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Fractal characteristics and reactivity evolution of lignite during the upgrading process by supercritical CO_2 extraction

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HIGHLIGHTS

- Fractal analyses were performed on two kinds of lignite and one subbituminous coal before and after $SCCO_2$ extraction.
- The pore structure evolution of upgraded coals during $SCCO_2$ extraction process was investigated.
- Relationships between fractal dimension and pore structure parameter were studied.
- Combustion reactivity of upgraded lignite was enhanced whereas upgraded subbituminous coals have little variation.

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ABSTRACT

In this study, an upgrading process of lignite with supercritical CO_2 extraction under rather mild temperatures was studied as a possible method for producing clean solid fuel with less moisture and enhanced combustion reactivity. The fractal characteristics and reactivity evolution of two typical lignites during the upgrading process by supercritical CO_2 extraction have been studied in present work. Two typical lignites and one subbituminous coal were extracted in different conditions by a semi-continuous supercritical CO_2 extraction device and the evolution of coal pore structure was investigated by N_2 and CO_2 adsorption/desorption isotherms. Two fractal dimensions D_1 and D_2, at relative pressures 0–0.45 and 0.45–1, respectively, were calculated by the Frenkel-Halsey-Hill model. The combustion reactivity of raw and upgraded coals was studied by a thermogravimetric analyzer. The results indicate that the N_2 quantity adsorbed in pores of upgraded lignite increases with the increase of extraction time and temperature which is consistent with the variation of specific surface area and total pore volume of upgraded lignite. The mesopores and micropores of upgraded HB lignite are developed whereas macropores and mesopores of upgraded ZT lignite are enlarged after supercritical CO_2 extraction. It was found, D_1 values of upgraded HB lignite decrease whereas D_2 values increase slightly. Meanwhile, the D_1 and D_2 values of upgraded ZT lignite are all decreased. The D_1 values are mainly affected by the influence of mesopores and macropores on specific surface area and D_2 values are mainly affected by the effects of fine mesopores and micropores on total pore volume. We found that D_1 values have a positive relationship with the average pore diameter whereas have a negative relationship with specific surface area and total pore volume. D_2 values have a negative relationship with average pore diameter whereas have a positive relationship with specific surface area and total pore volume for the raw and upgraded lignite. The combustion reactivity of upgraded lignite is enhanced after supercritical CO_2 extraction due to the improvement of specific surface area and total pore volume.

1. Introduction

Coal is currently the main energy source in the world [1–4] and lignite accounts for 45% of the total coal resources worldwide [5] whereas 12.69% in China [6,7]. Coal is the predominant energy source in China and would still occupy an important position in the coming decades [8,9]. Besides, lignite would play a more important role due to the significant decrease of bituminous coal and anthracite coal [10–13]. However, the high moisture content in lignite greatly limits its utilization [14,15]. Drying and upgrading of lignite is the first and a necessary step to its further application such as pyrolysis, gasification and combustion [11,16].

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Nomenclature

$SCCO_2$	supercritical CO_2
LRCs	low rank coals
SSA	specific surface area
TPV	total pore volume
APD	average pore diameter
FHH	Frankel-Halsey-Hill
HB	Hu Lun Bei Er lignite
TG-DTG	thermo-gravimetric and differential curves
M_{ar}	moisture content of as-received basis,%
A_d	ash content of dried basis,%
V_{daf}	volatile content of dried-ash-free basis,%
FC_{daf}	fixed carbon content of dried-ash-free basis,%
$E_{(wt\%,daf)}$	extraction yield of dried-ash-free basis,%
k_{mean}	average combustion rate (min^{-1})
ZT	Zhao Tong lingite
TGA	thermogravimetric analyzer

There are a number of drying and upgrading methods for lignite, and they can be divided into evaporative drying methods and non-evaporative drying methods [17]. Evaporative drying methods include rotary drying, fluidized bed drying, hot oil immersion drying and microwave drying. Non-evaporative drying methods contain hydrothermal drying, mechanical thermal drying and solvent extraction. Among these drying and upgrading methods, rotary drying suffers from high energy consumption [18]. Drying in hot air or flue gas in fluidized bed is widely used but has the risk of self-ignition and oxidation. The application of superheated fluidized bed drying method is limited in arid area because of requirements of large quantity of water [19]. The hot oil immersion drying is hard to separate oil and coal completely [17]. Microwave drying is considered to be a potential drying method [20]. However, most of the drained water is discarded without further utilization such as the steam reforming of methane (SRM) among these evaporative drying methods [20]. Non-evaporative drying methods of hydrothermal drying [21–23], mechanical thermal drying [17] and organic solvent extraction methods [24–26] are usually done at high temperatures.

Supercritical CO_2 ($SCCO_2$) is a solvent which has low viscosity and high diffusion capacity similar to gas and high density similar to liquid [27]. Hence, it is easy to diffuse in and out of coal and the moisture diffusion coefficient of $SCCO_2$ extraction is faster than fluidized bed drying when the flow rate of $SCCO_2$ is far smaller than the air medium in fluidized bed at the same drying temperature [16]. Meanwhile, CO_2 is safe and inert, so that self-ignition and oxidation of coal could not occur. CO_2 is easy to obtain, easy to separate with coal and can be recycled in the $SCCO_2$ extraction system. Hence, the $SCCO_2$ solvent has great superiority to other solvent. More than that, the green-house gas CO_2 can also be taken into utilization in order to mitigate climate change [8]. The loss of volatile matter can be lower and the low grade heat can be utilized because $SCCO_2$ extraction is conducted at low temperature. Therefore, the $SCCO_2$ extraction system maybe could be combined with a power plant or gasification system and make use of CO_2 and low grade heat they produced which can increase the efficiency of the power plant and gasification system. Some researches on $SCCO_2$ extraction have been done and the results show that $SCCO_2$ extraction can alter the structure and properties of coal [28,29], and there are studies revealed that $SCCO_2$ extraction may alter the structure of coal by extracting organic and inorganic constituents from the coal matrices [30,31]. Iwai et al. [32–34] conducted drying of three LRCs by using $SCCO_2$ and found the surface areas of Berau and Taiheiyo coals dried with supercritical CO_2 were larger than thermally dried coals. The swellability of low rank coals is enhanced by drying with supercritical CO_2. However, there are no investigations to research the pore structure and fractal dimension variation and combustion reactivity enhancement of upgraded lignite by $SCCO_2$ extraction systematically so far.

Fractal theory has been proven to be an effective method to evaluate the complex porous material not only on the pore structure but also on the diffusivity and permeability [35,36]. This includes description of pore irregularity and surface roughness for porous materials. It has been shown that the irregularity of surfaces and pores is important for processes such as diffusion, reaction dynamics, and adsorption [1,37]. Many methods such as quantitative X-ray CT image, nuclear magnetic resonance spectroscopy (NMR), high resolution transmission electron microscopy (HRTEM), small angle X-ray scattering (SAXS) and gas adsorption/desorption analyses have been applied to study the characteristics of the adsorption pores [38–42]. Among these technologies, N_2 adsorption/desorption has been proven to be an effective method to characterize fractal dimensions since adsorption/desorption measurements are relatively simple and convenient to calculate the fractal dimensions [43]. One method for fractal analysis based on adsorption isotherm is the Frenkel-Halsey-Hill (FHH) model [40]. This method has also been applied to coal for the fractal characterization of adsorption-pores [39,44,45]. As far as I know, studies about the pore structure variation and fractal characteristics evolution of lignite during an upgrading process by $SCCO_2$ extraction are rare. $SCCO_2$ extraction is a relatively new and potential upgrading method for lignite which deserving investigations for its merits we have discussed above. We found that the pore structure and the combustion reactivity of upgraded lignite are improved after $SCCO_2$ extraction while other upgrading methods have no similar effects [14,23]. Hence, it is of significance to investigate the upgrading method of $SCCO_2$ extraction in order to research the relationship of physicochemical properties such as pore structure and reactivity with experiment condition which is important to utilize the lignite resource.

In this paper, we collected three kinds of coal samples to study the effects of $SCCO_2$ extraction temperature and time on pore structure and fractal dimensions of upgraded coals. The Frankel-Halsey-Hill (FHH) equation was employed to characterize pore fractal dimensions including surface morphology and volumetric of coal samples. The thermogravimetric analyzer (TGA) was applied to evaluate the combustion reactivity of upgraded coals.

2. Experimental

2.1. Material

Two typical lignites obtained from Hu Lun Bei Er (HB), Zhao Tong (ZT) and a subbituminous coal obtained from Xin Jiang (XJ) were chosen to be investigated in this study. The raw coals were crushed and sieved, and the 0.18–0.25 mm fraction was chosen for further

Table 1
Properties of raw and upgraded HB lignite.

Samples	Proximate analysis (wt%)				
	M_{ar}	A_d	V_{daf}	FC_{daf}	$E_{(wt\%,daf)}$
HB	35.78	9.47	44.93	55.07	
62-15-15-HB	24.00	10.25	44.39	55.61	13.65
62-15-60-HB	7.23	10.31	44.06	55.94	33.25
62-15-180-HB	6.09	10.23	42.89	57.11	35.33
82-15-15-HB	20.82	10.18	44.49	55.51	17.23
82-15-60-HB	5.87	10.18	43.38	56.62	34.64
82-15-180-HB	4.86	10.16	42.42	57.58	36.42
102-15-15-HB	12.46	9.78	45.00	55.00	26.42
102-15-60-HB	4.03	10.19	43.16	56.84	36.59
102-15-180-HB	3.65	10.18	42.94	57.06	38.09