

The iron mineral changes occurring in lignite coal during gasification

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Abstract Representative lignite and gasified material samples were retrieved from a cooled down gasifier. The samples were taken at various heights in the gasifier that operated on lignite, under stable conditions. The proximate analyses, ash composition and temperature in the gasifier were determined according to standard procedures. The main minerals found in the present investigation were bassanite, illite, quartz, kaolinite, calcite and the only iron bearing mineral was found to be pyrite. The trend in the estimated particle surface temperature profile shows an increase in the drying, pyrolysis, gasification and combustion zones from about 300 °C to just over 900 °C. About 1/3 down the gasifier, an average particle temperature of about 400 °C and particle surface temperature of about 600 °C was measured where pyrite conversion started. About 2/3 down the gasifier, where an average temperature of about 700 °C and particle surface temperature of about 900 °C was measured, all the pyrite was converted and in the bottom part of the gasifier, oxidation of the iron started to play a role and hematite and an iron containing glass formed at an average temperature of > 800 °C and surface temperature of 900 °C.

Keywords Lignite · Gasification · Pyrite · Mineral changes

1 Introduction

The formation of coal occurs in three stages— aerobic decay, anaerobic decay and metamorphism/bituminisation, subsequent to the accumulation of plant debris in swampy conditions and the abundance and composition of mineral matter in the coal is determined by the conditions of coalification [1]. According to literature [2, 3], iron in the minerals in coal is mainly associated with minerals such as pyrite, jarosite,

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Table 1 The proximate analyses of the original lignite used for gasification [9]

	Calorific value MJ/kg	Moisture %	Ash %	Volatile matter %	fixed carbon %	Total sulphur
Lignite	28.0	32.5	12.5	42.2	45.2	1.1

troilite, pyrrhotite, ankerite, illite and siderite. Lignite, which accounts for almost half of the proven coal reserves in the world, can be seen as an important primary energy source and is generally characterised by a high moisture content, low heating values and low carbon content with typical minerals such as bassanite, illite, quartz, kaolinite, calcite and pyrite being present [4].

Coal gasification can be defined as the reaction of solid fuels, in this case lignite, with air, oxygen, steam, CO₂, or a mixture of these gases at a temperature of over 700 °C to produce synthetic gas that is suitable for use either as a source of energy or raw material for synthetic liquid fuels, chemicals or other gaseous fuels [5]. During the coal gasification process the mineral matter undergoes various transformations and non-mineral inorganics, which are common in low rank coals such as lignite, can also contribute significantly to ash formation during gasification.

In previous studies [6, 7] the changes occurring when pyrite, present in South African bituminous type coals, was gasified, showed that the pyrite decomposed to form hematite and an iron-containing glass in the ash. The temperatures in the gasifier, operating on the bituminous coal, varied between 200 °C at the top of the gasifier to about 1 200 °C in the hottest part, just before cooling to about 300 °C in the ash bed. Pyrite, being the main iron bearing mineral present, typically started to decompose at a temperature of 500 °C and reached a maximum decomposition at 650 °C [6].

In the present investigation the changes in pyrite, occurring in lignite, during gasification are investigated and the decomposition temperatures compared with theoretical values.

2 Experimental

Representative samples from various heights in the gasifier were taken after the whole gasifier had cooled sufficiently. Detail of the sampling methodology employed has been reported by Bunt [8]. Each sample was homogenized, riffled and split into equal quarters and subsequently analysed. The ash compositions, in terms of its oxides were determined according to the ASTM D3682 standard and the proximate analyses was conducted according to the SANS 5924, ISO 562 and 1171 standards. The temperature inside the gasifier was determined according to the standard ISO 7404-5 vitrinite reflectance profile technique.

The Mössbauer analyses were conducted on the powdered samples with the aid of a Halder Mössbauer spectrometer capable of operating in conventional constant acceleration mode using a proportional counter filled with Xe-gas to 2 atm. The samples were placed between Perspex plates and then irradiated with γ -rays from a 50 mCi ⁵⁷Co(Rh) radioactive source to obtain a room temperature Mössbauer spectrum. The Mössbauer spectrometer was calibrated using α -Fe as the reference.

Table 2 Average chemical composition (wt.%) of the various components in the lignite and ash sample studied [9]

	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	Fe ₂ O ₃	SO ₃	Minor
Lignite	19.1	9.0	21.6	5.8	4.9	9.2	27.6	2.8
Ash	25.3	16.5	28.8	9.4	6.7	7.2	1.1	5.0

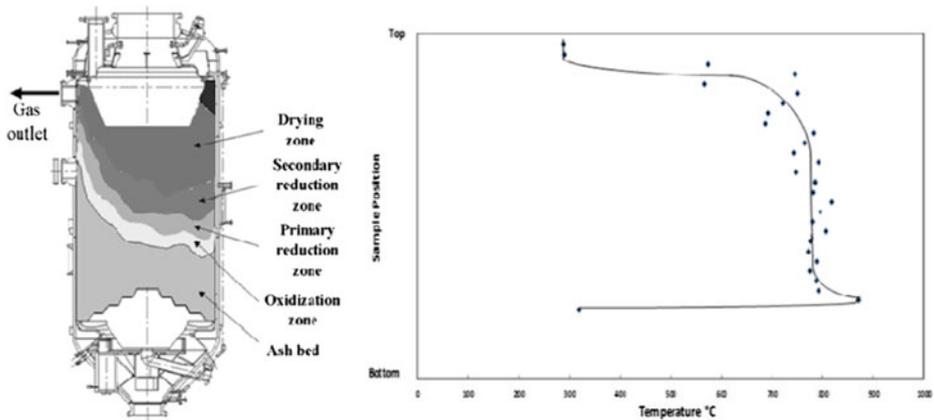


Fig. 1 Graphical representation of a gasifier with the resultant particle surface temperature profile observed in the gasifier

3 Results and discussion

The proximate analyses of the lignite (Table 1) shows that the amount of mineral matter, that changes to ash after gasification was just over 12 % with most of the sulphur associated with pyrite. The main minerals found in the present investigation were bassanite, illite, quartz, kaolinite, calcite and pyrite, consistent with reports in literature [4, 9]. Illite can contain iron, but no iron was detected in the illite in the present experiment and thus pyrite was found to be the only Fe-containing mineral present, suitable for Mössbauer spectroscopy.

The chemical composition of the mineral matter in the lignite and ash are shown in Table 2. From Table 2 it is clear that SiO₂ and Al₂O₃ form the bulk of the ash and in conjunction with the Fe₂O₃ forms the typical glass component in the final ash product. The Na₂O and CaO contents are high and can hence lead to low ash melting temperatures which have adverse effects on the gasification process.

The surface temperature (i.e. temperature on the surface of the particle) was determined as the mean of 15 % of the highest reflectance measurements per sample and the trend in the estimated particle surface temperature profile is in line with the expectations as the temperature increases in the drying, pyrolysis, gasification and combustion zones (see Fig. 1) from about 300 °C to just over 900 °C. The peak at the bottom of the gasifier can be attributed to the position of the oxygen inlet into the gasifier and thus a higher temperature is observed, but it is still below the ash fusion temperature of the lignite.

In Fig. 2 the Mössbauer spectra of the pyrite entering the gasifier is shown, as well as the changes observed as the material descended in the gasifier. The first appear-

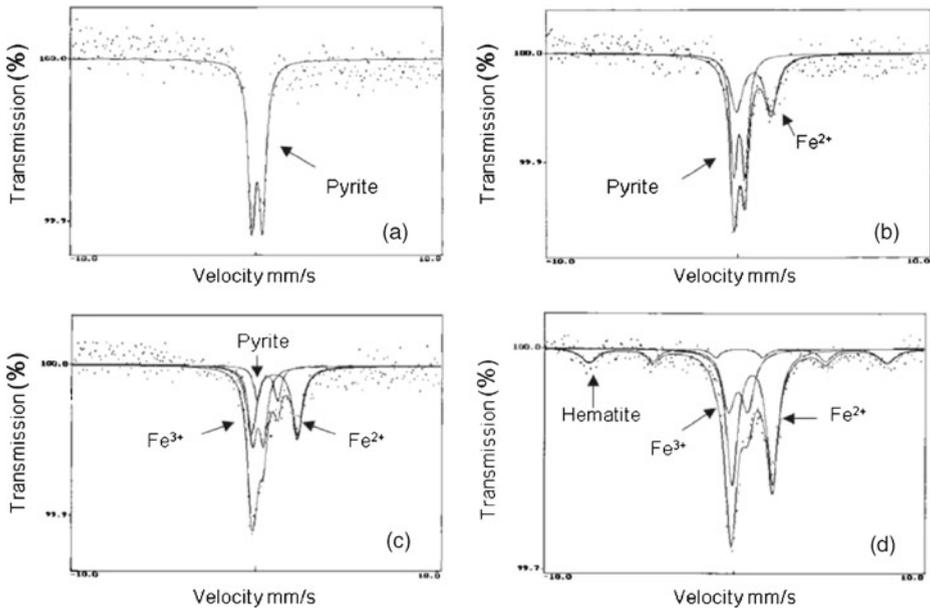


Fig. 2 Mössbauer spectra of (a) the pyrite occurring in the lignite, (b) the changes that occurred one third through the gasifier, half way through the gasifier and (c) the spectrum of the ash sample after gasification

ance of a Fe^{2+} phase occurred about one third down the gasifier, which correlates to an average temperature of about $400\text{ }^{\circ}\text{C}$ and particle surface temperature of about $600\text{ }^{\circ}\text{C}$, consistent with literature values [4, 9] for the start of pyrite conversion. As the pyrite and the coal further descended in the gasifier it was subjected to higher temperatures and the amount of pyrite decreased and no pyrite was visible about two thirds down the gasifier where an average temperature of about $700\text{ }^{\circ}\text{C}$ and particle surface temperature of about $900\text{ }^{\circ}\text{C}$ was measured. In the bottom part of the gasifier, oxidation of the iron starts to play a role and hematite formed at an average temperature of $> 800\text{ }^{\circ}\text{C}$ and surface temperature of $900\text{ }^{\circ}\text{C}$.

The highest temperatures occurred in the ash bed, with temperatures of above $900\text{ }^{\circ}\text{C}$ measured. At these high temperatures the SiO_2 and Al_2O_3 present in the coal agglomerate and form the final $\text{Fe}^{2+,3+}$ glass observed, as shown in Fig. 2. Thus the pyrite changed gradually to form, in conjunction with the SiO_2 and Al_2O_3 present in the coal, a Fe-containing glass and hematite at the bottom, or ash grate of the gasifier. It should also be noted that the amount of iron present in the coal will influence the ash fusion temperature (AFT) of the ash formed, as was reported in literature [7].

The Fe present in the pyrite is expected to form pyrrhotite (Fe_{1-x}S) and hematite (Fe_2O_3) respectively in the pyrolysis zone. The pyrrhotite can then react with hematite to form magnetite in the hotter gasification and combustion zones with the SO_2 formed in the reaction, not expected to survive the highly reducing environment higher up in the gasifier [8]. The surface temperature, as measured for the coal particles via vitrinite reflectance, gave a good indication of the temperature the

Table 3 Room temperature Mössbauer parameters of gasifier samples studied¹

Sample	Mineral	δ (mm.s ⁻¹) ± 0.01	Δ (mm.s ⁻¹) ± 0.01	H (T)	Rel area (%)
Top of gasifier	Pyrite	0.23	0.58		100
1/3 down	Pyrite	0.23	0.59		52
	Fe ²⁺	1.05	2.39		48
1/2 down	Pyrite	0.22	0.56		37
	Fe ²⁺	1.07	2.26		42
	Fe ³⁺	0.70	1.03		21
2/3 down	Fe ²⁺	1.05	2.36		67
	Fe ³⁺	0.69	1.02		33
Bottom of gasifier	Fe ²⁺	1.06	2.22		56
	Fe ³⁺	0.68	1.10	49.7	26
	Fe ₂ O ₃	0.33	-0.08		18

¹ δ = Isomer shift relative to α -iron, Δ = Quadrupole splitting and, H = magnetic hyperfine field

minerals experienced. Since the decomposition to pyrrhotite is relative fast [10] this phase was not observed in the current measurement.

Table 3 shows the Mössbauer parameters of the samples at the top, one third, then half way down the gasifier, two thirds down the gasifier and finally at the bottom of the gasifier with parameters observed for the mineral phases consistent with those found in literature [11].

4 Conclusion

Pyrite was the only Fe-bearing component present in the lignite and deformation of the pyrite started just less than about one third down the gasifier with the formation of a Fe²⁺ doublet as the pyrite started to decompose in the reduction or pyrolysis zone of the gasifier. Further down the gasifier the pyrite content reduced even more and about two thirds down the gasifier it finally disappeared. In the combustion zone, or bottom part of the gasifier the iron was oxidised to form the Fe-glassy component and hematite.

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