Fuel 215 (2018) 312–319

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Simultaneous disposal and utilization of coal chemical wastewater in coal and petroleum coke slurry preparation: Slurrying performance and mechanism

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ARTICLE INFO

Keywords:
Coal gasification wastewater (CGW)
Coal-water slurry (CWS)
Slurrying performance
Additive adsorption
Waste recycling

ABSTRACT

Preparation of coal gasification wastewater (CGW) into coal-water slurry (CWS) or petroleum coke (PC)-water slurry (PCWS), which is then used as a feed material for gasification, enables the recycling of CGW and consequently solves its environmental pollution problems. The present study focused on slurrying behavior of CWS and PCWS prepared with CGW. The slurrying mechanism was studied based on the coal (or PC)–additive adsorption and hydrophobic property of the coal (or PC). Results showed the additive and CGW inclusions exhibited synergistic effects when they were adsorbed onto the coal (or PC). Increasing the adsorption amount of the additive facilitated the formation of a stable hydration shell outside the coal (or PC) particles, which enhanced the separation and dispersion of particles in the suspension. Therefore, CWS (or PCWS) was easily prepared into a high-concentration suspension when CGW was used instead of clean water; that is, CGW improved the slurrying performance. Therefore, preparing CWS (or PCWS) with CGW is a favorable option for simultaneously treating and utilizing CGW.

1. Introduction

China has an energy structure that is characterized by “rich coal, deficient oil, and lean gas.” The development of the modern coal chemical industry, including coal-to-liquid and coal-to-gas technologies, has a realistic and long-term significance for fully utilizing the advantages of resources, filling in the demand–supply gap of petroleum and natural gas, and mitigating air pollution caused by coal combustion. Coal gasification is an important aspect of the coal chemical industry. This process has been considered one of the most promising alternatives to producing gaseous fuels. However, high water consumption and wastewater discharge are the main issues of the modern coal chemical industry.

Coal gasification wastewater (CGW), which is generated mainly from gas washing, condensation, and fractionation processes, has a high concentration of organic pollutants and high toxicity; it typically exhibits considerable fluctuations in water quality (such as phenols, ammonia, cyanide, and suspended solids) [1], thereby resulting in difficulty in treating it uniformly. This condition restricts the development of the coal chemical industry in the major coal-producing areas in China, where environmentally sensitive areas are located.

Currently available treatment methods for CGW include physical [2–4] (such as adsorption, precipitation, filtration, coagulation, and membrane separation), chemical [5] (such as oxidation), and biological [6,7] (such as aerobic and anaerobic treatments). However, existing methods face numerous problems during practical application [8]. Chemical oxygen demand (COD) can be efficiently reduced through the adsorption method; however, the regeneration and secondary contamination of adsorbents are critical obstacles. The catalytic oxidation method can effectively degrade biorefractory organic pollutants but requires a high operating cost. Aerobic or anaerobic treatments alone are incapable of producing effluents with COD and nitrogen concentrations that comply with discharge standards due to the presence of biorefractory organic pollutants and nitrification inhibitors. The combined anaerobic–aerobic method [7] can achieve desirable CGW treatment performance. Various combinations of anaerobic and aerobic processes have been successfully applied to remove phenols, polycyclic aromatic hydrocarbons, and long chained alkanes from CGW at the industrial scale. However, maintaining a stable up-to-standard discharge quality is difficult for biologically treated effluents when wastewater contains a high amount of refractory organics, and thus, advanced treatment units are required, which increases capital and

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https://doi.org/10.1016/j.fuel.2017.11.038
Received 20 July 2017; Received in revised form 14 October 2017; Accepted 13 November 2017
0016-2361/

Nomenclature

CGW	coal gasification wastewater
DIW	deionized water
PC	petroleum coke
CWS	coal-water slurry
PCWS	petroleum coke-water slurry
CGWS	CWS prepared using CGW
PCGWS	PCWS prepared using CGW
COD	chemical oxygen demand
NNO	sodium methylene bis-naphthalene sulfonate
SLS	sodium lignosulfonate
η_{100}	slurrying viscosity (the average apparent viscosity value presented at $100\,s^{-1}$)
SC_{max}	solid concentration of the slurry sample when its η_{100} is 1000 mPa·s
λ_{max}	the maximum absorbance wavelength
Γ	adsorption amount of the additive by unit mass of sample (dry basis), $mg\,g^{-1}$
c_0	concentration of the original additive solution, $mg\,L^{-1}$
c_e	equilibrium concentration remaining in the solution after adsorption, $mg\,L^{-1}$
V	volume of the additive solution, L
m	mass of the sample (dry basis) added to the additive solution, g
FTIR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy

operation costs [1,9]. The management of highly recalcitrant CGW using a cost-effective, environment-friendly, and universally applicable method is significant for the healthy development of the coal chemical industry.

Coal-water slurry (CWS) is a coal-based liquid fuel composed of pulverized coal (50–70 wt%), water (30–50 wt%), and a small amount of additive (0.5–1 wt%). This fuel, which originated from the oil crisis during the 1970 s, has been widely used in boilers, furnaces, and gasifiers as an oil substitute or a gasification feed in China [10,11]. CWS is also the main form of feed material for coal conversion in the coal chemical industry; it is widely used in direct [12] and indirect [13] coal liquefaction, as well as in coal-to-methanol [14] and coal-to-olefin [15] technologies. The preparation of CWS using coal chemical wastewater instead of clean water can save a huge amount of clean water and effectively use wastewater given the considerable amounts of water consumed for CWS preparation and wastewater discharge from the coal chemical industry. The high concentration of organics in wastewater increases the combustion heat of CWS. In this manner, wastewater is simultaneously treated and utilized. Miccio and Miccio [16] prepared the coal-waste-water mixture using organic sludge from alcohol production wastewater. A high value of co-combustion efficiency (larger than 98%) was attained in a 200 kWt fluidized bed combustion pre-pilot facility.

Slurrying properties, including apparent viscosity, solid loading, rheology, and stability, significantly influence the preparation, storage, pumping, combustion, and gasification performances of slurry fuel [10]. These properties should be extensively studied before the technology that prepares CWS using coal chemical wastewater can be widely applied. Related studies [17–19] have shown that the slurryability, fluidity, and stability of CWS are improved when industrial wastewater is fully or partially used instead of clean water to prepare CWS. Liu et al. [17] determined the effect of waste liquid produced from the hydrothermal treatment of both low-rank coal and sludge on the slurryability of coal sludge slurry, and the results showed that the slurry prepared using waste liquid instead of clean water had a higher slurrying concentration and better stability, due to the organic compounds and high-valent cations in the waste liquid. Liu et al. [18] prepared CWS using petrochemical wastewater and found that certain active ingredients of petrochemical wastewater improved the surfactivity and slurryability of coal particles. Zhan et al. [19] used unmodified black liquor, a waste and nuisance in the pulp and paper industry, to prepare petroleum coke (PC)-water slurry (PCWS); they found that black liquor functioned well as an additive and a stabilizer and remarkably improved the rheological properties, fluidity, and stability of PCWS. To date, however, research on the slurrying performance and mechanism of CWS prepared using coal chemical wastewater has rarely been reported. Accordingly, CWS was prepared using CGW in laboratory scale, and slurrying performances, including apparent viscosity and maximum solid loading, were obtained in the current study. The slurrying mechanism was analyzed by determining the coal–additive adsorption and hydrophobic property of the coal surface. Similarly, PCWS was prepared using CGW, and the slurrying properties were identified.

2. Experiment and methods

2.1. Materials

2.1.1. Coal and PC

Brown coal mined from the Xinjiang district in China and PC from TANECO (an oil and gas company in Russia) were selected for this study. The coal and PC were ground and sieved to a particle size of less than 150 μm before being prepared into slurry. The results of the proximate and ultimate analyses of the coal and PC are presented in Table 1.

The particles size distribution of the coal and PC was analyzed by the Mastersizer 2000 Granularity meter (Malvern, UK), and the results were shown in Fig. 1. The volume average particle diameter was 26.93 μm and 49.06 μm for coal and PC respectively.

The microscopic pore structure of the coal and PC samples was determined by an automatic surface area and pore analyzer (TriStar II3020, Micromeritics, USA). The samples were pre-heated at 200 °C for 4 h in vacuum and then nitrogen adsorption/desorption isotherms at 77 K was used to measure the specific surface area based on the Brunauer–Emmett–Teller (BET) method and the total pore volume based on the Barrett–Joyner–Halenda (BJH) method. The results are

Table 1
Proximate and ultimate analyses of coal and PC.

Sample	Proximate analysis (%)				Ultimate analysis (%)					HCV
	M_{ad}	A_d	V_d	FC_d	C_d	H_d	N_d	$S_{t,d}$	O_d	(MJ/kg)
Coal	11.30	21.32	32.58	46.10	60.99	2.96	1.11	0.47	13.15	22.08
PC	0.95	0.91	10.99	88.10	88.79	3.69	1.87	4.42	0.32	35.05

M_{ad} refers to the yield of moisture on an air-dried basis; A_d, V_d, and FC_d respectively refer to the yield of ash, volatile, and fixed carbon on a dry basis; ultimate analysis was conducted on a dry basis; HCV refers to the higher calorific value.