate analyses of ZT lignites.

Terms	Values		Methodology for measures	Uncertainty(%)
	As-received (%)	Dry ash free basis (%)		
Free moisture	33.14	–	GB/T211-2007	0.2817
Inherent moisture	12.33	–	GB/T211-2007	0.1089
Proximate analysis				
Moisture	41.38	–	**GB/T 30732-2014**	–
Fixed carbon	18.49	40.93	**GB/T 30732-2014**	–
Ash	13.44	–	**GB/T 30732-2014**	–
Volatile matter	26.69	59.07	**GB/T 30732-2014**	–
Ultimate analysis				
C	26.30	58.21	**GB/T 31391-2015**	–
H	3.74	8.28	**GB/T 31391-2015**	–
Sulfur	0.40	0.88	**GB/T 31391-2015**	–
O	13.79	30.52	**GB/T 31391-2015**	–
N	0.95	2.11	**GB/T 31391-2015**	–