Journal of Cleaner Production 168 (2017) 1032–1038

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Enhancement in floatability of sub-bituminous coal by low-temperature pyrolysis and its potential application in coal cleaning

Wencheng Xia [a], *, Chenkai Niu [a], Chuancheng Ren [b]

[a] School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, 221116, Jiangsu, China
[b] School of Information Management, Dezhou University, Dezhou, 250323, Shandong, China

ARTICLE INFO

Article history:
Received 2 July 2017
Received in revised form
12 September 2017
Accepted 12 September 2017
Available online 13 September 2017

Keywords:
Sub-bituminous coal
Low-temperature pyrolysis
Flotation
XPS
SEM

ABSTRACT

Sub-bituminous coal is one type of low rank coal, which is difficult to upgrade using flotation cleaning technology because of its high hydrophilic properties. Low-temperature pyrolysis is widely used to convert low rank coal to gas/liquid components and the coal char is burned for power generation. It is friendlier to the environment if the coal char is forwarded to the cleaning process prior to the burning/combustion. This investigation aimed to assess the possibility of upgrading the coal char obtained from the low-temperature pyrolysis of sub-bituminous coal. The scanning electron microscopy, X-ray photoelectron spectroscopy, attachment time, and flotation tests were used to reveal the changes of surface properties and floatability of sub-bituminous coal during low-temperature pyrolysis with different pyrolysis times, i.e. 30, 60, 90, and 120 min, respectively. The results indicated that many pores and cracks were created on the coal char compared to raw coal surface. The content of hydrophobic functional groups on coal surface was increased whereas the content of hydrophilic oxygen-containing functional groups on the coal surface was reduced after the pyrolysis. The attachment time of coal particle-bubble was significantly decreased while the flotation recovery of coal was increased after the pyrolysis. Throughout this paper, the pyrolysis time of 30 min may be suitable for the enhancement of coal floatability by considering the gas/liquid production as well as economy and time saving. It is also inferred that the floatability of coal char should be governed by both its surface morphology and its surface composition of functional groups.

1. Introduction

Even though energy researches regarding new energy sources and technologies are becoming more popular than those regarding fossil fuels nowadays, coal resource still plays an important role in the energy supply in many countries, such as China (Yu et al., 2013), Turkey (Balat, 2010), Australia (Li, 2013), the European Union (Burmistrz et al., 2016a) and the United States (Shafiee and Topal, 2009). However, the usage of coal is meeting its serious challenges, such as mining safety (Han et al., 2017), air pollution, water pollution (He et al., 2017), environmental protection (Wang et al., 2017a, 2017b), land subsidence etc (Krzemień et al., 2016).

Coal contains both the organic and inorganic matters. The organic matters, as well as pyrite are easy to be oxidized in the air (Li et al., 2017). Therefore, plenty of heat is released during the coal oxidation (Wang et al., 2003). If the heat is concentrated and the temperature of coal mine or piles reaches its self-ignition point, coal spontaneous combustion (under ~400–500 °C temperature conditions) will happen. The spontaneous combustion of coal is usually prevented by humans, the coal has already suffered a high-temperature heating process which is similar to a low-temperature pyrolysis process to some extent (Valdés et al., 2016). The heating or pyrolysis process not only changes the surface properties of coal but also plays an important role in the hydrophobicity and floatability of coal and hence affects the beneficiation of the heated coal. It has been partially reported that the surface wettabilities of bituminous and anthracite coals are increased after the heating process (Xia et al., 2017a). However, little attention was paid to a comprehensive study into the relationship between the physical/chemical properties and the hydrophobicity/floatability of coal particle before and after the heating or pyrolysis process (Niu et al., 2017).

Additionally, sub-bituminous coal is one type of low rank coal, which is difficult to upgrade using flotation cleaning technology because of its high hydrophilic properties (Schobert, 1995). In

---

* Corresponding author. .
E-mail addresses: xiawencheng@cumt.edu.cn, w.xia.cumt@gmail.com (W. Xia).

http://dx.doi.org/10.1016/j.jclepro.2017.09.119
0959-6526/© 2017 Elsevier Ltd. All rights reserved.

general, effective collectors are founded to improve the flotation of low rank coal (Wen et al., 2017). However, these newly created collectors are not efficient in the industrial application of coal flotation because these collectors are expensive or environmentally harmful. Nowadays, low rank coal flotation is a worldwide problem. For example, plenty of fine low rank coal particles are refused and wasted in the northwest of China, and it is a serious threat to the environment as well as a waste of energy sources (Xing et al., 2017). An effective utilization of low rank coal is urgently needed for the sustainable development of coal and energy resources. The low-temperature pyrolysis is widely used to convert low rank coal to gas/liquid components (Collot, 2006). Then, the coal char is burned for power generation or used as carbon materials (Burmistrz et al., 2016b). A proper conversion and utilization of coal resource can benefit the CO_2 capture as well as environmental protection (Mehrpooya et al., 2017). As is known, the low-temperature pyrolysis process will release most of volatile matter from coal particles. The ash content primarily consists of inorganic minerals, such as quartz, kaoline, and montmorillonite (Sauer and Seuring, 2017). The weight of these minerals does not obviously change during the low-temperature pyrolysis and hence the ash content of the coal char will higher than raw coal (Xiao et al., 2016). The high-ash coal char is not suitable and economic to be forwarded to the burning or power generation processes. Therefore, it is friendlier to the environment if the coal char is forwarded to the cleaning process prior to the burning/combustion.

Therefore, the purpose of this paper was to investigate the effects of low-temperature pyrolysis on the surface properties and floatability of sub-bituminous coal. A comprehensive study, including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), attachment time and flotation tests, was carried out to reveal the fundamental and applied aspects regarding the surface properties and floatability of sub-bituminous coal particles before and after the pyrolysis process.

2. Experimental

2.1. Coal samples

The <0.5 mm size fraction of low ash sub-bituminous coal was used as raw coal sample in this paper. The proximate and ultimate analysis of raw coal is listed in Table 1. For raw coal, the volatile matter content is very high, which indicates the coal sample is one type of low rank coal. In addition, the ash content of coal sample is very low, which benefits the investigation of the surface properties of organic materials on coal surface before and after pyrolysis process.

2.2. Low-temperature pyrolysis process and mass loss analysis

Low-temperature pyrolysis experiments were conducted in a controlled atmosphere furnace (Device Model: OTF-1200X). The terminal temperature was fixed at 500 °C, with an interval of 25 °C at a heating rate of 15 °C/min and an isothermal treatment of 30, 60, 90 and 120 min, respectively. The selection of terminal temperature is based on our previous studies and other publications that the temperature of 500 °C is suitable for both the gas/liquid production but also the economic aspects (Li, 2013).

Approximately 4 g of raw coal fines were paved in a quartz container under the N_2 gas environment with the gas flow of 80 ml/min. After the pyrolysis process, the coal chars were cooled under the N_2 gas until it was cooled to the normal atmospheric temperature. At last, the coal chars were stored under the N_2 gas and waited for the tests. In this paper, the mass loss of coal chars at various pyrolysis times was analyzed to reveal the mass changes at different pyrolysis times.

2.3. SEM tests

Quanta 250 SEM (FEI, USA) was used to analyze the surface morphology of raw coal and coal chars at various pyrolysis times. Before the SEM tests, the particle surface was sputter-coated with a layer of gold. The magnification of SEM was fixed at 1, 000.

2.4. XPS tests

The XPS experiments of raw coal and coal chars at various pyrolysis times were carried out at room temperature in an ultra-high vacuum (UHV) system with the surface analysis system (ESCALAB 250 Xi, America). The data processing (peak fitting) was performed with XPS Peak fitting software. The binding energies were corrected by setting the C1s hydrocarbon ($-CH_2-CH_2$-bonds) peak at 284.8 eV.

2.5. Attachment time tests

The raw coal and coal char particles were also forwarded to the attachment time tests. The bubble-particle attachment time measurements were conducted with the Attachment Timer (made by University of Alberta, Canada) (Gu et al., 2003).

First, the coal particle was transferred to a small cell filled with distilled water. A bubble holder was on the top of the coal bed. The bubble of about 1.5 mm in diameter was generated using a microsyringe and then held by the bubble holder. The distance between the bubble and the coal bed was adjusted as a constant in each test using the three-dimensional micro-translation stage. Next, the bubble was kept in contact with the coal bed for the controlled contact time from 10 ms to 5, 000 ms. The attachment behavior of coal particle to the bubble was visually observed through the lens and CCD camera linked to a monitor, as shown in Fig. 1. In order to obtain the accurate bubble-coal attachment time, repeated measurements were performed at different positions of the coal bed and the final attachment time was obtained using the arithmetic mean value.

2.6. Flotation procedure

All flotation tests were conducted in a 40 ml micro-flotation cell with the impeller speed of 1, 600 r/min. The pulp density was about 50 g/L. The collector is not used in order to investigate the natural floatability of raw coal and coal chars at various pyrolysis times. The frother was sec-octyl alcohols at a dosage of 1.5 μl.

First, the coal sample was added in flotation cell with water and pre-wetted for 3 min. Then, the frother was added and the pulp was

Table 1
Proximate and ultimate analysis of sub-bituminous coal sample.

Mad (%)	Ad (%)	FCd (%)	Vd (%)	Cdaf (%)	Hdaf (%)	Odaf (%)	Ndaf (%)	S(t, daf) (%)
8.1	10.0	59.8	30.2	79.3	4.7	14.7	1.1	0.2

Mad: moisture content on air-dry basis. *Ad*: ash content on a dry basis. *FCd*: fixed carbon content. *Vd*: volatile matter content on a dry basis. *Cdaf, Hdaf, Odaf, Ndaf,* and *S(t, daf)*: Element (*C, H, O, N* and *S*) content based on a dry ash free basis.