



# The effect of added minerals on the pyrolysis products derived from a vitrinite-rich demineralised South African coal



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## ABSTRACT

A better understanding of the behaviour of the inorganic matter present in coal will assist in more cost-effective operations and more consistency in product yield and composition during thermal processing. In this study, the effect of specific major coal minerals on pyrolysis product yield and composition was determined. 5 wt% calcite, dolomite, kaolinite, pyrite, or quartz was added to an acid washed South African medium rank C bituminous coal fraction and pyrolysed using a modified Fischer Assay procedure, using stainless steel retorts, and temperatures of 520 °C, 750 °C and 900 °C. It was found that mineral activity decreased in the order calcite/dolomite >> pyrite > kaolinite >>> quartz. Calcite and dolomite addition led to a highly significant decrease in tar yield, and tar producers should note this finding as the presence of these minerals in the coal feedstock could have a considerable effect on the tar yield and composition at their operations. Detailed characterization of the measured pyrolysis products provided valuable insight and data for the development of a pyrolysis yield and compositional model based on mineral addition.

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## 1. Introduction

The effect of mineral matter on coal conversion has been studied since the 1920s [1], but literature is limited with regard to aspects of pyrolysis yield and composition [2]. Since the 1980's mineral matter present in coal and the interactions occurring during pyrolysis has received a lot of attention [2–6]. Pyrolysis is the initial step in most coal conversion processes and it is largely dependent on the properties of the coal [7–10]. The mineral matter can be responsible for up to 45% of the total volatile yield in coal, depending on the coal type, particle size, thermal process and amount and type of mineral matter present [11]. It has a profound effect on coal reactivity, and during catalysis of gasification reactions [12,13]. Mineral matter is also responsible for various technological problems such as fouling, slagging and inconsistency with regard to product yield and composition [13].

From a catalytic gasification perspective, the inorganic components provide the advantage that they are already present in the coal matrix, are well dispersed, and coal-mineral interactions are

thus feasible during thermal processing. [3,14]. When considering the fact that pyrolysis is a step which is largely dependent on coal properties, a detailed understanding of the effect of mineral matter on the pyrolysis products is expected to provide valuable insight [11]. The most prominent minerals found in South African coals include: kaolinite, quartz, pyrite, calcite and dolomite, and infilling of calcite and dolomite within cleats have been reported for many of the coal seams, particularly the Highveld coalfield [15–17]. In this paper, the effects of the addition of these minerals on the pyrolysis products derived at 520, 750 and 900 °C to acid washed, medium rank C bituminous Highveld coal will be reported. The assumption is made that the acid leaching process does not significantly influence the coal structure, except through removal of the minerals [18]. Detailed characterization of the measured pyrolysis products is expected to provide valuable insight and data for the development of a pyrolysis yield and compositional model based on mineral addition; this attempt will be discussed in a future manuscript.

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## 2. Experimental procedure

### 2.1. Coal and mineral samples

A bituminous, vitrinite-rich coal sample from the Highveld coalfield was used (TWD). The acid washing procedure and characterization of the coal sample was discussed previously [19]. The coal sample was found to be a Medium Rank C bituminous coal, consisting of 55 vol.% vitrinite, 38 vol.% inertinite and 7 vol.% lipinitite, reported on a mineral matter free basis [19]. A hydrochloric (HCl) and hydrofluoric (HF) acid leaching process, as described previously, was followed [18]. The ash content was reduced from 14.9 wt% d.b. to 2.0 wt% d.b. after acid washing. The most prominent remaining mineral phase consisted of pyrite, as it was not successfully removed by the acid washing procedure used [18,19].

Table 1 provides the details of the minerals that were used in this investigation. The acid washed coal will be referred to as (AW TWD); the addition of 5 wt% calcite as AW-Cal, the addition of 5 wt% dolomite as AW-Dol, the addition of 5 wt% kaolinite as AW-Kao, the addition of 5 wt% pyrite as AW-Pyr, and the addition of 5 wt% quartz as AW-Qz.

### 2.2. Pyrolysis experiments

Pyrolysis experiments were conducted using the NWU Fischer Assay setup as reported earlier [20]. Pyrolysis experiments were carried out under N<sub>2</sub> atmosphere at 520, 750 and 900 °C using stainless steel retorts. Condensable volatiles were captured in round-bottom flasks immersed in ice and water, after which two gas washing stages with toluene followed and the gas fraction was captured with the aid of Tedlar® gas sampling bags. Water separation was effected and yields determined. The gas, tar and char fractions were captured and further analyzed.

Mineral addition was done by physical mixing on a 5 wt% basis to a 50.0 g coal sample, to ensure that the same amount of carbonaceous material was present in the retort and that differences observed were due to the addition of mineral matter. All mineral samples were size reduced to <100 μm.

### 2.3. Gas analysis

Gas chromatography (GC) analysis was carried out with the aid of an SRI 8610C multiple gas chromatograph, as used previously [20]. Gaseous products are separated by the aid of 3 packed columns, i.e. 6' HayeSep D, 6' molecular sieve and 3' 5 Å molecular sieve (all with an outer diameter of 1/8'). Gaseous products are quantified by a flame ionization detector (FID) and 2 thermal conductivity detectors (TCD1 and TCD2). Calibration of the equipment was done using a refinery gas standard and by evaluating the typical elution time frames for the expected gas product constituents, which include: O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, ethylene, ethane, C<sub>3</sub>–C<sub>6</sub>. GC results were further converted to a g gas species/g coal (d.m.m.f.) basis with aid of Equation (1).

$$g(i, j) \text{ g (coal, d.m.m.f.)} = \left( \frac{[(\text{wt.}\%)]_i}{100} \right) (G_j) / C_g(\text{d.m.m.f.}) \quad (1)$$

where *i* is the gas species, *G<sub>j</sub>* refers to the amount (g) gas derived from the coal at temperature *j* and *C<sub>g</sub>* refers to the amount of coal (g) on a dry, mineral-matter-free basis.

### 2.4. Tar analysis

#### 2.4.1. Simulated distillation

Simulated distillation analysis was conducted according to the ASTM D2887 standard as reported previously [20].

#### 2.4.2. Gas chromatography mass spectrometry

All tar samples were analyzed using a GC-FID (quantification) and a GC-MS (peak identification) fitted with PONA column (50 m × 0.2 mm × 0.33 μm) as reported previously [20].

#### 2.4.3. Size-exclusion chromatography (SEC-UV)

The SEC-UV analysis of the derived tars were carried out with an Agilent 1100 high-performance liquid chromatograph (HPLC) set at 80 °C using a 300 mm long, 7.5 mm internal diameter PLgel mixed-E (Varian) GPC column for separation and HPLC grade 1-methyl-2-pyrrolidone (NMP) from Merck Chemicals at a flow rate of 0.5 ml/min as eluent [21]. Integration of the SEC-UV data was done using the HP 1100 Data Analysis software and peak identification was done as highlighted previously [20,21].

### 2.5. Char analysis

Proximate analysis was carried out using the relevant standard methods (Inherent moisture – ISO 11722: 1999 [22]; Ash content – ISO 1171: 2010 [23]; Volatile matter content – ISO 562: 2010 [24] and Fixed carbon content – determined by difference). Ultimate analysis was carried out according to ISO 29541: 2010 [25]. The total sulfur content was determined by IR spectroscopy according to ISO 19759: 2006 [26]. All analyses were conducted by Bureaus Veritas, Pretoria, South Africa.

## 3. Results and discussion

### 3.1. Pyrolysis product yields

Table 2 provides the pyrolysis product yield results for the different mineral additions. The results have been corrected for mineral matter content and moisture loss, as well as contribution to the gas phase due to the decomposition of minerals as determined by TGA experiments [19]. The results are based on the 95% confidence interval values based on the average of 2 runs that were within the repeatability limits as specified by ISO 647 [27]. Material balance closure ranged between 93 and 95% without including the mass loss due to loss of moisture.

#### 3.1.1. Gas yield

It can be observed that the addition of calcite (AW-Cal) led to slightly lower gas yields, whilst AW-Kao and AW-Qz produced slightly more gas at 520 °C. In the case of the 750 °C experiments, the AW-Cal sample produced more gas, whilst AW-Pyr produced less gas, and all other gas yields were within repeatability limits [27]. From the 900 °C experiments, AW-Cal, AW-Dol and AW-Kao produced more gas than the AW TWD sample, whilst the addition of pyrite (AW-Pyr) and quartz (AW-Qz) had no significant effect.

The increase in gas yield observed with the addition of calcite (AW-Cal) and dolomite (AW-Dol) is consistent with previous findings [28–30]. In most cases the increased gas yield was attributed to tar cracking reactions [31]. The addition of kaolinite was associated with the cracking of tar to form increased yields of H<sub>2</sub> [4–6], and it was reported in previous studies that the overall gas yield could be increased by kaolinite addition [32]. This can explain the higher gas yields at 520 °C and 900 °C, although the bulk of H<sub>2</sub> is only formed at temperatures exceeding 690 °C [33,34]. The higher H<sub>2</sub> yield obtained for the 520 °C experiments also coincides with the temperature range wherein kaolinite transforms to meta-kaolinite, i.e. 450 °C to 600 °C [35–37].

The lower gas yield of the AW-Pyr sample for the 750 °C experiments is interesting to note if it is taken into account that the decomposition of the added mineral would have been completed at this temperature, yielding H<sub>2</sub>S and SO<sub>2</sub> gas [38,39]. The increase in gas yield observed at 520 °C from the addition of quartz (AW-Qz)

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