CHAPTER 7

Conclusions

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 extent and extraction yield). With South African coals the opportunity presented itself to study not only Permian-aged Gondwana vitrinite but also inertinite (which is the dominating maceral in most South African Permian coals).

NMR structural analyses found that inertinite-rich Highveld is more aromatic than vitrinite-rich Waterberg (86% and 76% respectively) and has a higher bridgehead value (30 % for inertinite and 23 % for vitrinite) indicating that the inertinite-rich aromatic structures are more polycondenced. The NMR derived lattice parameters indicated that vitrinite-rich and inertinite-rich coals have very similar sized aromatic clusters. The inertinite-rich coal is structurally more ordered and has a higher degree of crystalline stacking (evident from X-ray diffraction studies). The laser-desorption ionization time-of-flight mass spectrometry (LDTOF-MS) showed that both coals consist of similar molecular weight distributions ranging to approximately 1700 m/z with a maximum abundance of ~450 m/z for vitrinite and ~550 m/z for 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 structurally more ordered, more aromatic, and had less hydrogen than the vitrinite-rich Waterberg coal.

The data obtained from elemental, NMR, LDTOF-MS and high-resolution transmission electron microscopy analyses were used to construct molecular representations for vitrinite-rich Waterberg and inertinite-rich Highveld coals. The individual molecules were created from the analytical data and were comparable to experimental molecular weight distributions. The individual molecules were assembled into three-dimensional structures. The constructed models were structurally diverse with a molecular weight range of 78 to 1900 amu. The vitrinite-rich model consisted of 18,572 atoms and 191 individual molecules and the inertinite-rich coal consisted of 14,242 atoms and 158 individual molecules. Although these coals have very similar average molecular structures according to the various analytical data, subtle changes leads to significant behavioral differences in the models. The constructed molecular models were constructed for solvent interaction visualizations and simulations.

Coal swelling behavior was evaluated using the traditional pack-bed swelling method and a novel single-particle stop-motion videography swelling method using NMP and CS_2/NMP. The pack-bed swelling showed that vitrinite-rich coal had a greater swelling extent than the inertinite-rich coal, regardless of solvent. The swelling extent was greater in CS_2/NMP binary solvent than for NMP in the pack-bed experiments. Single-particle swelling experiments showed that both coals, regardless of solvent, exhibit overshoot-type and climbing-type swelling. Inertinite-coal had a faster swelling rate, regardless of solvent, than the vitrinite-rich coal. The swelling in CS_2/NMP was faster, regardless of coal, than in NMP. 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. Computed tomography was conducted on both coals over a 50-hour period and anisotropic swelling was observed in all particles. As expected, swelling was greater perpendicular to the bedding plane than parallel to it. Solvent swelling studies showed that even though these coals are similar in their average structural composition, they exhibit differences in solvent swelling behavior.

The petrographic changes (maceral-group composition and reflectance) with solvent swelling and extraction were also quantified. The literature is bereft of information regarding low-temperature solvent extraction petrography transitions. No changes in the maceral compositions were found. Solvent extraction residues exhibited the most significant observable changes: cracking of particles, decrease in reflectance, low-reflecting edges and formation of smooth rounded edges. Inertinite-rich Highveld coal exhibited extensive fracturing during solvent treatment, making maceral analysis difficult (distinction between vitrinite and low-reflecting inertinite is difficult for small particles). 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 reflectrograms). The current data suggests a relationship between solvent extraction and mean random reflectance, the higher the extraction yields the lower the mean random reflectance.

The final objective of this thesis was to determine if proposed molecular models could be used to study solvent behavior (swelling extent and extraction yield). A theoretical extraction yield could be determined from the proposed molecular models using the solubility parameters and showed agreement with experimental extraction trends. This method is only applicable for pure solvents and does not take the synergistic effect of more complex solvents into account. 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 extent seems to be a promising tool for solvent-coal interaction predictions, but more studies needs to be conducted.

Solvent swollen structures were constructed by the addition of solvent molecules to the original coal molecules. This method provided information regarding the changes in energy and non-bonding interactions when solvents are introduced into a coal. It was observed that NMP and CS_2/NMP have the ability to disrupt van der Waals interactions within the coal structure. The distributions of hydrogen bonds were calculated and provided a method to evaluate solvent-coal hydrogen interactions. It was found that hydroxyl groups associated with the coal structure is the dominating hydrogen bond donor in solvent interaction. It can be concluded from the current study that molecular modeling and simulation can be used effectively in the prediction of swelling extraction trends (using solubility parameters) and solvent swelling (using SAFT). In addition molecular modeling and simulation is a useful tool to investigate the changes in energies and non-bonding interactions in coal with various solvents.

The studies in this thesis showed that a large, structurally diverse representation of coal could be constructed using various analytical methods. Solvent swelling data showed that these coals had very different swelling extents and behaviors (for example, differences in swelling extent and swelling rate). This indicated that subtle differences in structure leads to significant differences in swelling behavior. Modeling visualizations and simulations were conducted in attempt to investigate the role non-bonding interactions play on solvent interactions. Construction of "swelled structures" showed that these questions could be probed and that non-bonding interactions play an important role with solvent interaction. SAFT is another method that showed promise as a modeling tool for solvent interaction (swelling and extraction) prediction.

Another contribution made was the development of series of PERL scripts (Appendix 1) that was used for automation and visualization of various modeling aspects. These scripts (e.g. NMR parameter calculation, molecular weigh distribution calculation, hydrogen bond distribution calculation, etc) were used to calculate parameters and obtain information that previously was very difficult to obtain and/or time consuming.