Ecotoxicology and Environmental Safety 112 (2015) 105–113

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Chemical and toxicological evaluation of underground coal gasification (UCG) effluents. The coal rank effect

Krzysztof Kapusta*, Krzysztof Stańczyk

Główny Instytut Górnictwa (Central Mining Institute), Plac Gwarków 1, 40-166 Katowice, Poland

ARTICLE INFO

Article history:
Received 4 August 2014
Received in revised form
28 October 2014
Accepted 30 October 2014
Available online 12 November 2014

Keywords:
Underground coal gasification
Condenser water
Groundwater pollution
Acute toxicity
Vibrio fischeri

ABSTRACT

The effect of coal rank on the composition and toxicity of water effluents resulting from two underground coal gasification experiments with distinct coal samples (lignite and hard coal) was investigated. A broad range of organic and inorganic parameters was determined in the sampled condensates. The physicochemical tests were supplemented by toxicity bioassays based on the luminescent bacteria *Vibrio fischeri* as the test organism. The principal component analysis and Pearson correlation analysis were adopted to assist in the interpretation of the raw experimental data, and the multiple regression statistical method was subsequently employed to enable predictions of the toxicity based on the values of the selected parameters. Significant differences in the qualitative and quantitative description of the contamination profiles were identified for both types of coal under study. Independent of the coal rank, the most characteristic organic components of the studied condensates were phenols, naphthalene and benzene. In the inorganic array, ammonia, sulphates and selected heavy metals and metalloids were identified as the dominant constituents. Except for benzene with its alkyl homologues (BTEX), selected polycyclic aromatic hydrocarbons (PAHs), zinc and selenium, the values of the remaining parameters were considerably greater for the hard coal condensates. The studies revealed that all of the tested UCG condensates were extremely toxic to *V. fischeri*; however, the average toxicity level for the hard coal condensates was approximately 56% higher than that obtained for the lignite. The statistical analysis provided results supporting that the toxicity of the condensates was most positively correlated with the concentrations of free ammonia, phenols and certain heavy metals.

1. Introduction

The increasing energy demand and energy prices observed today in many parts of the world in combination with environmental, political and socioeconomic concerns related to the energy sector favour research on alternative technologies for energy production and energy utilisation. One of the technologies is underground coal gasification (UCG). Coal is the most abundant fossil fuel in the world and is likely to outlast the gas and oil resources combined (IEA, 2013). Its current share in global power generation is dominant, and according to forecasts, it is expected to steadily increase in the future, mainly due to increasing energy demands in developing countries and the gradual depletion of the proven oil reserves (IEA, 2013). However, according to geological surveys, large amounts of the global coal resources, owing to technological or economic constrains, are currently beyond the range of traditional mining. These unmineable coal deposits may, in some cases, constitute suitable candidates for UCG technology.

The concept of UCG is not new and dates back more than one hundred years (Gregg and Edgar, 1978; Burton et al., 2006). During this process, coal is converted into a combustible gas directly in the seam (in situ). In its simple configuration, UCG involves drilling two vertical wells into the desired coal deposit, at some distance apart, enhancing the permeability of the coal between the two wells, (e.g., by directional drilling), igniting the coal seam in one well, and then injecting the gasification media (air, oxygen or steam) through the injection well. The product UCG gas, of which the primary components are hydrogen, carbon monoxide, carbon dioxide and methane, is recovered through the production well on the surface. The composition, as well as the heating value, of the produced gas depends mostly on the type of coal, gasification reagent applied and the gasification conditions (Khadse et al., 2007; Shafirovich and Varma, 2009; Kapusta and Stańczyk, 2009). The gas composition also determines its usefulness for possible downstream applications (Wang et al., 2011; Stańczyk et al., 2011). Liquid fuels by the Fischer–Tropsch process, production of substitute natural gas (SNG) and ammonia or urea synthesis are typical UCG syngas applications. Several research studies have proven that, under specific conditions, a product with a considerable

* Corresponding author. Fax: +48 32 3246522.

http://dx.doi.org/10.1016/j.ecoenv.2014.10.038
0147-6513/

contribution of hydrogen can be obtained in the UCG process (Yang et al. 2008; Shu-gin et al., 2009; Yang and Ding, 1990; Stańczyk et al., 2010, 2012). The low-calorific UCG gas, typical for air-blown UCG operations, is usually intended for energy applications (heat or electricity).

Although the UCG process has several advantages over surface coal gasification, such as lower capital investment costs, limited human labour, no coal transportation and no need for surface coal processing, the possible environmental risks associated with field UCG operations must be considered. One of the major environmental concerns addressed before UCG commercialisation is water quality. As a result of coal pyrolysis and the series of homo- and heterogeneous reactions occurring between the gasification products, a number of hazardous environmental contaminants can be produced during the UCG process. The major organic groundwater pollutants typical of UCG are phenols, benzene and its derivatives (BTEX), polycyclic aromatic compounds (PAHs) and certain heterocyclic compounds containing nitrogen, sulphur and oxygen heteroatoms. The inorganic matrix includes ionic compounds, such as ammonia, cyanides, sulphates, chlorides and wide range of metal and metalloid elements (Stuermer et al., 1982; Edgar et al., 1981; DeGraeve et al., 1980; Yang, 2009; Kapusta and Stańczyk, 2011; Liu et al., 2006a, 2006b).

Operating below the hydrostatic pressure is the main preventive measure to effectively control the migration of contaminants during UCG operation (Kapusta et al., 2013; Liu et al., 2007). However, during the production phase, in many parts of the surface gas-processing facility, considerable quantities of post-gasification condenser water are produced. These water effluents are formed as a result of gas–moisture condensation onto the cooler parts of the installation, and their production is strongly influenced by the overall balance of water available for the gasification process. Water in the UCG process derives from three distinct sources:

- water present in the coal seam as moisture (static resource);
- groundwater infiltrating into the UCG cavity from the surrounding strata (dynamic resource); and
- water (steam) supplied as a gasifying agent.

The production of such chemically complex wastewater is typical for the technologies of the thermochemical processing of coal (Jin et al., 1999; Parkhurst et al. 1981; Dong and Zhang, 2010). These effluents, if not treated appropriately on the surface, can cause serious environmental and ecological impacts.

Many of the individual chemical characteristics for the UCG condensates are reported to be refractory and toxic (DeGraeve et al., 1980; Hill and Kocornik, 1986). Because chemical analysis is usually limited to a selected list of substances, it may be complemented by the application of bioassays that provide an integrated measure of toxicity. Numerous standard procedures for toxicity testing have been developed, suggesting plants, microorganisms, invertebrates and vertebrate organisms (Loibner et al., 2004). Acute and embryo-larval toxicity studies with *Daphnia pulicaria*, rainbow trout and fathead minnows have indicated that UCG condenser waters are extremely toxic, even when highly diluted (DeGraeve et al., 1980). Although standard acute-toxicity tests with fish and aquatic macro invertebrates have long played a major role in aquatic hazard and risk assessments (Toussaint et al., 1995), a number of alternative (rapid) tests have been proposed for screening due to their experimental simplicity, sensitivity, reproducibility and short exposure time. Rapid toxicity tests are also less expensive than standard acute-toxicity tests (Toussaint et al., 1995). The luminescent bacterial toxicity test system using *V. fischeri* is a reliable and widely applied aquatic bioassay that shows good sensitivity to a broad range of organic pollutants (Loibner et al., 2004). In this method, the reduction in light emission by luminescent bacteria is attributable to the toxic effect of the tested sample (Gellert, 2000).

A study of the physicochemical and ecotoxicological characteristics of condenser waters originating from two UCG experiments with coals of different ranks, was performed in the course of field and surface gasification trials performed at the Experimental Mine "Barbara" in Mikołów, Poland. The ecotoxicity was investigated with the luminescent bacterial assay based on *V. fischeri* test organisms. In this report, the main findings of this research are presented.

2. Materials and methods

2.1. The origin of the water-condensate samples

The experiments were conducted both in natural (in situ) and surface (ex situ) conditions and among various aspects relevant to UCG: the influence of the coal rank on the composition and the efficiency of the gas production has been thoroughly investigated. The results of the experiments were described in a series of published research papers (Stańczyk et al., 2010, 2011, 2012; Wiatowski et al., 2012). Many ancillary factors related to UCG technology were also studied, including one connected to the environmental aspects of the in situ coal gasification (Kapusta and Stańczyk, 2011; Kapusta et al., 2013).

The raw UCG product gas contains water vapour, originating mainly from the evaporation of coal moisture, the coal-pyrolysis process (pyrogenic water) or undesired hydrogen combustion. This gas moisture tends to condense onto the cooler parts of the installations, such as the internal surfaces of gas pipelines or in particular devices of the gas-treatment module. To prevent environmental pollution during the UCG operations, the resulting post-gasification water condensates are systematically collected and transported for off-site treatment. The UCG effluent samples used in the study originated from two gasification trials. One was a 16-day hard coal in situ gasification trial performed in the Barbara Experimental Mine in Mikołów, Poland. The second set of effluents was from a surface (ex situ) experimental simulation with a large-block lignite sample, performed in an ex situ gasification unit. For each gasification experiment, the sampled water condensates represent four distinct periods of the overall process run time. Detailed descriptions of the installations were published in the reference papers (Wiatowski et al., 2012) and (Kapusta and Stańczyk, 2011) for hard coal and lignite trials, respectively.

2.2. Sample preparation and chemical analysis

The collected raw water condensates (four samples for each gasification trial) were pretreated by filtration in a separatory funnel with a 0.45-μm membrane filter for the removal of emulsified tars and oils as well as solid particles. The obtained filtrates were stored at 4 °C until analysed. Apart from the two standard water parameters as the conductivity and pH, the following inorganic parameters were determined in the condensates: total ammonia nitrogen, nitrites, chlorides, cyanides, sulphates, and 17 metal and metalloid trace elements (Sb, As, B, Cr, Zn, Al, Cd, Co, Mn, Cu, Mo, Ni, Pb, Hg, Se, Ti, and Fe). The organic analysis of the effluents included phenolics, benzene with its three alkyl homologues toluene, ethylbenzene and xylene (BTEX), and 15 polycyclic aromatic hydrocarbons (PAHs). The conductivity, pH, biological oxygen demand (BOD_5), chemical oxygen demand (COD_{Cr}) and total organic carbon (TOC) were additionally determined in the representative post-gasification effluents as typical nonspecific industrial wastewater parameters.