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# General Introduction

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A brief overview of the purpose for investigating the devolatilization behaviour of South African coal is provided in four sub-divided sections of this chapter. A brief account of the background information and the motivation for executing this investigation is given in Section 1.1. This section addresses the importance of coal as both an energy- and petrochemical commodity; and outlines the importance of studying devolatilization as it forms the most important step of all coal conversion processes. A subsequent formulation of the problem statement is provided in Section 1.2, while the research objectives are presented in Section 1.3. Finally the chapter is concluded with the scope and chapter overview of the investigation in Section 1.4.

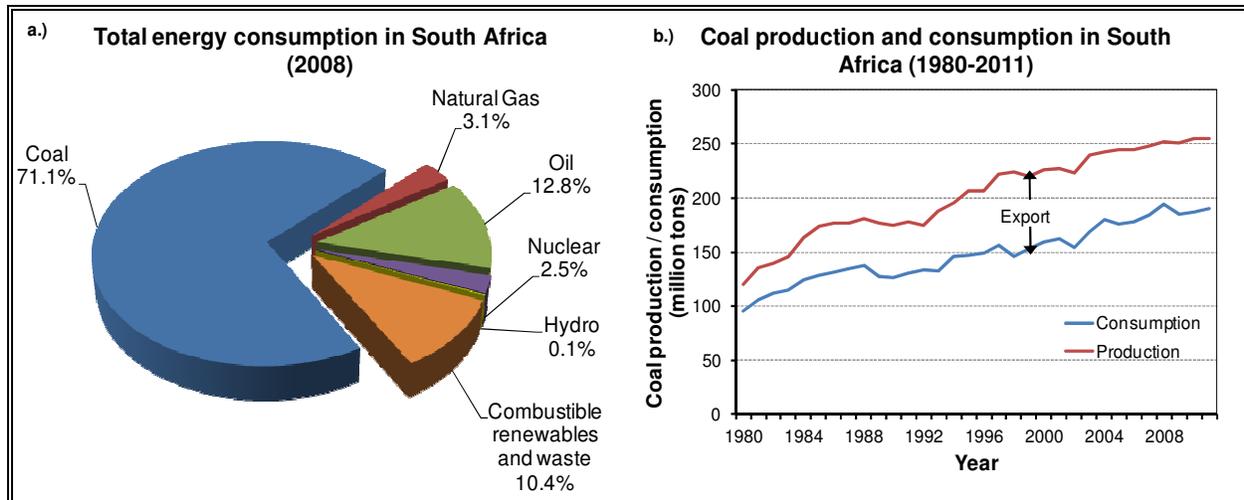
## **1.1 Background and motivation**

### *1.1.1 Coal as an energy source*

Currently the importance of coal lies in its ability to be converted into useful chemical products such as in the petrochemical industry; or to be used as a process utility in electricity generation, steel production, cement manufacturing and coke production (Miura, 2000; WCI, 2012a). Coal plays a significant role in the electricity generation sector, where it contributes approximately 39% to the world's electricity demand. Additionally, approximately 64% of steel production worldwide comes from iron made in blast furnaces fired by coal. Furthermore, coal provides close to 30.3% of the world's energy supply and it is expected that the demand for usage of this important resource will inevitably increase throughout the next decades, especially in developing sections of the world, like China and India, due to the abundance and economy of coal (Miura, 2000; WCI, 2012b). According to the World Coal Institute (2012b), oil currently contributes 34% to the global primary energy market, with coal and natural gas providing 30% and 24%, respectively, to this sector. Although oil constitutes the major part of primary energy usage, coal still contributes the largest portion (41%) to global electricity generation. The large demand for energy generation and petrochemical production requires sufficient recoverable coal reserves.

Coal reserves are available in almost every country, with close to 70 countries accounting for most of the recoverable coal reserves (WCI, 2012a). In contrast, however, over 66% of the world's oil- and gas reserves are mainly concentrated in the Middle East and Russia.

Current statistics have shown that world hard coal production reached an estimated capacity of 6637 million tons only in 2011, which accounted for a 19.3% increase from 2006 and more than a 100% growth over the past 25 years. At current production- and consumption levels of different fossil fuels, the life expectancy of proven coal reserves is estimated to be in the range of 118 years, whereas proven oil and gas reserves will only last 46 and 59 years, respectively (WCI, 2012b). It is therefore expected that the demand for fossil fuel processing will surge due to the abundance and economy of coal (Miura, 2000). Coal forms an important fossil fuel resource for developing countries like South Africa with large coal reserves, due to the expected continuous increase in oil and natural gas prices. South Africa is ranked as the fifth largest coal consumer and -producer in the world, with an annual production of 253 Mt/yr in 2011. This figure accounts for approximately 3.8% of the world coal production. With regard to current production rates, approximately 50 years of recoverable coal reserves are available in South Africa. South African coal contributes a staggering 93% to electricity generation (WCI, 2012b). Furthermore, the importance of coal utilization in South Africa is becoming more evident due to the eventual growth rate in coal consumption during the years 1980-2011 as depicted in Figure 1.1 b.) (EIA, 2011).



**Figure 1.1 Total energy consumption a.) and coal production-and consumption rates b.) in South Africa (DOE, 2012; EIA, 2011).**

The difference in the consumption- and production values is mainly attributable to the export of coal to global sectors (Figure 1.1.b.). According to the Energy Information Administration (2011) the contribution of coal to energy consumption in South Africa was close to 71.1% in 2008 as shown in Figure 1.1.a.). This value, however, is unlikely to change significantly over the next few decades due to the lack of suitable alternatives to replace coal as primary energy source in South Africa (DOE, 2012). From the available coal production feed stock in South Africa, nearly 21% is sold to the export market, another 21% is used locally (excluding coal used for electricity generation). The remainder is distributed to different local industries where almost 70% and 20% is respectively allocated to electricity generation and to the petrochemical industry (Sasol). Of the remaining 10%, 5% is provided to the general industry while 5% is fed to the metallurgical industry or sold to local merchants (Eberhard, 2011; Prevost, 2010). It should, however, be noted that although the preceding statistics reflect the overwhelming significance of coal usage on the South African economy, no explicit coal policy is currently available. The latest official energy policy statements include the Energy Policy White Paper published in 1998 as well as the more recent Integrated Resource Plan of 2010 which stipulated the need for efficient electricity regulation (Eberhard, 2011; South Africa, 2010). Although very out of date, the Energy Policy Paper did advocate a number of key policy issues which included continued deregulation, maintaining a coal resource database, the promotion of smokeless or low-smoke coals for household application, the efficient usage of coal discards, promotion of end-use efficiency and clean coal technologies (Eberhard, 2011). This tends to support the fact that the sustainable- and efficient use of coal in South Africa will become evidently more important in the long term.

### *1.1.2 Coal conversion technologies*

Apart from being combusted for electricity generation, coal is also a valuable source of petrochemical- and non-fuel substances. By the process of liquefaction coal can be converted to liquid fuels. The produced liquid fuels can be refined further into transport fuels and other chemical products (WCI, 2012a; Horsfall, 1993). In general three main strategies are available for converting coal to liquid fuels, which include (i) direct liquefaction such as hydrogenation (WCI, 2012a; Horsfall, 1993), (ii) devolatilization/carbonization (Horsfall, 1993; Kristiansen, 1996) and (iii) indirect liquefaction such as coal gasification (Horsfall, 1993; WCI, 2012a). The latter process alternative is currently the favoured non-fuel conversion route for South African coal. Coal fed to the gasifiers, are subjected to steam and oxygen under high temperatures and

pressures. CO<sub>2</sub> produced within the gasifier reacts with the coal to form synthesis gas or “syngas”, which is used for the production of long-chain hydrocarbons via either the Sasol Advanced Synthol (SAS) or Sasol Slurry Phase Fischer Tropsch proprietary technologies (Bunt & Waanders, 2008; Bunt & Waanders, 2009; Horsfall, 1993; Van Dyk *et al.*, 2006; WCI, 2012a;).

### 1.1.3 Non-fuel applications of coal

In addition to its use as a primary energy resource, coal also plays a beneficial role in the production of non-fuel substances. Although the coal utilization market is dominated by the application of coal for fuel purposes, the non-fuel use of coal was shown to have a higher value (Schobert & Song, 2002). Furthermore, it is expected that the processing of coal-derived oils in existing petroleum refineries will become more prominent in the nearby future, due to the decline in resources and quality of crude oils (Schobert & Song, 1995). Non-fuel products derived from coal include (Menendez *et al.*, 2000; Schobert & Song, 1995; Schobert & Song, 2002; Van Dyk *et al.*, 2006):

- Production of metallurgical coke from the high-temperature carbonization or devolatilization of sub-bituminous- and bituminous coals;
- Manufacturing of carbon materials such as activated carbon, carbon molecular sieves and chemicals such as phosphorus;
- The production of specialty materials such as graphite, fullerenes and diamonds;
- Devolatilization of coals for producing aromatic chemical feedstocks;
- Production of synthesis gases and other chemicals from coal gasification. This includes the recovery of valuable condensable co-products such as tar and oil during the subsequent cooling of the product gas stream;
- Production of aromatic- and phenolic chemicals from coal tar generated in devolatilization, gasification and carbonization;
- The use of coal tar pitch in the manufacturing of binder pitch, mesocarbon microbeads, carbon fibres and activated carbon fibres;
- Production of humic acids and calcium humulates for application in the soil modification and -fertilization industry;
- Manufacturing of coal/polymer composites and coal/conducting polymer composites.

Coal has several positive attributes, in comparison to the other fossil fuels, when considered as a feedstock for the above-mentioned non-fuel products (Schobert & Song, 1995). First of all, carbon (on a weight basis) dominates the composition of coal and a major part of the carbon is already contained within aromatic structures, therefore with the appropriate selection of operating conditions the production of active carbons, graphites and other carbon materials should be quite straightforward. In addition, coal may be a better feedstock in the production of aromatic chemicals than alternative feedstocks which contain more aliphatic carbon, whereas the aromatic structures of coals are mainly dominated by multi-ring systems, which can be of great significance in the production of new generation polymers such as polyethylene naphthalate and Hoechst Celanese's liquid crystalline powder, where naphthalene derivatives obtained from coal may be used as monomers (Schobert & Song, 1995; Schobert & Song, 2002).

#### *1.1.4 Significance of devolatilization*

The devolatilization of coal plays an integral part in the metallurgical industry for producing coke, as well as during coal gasification where it normally constitutes the initial step of this process. In addition, dissection studies done by Bunt and Waanders (2008) revealed the significant importance of the devolatilization zone within fixed-bed gasifiers, which typically involves the conversion of lump coal particles ranging between 5 mm and 100 mm. The devolatilization of coal yields many valuable chemicals in the tars and gases formed and has a marked effect on the further processing potentials of the formed char. Coal tars form an important source of aromatic chemicals such as phenols, naphthalenes, pyrenes, cresols and specialized products such as activated carbon and carbon fibre (Miura, 2000; WCI, 2012a; Wittcoff & Rueben, 1996). Aromatic chemicals such as benzene, toluene and xylenes (BTX) are consumed at a rate of 25 Mt/yr, whilst close to 5 Mt of naphthalene and 3- and 4-ring compounds are consumed annually (Collin, 1985; Murakami, 1987). Currently, coal tar accounts for about 10% to 15% of the total BTX production and constitutes approximately 95% of larger aromatics (Wittcoff & Rueben, 1996). Furthermore, coal tars are still used in the production of significant quantities of naphthalene, mainly for phthalic anhydride manufacture ( $\pm 100\ 000$  t/yr), and anthracene which is the source of anthraquinone. Smaller, but commercially important compounds such as acenaphthene, biphenyl, 1-methylnaphthalene, fluorene, phenanthrene, fluoranthene, pyrene, quinoline and isoquinoline are also derived from coal tar (Kandiyoti *et al.*, 2006; Menendez *et al.*, 2000). In addition, the properties of the subsequently formed chars or

cokes play an important role in the downstream processing of these valuable carbon products. Detailed process parameters for gasification, however, still remain obscure, although some improvements in gasification efficiencies were obtained over the last few years due to the application of enhanced engineering design- and maintenance procedures. In addition, past operating experiences have shown that not only gasifier operating conditions, but also coal characteristic properties play an important role in gasifier performance and operational stability (Bunt & Waanders, 2009).

Accordingly, it is important to evaluate the devolatilization behaviour of a coal feedstock in order to evaluate and optimize the production of valuable products such as char/coke, tar and gas. The yields and properties of the tars and chars as well as the kinetics of devolatilization depend on the coal properties, which include chemical properties (proximate, ultimate and structural), physical structure (porosity, surface areas), organic content (macerals, microlithotypes, carbominerites), mineralogy (ash analysis), devolatilization conditions (temperature, pressure and gases) and reactor type (Alonso *et al.*, 1999; Alonso *et al.*, 2001; Baruah & Khare, 2007; Hanson *et al.*, 2002; Khan, 1989; Ko *et al.*, 1987; Liu *et al.*, 2004; Solomon & Hamblen, 1985). As a result of all these variables the devolatilization process is very complex, consisting of progressive de-polymerisation, condensation and re-polymerisation with the formation of gases, tars and chars (Gürüz *et al.*, 2004). Empirical models consisting of single- and multiple step reactions and a distributed activation energy model have been evaluated, but do not incorporate the properties of the coal and are unable to predict the nature of the products formed. Recent advances in the elucidation of coal structures (NMR, FTIR, XRD, HRTEM, MALDI-TOF) have led to a more fundamental approach to modelling coal devolatilization, based on the structural properties of coal (Arenillas *et al.*, 2001).

### **1.2 Problem statement**

From Section 1.1 it is evident that an important research goal is to accurately predict the yields, product properties and rates of coal devolatilization from measurements of the parent coal properties. Extensive research has been done on northern hemisphere (Carboniferous) coals (Baruah & Khare, 2007; Hanson *et al.*, 2002; Jamil *et al.*, 2004; Liu *et al.*, 2004), which are characterised by their high proportions of vitrinite, large amounts of reactive inertinite and very low ash contents. These coals have been shown to be very much different from South African

coals, due to their differences in depositional environment (Cadle *et al.*, 1993; Cai & Kandiyoti, 1995; Cairncross, 2001). In contrast, “Permian aged Gondwanaland” coals are mainly rich in inertinite with a high abundance of minerals, while some coal deposits (Grootegeluk and Venda-Pafuri districts) also display higher abundances of vitrinite-rich coals.

In addition, many of the studies concerning the devolatilization behaviour of coal samples have been conducted on coal particles in the micrometer size range (Alonso *et al.*, 2001; Cai & Kandiyoti, 1995; Hu *et al.*, 2004; Jamil *et al.*, 2004) and typically do not address the range of applicability for lump coal conversion technologies. Also, the inter-relationship of the devolatilization reactivity, molecular properties of the parent coal, char and tars has not yet been examined in detail for typical “Permian-aged Gondwanaland coals”. A detailed study is therefore proposed to investigate the devolatilization product propensity and the reaction rate properties of large coal particles (greater than 5 mm) based on the chemical-structural properties of the chemical components present (as obtained from advanced analytical techniques), in combination with conventional analyses of the devolatilization of typical South African coals.

### **1.3 Objectives of the investigation**

The main goal of this investigation is to evaluate the devolatilization behaviour of typical South African coals based on both a product-characteristic- and reaction-modelling perspective. In order to meet this aim the following objectives are formulated:

- Characterisation of the parent coals using conventional analytical methods which include proximate-, ultimate-, petrographic-, structural (physical)- and mineral analyses.
- Characterisation of the parent coals using advanced techniques such as NMR, XRD, HRTEM, MALDI-TOF, GC-MS etc. to assess chemical structures (aromatic- and aliphatic groups, molecular weight distribution, etc.). Correlation of the results with conventional properties in order to determine inter-relationships.
- Experiments in a self-fabricated reactor system to assess the influence of operating conditions on devolatilization product yield from large coal particles.

- Product quality assessment of the generated chars, gases and tars using a combination of both conventional- and advanced techniques such as proximate (char) analysis, ultimate (char) analysis, char morphology, NMR, XRD, HRTEM, MALDI-TOF, GC-MS etc. in order to obtain a fundamental understanding of the chemical- and molecular structures of the respective devolatilization products. Correlation of the results with parent coal properties to determine inter-relationships.
- Evaluation of the devolatilization rate of large coal particles in a large-particle thermogravimetric analyser and reaction modelling of the overall devolatilization process incorporating the parent coal properties, transport effects and kinetic rate parameters. The latter subsequently requires the evaluation of the intrinsic kinetic behaviour (small particles) of each coal with the aid of a laboratory scale thermogravimetric analyser, in order to determine suitable kinetic rate parameters for inclusion into the overall rate model.

### **1.4 Scope of the study**

In order to achieve the above-mentioned research objectives, a specified scope for this study was constructed. A schematic illustration of the scope of this investigation is provided in Figure 1.2. The thesis is subdivided into eight chapters (including this one). In Chapter 1 the relevant background and motivation for investigating the product distribution and kinetics of coal devolatilization is provided. This includes the formulation of the problem statement and respective objectives of this investigation. A complete theoretical background and literature survey with regard to the research field of coal devolatilization is presented in Chapter 2.

The literature study provides a better understanding of the nature, chemistry and fundamental characteristics of coal as well as the factors influencing this complex process. In brief this will include an overview of the chemistry and mechanisms of the devolatilization process as well as current industrial devolatilization operations. Furthermore, insight will be provided into the factors (coal properties and experimental operating conditions) affecting product yields, product distribution and devolatilization kinetics, respectively. In addition, a brief overview of the important kinetic- and transport models applied in devolatilization modelling will also be given.

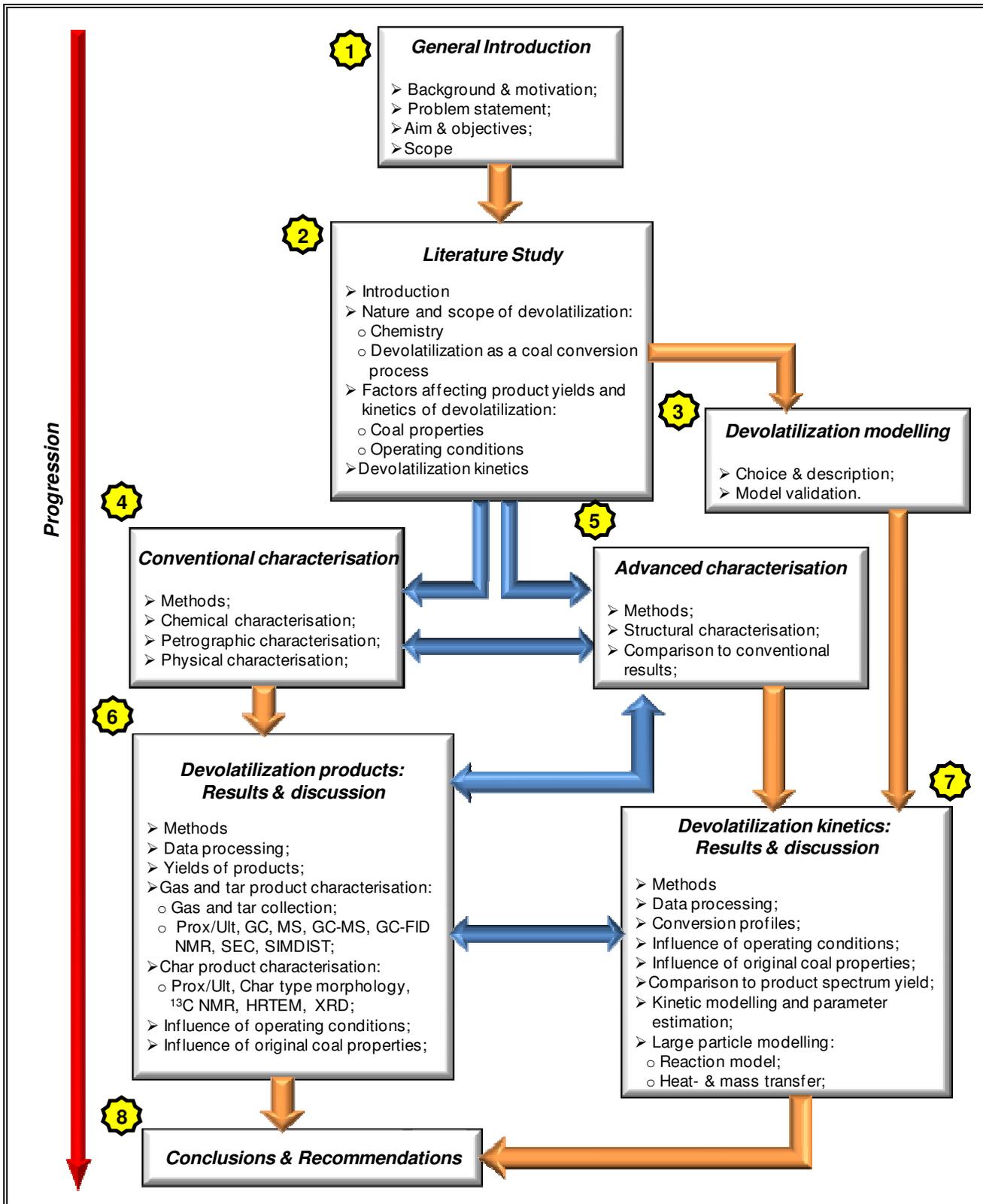


Figure 1.2 Scope of study.

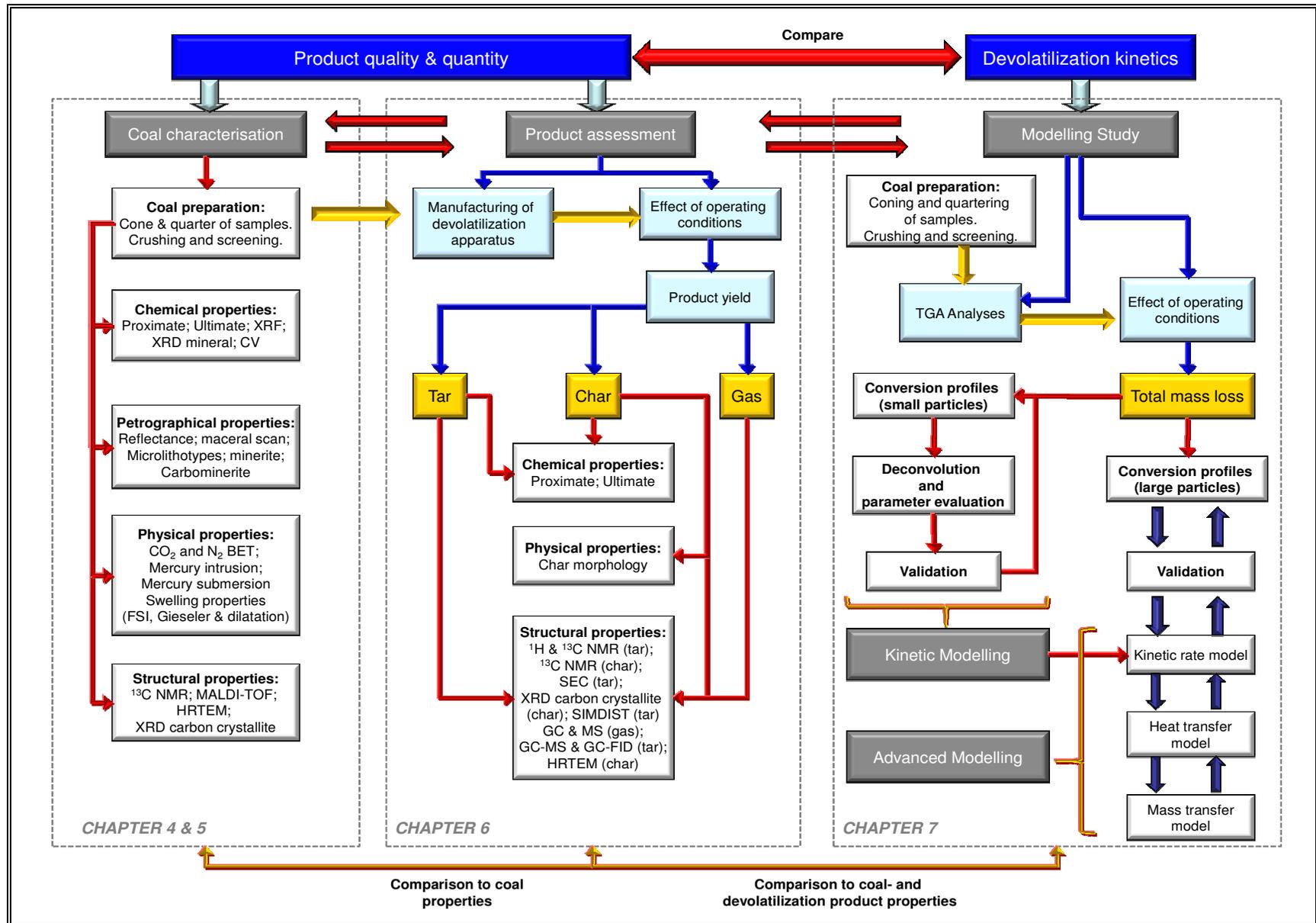


Figure 1.3 Simplistic research overview of chapters 4, 5, 6 and 7.

A discussion regarding the modelling of coal devolatilization and the choice of an appropriate kinetic particle model and transport model is provided in Chapter 3. This includes the validation procedure for mathematically solving the respective models. Chapters 4 and 5 focus on the characterisation (by conventional as well as advanced methods) of the parent coals used for the devolatilization investigation. An overview of the research scope of Chapters 4, 5, 6 and 7 is given in Figure 1.3. A discussion of the following topics is provided in Chapters 4 and 5:

- Sampling and coal preparation prior to coal analyses;
- Experimental techniques (Chapter 4 and 5);
- Chemical characterisation of the parent coals (Chapter 4);
- Petrographic characterisation of the parent coals (Chapter 4);
- Physical characterisation of the parent coals (Chapter 4);
- Advanced characterisation of the parent coals (Chapter 5);

Chapter 6 focuses on the production yields and analyses of the devolatilization products derived from the self-constructed tar capturing apparatus. An overview of the research scope of Chapter 6 is given in Figure 1.3. This chapter includes discussions on the following topics:

- Experimental techniques and protocols;
- Data processing of the results obtained;
- Yields of the different devolatilization products at different experimental conditions;
- Characterisation of the devolatilization products on conventional and advanced basis
- Influence of experimental conditions, such as temperature, on the yield, product distribution and product characteristics of the formed products;
- Comparison between the characteristics of the formed devolatilization products and the original coal properties.

Chapter 7 focuses on the reaction rates, kinetics and modelling of the devolatilization process as outlined in Figures 1.2 and 1.3. The following topics are addressed in Chapter 7:

- Experimental techniques and protocols;
- Data processing of the results obtained and construction of conversion profiles;
- Influence of experimental conditions on the reaction rate of each coal;
- Influence of parent coal properties on the reaction rate of each coal;

- Kinetic modelling of the reaction rate results and derivation of the important kinetic parameters;
- Incorporation of derived kinetic data into an overall large particle model including transport effects;
- Validation of modelling results.

Finally, Chapter 8 provides a summary of the important conclusions made during the investigation and gives an outlook and suggestions for future work.

### ***Bibliography***

Alonso, M.J.G., Borrego, A.G., Alvarez, D. & Menéndez, R. 1999. Pyrolysis behaviour of pulverised coals at different temperatures. *Fuel*, 78:1501-1513.

Alonso, M.J.G., Alvarez, D., Borrego, A.G., Menéndez, R. & Marbán, G. 2001. Systematic effects of coal rank and type on the kinetics of pyrolysis. *Energy & Fuels*, 15(2):413-428.

Arenillas, A., Rubiera, F., Pevida, C. & Pis, J.J. 2001. A comparison of different methods for predicting coal devolatilization kinetics. *Journal of Analytical and Applied Pyrolysis*, 58-59: 685.

Baruah, B.P. & Khare, P. 2007. Pyrolysis of high sulphur Indian coals. *Energy & Fuels*, 21(6):3346-3352.

Bunt, J.R. & Waanders, F.B. 2008. Identification of the reaction zones occurring in a commercial-scale Sasol-Lurgi FBDB gasifier. *Fuel*, 87:1814-1823.

Bunt, J.R. & Waanders, F.B. 2009. Pipe reactor gasification studies of a South African bituminous coal blend. Part 1-Carbon and volatile matter behaviour as function of feed coal particle size reduction. *Fuel*, 88:585-594.

Cadle, A.B., Cairncross, B., Christie, A.D.M. & Roberts, D.L. 1993. The Karoo basin of South Africa: type basin for the coal-bearing deposits of southern Africa. *International Journal of Coal Geology*, 23:117-157.

Cai, H.-Y. & Kandiyoti, R. 1995. Effect of changing inertinite concentration on pyrolysis yields and char reactivities of two South African coals. *Energy & Fuels*, 9(6):956-961.

Cairncross, B. 2001. An overview of the Permian (Karoo) coal deposits of southern Africa. *African Earth Sciences*, 33:529-562.

Collin, G. 1985. *Erdöl und Kohle-Erdgas Petrochem. (German journal)*, 38(11):489-496.

DOE (Department of Energy). 2012. South Africa Yearbook 2005/2006. <http://www.energy.gov.za/coal> Date of access: 12 September 2012.

Eberhard, A. 2011. The future of South African coal: market, investment, and policy challenges. Program on Energy and Sustainable Development, Stanford. [http://iis-db.stanford.edu/pubs/23082/WP\\_100\\_Eberhard\\_Future\\_of\\_South\\_African\\_Coal.pdf](http://iis-db.stanford.edu/pubs/23082/WP_100_Eberhard_Future_of_South_African_Coal.pdf). Date of access: 12 September 2012.

EIA (Energy Information Administration). 2011. Country analysis briefs: South Africa. <http://www.eia.doe.gov/> Date of access: 12 September 2012.

Gürüz, G.A., Ücetepe, Ü. & Durusoy, T. 2004. Mathematical modelling of the thermal decomposition of coal. *Journal of Analytical and Applied Pyrolysis*, 71:537-551.

Hanson, S., Patrick, J.W. & Walker, A. 2002. The effect of coal particle size on pyrolysis and steam gasification. *Fuel*, 81:531-537.

Horsfall, D.W. 1993. Coal Preparation and Usage. Parklands : Coal Publications (Pty) Ltd. 64p.

Hu, H., Zhou, Q., Zhu, S., Meyer, B., Krzack, S. & Chen, G. 2004. Product distribution and sulphur behaviour in coal pyrolysis. *Fuel Processing Technology*, 85:849-861.

Jamil, K., Hayashi, J. & Li, C.-Z. 2004. Pyrolysis of Victorian brown coal and gasification of nascent char in CO<sub>2</sub> atmosphere in a wire-mesh reactor. *Fuel*, 83:833-843.

Kandiyoti, R., Herod, A.A. & Bartle, K.D. 2006. Solid fuels and heavy hydrocarbon liquids. London : Elsevier Ltd. 353p.

Khan, M.R. 1989. A literature survey and an experimental study of coal devolatilization at mild and severe conditions: influences of heating rate, temperature, and reactor type on products yield and composition. *Fuel*, 68:1522-1530.

Ko, G.H., Peters, W.A. & Howard, J.B. 1987. Correlation of tar yields from rapid pyrolysis with coal type and pressure. *Fuel*, 66:1118-1122.

Kristiansen, A. 1996. Understanding coal gasification. London : IEA Coal Research. 70 p.

Liu, Q., Hu, H., Zhou, Q., Zhu, S. & Chen, G. 2004. Effect of inorganic matter on reactivity and kinetics of coal pyrolysis. *Fuel*, 83:713-718.

Menendez, R., Bermejo, J. & Figueiras, A. 2000. Chapter 5 in H. Marsh and F. Rodriguez-Reinoso eds *Science of Carbon Materials*, Universidad de Alicante, Spain.

Miura, K. 2000. Mild conversion of coal for producing valuable chemicals. *Fuel Processing Technology*, 62:119-135.

Murakami, H. 1987. *Nenryo Kyokai-Shi (Japanese journal)*, 66(6):448-458.

Prevost, X.M. 2010. Unpublished SA coal statistics. Pretoria: DME / XMP Consulting. (Unpublished)

Schobert, H.H. & Song, C. 1995. Non-fuel uses of coals and the synthesis of chemicals and materials. *Fuel*, 75(6):724-736.

Schobert, H.H. & Song, C. 2002. Chemicals and materials from coal in the 21st century. *Fuel*, 81:15-32.

Solomon, P.R. & Hamblen, D.G. 1985. Chapter 5: Pyrolysis in R.H. Schlosberg ed *Chemistry of coal conversion*, New York : Plenum press. p. 121-251.

South Africa. 2011. Electricity Regulations on the Integrated Resource Plan 2010-2030. Notice (9531). *Government gazette*, 34263:2, 6 May.

Van Dyk, J.C., Keyser, M.J. & Coertzen, M. 2006. Syngas production from South African coal sources using Sasol-Lurgi gasifiers. *International Journal of Coal Geology*, 65:243-253.

WCI (World Coal Institute). 2012a. Uses of coal. <http://www.worldcoal.org>. Date of access: 20 July 2012.

WCI (World Coal Institute). 2012b. Coal Facts. <http://www.worldcoal.org>. Date of access: 20 July 2012.

Wittcoff, H.A. & Rueben, B.G. 1996. Industrial organic chemicals. 2<sup>nd</sup> ed. New York: Wiley. 560p.