The fate of sulphur during pyrolysis and steam gasification of high-sulphur South Australian low-rank coals

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DECLARATION

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ABSTRACT

Australia’s economy is underpinned by access to cheap electricity, and over 85% of the country’s power generation capacity is based on pulverised coal combustion. South Australia has abundant resources of low-rank coal but its high sulphur content (typically 5% w/w db) raises both operational and environmental concerns in its utilisation. Depletion of current sub-bituminous coal reserves used for power generation means that competitive future coal-based energy supply may depend on efficient, cost-effective and environmentally-friendly utilisation of local lignite resources. Other unique properties such as high moisture, ash, sodium and chlorine content currently limit their utilisation and the study of their behaviour during fluidised-bed gasification (FBG) processes has been the focus of research by the Cooperative Research Centre (CRC) for Clean Power from Lignite.

Sulphur containing compounds in coal transform to sulphur dioxide (SO₂) in an oxidising atmosphere and hydrogen sulphide (H₂S) in a reducing atmosphere. The phenomenology of these transformations is detailed in the literature under a variety of conditions (pyrolysis, oxidation and reduction) but quantitative data for specific gasification processes is lacking. These gaseous sulphur compounds are precursors to acid rain on release to the atmosphere and cause corrosion in downstream processing units, requiring the need for effective desulphurisation strategies. Understanding the conversion of coal-bound sulphur to gas phase sulphur will enable the development of such strategies in order to comply with ever increasing emissions control.

The main objective of this study was to examine the extent of conversion and re-distribution of sulphur during the pyrolysis and gasification of two coals from South Australia: Lochiel and Bowmans. Both of these coals show similar proximate and ultimate analyses, and both contain significant quantities of sulphur, mainly in organic form. To this end, an experimental programme was designed to enable the accurate determination of the gas phase products of pyrolysis and gasification – on a continuous...
basis as they formed throughout the processes – and determine the impact of varying key parameters such as final pyrolysis temperature, heating rate and gasification temperature.

Temperature Programmed Pyrolysis experiments (heating samples from ambient to 1200°C at 15 K.min\(^{-1}\)) employing Lochiel and Bowmans coal were employed with continuous gas phase measurement of product gases. This enabled the determination of carbon and sulphur mass balances, along with the correlation of temperature with the source of particular sulphur (and other) products, and hence original sulphur species in the coal. Over 85% of the gas phase sulphur species were detected as hydrogen sulphide (H\(_2\)S) with methyl mercaptan (CH\(_3\)SH) and carbonyl sulphide (COS) comprising the balance. For the acid-washed Lochiel and air-dried Bowmans samples, sulphur dioxide (SO\(_2\)) was also detected. The absolute sulphur conversion to the gas phase was, however, only 30-40% across the two coals and with acid-treatment. Sulphur conversion for small particle (less than 0.5mm particle diameter) acid-washed Lochiel coal was in excess of 41%, and the presence of calcium and sodium led to significant retention of sulphur in the ash phase post pyrolysis.

Fixed-bed, fast pyrolysis experiments were also undertaken to elucidate the effect of final temperature (700°C, 800°C, 900°C, 1000°C) on the extent of pyrolysis and the distribution of products. Final sulphur conversion did not increase with increasing final temperature with a complex re-attachment mechanism whereby evolved sulphur re-reacts with the organic carbon matrix and inorganic species in the ash being the cause of this behaviour. Not only did the faster heating rates impact on the distribution of sulphur via an increase in conversion as H\(_2\)S and no SO\(_2\) in the product gas, the effect on carbon conversion and distribution of carbon between CO and CO\(_2\) was significant. In fluidised-bed pyrolysis experiments, the total sulphur and carbon conversion increased markedly relative to the fixed-bed heating rate processes, with a greater distribution of sulphur among CH\(_3\)SH and COS (at the expense of H\(_2\)S) and carbon among CO\(_2\) and methane.
Steam gasification experiments were carried out on small quantities of char in the fixed-bed apparatus (25%v/v steam in nitrogen), enabling the determination of a relationship between sulphur and carbon conversion. Contrary to the assumption in the literature that sulphur and carbon convert in equal and direct proportion, sulphur conversion was found to lag carbon conversion by up to 60% for both coals and at gasification temperatures of 800°C and 850°C. At 750°C, however, Lochiel and Bowmans coal did not exhibit similar behaviour. Acid washing was found to have a dramatic effect on the char’s reactivity, and in particular, on sulphur conversion up to around 20% carbon conversion.

Steam gasification experiments in the fluidised-bed, however, achieved a much slower gasification rate for the equivalent conditions of steam concentration and temperature. While the pyrolysis in the fluidised-bed was comparatively violent compared to the fixed-bed pyrolysis used to develop char for the experiments described above (Chapter 6), it was believed that such an environment led to a loss of both catalyst precursors from the char (largely sodium chloride, NaCl) and carboxyl groups to which those precursors organically bind in order to achieve their catalytic activity.

The implication of this work for industrial processes may be significant: it would appear that in order to achieve sufficient char reactivity during gasification, the creation of that char must be carried out at relatively mild conditions (of final temperature and heating rate).

The results from this suite of pyrolysis and gasification experiments provide a fundamental gas phase knowledge base on which further work can be carried out, and recommendations for the next steps along the commercialisation pathway for the effective utilisation of these coals is presented.
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