Fuel 104 (2013) 36–40

Contents lists available at ScienceDirect

Fuel

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

Ecotoxicity of effluents from hydrothermal treatment process for low-rank coal

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ARTICLE INFO

Article history:
Available online 6 July 2010

Keywords:
Low-rank coals
Hydrothermal treatment
Total organic carbon
Mutagenicity
Acute toxicity

ABSTRACT

Four low-rank coals (two lignites and two sub-bituminous coals) were hydrothermally treated at 200–350 °C. The effluent obtained was examined from the aspect of ecotoxicity, using the Ames *Salmonella* mutagenicity assay and the acute toxicity test for freshwater organisms. The total organic carbon in the effluent was increased with an elevation of the temperature of hydrothermal treatment (HTT). When the HTT temperature was 350 °C, the effluent showed a weak mutagenicity for all of the coals. The acute toxicity of HTT effluent was examined by use of *Daphnia magna* (water flea) and *Oryzias latipes* (Japanese medaka). The effluent obtained from a hot water extraction (HWE) at 80 °C showed no toxicity. However, the HTT effluent gave toxicity, and the degree of toxicity was increased as the HTT temperature was elevated. The toxicity of 350 °C-HTT effluent was comparable to those for phenols when *D. magna* and *O. latipes* were used. The HTT and HWE effluents were analyzed by the size exclusion chromatography (SEC). The degree of toxicity was discussed in terms of the molecular weight of organic component present in the effluent.

1. Introduction

Low-rank coals, such as lignites and sub-bituminous coals are frequently upgraded by a hydrothermal treatment (HTT) in which coal is treated with water under a high temperature (300–350 °C) and a high pressure (80–180 kg/cm^2). The decomposition of hydrophilic functional groups in coal as well as the sealing of surface micropore by the tar eluted from coal occurs during the HTT process, which leads to the irreversible reduction in the hygroscopicity of coal [1,2]. It has been reported that the effluent from the HTT process usually shows high total organic carbon (TOC) [3–5], suggesting that various organic compounds eluted from coal are present in the effluent.

There have been several studies about the ecotoxicity of effluent from coal utilization processes. In our previous studies [6,7], the ecotoxicity of eluent obtained by a hot water extraction (HWE) of coal was assessed by the Ames *Salmonella* mutagenicity assay. It was found that the eluent showed almost no mutagenicity, whereas chlorination of the eluent resulted in high mutagenicity. A similar result was obtained when an aqueous solution containing humic substances was tested [8–10]. Jin et al. conducted the acute toxicity test using *Daphnia magna* for the effluent from a coal gasification process [11]. Schacht et al. reported the acute toxicity test for some products derived from coal by use of several freshwater organisms [12]. However, there have been no studies about the ecotoxicity of effluent from the HTT process for low-rank coals, although the effluent contains various organic compounds as mentioned above.

In this study, low-rank coals (two lignites and two sub-bituminous coals) were subjected to HTT under various conditions. For the effluent obtained, the mutagenicity was assessed by the Ames *Salmonella* assay, and the effect of reaction temperature as well as liquid per solid (L/S) ratio in HTT upon the mutagenicity was investigated. Further, the acute toxicity test was carried out for the HTT effluent by use of freshwater organisms; *D. magna* (water flea) and *Oryzias latipes* (Japanese medaka) which were frequently used in ecotoxicity test [11–15]. Also, the degree of toxicity was discussed in terms of the molecular weight of organic component present in the effluent.

2. Materials and methods

2.1. Coals

Two Indonesian sub-bituminous coals (Adaro, AD and Banko, BA), and two Australian lignites (Loy Yang, LY and Yallourn, YL) were used in this study. AD was provided from the National Institute of Advanced Industrial Science and Technology (AIST), Japan, while BA, LY, and YL were kindly supplied by Kobe Steel, Ltd. The analytical data of these coals was obtained by the each supplier (AIST and Kobe Steel, Ltd.) and listed in Table 1. Those are analyzed by using standard method (JIS M 8813). The particle size of the coals was less than 149 μm (100 mesh).

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doi:10.1016/j.fuel.2010.06.040

Table 1
Analytical data of coals.

Sample coals	Proximate (wt%, d.b.)				Ultimate (wt%, daf)			
	I.M.[a]	Ash	V.M.[b]	C	H	N	0	O/C
LY (AUS)	11.60	0.88	39.80	69.57	5.00	0.60	26.20	0.28
YL (AUS)	24.90	2.30	45.20	66.40	4.60	0.50	28.30	0.32
AD(IND)	10.84	1.60	43.57	72.70	5.36	1.04	20.85	0.22
BA(IND)	10.70	0.60	44.80	71.20	5.20	1.10	22.10	0.23

[a] I.M., inherent moisture.
[b] V.M., volatile matter.

2.2. Hydrothermal treatment (HTT)

Powdered coal was mixed with 200 mL deionized water and the mixture was placed in a 500 mL autoclave (Suzuki Rika Seisakusho Co., Ltd.). The L/S ratio was varied from 3 to 100 in this study. The atmosphere in the autoclave was purged by N_2. The autoclave was heated at a rate of 3–4 degree/min to a desired temperature (200–350 °C) and the temperature was kept for 1 h under agitation. After cooling, the effluent was separated from coal by filtration (ADVANTEC, No. 5C, the holding size is 1 μm). Also, the HWE process was carried out for the coals in a similar manner to that described in our previous papers [6,7], and the 80 °C-HWE effluent was obtained.

2.3. Analysis of organic matters in the effluent

Total organic carbon (TOC) in the effluent obtained was determined by an automatic TOC analyzer (Shimadzu TOC-V CSH) after filtration with a membrane filter (ADVANTEC, 0.45 μm). The molecular weight of effluent component was analyzed by size exclusion chromatography (SEC). The SEC system consisted of a HPLC pump (JASCO PU-2080), a packed column, a UV–vis detector (Shimadzu SPD-10A), and a RI detector (JASCO RI-2031) was used. The UV-absorbance was measured at 254 nm. The SEC column was 300 × 7.5 mm Shodex Asahipak GF-310 HQ column. Deionized water was used as a mobile phase at a flow rate of 0.4 mL/min. The SEC column was calibrated using pullulan (Shodex), kDa: 5.9, 11.8, 22.8, and 47.3, and polyethylene glycol (Wako), kDa: 0.2, 0.5, and 1.0. Pullilan is polysaccharide polymer consisting of maltotriose units and is usually used as a water soluble GPC standard.

2.4. Mutagenicity assay

The mutagenicity of HTT effluent was evaluated by the Ames *Salmonella* mutagenicity assay by using the standard method [13]. The HTT effluent obtained was diluted with deionized water until the TOC reached 3–4 mg-C/L. The resulting effluent was concentrated 1000 times into a dimethyl sulfoxide (DMSO) solution by a solid phase extraction (SPE) method using an adsorbent cartridge (Nihon Waters Sep-Pak Plus CSP-800) according to a literature method [14]. Two *Salmonella typhimurium* strains TA98 and TA100 which were obtained from the National Institute of Public Health, Japan, were used. Dose–response tests were carried out using three dose-steps and one negative control. For each dose, the experiment was performed twice (four times for the negative control) according to the Ames assay protocol in Japan [16]. After incubation at 37 °C for 48 h, the number of colonies on the plate was counted. The degree of mutagenicity was expressed as the mutation ratio (MR), which was calculated as follows.

MR = (Mean number of revertant colonies in maximum dose sample plate)/(Mean number of revertant colonies in negative control plate)

2.5. Toxicity test using freshwater organisms

In order to evaluate the toxicity of HTT effluent against freshwater organisms, the acute toxicity test was carried out for *D. magna* and *O. latipes* according to the OECD guideline for the testing of chemical 202 and 203, respectively [18,19]. In the *D. magna* acute immobilization test, the test effluents were adequately diluted by the medium described in ISO 6341, and five *D. magna* juveniles (<24 h) were exposed to 20 mL of diluted effluent for 48 h in the test tube. The test tube was incubated at 20 ± 1 °C under a 16 h light (1000 lx)/8 h dark photoperiod. After 48 h exposure, the number of immobilized organisms was counted, and the concentration of organic component in the effluent, which gave 50% immobilization of *D. magna* [EC_{50} (mg-C/L)], was calculated by Probit analysis which is a statistical analyzing method for a dose and response curve [13]. Each test was replicated four times and also calculated a confidence interval at 95%.

In the fish acute toxicity test, the test effluent was appropriately diluted by the dechlorinated tap water, and ten test fish (*O. latipes*) were exposed to 2 L of diluted effluent for 96 h in the glass vessel. During the test period, the water temperature in the vessel was kept 24 ± 1 °C under a 16 h light (1000 lx)/8 h dark photoperiod. The testing medium in each vessel was renewed after 48 h exposure, and dead fish were counted and removed from the vessel every 24 h. After 96 h exposure, the number of dead fish was totalized, and the concentration of organic component in the effluent, which provided 50% mortality of *O. latipes* [LC_{50} (mg-C/L)], was calculated by Probit analysis. A low value in EC_{50} or LC_{50} indicates that the organic component in the effluent gives a high toxicity.

3. Results and discussion

3.1. TOC in the HTT effluents

When the HTT procedure at 200–350 °C was performed for lignite LY in various L/S ratios, The TOC in the effluent was measured. As shown in Fig. 1, the degree of TOC was greatly increased as the L/S was reduced from 100 to 3. When the 350 °C-HTT procedures were carried out for L/S = 20 and 3, the TOC in the HTT effluents were ca. 4500 and 18,000 mg-C/L, respectively. According to our previous study, the TOC for the HWE effluents was much lower (ca. 13–47 mg-C/L) when the same four coals were subjected to the 80 °C-HWE (L/S = 100) [7]. For LY, YL, BA, and AD coals, the effect of HTT temperature upon the degree of TOC in the effluent was examined when the HTT was performed in L/S = 100. As shown in

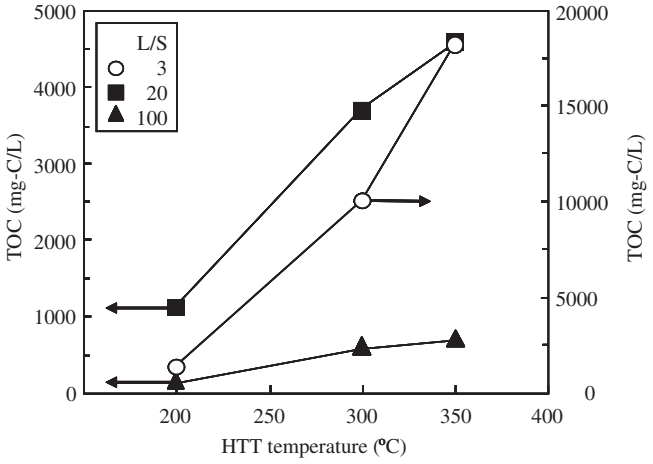

Fig. 1. Effect of HTT temperature upon TOC in the effluent (LY).