PROCESS SAFETY AND ENVIRONMENTAL PROTECTION xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Co-utilization of two coal mine residues: Non-catalytic deoxygenation of coal mine methane over coal gangue

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ABSTRACT

The deoxygenation of coal mine methane (CMM) is a necessary process for concentrating methane by pressure-swing adsorption technology. Removal of oxygen in CMM by the reaction between oxygen and carbon in coal gangue is a novel solution for simultaneously utilizing two kinds of byproducts of coal mine, CMM and coal gangue. Process conditions for the deoxygenation of CMM were investigated systematically by using a fixed-bed reactor. The results show that higher temperature and lower gas flow rate not only decreased the residual oxygen concentration in the outlet gas but also increased the methane loss, and that the particle size of gangue did not influence deoxygenation within the experimental conditions used. Under optimal conditions (650 °C and 250 mL/min), there was no residual oxygen in the outlet gas and the methane concentration decreased by less than 0.5 mol%. XRD results show that coal gangue was activated during deoxygenation, and that activated gangue was suitable for utilization as a main component in cementitious materials.

Keywords: Coal gangue; Coal mine methane (CMM); Deoxygenation; Compressed natural gas (CNG); Cementitious material

1. Introduction

Methane, an important greenhouse gas (GHG), is over 20 times more effective than carbon dioxide in trapping heat in the atmosphere (Warmuzinski, 2008). Coal mine methane (CMM), which contributes to methane emissions (Cheng et al., 2011), is released mainly during and after mining operations. It shows great variability in release rate and composition of CMM (Karacan et al., 2011). When the released CMM is mixed with air, the concentration of CH_4 and O_2 in the mixture are approximately 30–50 mol% and 10 mol%, respectively, and N_2 comprises the balance gas (Zhong and Englezos, 2012).

Over the past 10 years, CMM emissions have been given more attention because of their status as a GHG and their potential use as a clean energy resource. China is the world's top producer and consumer of coal, and coal accounts for approximately 70.0% of the country's total national energy consumption (Karacan et al., 2011). Nearly 90% of China's coal production is from underground mining, and approximately 85–95% of total CMM emissions come from underground mines. In China, about 30% of CMM is utilized, but the quality of the remaining 70% is too poor for use (actual methane concentration of 3–25%) and is therefore released to the atmosphere (Su et al., 2011).

Because of the low content of methane in CMM, it is necessary to separate CH_4 from other gases to obtain methane-rich gas and then deliver it to supply systems for natural gas. In the last few decades, methane separation technologies, including low-temperature liquefaction (Fuertes, 2001), pressure-swing adsorption (PSA) (Olajossy et al., 2003), solvent absorption, molecular gate, and membrane separation (Wu et al., 2009) have been developed. The PSA method can be used to recover methane from CMM, in which both methane and oxygen in emissions are concentrated. However, it is a dangerous

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Received 24 April 2013; Received in revised form 19 September 2013; Accepted 6 October 2013
0957-5820/$ – see front matter
http://dx.doi.org/10.1016/j.psep.2013.10.002

Table 1 – Properties of coal gangue.

Sample	Proximate analysis of coal gangue (wt%)[a]			
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}
Coal gangue	1.4	45.3	16.6	36.7
	Main chemical compositions of coal gangue (wt%)[b]			
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2
	23.8	17.7	0.8	1.0

[a] M, moisture content; A, ash; V, volatile matters; FC, fixed carbon content; ad, on air dry basis.
[b] On coal gangue basis.

process because CMM contains 5–15% oxygen, a level within the threshold of methane explosion. Therefore, it is necessary to remove oxygen in the drained gas before using it.

There are two main methods used in CMM deoxygenation: catalytic and non-catalytic deoxygenation (Wang et al., 2012). Catalytic deoxygenation involves catalytic combustion of methane to remove oxygen under a lean oxygen environment. Its reaction is given as follows: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. Catalytic combustion of methane is a strongly exothermic reaction, which induces temperature runaway of the catalyst bed, resulting in catalyst deactivation due to sintering at high temperatures. A disadvantage of catalytic deoxygenation is methane consumption and susceptibility of the catalyst to deactivation; therefore, the choice of catalyst is critical. Noble metal catalysts are widely used in the catalytic combustion of CH_4 because of their higher activity, lower ignition temperature, and better poison resistance. Another catalytic deoxygenation process (Zhang et al., 2009) involves the use of Na_2S as deoxygenation agent in the presence of molecular sieves. However, this process is complicated because of the recycling of Na_2S, which may increase the levels of sulfur-containing compounds in the outlet gas. In non-catalytic deoxygenation, coke combustion can effectively remove oxygen in CMM. However, the use of coke involves high energy consumption (Wang et al., 2012).

Coal gangue is an industrial residue that is discharged when coal is excavated and washed. It is one of the industrial solid wastes with the largest levels of discharge (Liu and Liu, 2010). According to statistics (Li et al., 2006), the accumulative total of its stockpile may reach more than 7×10^9 tons. In China, about 1600 sites of coal gangue hills, amounting to 4.5×10^9 t, occupy about 1.5×10^4 hm^2 of land, and the amount increases by (1.5–2.0) $\times 10^8$ t annually.

Large quantities of coal gangue have become a serious environmental problem; it contributes to pollution of water and soil, as well as to soil erosion. Approaches to fully utilize gangue are a therefore technical concern worldwide. Coal gangue contains carbon and large amounts of valuable mineral resources such as SiO_2, Al_2O_3, Fe_2O_3, and other oxides (Liu and Liu, 2010). As it has high levels of clay minerals and carbonaceous materials, coal gangue could also be a source of useful byproducts. In recent years, techniques to utilize coal gangue have been focused on power generation and input material for construction materials. Coal gangue can be used as raw material for the production of cementitious material. However, the cementitious capability of coal gangue is very weak. One method of improving the cementitious activity of coal gangue is calcination (Li et al., 2006). High-temperature activation is necessary for utilization of coal gangue in cement. However, the utilization percentage of coal gangue is only about 43% in China, which is far lower than that in developed countries (about 90%) (Wang et al., 2009).

The carbon present in coal gangue provides the possibility of replacing coke, which is used in the combustion deoxygenation of CMM. Furthermore, activation of coal gangue can be completed during deoxygenation and then used as cementitious material. Notably, two kinds of mining byproducts, CMM and coal gangue, can be utilized at the same time by this new process. This advantage accounts for the appeal of the process and warrants its detailed investigation.

In the present work, we investigated the deoxygenation of CMM performed by passing CMM through heated coal gangue powder. The effects of temperature, flow rate of feed gas, and particle size of coal gangue on the deoxygenation of CMM were studied, and optimized operating conditions were obtained. The treated coal gangue samples were characterized by thermogravimetric analysis (TGA) and X-ray diffraction (XRD).

2. Experimental

2.1. *Materials*

2.1.1. *Simulated CMM*

The CMM prepared in the laboratory was composed of CH_4 (42.56 mol%), O_2 (12.06 mol%), and N_2 (45.38 mol%). It was stored in a cylinder.

2.1.2. *Coal gangue sample*

The coal gangue sample was collected from the roof of a coal seam at Malan Mine of the Xishan Coal Electricity Group Co., Ltd. The coal gangue sample was stored immediately in a sealed plastic bag to prevent weathering and contamination. After they were brought to the laboratory, the coal gangue samples were air-dried and crushed to different particle sizes for the experiments. Samples were prepared by passing them through a commercial sieve shaker and were then set aside for subsequent use. The coal gangue was twice sieved to ensure that coal gangue fines, which tend to adhere onto larger particles, were removed from the samples. Results of proximate analysis of the coal gangue and the ash composition are shown in Table 1.

2.2. *Deoxygenation of CMM*

The deoxygenation reaction of CMM with coal gangue in a continuous-flow system (Fig. 1) with a fixed-bed reactor at atmospheric pressure was investigated. The reactor was constructed from a stainless steel tube having an inner diameter of 8 mm and a length of 60 cm. About 4.0 g of coal gangue