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Enhancing the storage stability of petroleum coke slurry by producing biogas from sludge fermentation

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ABSTRACT

Huge amounts of highly concentrated organic wastewater and sludge, which are main environmental pollutants that are highly difficult and costly to dispose of, are generated along with rapid industrialization and urbanization. Petroleum coke slurry (PCS) is an established liquid fuel that can be used as a substitute to oil and as a gasification material. However, the poor storage stability of PCS significantly constrains its applications. In this study, highly concentrated organic wastewater, sludge, and petroleum coke were mixed to prepare a new PCS with high storage stability. During sealed storage, biogas bubbles were produced and diffused in the prepared PCS because organic matter in wastewater was consumed by microorganisms in the sludge. Biogas bubbles bonded with petroleum coke particles and formed gas–solid combos. The lifting and steric hindrance effects of biogas effectively prevented petroleum coke particles from settling and coagulating, thus enhancing PCS storage stability and extending the application range of PCS. Based on the mathematical model and the stability results, the sludge significantly increased the spatial structure strength of PCS, and the fermentation biogas diffused in the slurry further increased structure strength and enhanced slurry stability.

1. Introduction

Along with rapid industrialization and urbanization, huge amounts of highly concentrated organic wastewater and sludge are generated. If not disposed of properly and immediately, highly concentrated organic wastewater will generate foul smell and pollute the environment because of decomposition. Sludge contains more salts, heavy metals, pathogens, nutrient substances, organic pollutants, etc., the untreated sludge will also pose dangerous environment consequences when discharged into the environment. They have become the main environmental pollutants, and therefore, they have to be disposed of properly to avoid secondary pollution. According to previous reports [1, 2], waste water and sludge can be made into slurry fuel by blending with pulverized coal. This method can solve the way out and environmental issues of waste water and sludge, and also use their caloricity so as to realize sustainable development.

As we also know, the successful development of coal–water slurry (CWS) technology has produced petroleum coke slurry (PCS). This substance, which is made from petroleum coke and water, provides a new, clean, and efficient way to use petroleum coke. PCS can be used as a substitute to oil and as a gasification material because its fluidity and rheological properties are similar to those of oil and CWS [3, 4]. PCS has numerous advantages over CWS, including high slurrying concentration, high calorific value, and low ash content. However, petroleum coke particles in PCS always agglomerate and settle very easily, thus causing significant solid–liquid separation in the PCS system during storage [5]. Poor storage stability significantly prohibits the development and applications of PCS.

Solving the storage stability problem will improve the industrial applicability and widen the application range of PCS. Zhan et al. [6] attempted to enhance the stability of PCS by using black liquor as an additive. Black liquor improved surface wettability of petroleum coke particles and increased the Zeta potential of particle surface [7], i.e., the electrostatic repulsive effects among particles were increased, and thus, the stability of PCS was improved. However, the effect of the method is extremely limited. Wang et al. [8] applied ultrasonic treatment to petroleum coke oil slurry and found that treatment at 20 kHz, 50 W/cm^2 for 4 min could achieve the optimum effect to decrease apparent viscosity and improve

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Abbreviations

COD	Chemical oxygen demand
CWS	Coal–water slurry
MOM	Macromolecular organic matter
PCS	Petroleum coke slurry
PR	Penetration rate
S0	Clean water–petroleum coke slurry
SS0	Clean water–sludge–petroleum coke slurry
SCD_{max}	Maximum difference of solid concentration in PCSs/WSSs
SEM	Field-emission scanning electron microscope
VSS	Volatile suspended solid
W1, W2, W3, W4	Starch solutions with COD of 2500, 6000, 12,000, and 18,000 mg O_2/L, respectively.
W_m	Total energy dissipation per unit mass of slurry
W_V	Total energy dissipation per unit volume of slurry
WSR	Water separation ratio
WSS	Starch wastewater–sludge-petroleum coke slurry
η	Apparent viscosity
η_c	Characteristic viscosity

static stability. However, ultrasonic treatment is expensive and difficult to promote in actual applications, and more, the static stability improving effect is also not significant. Wang et al. [9] effectively improved the stability of PCS by blending sludge into PCS. Sludge flocs have abundant voids and pores [10]. When petroleum coke and sludge are co-slurrying, the thin petroleum coke fills in the voids and pores and combines with sludge flocs to form a stable network structure, which prevents particles from settling and flocculating. But at the same time, adding sludge significantly increased the viscosity of PCS. Inspired by flotation process[11], Bubble PCS is proposed, which is a gas–liquid–solid three-phase mixture formed by adding or producing bubbles in PCS. Compared with common PCS, Bubble PCS is enhanced in the storage stability, depending on the lifting and steric hindrance effects of the bubbles, which prevent petroleum coke particles from settling and agglomerating. Gao [5] used an air compressor to blow air into PCS through a sand core plate and systematically studied the effects of various factors on the stability of PCS. The experimental study showed the stability of PCS was effectively enhanced by the air bubbles.

Interestingly, sludge contains large amounts of microorganisms that can utilize hydrocarbons, proteins, and lipids in sludge flocs to ferment and generate biogas [12–14]. When sludge is blended into PCS, biogas bubbles are generated from sludge fermentation and diffuse in the slurry system. Not like the air bubbles injected by compressor from outside in Gao's study [5], biogas bubbles here are automatically formed inside the slurry system, and also act as combustible component [15]. To increase biogas production, waste and wastewater with high concentration of organic matter are always added to enhance fermentable substrate concentration [16, 17]. Highly concentrated organic wastewater is generated from various industries, such as agricultural processing, starch/sucrose factory, winery, and meat processing. Organic wastewater always has a high chemical oxygen demand (COD) value. For example, brewery wastewater contains COD of 80,000 mg O_2/L to 90,000 mg O_2/L [18]; cheese whey, ~55,000 mg O_2/L; poultry wastewater, ~123,000 mg O_2/L; olive oil processing wastewater, ~140,000 mg O_2/L [19]; cane sugar refinery wastewater, more than 5000 mg O_2/L; cassava starch processing wastewater, more than 8000 mg O_2/L; cassava alcohol wastewater, more than 25,000 mg O_2/L [20], and potato–maize wastewater, 5300 mg O_2/L to 18,100 mg O_2/L [21]. The high COD in wastewater can increase the biogas production when co-digested with sludge.

In the current study, highly concentrated organic wastewater, sludge, and petroleum coke are mixed to prepare PCS. The sludge provides the necessary microorganisms, and the organic wastewater provides the carbon and nitrogen sources for fermentation. In addition, highly concentrated organic wastewater is used to prepare slurry fuel instead of clean water. Environmental problems resulting from organic wastewater are solved, the organic loads for fermentation in the slurry are increased, and matter undigested by microorganisms also increases the caloric value of the prepared PCS. This study focuses on the PCS stability improving effects by biogas bubbles generated from sludge fermentation, and try to develop the industrial application potential of this method.

2. Experimental

2.1. Materials

Starch solution, which was used as a model of complex wastewater, was formulated using cassava starch and peptone at a mass ratio of 100:10, i.e., $m(C):m(N) = 100:5$, at which condition the microorganisms were more likely to have higher activity. In the experiment, four solutions with different COD concentrations were prepared by adjusting the concentration of cassava starch and peptone proportionally. The four solutions were labeled as W1, W2, W3, and W4; and their COD values were 2500, 6000, 12,000, and 18,000 mg O_2/L, respectively. To maintain normal microorganism activity, suitable amounts of mineral salts, such as NaCl (3.0 g/L), $(NH_4)_2SO_4$ (0.1 g/L), KH_2PO_4 (0.06 g/L), $NaHCO_3$ (0.1 g/L), $MgSO_4$ (0.09 g/L), and $CaCl_2$ (0.03 g/L) were added into the solutions.

Petroleum coke powders with a volume weighted mean size of 27.67 μm were obtained from Jinshan Petrochemical Company (Shanghai, China). Sludge was collected from a waste water treatment plant (WWTP) in Hangzhou city, China with a daily flow rate of 1,200,000 m^3/d. The wastewater treatment is performed by the activated sludge process. All sludge samples were stored at 4 °C until use.

The proximate and ultimate analysis of applied petroleum coke and sludge are shown in Table 1. The sludge has extremely high contents of moisture (82.42%) and ash (54.95% on dry basis). The dry-basis higher heating value of the sludge is relatively low (10.36 MJ/kg) when compared with petroleum coke (36.00 MJ/kg), because of its very low fixed carbon content (4.96% on dry basis). In addition, the total COD of the collected sludge is 254.99 mg O_2/g dry sludge, and its dry-basis volatile content is 40.09%.

Chemical additives are important components of CWS/PCS. A suitable additive decreases aggregation forces among particles and increases the surface charge of particles, thus enhancing slurry stability. A copolymer of methylene naphthalene, sulfonate styrene, and sulfonate maleate, which was proven to have better dispersing effect [22, 23], was selected as the chemical additive in the present study. This copolymer was added to PCS at a constant dosage of 0.8% on a dry-coal basis.

2.2. Methods

2.2.1. Preparing the new PCS

Given the different effects of slurrying process [24], all slurry samples were prepared as follows. First, the required masses of the slurrying materials, including those of petroleum coke powder, sludge, starch wastewater, and chemical additive were weighed. The mass ratio of wet sludge to petroleum coke was 16:100. Next,