Fuel Processing Technology 144 (2016) 282–289

Contents lists available at ScienceDirect

Fuel Processing Technology

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

A comparison of acid treatment in the dewatering of Chinese and Australian lignites by mechanical thermal expression at high temperatures

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ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form 9 January 2016
Accepted 10 January 2016
Available online 23 January 2016

Keywords:
Lignite
Mechanical thermal expression
Dewatering
Acid treated
Waste water treatment

ABSTRACT

Mechanical thermal expression (MTE) is an effective and efficient method of dewatering high moisture content lignite. However the high total organic carbon (TOC) of the wastewater requires further chemical treatment, before discharge to the environment. In this work, changes in the characteristics of the solid products and the wastewater are reported, when sulphuric acid is used as part of the MTE process.

Two lignites were tested: Loy Yang (LY) from Australia and ShengLi (SL) from China. The characteristics of the solid products and wastewater were analysed for both. The effect of expression temperature (200 °C and 240 °C) on moisture content reduction is evident for LY, but it is only marginal for SL. The final moisture content of the solid product in either case is not impacted by the addition of sulphuric acid, but the mercury porosimetry intrusion analysis showed a greater reduction in pore volume for LY. It is postulated that acid treatment suppresses the solubilization of phenols and carboxylic groups in the case of LY. For SL with a different maceral structure, as the concentration of the solubilized phenolic compounds is much lower when no acid is used, the impact of acid addition is much less significant. It appears that the addition of acid inhibits the dissociation of organics from the lignite macerals and also reduces the rate of dissolution, leading to lower TOC in the wastewater. Thus, the wastewater becomes easier to treat after sulphuric acid addition during MTE. The MTE process also removes dissolved salt and organically-bound minerals which aids in reducing the fouling components in the lignite and possibly the PM_{10} concentrations in the flue gas following combustion.

1. Introduction

The high moisture content in low rank coal (lignite and brown coal) is a major impediment in using these coals for efficient power generation. An efficient dewatering process is needed to improve the low rank coal utilisation for power generation. MTE is one such process proposed for dewatering low rank coal. However wastewater is also a subject for concern. Depending on the coal type, wastewater contains minerals, fine particles and organics that need to be treated before being released to the environment. MTE dewatering from high moisture content (about 60%) to low moisture content (about 25%) resulted in large quantities of wastewater. Butler et al. [1] showed that the Latrobe Valley power stations could produce about 20 GL of expressed water per annum using the MTE process. Therefore, wastewater treatment after the dewatering process is an important issue which needs to be addressed. One of the advantages of the MTE process over other dewatering processes (such as Hydrothermal Dewatering (HTD) [2] and pressurised steam drying [3]) is that the levels of organic compounds in MTE product water are lower. Temperature plays an important role in the release of organics into the wastewater. The TOC of the product water from processing at 200 °C in the MTE process has been measured as 0.8 g per kg of dry feed coal [4]. In comparison, HTD process reported product water TOC measurements of 2–50 g/kg [2].

Several methods are used in detecting organics in the wastewater. Qi [5] used solid phase extraction-gas chromatography–mass spectrometry (SPE-GC–MS) to identify the low molecular organic compounds in the MTE product water. Other researchers [1,5] reported that 20% of the organic carbon could be identified by this method and more than 97% of the identified compounds are carboxylic acid compounds, while the remainder are mainly phenolic, carboxylate, aldehyde and ketone compounds. The organic species in the product water increases with processing severity (high temperature and pressure) and the extent of moisture reduction [5]. Artanto and his co-workers [6] used pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS) to analyse dried MTE water samples and detected benzene, styrene, 2-methyl phenol, 3-methyl phenol and 1-phenyl-1-butanone in the water.

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http://dx.doi.org/10.1016/j.fuproc.2016.01.010
0378-3820/

To reduce organic compounds in the water, researchers tried acid treatment in the MTE process [7,8]. Vogt and his co-workers [7] treated the lignite from Australia, Germany and Greece with 0.01 M and 0.1 M HCl at room temperature, before undergoing MTE tests at 200 °C. Chemical Oxygen Demand (COD) was used to assess the organic removal. They reported no obvious change in COD in the wastewater from the LY [7], while the COD data for Bowman coal from Australia and Hambach coal from Germany showed an apparent dependence on the concentration of the acid added [7,8]. Domazetis and his co-workers [9] also found that acid treatment could reduce the COD in wastewater in the temperature range of 100–210 °C. Murakami and his co-workers [10] also found that the amount of dissociated carboxyl groups in solution decreased gradually with decreasing pH in the range of 2–8. They reported an increased level of inorganic cation (Na, K, Mg and Ca) in the product water and their concentrations are dependent on the concentration of HCl solutions used. The reduction in the ash content was found to be more apparent in higher temperature treatments using acid washed coal [9,11–13].

It is important that organic compounds in the wastewater are minimised for health reasons. Many health risks are associated with the organic compounds released to the environment. Maharaj found that the Balkan endemic nephropathy caused by phenols, PAHs, benzenes, and/or lignin degradation compounds was related to the leaching of toxic organic compounds from Pliocene lignite [14,15]. Researchers also found many other health risks, like endocrine disruption, nephrotoxicity, and cancer which might have potential relation to the organic compounds leached from coal [16–19]. Toxic phenols are one of the major groups of contaminants in wastewater during lignite processing [15]. Therefore, reducing phenol content and the other organics in wastewater is important as it will reduce the wastewater treatment cost. The inorganics in lignite also cause problems in the combustion, gasification and other chemical processing of the coal. It was reported that organically bound minerals contributed to the emission of inorganic PM_{10} (both PM_1 and PM_{1-10}) directly during lignite combustion [20].

Although the organic compounds in wastewater from the MTE process are lower than other non-evaporative process, it is still one of the limiting factors preventing the development of MTE. This study aims to evaluate whether sulphuric acid can assist in improving the quality of wastewater from the MTE dewatering process.

2. Experimental

2.1. Lignite samples and analysis

Lignite from two lignite deposits, one from Australia and one from China were used for experiments. Run-of-mine lignite samples from Loy Yang (LY), Victoria, Australia and from the ShengLi (SL) coalfield mine, Inner Mongolia, China were collected. The samples were milled and then sieved to minus 3 mm. Ultimate and proximate analyses were carried out using Vario MACRO cube from Elementar Co. Ltd. and 5E-MAG6700 from Changsha Kaiyuan Instrument Co. Ltd., respectively. The results are shown in Table 1. The mineral content of the raw lignite was analysed using X-Ray diffraction (XRD) with D8 Advance from the Bruker Company. The samples were scanned from 3° to 80° in the 2θ range. X-Ray Fluorescence Spectroscopy (XRF) was analysed by S8 Tiger from the Bruker Company with the lignite ash, and the detection limit is 1 ppm–100%. The XRD and XRF results are in good agreement with each other.

2.2. MTE experimental procedure

The MTE dewatering device and the experimental procedure have been provided in the literature [21–23]. The diameter of the cell used is 50 mm and the pore size of the sintered plate filter in the bottom is 40 μm.

2.2.1. Lignite pre-treatment before MTE tests

For the acid treated MTE (ATMTE) tests, 50 g lignite was mixed with 40 ml sulphuric acid of different concentrations (0.05 M, 0.1 M, 0.5 M and 1 M) in a beaker. The mixture was then stirred by a magnetic stirrer at a constant speed of 300 rpm for 30 min at room temperature. The water treated MTE (WTMTE) tests followed the same procedure, except that distilled water was used instead of sulphuric acid.

2.2.2. The MTE procedure

The water or acid was mixed with the coal prior to transferring into the MTE cell. Prior to compression, the piston was pressed slowly to repel water through both the pipeline in the piston and the wastewater outfall until the system was free of air inside. The cell was then heated to the desired temperature and then held for 30–40 min in total.

Table 1
Proximate analysis of LY and SL lignites and MTE products, pH of lignite slurries.

Sample	MTE temperature (°C)	Acid concentration (M)	Moisture (wt.%, wb)	Ash (wt.% db)	Volatile matter (wt.% db)	Fixed carbon (wt.% db)	pH of slurry before MTE tests
LY raw			46	8.02	50.07	41.91	
LY	200	0 (water)	28.38	7.66	46.41	45.93	3.47
LY	200	0.05	27.81	8.56	46.11	45.33	2.36
LY	200	0.1	28.5	7.98	47.3	44.72	1.57
LY	200	0.5	27.23	8.1	47.23	44.67	0.96
LY	200	1	26.85	7.91	47.65	44.44	
LY	240	0	24.16	8.13	46.16	45.71	
LY	240	0.05	25.60				
LY	240	0.1	25.06	7.11	47.15	45.74	
LY	240	0.5	24.79	7.83	46.74	45.43	
SL raw			30.58	22.27	32.41	45.32	
SL	200	0	28.6	18.29	34.09	47.62	5.66
SL	200	0.05	28.85				4.81
SL	200	0.1	27.58	15.94	36.08	47.98	
SL	200	0.5	28.94	17.53	35.47	47	1.53
SL	200	1	26.65	17.01	36.64	46.35	0.95
SL	240	0	27.37	20.7	33.01	46.29	
SL	240	0.05	27.66				
SL	240	0.1	27.64	20.84	32.97	46.19	
SL	240	0.5	27.26	19.6	35.82	44.58	

The sample name was tagged as sample-MTE-temperature-acid concentration, for example, the LY sample treated with 0.1 M acid at 200 °C was recorded as LY-MTE-200-0.1 M. All data in this table corresponds to a final pressure of 12 MPa.