8 Conclusions and recommendations

8.1 Introduction

The characteristic properties and devolatilization behaviour of four typical South African coals: UMZ, INY, G#5 and TSH have been the topic of discussion in this thesis. This chapter concludes the work of this thesis by providing a summary of the main conclusions made during this investigation as well as some relevant recommendations for future work regarding the evaluation of coal devolatilization behaviour.

8.2 Conclusions

8.2.1 Coal characteristic properties as determined by conventional methods

- All four coals were classified as bituminous Medium rank coals (Medium rank B to C) containing relatively low amounts of ash (13.5 wt.% (d.b) to 18.6 wt.% d.b), with vitrinite contents ranging between 24.4 vol.% (m.m.f.b.) and 69.2 vol.% (m.m.f.b.). A comparison between the four coals also revealed the presence of significant amounts of liptinite (close to 10 vol.% m.m.f.b.) confined to the organic structure of coal G#5.
- Volatile matter contents reported to be well above 20 wt.% (d.b) and increased in the order TSH < UMZ < INY < G#5, while XRD and XRF results confirmed the dominant presence of inorganic species such as kaolinite, quartz, calcite, dolomite and pyrite within the four coals.
- True densities were found to range between 1333 kg/m^3 and 1460 kg/m^3, while total porosities (as determined from mercury porosimetry) varied between 8.1% and 11.8%. CO_2- and N_2 adsorption isotherms also confirmed the presence of both micro- and mesopore structures within the four coals.

- From thermoplasticity measurements it was evident that only coal TSH exhibited extensive coking/caking properties, whilst the other three coals were found to only display some contraction upon heating under an inert atmosphere.

8.2.2 Coal characteristic properties as determined by advanced methods

- From ^{13}C NMR (CP-MAS) it was evident that the vitrinite-rich (69.5 vol.%, m.m.f.b.), higher rank (Medium B) coal TSH was more aromatic (81%) and more poly-condensed (as a result of both its larger, aromatic bridgehead- and aromatic carbon content (40% and 24 aromatic carbons per cluster)), while coal G#5 was found to be the least aromatic (66%) with larger abundances of protonated aliphatic functionalities. No significant discrepancy could be observed in the aromaticity of coals UMZ (77%) and INY (74%) to correlate with current depth of coal seam deposition.
- XRD derived parameters, such as the fraction of amorphous carbon (X_A) and degree of disorder index (*DOI*), obtained for coal G#5 (0.67 and 0.78, respectively) provided additional evidence of its less ordered structure, therefore explaining the higher volatile matter content of this particular coal. In contrast, lower values of X_A and *DOI* for coal TSH (0.52 and 0.61, respectively) confirmed the more poly-condensed nature of this coal.
- From the MALDI-TOF MS and HRTEM results it was evident that all four coals displayed similar molecular weight distributions ranging to approximately 1800 m/z. Average molecular weights were typically between 300 m/z and 500 m/z for coals UMZ, INY and G#5, while the MALDI-TOF MS spectrum of coal TSH was characterised with a maximum abundance at a higher average molecular mass (609 m/z), suggesting the presence of larger aromatic functional units.

8.2.3 Influence of operating conditions on the yield of devolatilization products

- Reaction temperature was found to be the dominating factor controlling product yield,- quality, and -evolution rate, while the influence of particle size was less significant.
- Tar yields reported typical values of between 3.6 wt.% and 10.1 wt.%, while the yield increased in the order UMZ < INY < TSH < G#5.

- A comparison with coal characteristic properties, revealed that the higher tar yield of coal G#5 could be ascribed to the high vitrinite (60.2 vol.% m.m.f.b.) and liptinite content (9.7 vol.% m.m.f.b.) of this coal, while tar yields for coal TSH were found to be comparable to those obtained for the inertinite-rich coals as a result of its rank and more profound swelling nature causing larger internal mass transfer resistances.
- It was found that both gas and -total volatile yield increased significantly with increasing temperature, while tar yield remained relatively unchanged for coals UMZ, INY and TSH. This shift in product spectrum, favouring the formation of more gaseous species, was attributed to additional bond cleavage- and secondary cracking reactions becoming more apparent at higher temperatures.

8.2.4 Product quality of generated gases, tars and chars

- Gaseous products evolved during devolatilization consisted mainly of H_2, CH_4, CO, CO_2, low molecular weight paraffins (ethane and propane) and –olefins (ethylene and propylene) as well as some C_4 homologues. Increases in the amount of gaseous species at higher devolatilization temperatures could again be attributed to both hydrocarbon cracking and additional bond cleavage of aromatic structures within the formed chars.
- Higher proportions of H_2 and CH_4 obtained from coal TSH indicated that secondary cracking was more extensive for this coal, while the presence of larger amounts of low molecular weight aliphatics from coal G#5 could be ascribed to its higher aliphatic nature (fraction aliphatics: 0.34) and larger liptinite content (9.7 vol.% m.m.f.b.).
- From SIMDIST results it was concluded that the weight average boiling points (*WABP*) of the different tars ranged between 337°C and 377°C, while an increase in temperature led to a subsequent increase in the amount of lower boiling fractions such as naphthas and kerosenes due to more extensive hydrocarbon cracking.
- GC-MS, GC-FID, ^{1}H NMR and ^{13}C NMR indicated that tar samples became progressively more aromatic with increasing temperature, constituting molecular compounds with lower degrees of aliphatic substitution, such as phenols, higher order aromatic derivatives (naphthalenes etc.) and PAHs. In contrast, lower temperature tars were characterised by the presence of long chain aliphatic homologues and simple aromatics, while carbon aromaticity (f_a) increased in the order G#5 < INY < UMZ < TSH.

- SEC-UV analyses revealed that a large proportion of tar material was confined to molecular weights below 1000 m/z, while larger molecular constituents with molecular weights as large as 5000 m/z were also apparent in all cases. In addition, an increase in temperature was found to contribute to noticeable shifts in the molecular weight distributions of each tar, confirming the presence of more extensive hydrocarbon cracking at higher temperatures.
- Generated chars were found to contain different char types, of which devolatilized coal structures were most commonly observed at 450℃, while honeycomb- and cracked dense chars formed the main structures present in chars generated at 750℃.
- From ^{13}C NMR (CP-MAS), XRD and HRTEM results it was concluded that the chars became increasingly more aromatic and poly-condensed with an increase in temperature, subsequently leading to the formation of more aligned and structurally orientated aromatic functional units (aromatic fringes). In addition, a comparison between HRTEM results for the different chars revealed that structural orientation was more significant for the coking coal (TSH) and that the higher degree of structural alignment of the latter could be attributed to its extensive thermoplastic behaviour.
- Differences in conventional char properties such as volatile matter, H/C and O/C ratio, etc. could be related successfully to more advanced structural parameters such as *DOI*, X_A as well as parent coal aromaticity.

8.2.5 Reaction rate modelling of the devolatilization of large coal particles

8.2.5.1 Assessment of the intrinsic kinetic behaviour of coal devolatilization

- Non-isothermal rate measurements (intrinsic rate assessment) indicated that volatile evolution increased monotonously with temperature, while two stages of devolatilization could be distinguished and be ascribed to the initial loss of mass due to the release of moisture and occluded gas (< 350℃) followed by the subsequent production of tars, gases and chars (> 350℃).
- A shift in main peak temperature (main devolatilization peak) to higher temperatures for coal TSH could be attributed to both the higher aromaticity (rank) and more extensive thermoplastic nature of this coal.

- Primary decomposition rates were higher for the vitrinite-rich coals in comparison to coals UMZ and INY, due to the presence of more reactive material (vitrinite and liptinite) in the organic structures of these coals.
- Intrinsic rate modelling involved the simultaneous, non-linear regression of DTG data of all four heating rates, according to a first order, pseudo-reaction kinetic modelling strategy. In all cases, experimental DTG and TG profiles could be adequately described assuming 8 pseudo-component reactions, although sufficient predictions with the use of 4 pseudo-component reactions could even be obtained for coals TSH and G#5. Typical activation energies reported to be between 22.3 kJ/mol and 244.3 kJ/mol for the different coals and were found to be within the acceptable limits specified in other investigations (11.1 kJ/mol to 827.1 kJ/mol).

8.2.5.2 Devolatilization behaviour of large coal particles

- "Pseudo"-isothermal rate assessments performed on 20 mm coal particles, at different temperatures, confirmed the increase in both the rate of mass loss and ultimate volatile yield with increasing temperature.
- For all four coals, large particle devolatilization behaviour could be accurately described with a model allowing for the derived intrinsic kinetics (moisture- and volatile evolution), coal swelling/shrinkage, as well as heat- and mass transport limitations.
- From simulation studies it could be concluded that volatile evolution at the particle surface was always higher in comparison to the particle centre, as a direct result of higher temperature gradients in the vicinity of the particle surface. At low temperatures, volatile evolutions occurred according to a volume reaction mechanism, while the devolatilization mechanism at higher temperatures approached shrinking core behaviour.
- Increases in particle size (simulation study) led to not only substantial increases in the time to reach thermal equilibrium, but also significant decreases in the evolution rate of volatile products from the coal structure due to larger conduction resistances.
- Heat losses due to the effect of internal convection of volatiles, heat of reaction and vaporization were found to be quite significant, confirming the need for incorporating these terms in the general heat equation.

- Analogous to the effect of particle size, coal swelling effects could be attributed to larger conductive resistances yielding lower particle heating rates (slower volatile evolution), while the opposite was found to be true for particles exhibiting shrinkage behaviour.

8.3 Contribution to knowledge of coal science and technology

The following achievements were considered valuable contributions to the field of coal science and technology:

- A full account of chemical-, mineralogical-, petrographical- and physical features for the four different coals provide valuable information for assessing feedstock suitability to coal conversion processes such as carbonization, gasification, etc. and can be included in any international coal data bank. Furthermore, the determination of molecular properties/characteristics from advanced analytical techniques is considered an important contribution as it provides valuable insight into the molecular composition of each respective coal, which prior to this investigation has not been reported for these coals in open literature.

- Product evolution studies revealed valuable information regarding the product yielding potential (tar, char and gas yield) of coal particles confined to sizes used in lump coal conversion operations. In addition, results obtained from the conventional (proximate, ultimate and char morphological petrology)- and advanced analyses (GC-MS, GC-FID, SEC, NMR, HRTEM and XRD) provided a detailed description of the chemical-, physical- and molecular nature of the respective products (chars, gases and tars) derived at the different experimental conditions. The preceding developments are considered major achievements in the field of coal science and technology, especially in the South African context, as they provide the first noteworthy description of the molecular properties of tars and chars derived from large, South African coal particles.

- The use of coal characteristic predictors such as f_a, X_A, *DOI,* O/C*,* H/C and *MI* does not only provide an efficient way of predicting feed stock behaviour but also contributes to a better fundamental understanding of the possible nature and quality of products generated during the process of devolatilization. This is of great importance as most published works involving the assessment of devolatilization behaviour do not consider the interrelationships between parent coal characteristics and that of the subsequently formed devolatilization products.

- The application of the pseudo-component reaction model for describing the intrinsic kinetics of coal devolatilization, is considered to be a valuable contribution, especially in the South African context where, prior to this investigation, no kinetic information regarding devolatilization of these four coals were available. Furthermore, mathematical description of large particle devolatilization behaviour for the different coals involved the evaluation of a transient large particle model, which consisted of coupling the derived intrinsic kinetics (moisture- and volatile evolution) and particle thermoplasticity with the well known conservation laws for heat- and mass transfer. Currently this is one of the most comprehensive particle models to be applied in the description of the devolatilization of large South African coal particles and can be subsequently incorporated further in typical reactor modelling scenarios involving the devolatilization, gasification and/or combustion of coals with different volatile contents.

8.4 Recommendations

Based on the findings made from this investigation, the following recommendations are proposed to aid in the expansion of knowledge regarding the devolatilization behaviour of South African coals:

- The use of He pycnometry and small angle X-ray scattering (SAXS) in conjunction with gas adsorption (CO_2 and N_2) and mercury porosimetry to obtain a more detailed understanding of the evolution of the porous structure of char during coal devolatilization.

- Application of more advanced methods such as GC-GC-MS, 2D NMR, Raman spectroscopy, tomography, FTIR and MALDI-TOF MS could be valuable in elucidating further fundamental features of coal-derived tars and chars. As an example, application of GC-GC-MS can assist in the better separation of co-eluting compounds within the retained tars, while 2D NMR techniques such as COSY (correlation spectroscopy), HETCOR (heteronuclear correlation), HMQC (heteronuclear multiple quantum correlation) and HMBC (heteronuclear multiple bonding correlation) can be useful for evaluating possible associations existing between different hetero-functionalities.

- Application of reactive force field modelling strategies (such as ReaxFF) in conjunction with the development of representative molecular coal models should be considered in order to dynamically simulate the devolatilization behaviour of the four different coals on a molecular level. Currently, no dynamic simulations are available for describing the devolatilization behaviour of South African coals, although some molecular models have already started to emerge over the past few years.

- Although the pseudo-component modelling approach was found to be most satisfactory, application of more advanced modelling techniques such as DAEM, FG-DVC, FLASHCHAIN, percolation theory etc. can provide additional insight into the numerous amounts of chemical reactions believed to occur during coal devolatilization and should be considered for future investigations

- For this investigation, coal swelling and/or shrinkage could be adequately described with the use of empirical models. It is, however, recommended that a detailed investigation regarding the mechanisms controlling swelling/shrinking of coal during devolatilization be undertaken in order to propose more fundamentally advanced swelling/shrinking models.

- Some of the thermo-physical properties used in the large particle devolatilization model have been taken directly from literature and are based on investigations performed on coals originating predominantly from the northern hemisphere. Improved accuracy of model predictions therefore necessitates the determination of thermo-physical property relationships characteristic of South African coals.

- Integration of knowledge obtained from coal characterisation (both conventional and advanced) with the developments of devolatilization modelling in order to provide a better interpretation of devolatilization behaviour with respect to new insights gained on coal structure.