Sulphur Transformations during
Pyrolysis of Low-Rank Coals and
Characterisation of Ca-based
Sorbents

by

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SUMMARY

The high sulphur content in South Australian Low-rank coals causes serious constraints for the utilisation in fluidised-bed gasification systems for power generation. During the initial pyrolysis stage of the process, sulphur in coal evolves toxic compounds such as H₂S, COS and CS₂, which are precursors of acid-rain. Sulphur remaining in the char contributes to processing problems such as slagging, fouling, agglomeration and defluidisation.

Temperature-programmed Pyrolysis experiments employing Bowmans and Lochiel low-rank coal and treated Bowmans coals, were conducted to investigate the sulphur transformations during pyrolysis. Effects of sulphur distribution and inorganic matter were studied. Roughly 60% of the initial organic sulphur evolved over a range of temperatures, indicating the presence of aliphatic sulphides and disulphides, aliphatic/aryl thiols and some aryl sulphides in the original coal had decomposed. Solid-state sulphate transformations occurred between 400 and 600 °C to form organic sulphur in the char. The retention was greater for higher sulphate concentrations and less volatile sulphate compounds. Decomposition of reactive aliphatic sulphide and disulphide compounds decreased retention. In turn, the presence of sulphate sulphur suppressed organic sulphur decomposition between 300-500 °C.

Acid soluble/organically bound inorganics retained organic sulphur between 500-600 °C. Chemical and SEM analysis of acid-washed calcium exchanged chars removed at 800 °C and 900 °C, supplied evidence that calcium, enriched in the char, formed calcium sulphide between 700-900 °C by suppressing organic sulphur decomposition between 500-700 °C and facilitating the reactions with stable organic sulphur species in the char after 700 °C. Similar results were not observed for calcium carbonate added to coal, emphasising the importance of the intimate/organic bonding nature of calcium and the ability to facilitate reaction with sulphur. Organically-bound sodium in acid-washed sodium-exchanged coal formed significant proportions of water-soluble silicates in the char. A concentrated coating of sulphur around the silicates providing further evidence...
of sulphur’s role in ash agglomeration. Sodium also formed acid-insoluble constituents with sulphur. Total sulphur retention increased by 10% as the sodium acetate solution concentration in the ion-exchanging step increased from 0.25 M (2 wt% total Na) to 1.0 M (3.2 wt% total Na).

Sulphur transformations during fixed and fluidised-bed pyrolysis were performed to ascertain the effect of heat and mass transfer on sulphur transformations. Interpretation was aided by a heat transfer model. Sulphate and organic sulphur in coal decomposed to H₂S during the initial devolatilisation stage of pyrolysis, to an extent and at a rate proportional to the heating rate and inversely proportional to particle size. A decrease in the devolatilisation rate initiated solid-state sulphate transformations to retain organic sulphur in coal. The retention was enhanced for pyrolysis at faster heating rates and smaller particle sizes. A slower thermal response and an edge-wise distribution of sulphur across particle diameter implied that both heat and mass transfer resistances encouraged sulphur retention during the fluidised-bed pyrolysis of larger coal particles.

Atmospheric and pressurised TGA calcination experiments were conducted on a number of South Australian limestones and dolomites. The mechanism of calcination, effect of particle size, sorbent type and CO₂ partial pressure under fluidised-bed gasification conditions were studied. For the calcination experiments, particle size had varying effect for the sorbents investigated. The rate and mechanism of calcination were mainly influenced by the initial magnesium carbonate content, initial porosity and the occurrence of thermally induced fractures. The low initial porosity and particle size dependency of the calcination reaction of Angaston Limestone implied that the shrinking core model (SCM) was the most suitable to predict calcination conversion. The model predictions were successful to approximately 30% conversion, due to limitations in accounting for physical changes during the reaction. A two-stage shrinking core model, applied after 30% conversion, was found to accurately predict the calcination of 53-64 μm Angaston Limestone and 212-355 and 53-64 μm particles of Caroline Limestone. For the latter sorbent, the two stage SCM provided better predictions than a grainy pellet and homogenous model. It was concluded that the calcination reaction proceeds at a definite CaCO₃-CaO reaction interface for sorbents of high and low initial porosity. Finally, a constant mole fraction, y₁, was necessary to relate the calcination rate of Caroline
Limestone with CO\textsubscript{2} partial pressure, due to heat and mass resistances present during the calcination of CaCO\textsubscript{3} under significant partial pressures of CO\textsubscript{2} and for total pressures greater than 1 atm.

The results from the coal pyrolysis and sorbent calcination investigations provide a fundamental knowledge base for which models of sulphur emissions and sulphur capture during fluidised-bed gasification can be derived from.
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