

The Pennsylvania State University
The Graduate School
Department of Energy and Mineral Engineering

**STRUCTURAL ELUCIDATION, MOLECULAR REPRESENTATION AND SOLVENT
INTERACTIONS OF VITRINITE-RICH AND INERTINITE-RICH SOUTH AFRICAN
COALS**

A Thesis in
Energy and Geo-Environmental Engineering

by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Energy and Geo-Environmental Engineering

August 2008

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ABSTRACT

Two Permian-aged South African coals, vitrinite-rich Waterberg and inertinite-rich Highveld coals (similar rank, carbon content and Permian age) were studied to determine the structural differences and similarities of these two maceral diverse coals and how it impacts solvent interaction behavior (solvent swelling and extraction). With South African coals the opportunity presented itself to study not only Permian-aged Gondwana vitrinite but also inertinite. It was concluded from various structural data that both coals, although different in maceral composition and depositional basins, are similar in their base structural composition. The main differences were that the inertinite-rich Highveld coal was more ordered, more aromatic, and had less hydrogen than the vitrinite-rich Waterberg coal. Analytical data were used to construct advanced molecular representations for vitrinite-rich Waterberg and inertinite-rich Highveld coals. The individual molecules were created from the analytical data and were comparable to experimentally derived molecular weight distribution. The three-dimensional models were structurally diverse with a molecular weight range of 78 to 1900 amu. The vitrinite-rich model consists of 18,572 atoms and 191 individual molecules and the inertinite-rich coal consists of 14,242 atoms and 158 individual molecules. Various PERL script were developed to automate various visualization and analytical aspects.

Coal swelling behavior was determined using the traditional pack-bed swelling method and a new novel single-particle stop-motion videography swelling method with NMP and CS₂/NMP solvents. The pack-bed swelling showed that vitrinite-rich coal had a greater swelling extent and that swelling extent for both coals was greater in CS₂/NMP binary solvent than for NMP. Single-particle swelling experiments showed that both coals, regardless of solvent, exhibit overshoot-type and climbing-type swelling behaviors. Inertinite-coal had a faster swelling rate, regardless of solvent, than the vitrinite-rich coal. The single-particle swelling data was used to calculate the kinetic parameters and it was found that the swelling was governed by relaxation of the coal structure (super-Case II swelling). X-ray computed tomography was conducted confirming anisotropic swelling (swelling greater perpendicular to the bedding plane than parallel to it).

The petrographic changes (maceral-group composition and reflectance) with solvent swelling and extraction were also quantified. No changes in the maceral compositions were found, but changes in some coal particles were observed. Random reflectance analysis showed that, for both vitrinite and low-reflecting inertinite, there is a decrease in reflectance values with solvent treatment. Vitrinite reflectograms showed a shift from the dominant reflecting V-types to lower V-types. The low-reflecting inertinite reflectograms exhibited an increase in number of I-types (broadening of reflectograms). The changes in reflectance between the original and solvent treated coal could not be explained satisfactory and more studies is needed to understand this phenomenon.

The application of molecular simulation and visualization were studied using the proposed models. A theoretical extraction yield was determined from the proposed molecular models using the solubility parameters and showed agreement with experimental extraction yield trends. Statistical Associating Fluid Thermodynamics (SAFT) modeling was explored to test whether this method could predict swelling extent using current data. The predicted swelling trends of SAFT were comparable to that of the experimental swelling results. SAFT seems to be a promising tool for solvent-coal interaction predictions. Solvent swollen structures were constructed by the addition of solvent molecules to the original coal molecules. This method showed that coal-coal non-bonding interaction changes with the introduction of solvent. A decrease in the van der Waals interaction energies and a change in hydrogen bond distributions were observed in the swollen coal models

It was concluded that small changes in coal structure translates to significant changes in solvent interaction behavior. These changes can be visualized using computational molecular representations. The molecular models exhibited agreement to experimental data and it was proposed that they would also behave similar to that of the original coal. Various molecular visualization and simulation techniques were explored to study solvent-coal interactions using the proposed molecular models.

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