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The effect of acid washing on the pyrolysis products derived from a vitrinite-rich bituminous coal

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ABSTRACT

Extensive characterization of the pyrolysis products, derived from raw and acid washed samples of a vitrinite-rich South African bituminous coal is reported. Pyrolysis experiments were carried out with use of a modified Fischer Assay setup at 520, 750 and 900 °C. Gaseous products were analyzed by gas chromatography (GC); tar yields by simulated distillation (SimDis), gas chromatography mass spectrometry and –flame ionization detection (GC–MS and –FID) and size exclusion chromatography (SEC-UC), and the char yields by proximate, ultimate and Brunauer–Emmett–Teller (BET) CO_2 adsorption analyses. The water and tar yields of the acid washed coal fraction (AW TWD) was found to be lower, whilst the gas yields were found to be significantly higher than that of the raw coal fraction (TWD). The char yields were not significantly affected by acid washing. Some of the differences in pyrolysis product yields can be related to increased porosity of the acid washed coal fraction. GC analysis of the derived pyrolysis gases indicated that the AW TWD derived gas contained higher yields of H_2, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6 and C_4s when compared to the gas derived from the TWD fraction, whilst the CO yield from the TWD fraction was greater at all final pyrolysis temperatures. Analyses of the tar fraction by means of SimDis, GC–MS and –FID and SEC-UV indicated that the acid washed coal derived tars where more aromatic in nature, containing more higher boiling point components, which increased with increasing final pyrolysis temperature. On the other hand, the tars derived from the TWD coal contained lighter boiling point components with increasing final pyrolysis temperature. The changes in the pyrolysis behavior of the bituminous coal are due to the removal of the mineral matter and also the influence of the acid washing process. This study confirmed that acid washing of coal changes the pyrolysis products composition of a bituminous coal.

1. Introduction

Coal has a complex and heterogeneous chemical structure, containing various organic and inorganic species [1]. The inorganic fraction consists of various minerals, of which more than 125 have been identified [2,3]. Most of these minerals (approximately 100) are described as trace minerals (minerals present in a very low concentration with grain sizes smaller than 10 μm), with only a few considered to be of significance [3]. The most common major minerals in bituminous coal are: quartz, kaolinite, gypsum, pyrite, calcite, illite and feldspars [4]. The major mineral matter that is present in coal plays a significant role during thermal conversion processes (e.g. combustion, gasification, pyrolysis, etc.). Coal properties such as heating value, coal rank, reaction rate and ash content may be affected by the mineral matter content. The mineral matter may also affect final product yields due to the effect on the secondary pyrolysis reactions, as well as affect the composition of these products, as has been observed during tar production [5].

Pyrolysis is the initial step in most thermal coal conversion processes and it is largely dependent on the coal properties [6,7]. Pyrolysis is the thermal process by which coal undergoes thermal decomposition and recombination reactions to form char, volatile liquids (containing tars, oils and aqueous compounds) and gaseous products in the absence of oxygen [1]. The characterization of pyrolysis products of various coal samples has been reported extensively in literature [1,5–7].

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Acid leaching or demineralization of coals is not used on a commercial scale, but it is an important technique to study the effect of mineral matter on coal behavior. In order to determine the effect of minerals on coal thermal treatment products, the coal behavior without these minerals present, should be investigated. Leaching agents used to remove mineral matter include NaOH, HCl, HF, H_2SiF_6, and HNO_3 [8]. It has been found that hydrochloric acid (HCl) effectively reduces most mineral matter, whilst hydrofluoric acid (HF) is effective in dissolving the aluminum and silicon containing compounds [9]. Pyritic compounds, however, are not effectively removed by these acids. Studies found that the use of solutions containing ferric ions or HNO_3 extraction methods can be utilized to remove associated pyrite from coal [10,11].

Manoj et al. [12] investigated changes in the structure of a Godavari coal sample after leaching with EDTA and HF. Rubiera et al. [13] reported an increase in volatile matter, oxygen and nitrogen for a high-volatile bituminous coal char from the Harworth colliery in UK after leaching with a 1:1 mixture of HF/H_2SiF_6. An investigation into the influence of acid leaching procedures on a South African inertinite-rich bituminous coal, indicated that small amounts of oxygen and nitrogen containing species are incorporated in the coal structure during a HF/HNO_3 leaching process, but not during a HCl/HF/HCl procedure [14]. The remaining coal structure contains increased amounts of ═N—OH groups after HF/HNO_3 leaching, whereas the —COOH content was slightly increased after HCl/HF/HCl treatment [14]. Reported studies focused on the characterization of the remaining coal sample and not on the influence of acid leaching on thermal treatment products. Limited studies have been undertaken to investigate the influence of acid leaching treatment of coal on the pyrolysis products.

Differences in coal type, acid leaching method and pyrolysis procedure influence the results obtained. Most of the studies focused on the use of flash pyrolysis or thermogravimetry to investigate pyrolysis products. Limited reports on the quantitative characterization of the pyrolysis products derived from a South African bituminous coal and the influence of acid washing on the pyrolysis products could be found in literature [14,15] In this paper a South African vitrinite-rich bituminous coal was subjected to an acid leaching process and a detailed characterization of the pyrolysis products, including the gas and tar yields, was conducted. The validity of using an acid washing procedure to produce a relatively mineral-free coal to investigate the influence of minerals on thermal processing of coal is discussed.

2. Material and methods

2.1. Coal samples: preparation and characterization

A washed and air dried sample from the South African Highveld coalfield was obtained. The coal was a beneficiated product, having a low ash content (<15 wt% d.b.). The coal sample was milled and crushed to a particle size <75 μm, divided into two representative fractions and sealed under a nitrogen atmosphere. The first fraction served as the raw coal sample, referred to as TWD, whilst the other fraction underwent acid washing and is referred to as AW TWD.

A hydrochloric (HCl) and hydrofluoric (HF) acid leaching process, as described previously, was followed [8]. The analytical grade acids were obtained from MERCK. Five hundred grams (500 g) of the coal sample was added to 4 L 5 mol dm^{-3} (32 wt%) concentrated HCl in a glass beaker and stirred for 24 h using a polyethylene coated magnetic stirrer. The liquor was removed by filtration under reduced pressure. The insoluble solid fraction from the filtration stage was added to 2.5 dm^3 of 29 mol dm^{-3} (48 wt%) HF in a polyethylene beaker. The mixture was stirred for 24 h, after which the liquor was again removed by filtration, and the HF insoluble fraction further leached in HCl using a step similar to the initial step. The liquor was separated by filtration and the insoluble fraction was washed copiously using ultrapure water until the pH of the filtrate was close to 7.0. The acid insoluble solid was dried in a vacuum oven at 80 °C until constant weight.

Petrographic analyses, including vitrinite reflectance and maceral composition, were carried out according to ISO 7404:1999 [16].

X-ray fluorescence (XRF) ash analysis was carried out according to the ASTM D4326 method [17]. For the mineral XRD analyses, the samples were dried overnight in a vacuum oven at 80 °C to remove surface moisture. The samples were prepared prior to analyses by a back loading preparation method. A McCrone micronising mill was used along with addition of 20% Si to determine the amorphous content. XRD analysis was performed on a Phillips X'Pert PW1830 powder diffractometer. X'Pert Highscone software was used for phase identification. The Rietveld method (Siroquant software) gave an estimation of phase amounts. For QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) analysis a representative sample was mixed with graphite and mounted in Araldite epoxy-resin. After the sample has cured it was polished to a diamond finish of 1 μm and prepared by use of Carnauba wax. These samples were analyzed using a scanning electron microscope (SEM) to determine the mineralogical composition [18].

2.2. Pyrolysis experiments

Pyrolysis experiments were conducted using a modified Fischer Assay setup as reported previously [19]. The setup was modified to accommodate temperatures up to 900 °C using stainless steel retorts, capable of measuring tar, char and water content and also to capture gas fractions (Fig. 1). The Fischer Assay setup was operated at a constant heating rate of 6.2–6.3 °C/min up to 520 °C, 750 °C or 900 °C, with a holding time of 10 min, at atmospheric pressure conditions. Fischer Assay preparation under ISO 647 is specified at 520 °C [20]. The temperatures of 750 °C and 900 °C were selected as temperatures to study the effect of mineral matter on pyrolysis products and composition. A temperature of 900 °C is generally considered to be at the end of the pyrolysis stage of coal, and therefore a good indication of the last pyrolysis product yields and composition. The temperature of 750 °C was chosen to represent the mid-stage of pyrolysis. The setup was purged with nitrogen before the pyrolysis experiments commenced to limit oxidizing reactions.

Condensable volatiles were captured in round-bottom flasks immersed in an ice/water mixture. Two gas washing stages (solvent scrubbers) using toluene were added in series to the outlet of the round-bottom flasks. The final gas fractions from the solvent scrubbers were captured in Tedlar® gas sampling bags for analysis. Water separation was done and yields determined as reported previously [19].

2.3. Gas analysis

Gas yields were determined by difference after quantification of the char, tar and water yields after conventional Fisher Assay analyses. The gas yields were determined by using volume calculations along with compositional data for the derived gases. The gas products were sampled in 10 L Tedlar gas sampling bags for the duration of the experiment. After completion of the experiment, the volume occupied by gas in the bags was measured. The pressure for the system was noted, and using of the ideal gas law, the GC results and the gas volumes, the weights of the produced gases were calculated.

The captured gas samples were analyzed in a SRI 8610C Multiple Gas Chromatograph (GC). The GC was operated with a hold time of 7 min at 60 °C, ramping up to 280 °C with a heating rate of 15 °C/min and holding time of 20 min. The thermal conductivity