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Exploring on aqueous chemistry of micron-sized lignite particles in lignite–water slurry: Effects of pH on humics dissolution

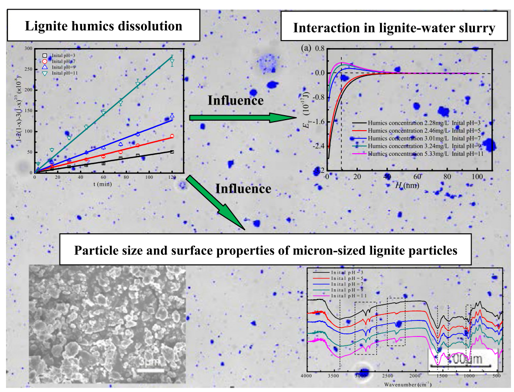
Yanfang Huang [a,1], Wenjuan Wang [a,1], Longjie Xing [a], Guihong Han [a,*], Jiongtian Liu [a,b,*], Guixia Fan [a]

[a] School of Chemical Engineering and Energy, Zhengzhou University, 450001 Zhengzhou, PR China
[b] National Engineering Research Center of Coal Preparation and Purification, PR China

HIGHLIGHTS

- The aqueous chemistry of lignite–water slurry was studied.
- The outer diffusion is the rate controlling step of humics dissolution.
- The particle size of lignite is decreased when the slurry pH is increased.
- Humics dissolution increases the surface hydrophilicity of the residual lignite.
- The dispersion stability of lignite is improved with humics dissolution.

GRAPHICAL ABSTRACT



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ABSTRACT

The aqueous chemistry of lignite can change the properties of coal–water slurry. The aqueous chemistry of lignite–water slurry including dissolution kinetics of humics and properties of the residual lignite was studied using optical microscope imaging, SEM, FTIR, zeta potential and contact angle analysis. Also, the influence of humics dissolution on the interaction of micron-sized lignite particles was discussed by EDLVO theory. The dissolution kinetics demonstrates that humics concentration increases with increasing the slurry pH. The outer diffusion through the product layer is the rate controlling step according to shrinking unreacted core model. The value of D_{50} defined as the apparent particle size relevant to 50% of cumulative distribution is decreased when the lignite slurry pH is increased. The FTIR, zeta potential and contact angle results show that humics dissolution increases the surface hydrophilicity of the residual lignite. The total energy E_T of the residual lignite particles at 10 nm of separation distance is enhanced from -0.70×10^{-17} to 0.34×10^{-17} J with the humics concentration is increased from 2.28 to 5.33 mg/L. The EDLVO calculation indicates that the dispersion stability of micron-sized lignite particles is improved with humics dissolution.

1. Introduction

Lignite, as a low-rank coal, originates from biomass by coalification. It is considered as the intermediate form between peat and bituminite [1]. Approximately 80% of lignite is used for power generation, and 20% is applied to produce synthetic natural gas,

* Corresponding authors at: School of Chemical Engineering and Energy, Zhengzhou University, 450001 Zhengzhou, PR China (G. Han).
E-mail addresses: guihong-han@hotmail.com (G. Han), scetljt@126.com (J. Liu).
[1] These authors contributed equally to this work as co-first authors.

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Table 1
The proximate analyses, elemental composition and humics content of lignite.

Proximate analyses				Elemental analysis (%daf)					Humics content (%)	
Total moisture (%arb)	Ash (%db)	Volatile matter (%daf)	Fixed carbon (%daf)	C	H	O_{diff}	N	S	Total humics	Free humics
61.60	19.91	58.75	41.25	67.12	3.54	26.00	1.56	1.78	45.79	42.20

Note: Free humics refers to the soluble organic fractions; Total humics refers to the soluble and the insoluble organic fractions associated with calcium and magnesium ions.

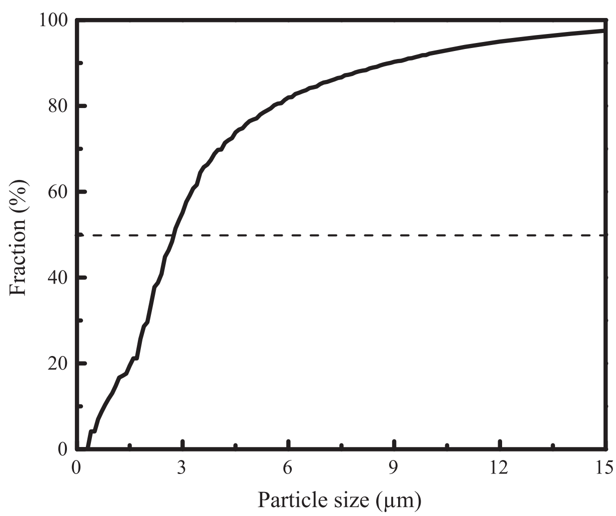

Fig. 1. The particle size distribution of the milled lignite particles.

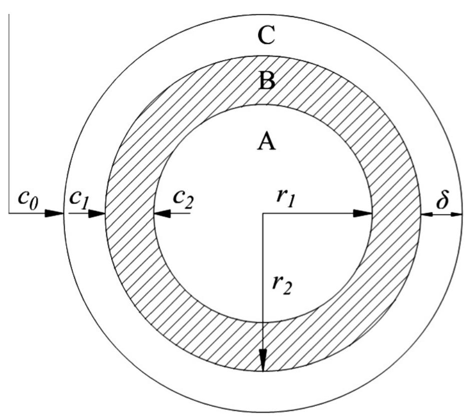

Fig. 2. Shrinking unreacted core model of dissolution reaction. (A – unreacted core; B – product layer; C – boundary layer; r_1 – radius of unreacted lignite particle; r_2 – radius of humics product layer; c_0 – concentration of Na^+ or H^+; c_1 – concentration of Na^+ or H^+ on surface of lignite particle; c_2 – concentration of Na^+ or H^+ in region of reaction; δ – thickness of Na^+ or H^+ on surface of lignite particle).

fertilizer products and soil conditioners in the world [2–5]. Lignite has the characteristic of high moisture content which is sometimes up to 60 wt.%. The high moisture has obvious negative effects on the utilization processes of lignite, such as liquefaction, gasification and combustion [6–10]. But lignite also has some remarkable advantages over high rank coal, such as high amount of volatiles, high reactivity and low sulfur [11,12]. It is estimated that the inventory of lignite is approximately 130 billion tons, which accounts for 13% of total coal reserves in China [13]. At present, lignite has not been massively utilized. The study on the efficient utilization of lignite resources has been expected.

Coal–water mixture (CWM) can often be found in the processing fields of lignite including coal washing processes (lignite flotation), transport in coal–water slurry, and disposal of coal [14–16]. The contact of lignite with water generally results in the dissolution of organic humics and water coloring. For example, lignite can be used to produce organic fertilizers and soil conditioners as the origin of humics. It was found that the interaction of lignite with water lead to the dissolution of humics fractions into underground water and the soil [17]. Coal–water system also exists in the flotation of low rank lignite. Lignite flotation is hard to be operated because lignite is relatively more hydrophilic than high rank coal, with more oxygen functional groups being exposed to water [18]. The producing of coal–water slurry fuel from lignite for combustion and gasification is a promising technology in clean lignite utilization [19]. The surface properties and the particle size distribution of lignite significantly influence the coal–water slurry properties. Some works have been conducted to examine the effects of oxygen functional groups on the surface properties and subsequent flotation behavior or slurryability in lignite flotation and clean lignite technology, by adopting hydrothermal drying and microwave-heating treatments [20,21]. For example, the hydrophilic oxygen functional groups were effectively decreased by microwave irradiation, and the lignite slurryability was improved [21,22]. Humics is hydrophilic matter, which has lots of oxygen functional groups such as carbonyl, carboxyl, and alcohol hydroxyl [23]. The release of humics from lignite into water certainly would change the properties of lignite and the solution composition in lignite–water system. The important property of coal–water slurry is its stability. Lignite particles in coal–water slurry should be kept their stability, homogeneity and the sedimentation should be prevented in their storage process. The stability of coal–water slurry depends on the dispersion, particle size distribution, concentration of lignite particles [24–27]. However, limited works have been done to study the aqueous chemistry of micron-sized lignite particles in the clean lignite technology, particularly the effects of humics dissolution on the properties of coal–water slurry.

In order to investigate the influence of interactions between coal and water that might occur in lignite–water mixture during the lignite flotation, or in the clean lignite technology, it is absolutely necessary to obtain more information about the effects of humics dissolution on the aqueous chemistry of micron-sized lignite particles. In this work, a typical Chinese lignite was subjected to acid/alkaline dissolution with different slurry pH, and the dissolution kinetics of humics in micron-sized lignite were described by shrinking unreacted core model. The particle size changing and surface properties of the residual lignite under different humics dissolution conditions were characterized using a serial of analytical techniques, i.e., optical microscope imaging, and SEM, FTIR, zeta potential and contact angle analysis. In addition, the influence of slurry pH corresponding to humics dissolution on the interactions between the residual lignite particles was examined by the EDLVO calculation.

2. Experimental

2.1. Materials

The sample of lignite was obtained from Zhaotong mining plant, China. The lignite was dried in a vacuum drying chamber at 30 °C