



6

Product yield and quality assessment from coal devolatilization

6.1 *Introduction*

The evaluation of the quality and properties of devolatilization products requires the use of an appropriate experimental system for the production of coal derived tars, gases and chars. Knowledge of the quality and quantity of different products obtained during the process of devolatilization can provide valuable insight into further processing potentials of said products for a certain coal. In this chapter an overview of the experimental procedures and analytical methods for assessing both devolatilization product yield and -quality will be given. The presentation and discussion of the subsequent results obtained is also included within this chapter. An overview of the materials used within this investigation is provided in Section 6.2, while Section 6.3 addresses the selection and preparation of coal particles suitable for the study. A detailed discussion of the particular experimental system used for producing devolatilization products is provided in Section 6.4. This includes a discussion of the relevant methods used for recovering the different products as well as the analytical techniques performed in order to assess the characteristic properties of the different products. This is subsequently followed by the presentation and discussion of the results obtained in Section 6.5. The chapter is concluded in Section 6.6, with a summary of some important conclusions made during this investigation.

6.2 *Materials used*

6.2.1 *Coals*

Three non-caking coals from the Witbank coalfields (seams 2, 4 and 5) as well as one caking coal from the Venda-Pafuri coalfield in the Limpopo province was used to assess coal

devolatilization behaviour of typical South African coals. The names of the four coals are omitted and conveniently annotated by the following (Chapter 4):

- Coal INY (seam 2, Witbank coalfield);
- Coal UMZ (seam 4, Witbank coalfield);
- Coal G#5 (seam 5, Witbank coalfield);
- Coal TSH (Venda-Pafuri coalfield);

An overview of the characteristic properties of these four coals, as obtained from both conventional and advanced analytical techniques, was provided in Chapters 4 and 5, respectively. A mean coal particle size of 5 mm and 20 mm, respectively, was used for all experiments. The particle selection methodology is discussed in more detail in Section 6.3.

6.2.2 Gas

The evaluation of coal devolatilization behaviour requires the use of an inert carrier medium. The use of an inert gas has a two-fold application: (1) ensuring that no reactive gas such as oxygen is in contact with the coal particles, and (2) the removal of formed product gases from the coal particle to ensure the minimization of any possible secondary surface reactions. For this purpose, ultra pure N₂ gas (ultra high purity grade: 99.999%; product no.: 511204-SE-C), as supplied by African Oxygen (AFROX), was chosen as carrier gas.

6.2.3 Solvents and analytical compounds

A number of solvents and analytical reagents were used for sample preparation, product recovery as well as product analysis. A summary of the solvents and analytical compounds used for this investigation is provided in Table 6.1. Information regarding the chemical grade, specification, manufacturer/provider and the application purpose of the specific solvent and/or analytical reagent is also included in Table 6.1. The use of each solvent and analytical reagent will be elaborated on in more detail in the following relevant sections of this chapter. Mercury was used as analytical reagent during coal particle selection (Section 6.3), while acetone and toluene were used for capture and recovery of tar generated from each experiment.

Table 6.1 Solvents and analytical compounds used.

Chemical entity	Purity	CAS number	Provider	Purpose
Mercury	≥ 99.5%	7439-97-6	ACE chemicals	Analytical reagent
Acetone	≥ 99.5%	67-64-1	ACE chemicals	Solvent
Toluene	≥ 99.5%	108-88-3	ACE chemicals	Solvent
Dichloromethane	99.9%	75-09-2	Merck	Analytical solvent
d-CDCl ₃	≥ 99.96%	865-49-6	Sigma-Aldrich	Analytical solvent
TMS	≥ 99.96%	75-76-3	Sigma-Aldrich	Internal standard
TKS	≥ 97%	4098-98-0	Sigma-Aldrich	Internal standard
Cr(acac) ₃	97%	21679-31-2	Sigma-Aldrich	Analytical reagent
NMP	≥ 99%	872-50-4	Sigma-Aldrich	Analytical solvent
HF	48 vol. %	7664-39-3	ACE chemicals	Analytical reagent
HCl	32 vol. %	7647-01-0	ACE chemicals	Analytical reagent
Samarium(II)iodide	0.1 M in THF	32248-43-4	Sigma-Aldrich	Analytical reagent

For analytical purposes, dichloromethane was used as analytical solvent for the GC-MS and GC-FID analyses conducted on the recovered coal tars. For NMR analyses conducted on the obtained tars, deuterated chloroform (d-CDCl₃) and tetrakis(trimethylsilyl)silane (TKS) with the addition of chromium(III) acetylacetonate (Cr(acac)₃) as a relaxation agent, were used (Section 6.4.3). N-methyl-2-pyrrolidinone (NMP) was used as eluent during SEC analyses on the tars (Section 6.4.3). Finally HF, HCl and SmI₂ were used during the preparation of coal chars for advanced analyses (Section 6.4.3), similar to what was done for the raw coal samples (Chapter 5).

6.3 Coal particle preparation and selection

6.3.1 Sample preparation

A full account of the coal sample preparation has been described in detail in Section 4.3. Two particle size ranges (i.e.: 5 mm and 20 mm) were used to investigate coal devolatilization behaviour of large coal particles. Coal particles with an average size range of 5 mm (-5.6 + 4.75 mm screening cut) were obtained by screening the -10 mm size fraction that was generated

during the crushing of the cone and quartered sub-samples of each coal. The selection and preparation of the 20 mm coal particles were done by manual selection and mercury submersion techniques as described in the text to follow.

6.3.2 Hand selection and grinding of larger particles

Coal particles in a size range of approximately 20 mm were hand-selected based on the content of vitrinite and inertinite macerals as obtained from petrographical analyses (Chapter 4). A measuring grid of 20 mm x 20 mm was used to ascertain the correct particle size. Rough edges on the particles were rounded down with the aid of pliers to produce particles that are approximately spherical (sphericity between 0.8 and 0.9). This method has also been previously applied by Beukman (2009) and Van der Merwe (2010a).

6.3.3 Mercury submersion tests

The sole use of qualitative methods for selection of coal particles, was further refined by the use of mercury submersion. Mercury submersion tests were performed on single 20 mm coal particles in order to establish the true/particle density of each coal particle. Particles for devolatilization experiments were further selected based on the comparison between particle density obtained from mercury submersion and particle density as obtained from mercury porosimetry (Section 4.6.1.3). A schematic overview of the mercury submersion test-rig is provided in Figure 6.1.

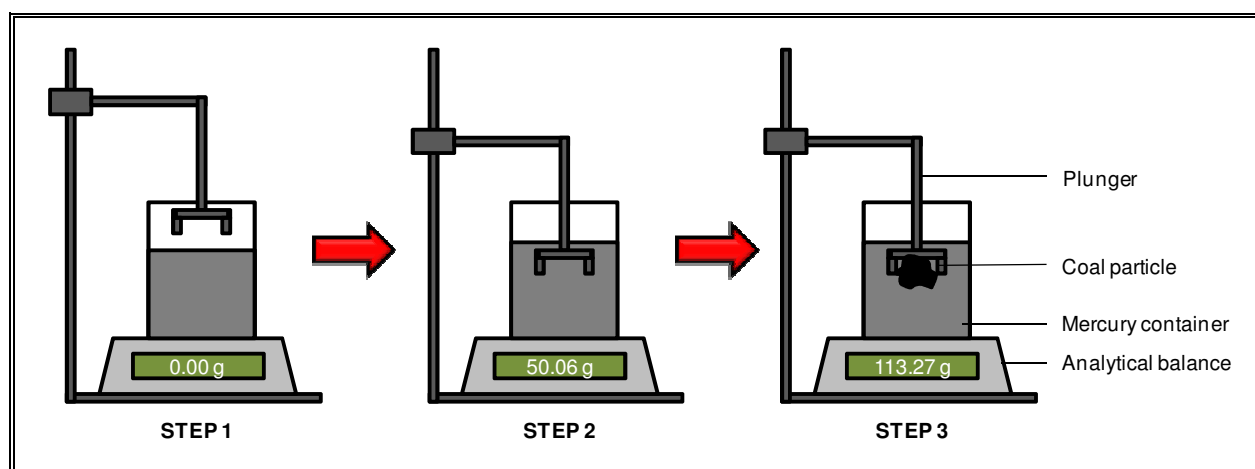


Figure 6.1 Mercury submersion test-rig.

The method consists of submerging a coal particle with a plunger in mercury and measuring the submerged weight, m_{sb} . A plunger is used to prevent the coal particle from floating due to its lower density compared to mercury. The plunger alone is also submerged, in order to account for the effect of the plunger weight during the analyses. The subsequent weight obtained from submerging only the plunger is annotated as m_{pl} . The particle density can therefore be determined from Archimedes' principle and the weight of the particle, m_p by Equation (6.1) (Van der Merwe, 2010a):

$$\rho_p = \left(\frac{m_p}{m_{sb} - m_{pl}} \right) \cdot \rho_{f,Hg} \quad \text{Equation (6.1)}$$

Details of the derivation of the above equation are provided elsewhere (Van der Merwe, 2010a). A total of 150 particles for each coal were mercury submerged in order to determine a density distribution curve as a selection guide. Particles selected for devolatilization studies were confined to a particular density range, which can be described by the following equation:

$$\rho_{coal} = \rho_{avg} \pm 2\sigma \quad \text{Equation (6.2)}$$

An overview of the results of the mercury submersion tests are provided in Section 6.5.

6.4 Experimental equipment and -methodology

6.4.1 Experimental equipment

6.4.1.1 Overview

A large number of strategies currently exist for evaluating the devolatilization behaviour and devolatilization products of carbonaceous substances. Some of these systems include: thermogravimetric equipment, fixed- and fluidised bed reactors, entrained flow (drop tubes) reactors and versatile wire-mesh (heated grids) instruments (Kandiyoti *et al.*, 2006). A brief overview of the above-mentioned experimental equipment has been provided in Chapter 2.

A versatile fixed-bed reactor system was designed and developed for this particular study to mainly adhere to the constraints of heating rate and particle size. The apparatus (henceforth indicated as the TCR (tar capturing reactor) facility) was constructed to conform to the following main operating specifications:

- The ability to capture gaseous and liquid products from devolatilization and other possible reactions;
- The ability to be operated in either isothermal or non-isothermal mode;
- The ability to be handle large sample sizes with reference to both mass (1 kg) and particle size (35 mm);
- The ability to be handle temperatures up to 900 °C;
- Reactor flexibility with respect to change in carrier- or reactant gas.

6.4.1.2 Operation of TCR facility

A schematic overview, with additional photographic details, of the TCR facility is provided in Figure 6.2. From the Figure it can be seen that the TCR facility consists of three main sections i.e.; the sample loading section, reactor section and the product capture and analysis section. The main segments of the loading- and reactor section was constructed of ASTM 316 Grade stainless steel, due to the fact that the apparatus had to endure moderate to high temperatures. The operation of the TCR facility entails the loading of a solid sample (coal in this case) into the sample loading section (pipe dimension: 2" schedule 40S) of the apparatus. The reactor section (pipe dimension: 3" schedule 80S, length: ± 0.5 m, capacity: ± 3 L) of the apparatus can be operated in either isothermal or non-isothermal mode by selective programming and operation of the installed high temperature Lenton[®] TMH 12/100/940 three-zone oven/furnace. The furnace/oven is lifted over the reactor section with the aid of a guide rail frame connected to a pulley-winch system. Once lifted over the reactor, the furnace can be switched on to start the respective heating cycle for warming the reactor. Reactant- or carrier gas is introduced at the bottom of the reactor and is subsequently warmed up to the required experimental temperature with the aid of a gas warming coil. In addition, a purge gas stream has been installed for flushing the sample loading section with inert/reactant gas prior to sample introduction and reactor warm-up. This ensures the homogenous distribution of reactant/inert gas within the system once the sample is introduced within the reactor section.

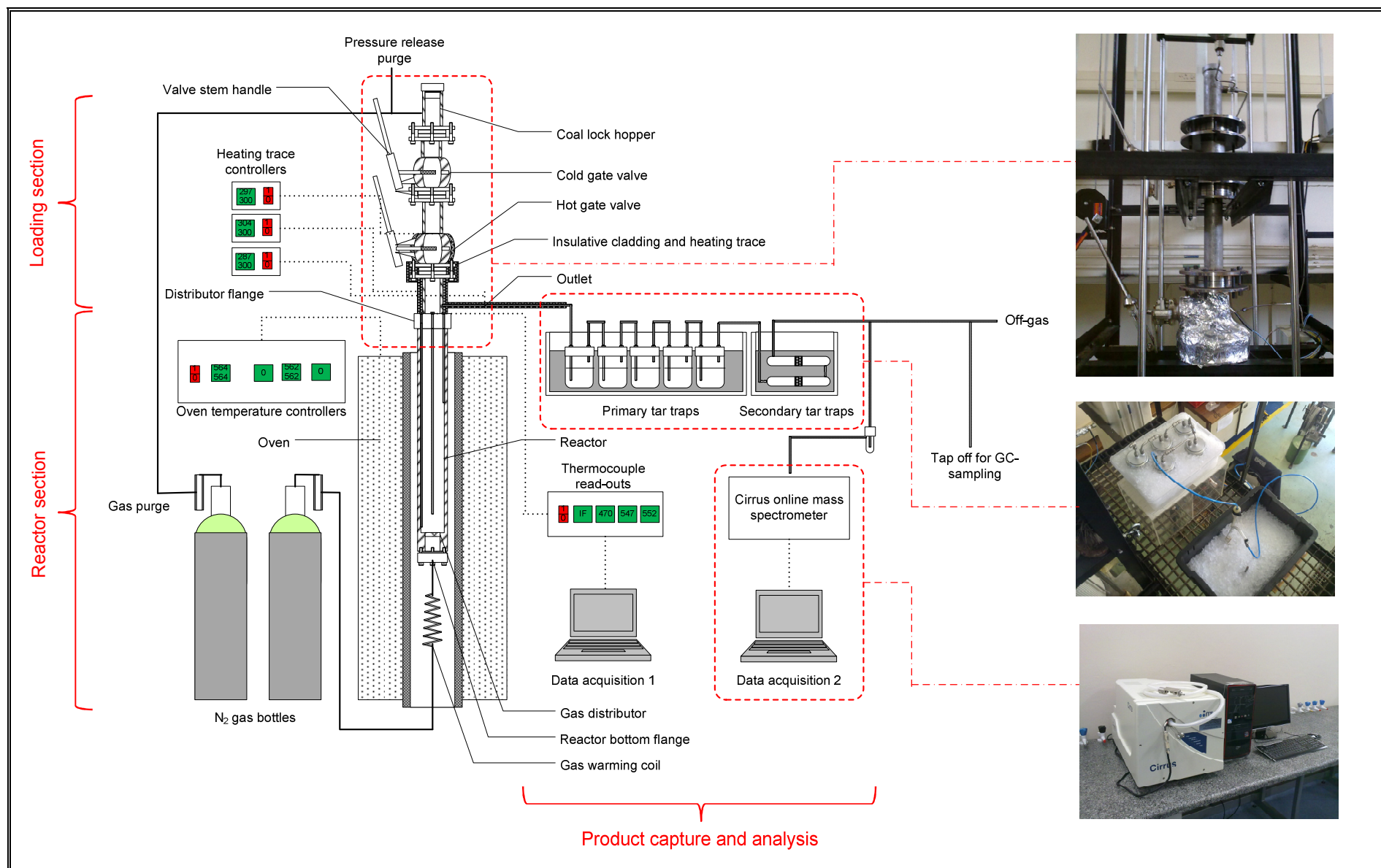


Figure 6.2 Schematic overview of TCR facility.

Gas introduced into the reactor is distributed evenly with the aid of a gas distributor plate fixed to the reactor bottom flange. Experimental temperatures within the reactor were monitored individually by three K-type thermocouples situated at different heights i.e.: 5 mm, 50 mm and 0.4 m from the gas distributor plate. Thermocouple readings were logged continuously on Data acquisition interface 1 to evaluate when the reactor temperature stabilises and reaches steady state. Once the required experimental temperature is reached, the coal sample is introduced within the reactor pipe via a two phase gate valve system (ASTM 304 stainless steel, maximum operating temperature and pressure: 400 °C and 1 bar). The cold gate valve ensures that the loaded coal sample does not come into contact with the warm reactor section, and provides the temporary storage of the sample before sample introduction. In contrast, the hot gate valve provides the direct link between the coal loading section and the reactor section. Both valves have been fitted with valve stem handle mechanisms to ensure that the valves can be quickly opened and closed during sample introduction and to minimize product gas losses. The introduced sample forms a fixed bed on the gas distributor plate. The evolved product gases and tars travel through the reactor to the outlet pipe, where the tars can be captured and the product gas cleaned.

A wide variety of tar capturing strategies are currently available which include direct gas bag sampling, dry- and cold trapping, solvent washing, impingement, electrostatic precipitation, solid-phase adsorbent, etc. techniques (Baruah & Khare, 2007; Dufour *et al.*, 2007; Hu *et al.*, 2004; López *et al.*, 2010; Luo *et al.*, 2010; Miura *et al.*, 1992; Sathe *et al.*, 2002; Wang *et al.*, 2010; Watt *et al.*, 1996). Some of the traditional methods of coal tar sampling are based on cold trapping techniques with the use of absorptive solvents and/or impingers (Dufour *et al.*, 2007).

For this particular system, the outlet pipe (1/4", ASTM 316 Stainless steel) from the reactor section is connected to a series of primary- and secondary cold product traps for scrubbing the product gas and retaining any formed liquid products. Schematic representations of the different stages of tar trapping are shown in Figure 6.3. The primary tar traps consist of glass washing bottles with aluminium caps to which 1/4" stainless steel pipes were fitted. The glass bottles are filled with the necessary solvent for dissolving the liquid products generated during the experiment.

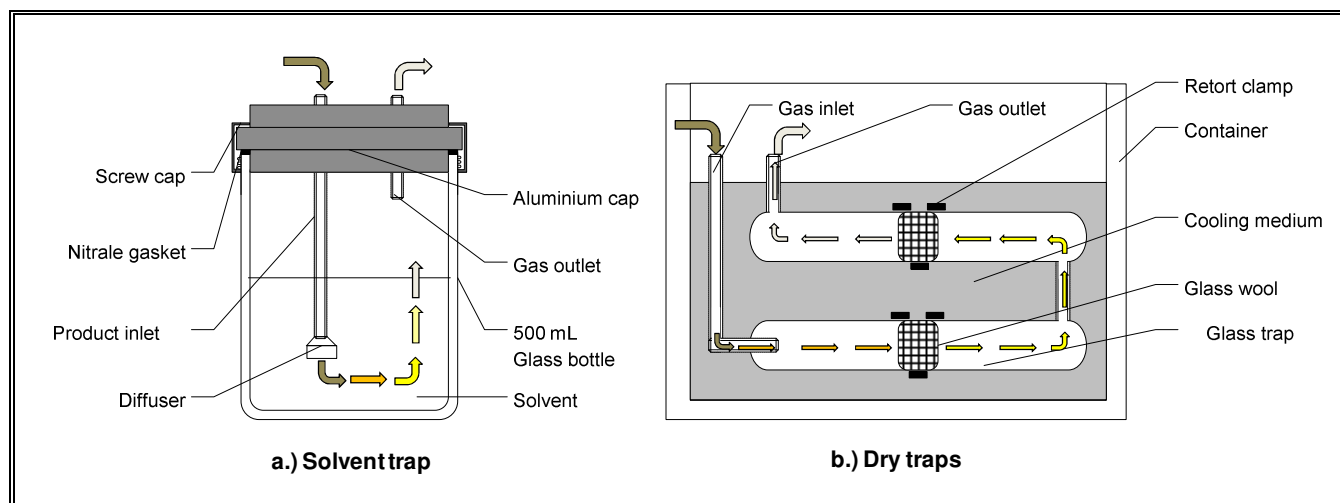


Figure 6.3 Schematic representation of the a.) primary solvent trap and b.) secondary dry traps.

The secondary dry traps were also manufactured of glass, with a glass wool packing to filter out any volatile liquid products still contained in the product gas. The cleaned product gas is subsequently sent to an online mass spectrometer to evaluate the formed gas species, while gas bag samples captured from the tap off line are analysed by a separate gas chromatograph. The exposed flange and reactor pipe, the hot gate valve and the outlet pipe close to the reactor are controlled at a constant temperature of above 300 °C with the aid of fibre glass heating trace and insulative fibre glass- and aluminium cladding. This is done to prevent the occurrence of any cold spots during experimentation which can cause the generated tars to condense within the system.

After an experiment has been conducted the furnace can be lowered to allow the reactor to cool down naturally while inert gas flushes the system. The primary- and secondary traps can be removed and the retained liquid products can be recovered with methods that will be described in Section 6.4.3. Once the reactor has cooled down to room temperature, the bottom flange can be disconnected and the char within the reactor can be removed.

6.4.2 Experimental plan and protocol

6.4.2.1 Experimental conditions

Experimental conditions were chosen to closely resemble typical coal devolatilization conditions. A summary of the experimental conditions used for this investigation is given in Table 6.2. A low

and a high experimental temperature (450 °C and 750 °C) was chosen to investigate the effect of temperature on product yield and quantity in the primary degradation regime of devolatilization (Ladner, 1988). It has been shown that an increase in heating rate increases both volatile and tar yield (Gibbins & Kandiyoti, 1989; Gibbins-Matham & Kandiyoti, 1988; Kandiyoti *et al.*, 2006; Ladner, 1988). In order to maximise tar yield, the reactor section was heated to the desired operating temperature prior to sample introduction. This was done due to the fact that the furnace only has a maximum heating rate of 25 °C/min when in non-isothermal operation and that the maximum heating rate of a coal particle is normally restricted by its thermal properties. Typical, lump-size particles were chosen to investigate the effect of particle size, while a relatively small sample mass was used to ensure a minimal packing depth within the reactor.

Table 6.2 TCR experimental conditions.

Variable	Range specification or composition
Coal feedstocks	INY, UMZ, G#5 and TSH
Coal particle size	5 mm and 20 mm
Operating temperature	Isothermal reactor temperatures of 450 °C and 750 °C
Heating trace temperature	≥ 300 °C
Operating pressure	Loading section: Slight overpressure Reactor section: Atmospheric
Gases used	Nitrogen (N ₂)
Gas composition	99.999% Ultra high purity gas
Total gas flow rate	± 8 L/min
Gas residence time within reactor	≤ 20 s
Sample mass	60 g for both particle sizes
Coal residence time	2 hours

The coal sample was devolatilized for a total of 2 hours before cooling the reactor. A high total gas flow rate was chosen to reduce any external diffusion effects as well as secondary reactions, and to comply with a differential reactor. After the coal sample was introduced to the warm reactor, the loading section extending to the hot valve was slightly pressurized (± 1 bar (g)) to ensure that no product gas or tar could leak to the coal loading section.

6.4.2.2 Experimental protocol

The whole TCR facility was purged from air with N₂ prior to and during reactor warm-up, while the two-phase valve system was kept open. Once the required experimental temperature was reached, the bottom hot gate valve was locked, followed by the top cold valve. Hereafter the required coal sample was loaded into the coal lock hopper and continuously flushed with the N₂ purge gas. Before coal sample was introduction into the reactor, the primary- and secondary tar traps were assembled and respectively filled with solvent and glass wool. Some of the more common solvents for tar capturing include: acetone (Aiken *et al.*, 1983), dichloromethane (Oesch *et al.*, 1996), mixture of ethanol and tetrahydrofuran (Beall & Duncan, 1980), methylene chloride (Mudge *et al.*, 1987), toluene (Paisley, 1993), methanol (Arauzo *et al.*, 1997), 2-propanol (Dufour *et al.*, 2007) and chloroform and methanol (Sathe *et al.*, 2002; Li *et al.*, 1993a & b). Toluene was used as capturing solvent in the primary tar traps of the TCR, due to its capability of dissolving most organic compounds and the fact that it does not dissolve in water. Glass wool was separately weighed and packed into the glass tubes of the secondary traps. Furthermore, cooling mediums for cold traps typically include ice at 0°C (Dufour *et al.*, 2007), mixtures of 2-propanol and liquid nitrogen at -60°C (Dufour *et al.*, 2007), ice water and CaCl₂ at -2°C (Shamsi, 1996), acetone and dry ice at -68°C (Shamsi, 1996), dry ice and methanol at -70°C (Hayashi *et al.*, 1994). An ice-acetone mixture was used as cooling medium for both primary- and secondary tar traps. Once the traps were assembled, they were connected to the outlet pipe of the reactor and the mass spectrometer was switched on. The inert gas was allowed to flush the reactor and tar trap phases for an additional 15 minutes to ensure the removal of any air still contained in the tar traps. Finally, the gate valves were opened and the coal sample was dropped into the reactor. Gas samples for gas chromatography were acquired at set intervals during each experimental run by collecting the off-gas in 1 L and 5 L Tedlar sample bags respectively. The volumetric flow rate of the gas was measured at regular time intervals with a soap-bubble meter before and after coal sample introduction.

6.4.3 Product recovery and yield assessment

After two hours the furnace was switched off and lowered to allow the reactor to cool down. This included the disconnection of the primary- and secondary tar traps from the outlet pipe. The tar-toluene solution in the primary tar traps was removed and the traps thoroughly cleaned with clean toluene before subjecting it to a Dean-Stark distillation technique (ASTM D95, ISO 3733)

(ASTM, 2010; ISO, 1999) in order to remove any forms of inherent- and pyrolytic water from the product. Hereafter, toluene was removed by application of rotational vaporization in a Buchi Rotavap R-II. A water bath temperature of 60°C and the sequential lowering of the internal pressure to 27 mbar were used to evaporate the toluene from the tar-toluene mixture. Once most of the toluene was evaporated, the retained tars were kept at a fixed temperature of 60°C and a pressure of 27 mbar for 5 minutes to ensure that all the toluene was completely removed. The glass wool removed from each secondary trap was dried overnight to remove any condensed toluene and subsequently reweighed. The yield of tar from each experiment was calculated by the following equation:

$$wt.\%_{tar} = \frac{(m_{rotavap} + m_{gw,1} + m_{gw,2})}{m_{coal}} \times 100 \quad \text{Equation (6.3)}$$

Water yields were determined directly after Dean-Stark distillation by measuring the amount of water produced with a minute volumetric flask. Due to its instability and uncertainty in prediction with external conditions, water yields were not reported for this investigation. In addition, char yield could be determined from the amount of char weighed after the char was removed from the reactor. Total gas yield was quantified by calculation of the area under the total evolution profile of each gas species identified by the gas chromatograph. A detailed account of the calculation is provided in Section 6.4.4.2.

6.4.4 Product quality assessments

6.4.4.1 Overview of quality assessments

A quality (composition and structure) assessment of devolatilization products provides an additional perspective on the difference and importance of products generated at different operating conditions. A number of methods for evaluating the composition and structure of products obtained from coal devolatilization exist. Conventional- and advanced analytical techniques were employed in order to evaluate characteristic properties of typical devolatilization products which include: tar, gas and char. A summary of the analytical techniques used, as well as the laboratories responsible is provided in Table 6.3. Details

regarding the preparation- and experimental methodology of each respective analysis are provided in the relevant text to follow.

Table 6.3 Analyses conducted on obtained devolatilization products.

<i>Characteristic property</i>	<i>Analyses</i>	<i>Products to be analysed</i>	<i>Laboratory responsible</i>
Chemical	Proximate	Char	Advanced Coal Technology
	Ultimate	Char	Advanced Coal Technology
Physical	Char morphology	Char	University of Witwatersrand
Molecular	GC (-TCD and -FID)	Gas	North West University
	MS	Gas	North West University
	GC-MS & GC-FID	Tar	Sasol Infrachem®
	SIMDIST	Tar	Sasol Infrachem®
	SEC	Tar	Sasol Technology
	^1H & ^{13}C NMR	Tar	University of Stellenbosch
	Solid state ^{13}C NMR	Char	University of Stellenbosch
	XRD carbon crystallite	Char	XRD Analytical & Consulting
	HRTEM	Char	University of Cape Town

6.4.4.2 Gas analysis

Gases evolved during the devolatilization studies were constantly monitored and analysed with the aid of gas chromatography and mass spectrometry.

Mass spectrometry (MS):

Gas evolved during each of the devolatilization experiments was constantly monitored online with the aid of mass spectrometry. A CirrusTM (Serial no.: LM92-00510020) atmospheric pressure gas monitoring mass spectrometer with multiple inlet system was used for this purpose. For optimized sensitivity and long term stability, the mass spectrometer is fitted with a precision built quadrupole analyzer with a closed ion source, a triple mass filter, as well as a dual (Faraday and secondary electron multiplier) detector system. Although the mass

spectrometer is capable of measuring molecular masses of up to 300 m/z, it was set to only acquire results for products with molecular masses up to 100 m/z. This was done due to the fact that larger molecular weight compounds are retained in the product traps of the TCR, and due to the uncertainty of product identification at higher molecular masses. A detector gain of 30 and an accuracy setting of 4 were used for all experiments, while product gas was introduced into the mass spectrometer at atmospheric conditions. Mass species evolution was measured in partial pressure intensity (Torr). Data acquisition was performed every four seconds on the Process Eye Professional 8.0 acquisition software.

Gas chromatography (GC):

In addition to online MS measurements, gas samples collected in Tedlar bags during each experimental run was subjected to gas chromatography analysis on a SRI 8610C multiple gas chromatograph. The relevant instrument information, oven programme, carrier gas flow rates and detector temperatures are listed in the Table 6.4.

Table 6.4 Experimental conditions used for gas chromatography.

GC conditions	Specification
Inlet temperature	25 °C
Injection volume	0.5 µL
Detector cell temperatures	TCD1: 300 °C TCD2: 150 °C
Carrier gases and gas flow rates	FID: He (25 psi and 20 mL/min). Methanizer: H ₂ (20 psi and 25 mL/min) and Air (5 psi and 250 mL/min). TCD1: He (25 psi and 20 mL/min). TCD2: Ar (7 psi and 10 mL/min)
Oven programme	Hold for 7 min at 60 °C, 60 °C to 280 °C at 15 °C/min, hold for 20 min at 280 °C.
Calibration standard and unit of measure	Refinery gas #1 and mol. %

The chromatograph was fitted with three packed columns i.e.: 6' HayeSep D, 6' 13X molecular sieve and 3' 5 Å molecular sieve (all with an outer diameter of 1/8'), to facilitate the necessary separation of gaseous products. A flame ionization detector (FID) and two thermal conductivity detectors (TCD1 and TCD2) were used for quantifying the relevant amounts of gaseous products. The gas samples were injected manually, while the chromatographs were logged and stored by the Peak-382 acquisition software. A refinery gas standard was used for calibration (mol.%) and to evaluate the typical elution time windows for the expected hydrocarbon products, which include: O₂, N₂, CH₄, CO, CO₂, ethylene, ethane, C₃s (propylene, propane, propadiene, cyclopropane, methyl-acetylene), C₄s (isobutene, n-butane, isobutylene, 1,3-butadiene, cis-2-butene, trans-2-butene, butane-1), C₅s (isopentane, n-pentane) and C₆s (n-hexane, 4-vinyl-1-cyclohexene). The quantification of the total amount of gas produced involved the numerical estimation of the total amount of each individual gas species evolved during the course of the experiment. The total amount of gas species, *i*, (mol.%) evolved was estimated using Equation (6.4):

$$mol.\%_{i,Total} = \frac{1}{t_T} \int_0^t mol.\%_i dt \quad \text{Equation (6.4)}$$

Conversion to wt.% of the total coal mass could be accomplished by using the following equation:

$$wt.\%_{i,Total} = 100 \times mol.\%_{i,Total} \cdot \frac{n_T \cdot M_{r,i}}{m_{coal}} \quad \text{Equation (6.5)}$$

The numerical integration of the evolution curves according to Equation (6.4) was done with the aid of Origin 8.0 software.

6.4.4.3 Tar analysis

Simulated distillation (SIMDIST)

Simulated distillation provides a valuable way of determining the boiling point range of petrochemical products via gas chromatography. Knowledge of the boiling point distribution can provide insight into the composition of products (such as coal-derived tars) related to

petrochemical refining processes (ASTM, 2008). SIMDIST analyses were performed on all tar samples at Sasol Infrachem® according to the ASTM D2887 method. Samples were prepared by dissolving 200 mg tar in 2 mL HPLC-grade, dichloromethane (CH_2Cl_2). The SIMDIST procedure as outlined in the ASTM D2887 method is applicable to petrochemical fractions confined to a boiling range between 55.5°C and 538°C. Distillation measurements were performed on a high-temperature GC-FID fitted with an ARX 2887 Restek column (10m x 0.53 mm x 0.53 μm). Approximately 0.2 μL of the sample per analysis was injected into the GC column, while the GC oven program was operated as follows: (1) initial temperature of 40°C, (2) heating at 15°C/min to 540°C and (3) isothermal at 540°C for 10 minutes.

Gas chromatography-mass spectrometry and-flame ionization detection (GC-MS and GC-FID)

GC-MS and GC-FID analyses on the retained coal tars were carried out at Sasol Infrachem® using an Agilent 7890 GC equipped with a FID and an Agilent 7890N GC connected to a mass selective detector (MSD). For peak identification, GC-MS analyses were performed prior to GC-FID. Quantification of the inherent species of the tars was accomplished with the GC-FID. GC samples were prepared by dissolving approximately 200 mg of tar in 2 mL of dichloromethane (CH_2Cl_2). During analyses, about 0.2 μL of sample was injected into the respective systems at a split ratio of 100:1. An HP-PONA (PONA-paraffins, olefins, naphthenes and aromatics) petrochemical, fused silica column (100% dimethyl polysiloxane) with a 0.25 mm internal diameter and 0.25 μm phase thickness, capable of operating at a maximum temperature of ~350°C was used for both analyses. The detector- and injector temperatures were controlled at 280°C, while He was used as carrier gas with a flow rate of 1.2 mL/min. The column temperature was operated as follows: (1) 120°C for 10 minutes, (2) heating to 290°C at 5°C/min and (3) isothermal at 290°C for 30 minutes, or until all possible species have evolved. Helium and hydrogen gas were respectively used as carrier gases for the MS and FID. Only species with a relative abundance above 0.005 wt.% were taken into consideration for quantification of the tar components.

Size exclusion chromatography (SEC)

Size exclusion chromatography was conducted on all tar samples in order to obtain an estimate of the molecular weight distribution of each sample. SEC analyses were performed on an Agilent 1100 high-performance liquid chromatograph (HPLC) equipped with a 300 mm long (7.5

mm I.D.) PLgel mixed-E (Varian) GPC column and two detectors in series (UV-Visible light detector (UV-VIS) and refractive index detector (RID)). A constant column temperature of 80 °C and a flow rate of 0.5 mL/min were used during all analyses. Approximately 200 mg of each tar sample was dissolved in 1 mL of a suitable mobile phase. HPLC-grade N-methyl-2-pyrrolidone (NMP) was used for this purpose. The sample was diluted further by dissolving 200 µL of the first solution in an additional 1.3 mL of NMP. 10 µL of tar sample solution was injected into the column per analysis. A total analysis time of 30 min was found to be sufficient for each sample. NMP was degassed via an auto degasser prior to each analysis. For quantification purposes, the UV-VIS detector was set to multiple wavelengths (280 nm, 300 nm, 350 nm and 370 nm). The determination of the molecular weight distribution of each tar sample required the use of the necessary calibration standards. Ten polystyrene standards (molecular weight ranging from 162 g/mol to 19640 g/mol) from Varian were dissolved in NMP and used as external calibration for the SEC column. As NMP is opaque at 254 nm, calibration on the polystyrene standards was conducted at a UV-VIS wavelength of 260 nm, due to the partly transparent nature of NMP at this wavelength (Herod *et al.*, 2000). Although the system is equipped with a RID, it was not utilized for this investigation. A molecular weight calibration curve was constructed based on the peak molecular weights (M_p) and retention times (min) of each polystyrene standard. A detailed account of SEC calibration and mass estimation can be found elsewhere (Herod *et al.*, 2007; Kandiyoti *et al.*, 2006; Karaca *et al.*, 2004; Morgan *et al.*, 2005).

Solution state proton and carbon-13 nuclear magnetic resonance spectroscopy (^1H - and ^{13}C NMR)

Solution state proton (^1H) and carbon 13 (^{13}C) NMR analyses were conducted on all the tar samples using a Varian 600 MHz spectrometer. Samples were prepared similarly to the method proposed by Morgan *et al.* (2008a). For both ^1H and ^{13}C NMR, respectively, 20% (% w/v) of the analyte was dissolved in deuterated chloroform (d-CDCl_3). Tetrakis-(trimethylsilyl)-silane (TKS) was chosen as both the chemical shift- and quantitative reference for all the subsequent analyses, due to the highly volatile nature of tetramethylsilane (TMS) (Boiling point of $\pm 27^\circ\text{C}$) (Morgan *et al.*, 2008a). For calibration purposes, TKS was measured initially against the more commonly used TMS to assess the change in chemical shift for both ^1H - and ^{13}C NMR analyses. Chromium (III) acetyl acetonate ($\text{Cr}(\text{acac})_3$) was added as relaxation agent, in different concentrations to samples prepared respectively for proton (^1H) and carbon 13 (^{13}C) NMR analyses. An overview of sample concentrations and NMR operating parameters are

provided in Table 6.5. The effect of $\text{Cr}(\text{acac})_3$ concentration on NMR lock was conducted prior to sample analyses. PROTON (ZGPS) and CARBON (inverse gated) NMR microprograms were used for quantitative ^1H and ^{13}C NMR analyses, respectively. Acquired spectra were manually processed with the aid of the Spinworks 3.0 software. Typical aliphatic- and aromatic spectral regions as proposed by Andrésen *et al.* (2001), Díaz and Blanco (2003), Guillén *et al.*, (1998), Khan *et al.* 2003, López *et al.* (2010), Morgan *et al.* (2008a) and Wang *et al.* (2010) were used for quantification of peaks in the different NMR analyses. Typical chemical shift values of 0.5 ppm to 5 ppm for aliphatic functionalities and 6 ppm to 9 ppm for aromatic functionalities were used during quantitative ^1H NMR. For ^{13}C NMR the spectral regions are respectively given as: 0 ppm to 100 ppm (aliphatic) and 100 ppm to 160 ppm (aromatic). Further subdivisions of functionalities are provided in Section 6.5.3.

Table 6.5 Experimental parameters for NMR analyses.

Experimental parameters	Specifications	
	^1H NMR	^{13}C NMR
Varian microprogram (pulse sequence)	PROTON	CARBON (Inverse gated)
Sample concentration (% w/v)	20	20
$\text{Cr}(\text{acac})_3$ concentration (% w/v)	0.0-0.3	3
Reference material concentration (% w/v)	2	2
Solvent volume (mL)	1	1
Frequency (MHz)	600	150
Spectrum width (Hz)	9599.2	37718.1
Data points (K)	6.7	32
Digital resolution (Hz/point)	1.17	1.15
Pulse width (μs)	6.10 (90°)	9.10 (90°)
Acquisition (μs)	0.706	0.869
Number of transients	16	~ 30000

6.4.4.4 Char analysis

Chars obtained from the different coal samples were subjected to different analyses (proximate, ultimate, morphological, ^{13}C NMR, XRD and HRTEM) in order to investigate and relate the change in coal properties during a change in devolatilization conditions. Similar methods as

discussed in the relevant sections of Chapter 4 and 5 were followed to prepare the chars for the subsequent analyses. Proximate and ultimate analyses were performed on both the 5 mm and 20 mm chars, while only the 5 mm chars were used for the other analyses. For the advanced analyses, 5 mm particles were milled and sieved to an ultra-fine size fraction of -75 μm as discussed in Section 5.3.1.1.

Proximate and ultimate analysis

Char samples with a particle size range of -3 mm were used for both proximate and ultimate analyses. Preferential crushing in a ball mill was conducted in order to reduce the 20 mm chars to the particular size range. Ash, volatile matter and inherent moisture contents, were determined according to the SABS ISO 562:1998 (SANS, 1998), SABS ISO 1171:1997 (SANS, 1997) and SANS 5925:2007 (SANS, 2007) standards, respectively, while fixed carbon was determined by difference. The ISO 12902 (C-, H- and N content) and ISO 19759 (S content) standard procedures were followed to determine the relevant amounts organic elemental constituents of the chars (ISO, 2001 & 2006).

Char morphological analyses

The retained 5 mm char samples were subjected to char morphological analyses at the University of Witwatersrand, following the work done by Bailey *et al.* (1990), Bunt *et al.* (2009), Chabalala *et al.* (2011), Malumbazo *et al.* (2012) and Wagner (1998). The analysis was performed in order to quantify the proportion of porous and dense char constituents generated during the devolatilization experiments. Char samples were crushed to -1 mm and subsequently mounted in resin to produce the relevant petrographical blocks according to ISO standard for routine preparation (ISO 7404/2) (ISO, 1985). A Struers TegraForce-1 polishing machine was used for polishing the blocks, while the polished blocks were examined under a Leica DM4500P petrograph equipped with an oil immersion lens (Bunt *et al.*, 2009; Chabalala *et al.*, 2011; Malumbazo *et al.*, 2012). Examinations were performed at a magnification of 500x, while employing a point count analysis technique for assessing the relative proportions of char types within each sample block. More than 400 points were recorded per sample. For illustrative purposes, qualitative pictures of the respective char types were also recorded.

Solid-state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR)

The ultra-fine char samples were subjected to an extensive HCl/HF acid wash, similar to what was done for the parent coals (Section 5.3.1.1.). Demineralized char samples were further treated with Sml_2 under an inert atmosphere to eradicate the presence of any free radicals within the char structures (Section 5.3.1.1.). Solid-state ^{13}C NMR analyses were conducted at the University of Stellenbosch on chars produced at 450°C and 750°C. ^{13}C CP-MAS (Cross-Polarization Magic-Angle-Spinning) and DD experiments were performed with the aid of a Varian VNMRs 500 MHz two channel spectrometer containing 4 mm zirconia rotors and a 4 mm Chemagnetics TM T3 HXY MAS probe (Assumption, 2010). Similar operational parameters as outlined in Section 5.3.1.2 were used for the analyses of the chars. As for the parent coal samples, respective structural (aromatic- and aliphatic species) parameters were calculated from the integral values according to the method proposed by Solum *et al.* (1989a & 2001).

X-ray diffraction (XRD)-carbon crystallite analyses

XRD carbon crystallite analyses were performed on the demineralized char samples in order to evaluate the change in carbon crystallite structures during devolatilization. Co K α radiation was used for this purpose on the same apparatus as described in Section 4.5.1.1. Approximately 2 g of each of the demineralized char samples (produced at 450°C and 750°C for the four different coals) were provided for the analyses. An overview of the apparatus settings and analysis parameters used for the carbon crystallite analyses on the chars is provided in Table 5.2 of Section 5.3.1.3 (Okolo, 2010). A similar processing and calculation methodology as outlined in Section 5.3.1.3 was used to evaluate the carbon crystallite- and structural parameters of the chars (Feng *et al.*, 2003; Lu *et al.*, 2001; Lu *et al.*, 2002; Okolo, 2010; Takagi *et al.*, 2004; Trejo *et al.*, 2007; Oya *et al.*, 1979; Van Niekerk, 2008; Wang *et al.*, 2001; Wu *et al.*, 2008). The reader is referred to this section for details regarding the calculations.

High-resolution transmission electron microscopy (HRTEM) and image analyses

Char particles smaller than 75 μm were hand-ground for 15 minutes with a pestle and mortar to produce an ultrafine powdered sample to be analysed by HRTEM. The finely ground samples were applied to a 300 mesh Quantifoil R2/2 holey carbon copper grid with the use of acetone as discussed in Section 5.3.1.5. Image acquisition was performed at 200 kV using a Tecnai F20

FEGTEM and a Gatan CCD camera (Model 895). A detailed account of the method is provided in Section 5.3.1.5. Lattice fringe extraction and image analysis was performed with Adobe Photoshop CS5 according to the method proposed by Mathews *et al.* (2010) and Sharma *et al.* (1999). The methodology for fringe extraction and determination of aromatic raft size distribution has been attended to in detail in Section 5.3.1.5.

6.5 Results and discussion

6.5.1 Large particle selection via mercury submersion

The selection of coal particles for the devolatilization experiments entailed the use of mercury submersion as described in Section 6.3.3. Density distributions as obtained from the mercury submersion analysis are reflected in Figure 6.4 for all four coals.

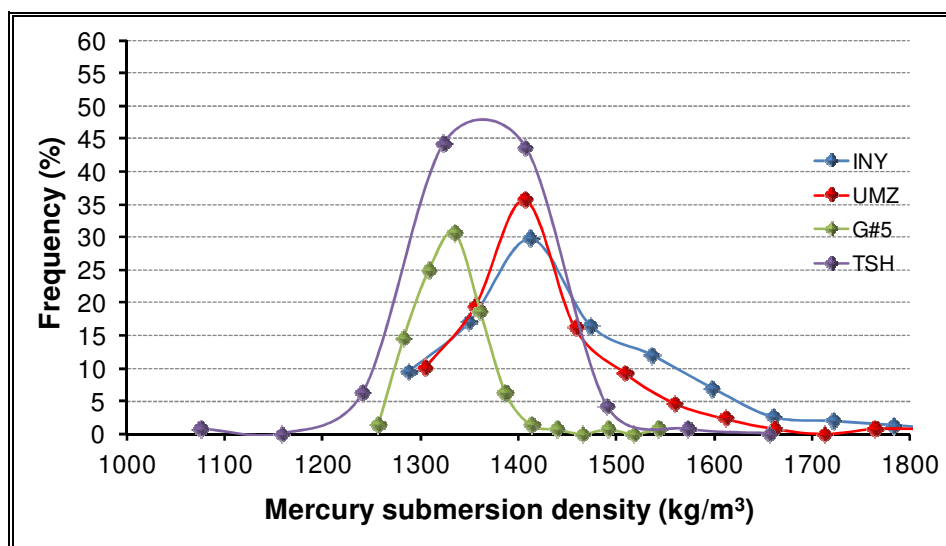


Figure 6.4 Density distribution of coal particles.

From Figure 6.4 it is evident that the density distribution for all four coals showed Gaussian-type behaviour, with the apex of all four distributions concentrated in the 1300 kg/m³ to 1450 kg/m³ density range. The density distributions were used to estimate the average particle density and the respective standard deviation, to determine density selection ranges as described by Equation (6.1). The obtained mercury submersion densities (average- and selection limits) and the particle density as obtained from mercury porosimetry are provided in Table 6.6. The use of

mercury porosimetry for determining particle density has been attended to in Section 4.5.1.3. The results obtained from the mercury submersion correlated very well with what was obtained with mercury porosimetry (Chapter 4), thus providing a benchmark for appropriate selection of larger coal particles. Acquired average densities correspond to particle densities reported for bituminous coals (Speight, 2005). This provides a suitable way of selecting large coal particles with similar maceral- and mineral composition. Only particles confined to the density selection limits were selected for devolatilization experiments in the TCR.

Table 6.6 Comparison between mercury intrusion and -submersion results.

Mercury densities	Unit	INY	UMZ	G#5	TSH
Particle density (mercury porosimetry)	kg/m ³	1442.0	1460.0	1333.0	1368.0
Average particle density (mercury submersion)	kg/m ³	1442.4	1450.3	1334.2	1397.5
Standard deviation, σ	kg/m ³	48.31	42.5	33.9	43.2
Upper density selection limit	kg/m³	1539.0	1535.2	1402.0	1483.9
Lower density selection limit	kg/m³	1345.7	1365.5	1266.5	1311.0

6.5.2 Product yields

Large coal particles (20 mm) selected according to the mercury submersion tests were subjected to devolatilization experiments as outlined in Section 6.4.2. Particles in a smaller size range (± 5 mm) were also used to assess the effect of particle size on coal devolatilization. Large coal particles were used in this investigation in an attempt to understand the devolatilization behaviour of coal in typical lump coal conversion processes. The effect of coal type, temperature and particle size on the product yields from devolatilization is subsequently addressed and discussed in the following text.

6.5.2.1 Effect of coal type

Table 6.7 provides an overview of the results obtained from the TCR facility for the 20 mm particle size experiments at a constant temperature of 450 °C for the four different coals.

Table 6.7 Effect of coal type on the product distribution during devolatilization at 450 °C.

Devolatilization products	Unit	Inertinite-rich coals		Vitrinite-rich coals	
		UMZ	INY	TSH	G#5
Tar ^a	wt. %	3.6 ± 0.38	4.1 ± 0.43	5.0 ± 0.40	10.1 ± 0.42
Gas ^{a,b}	wt. %	3.6 ± 0.31	3.1 ± 0.20	3.7 ± 0.42	5.6 ± 0.12
Char ^a	wt. %	92.8 ± 1.12	92.9 ± 0.8	91.4 ± 1.22	84.3 ± 0.71
Total	wt. %	100.0	100.0	100.0	100.0

^a Values reported on a water and loss free basis. ^b Values estimated from species detected by gas chromatography.

An increasing trend was observed for the amount of gaseous volatiles produced from each coal, whereas a decreasing behaviour was observed for the yield of char with increasing temperature. This is in agreement with what was obtained from the Fischer-assay conducted on the four coals (Section 4.6.1.1.) Accordingly, both volatile- and tar yields decrease in the order liptinite, vitrinite and inertinite (Strugnell & Patrick, 1996). Apart from its high vitrinite content, the significant amount of tar (10.1 wt.%) and gas (5.6 wt.%) obtained from the devolatilization of coal G#5 could therefore also be attributed to its higher liptinite content in comparison to the other coals.

Although coal TSH contained the largest amount of vitrinite, it only produced the second largest amount of tar. The lower tar yield from coal TSH in comparison to coal G#5 could, however, be attributed to this coal's higher rank, which has been found to contribute to the total amount of volatile matter that can be released (Borrego et al., 2000; Fletcher *et al.*, 1990 & 1992; Pugmire *et al.*, 1991; Smith & Smoot, 1990; Smith *et al.*, 1994; Solum *et al.*, 1989a). In addition, it has been found that the devolatilization behaviour of non-softening coals and softening coals are profoundly different (Smith *et al.*, 1994; Yu *et al.*, 2007). Internal mass transfer restrictions such as pore collapse, metaplast formation and bubble formation due to the strong coking nature of coal TSH (FSI of 9) could therefore also have attributed to the lower amount of tar yielded from coal TSH in comparison to coal G#5. Similar observations were made for the smaller particle and higher temperature experiments. The Maceral Index (*MI*) is a well known parameter for describing both the effect of maceral content and rank on coal conversion, and was described in detail in Section 4.6.1.2 (Hattingh, 2009; Su *et al.*, 2001a). Tar yield, for both particle sizes and temperatures, as a function of *MI* is provided in Figure 6.5.

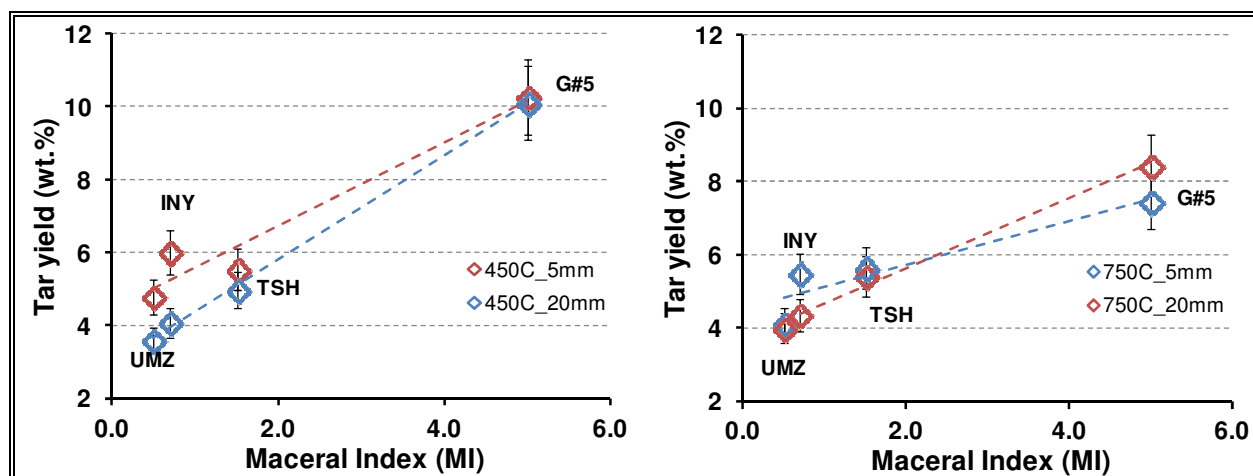


Figure 6.5 Comparison between tar yield and Maceral Index (MI).

From the Figure it is clear that tar yield could be predicted satisfactorily with the aid of the *MI* in all cases.

6.5.2.2 Effect of final temperature

Final temperature is one of the key variables controlling the devolatilization behaviour of coals. A comparison between the product yields at the two different temperatures for the 20 mm particles is summarised in Table 6.8. In addition, the effect of temperature on product yield is illustrated graphically for both particle sizes (5 mm and 20 mm) in Figure 6.6.

Table 6.8 Effect of temperature on the product distribution during devolatilization.

Temperature	Products	Unit	Inertinite-rich coals		Vitrinite-rich coals	
			UMZ	INY	TSH	G#5
450 °C	Tar ^a	wt. %	3.6 ± 0.38	4.1 ± 0.43	5.0 ± 0.40	10.1 ± 0.42
	Gas ^{a,b}	wt. %	3.6 ± 0.31	3.1 ± 0.20	3.7 ± 0.42	5.6 ± 0.12
	Char ^a	wt. %	92.8 ± 1.12	92.9 ± 0.76	91.4 ± 1.22	84.3 ± 0.71
	Total	wt. %	100	100	100	100
750 °C	Tar ^a	wt. %	4.0 ± 0.10	4.4 ± 0.44	5.4 ± 0.19	8.5 ± 0.67
	Gas ^{a,b}	wt. %	16.6 ± 1.43	14.8 ± 0.20	12.7 ± 0.84	20.9 ± 1.58
	Char ^a	wt. %	79.4 ± 0.22	80.9 ± 0.92	81.9 ± 1.23	70.6 ± 0.53
	Total	wt. %	100	100	100	100

^a Values reported on a water and loss free basis. ^b Values estimated from species detected by gas chromatography.

From both Table 6.8 and Figure 6.6 it could be observed that total volatile matter increased with increasing temperature, irrespective of particle size. This corresponds to the findings of numerous authors which include: Hu *et al.* (2004), Kandiyoti *et al.* (2006), Kristiansen (1996), Ladner (1988) and Smith *et al.* (1994). The behaviour of tars and gases does, however, differ from the general trend of the evolution of the total amount of volatiles. For coals UMZ, INY and TSH, no significant difference in tar yield (for both the 5 mm and 20 mm particles) could be observed with an increase in temperature. In contrast however, a significant decrease in tar yield with an increase in temperature was observed for coal G#5.

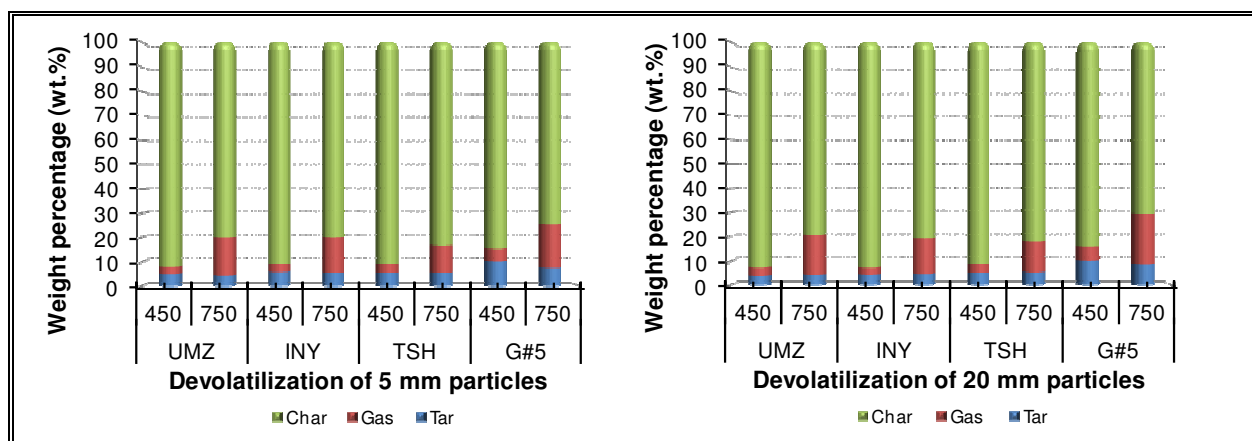


Figure 6.6 Effect of temperature on product yield for both particle sizes.

A tar reduction of approximately 16.4% and 27.6% occurred for the 5 mm and 20 mm experiments, respectively. According to Kandiyoti *et al.* (2006), tar cracking reactions begin to affect tar yields at higher temperatures. In addition, tar yield subsequently reaches a maximum value and declines with an increase in temperature if the increase in tar production is matched by tar cracking reactions (Kandiyoti *et al.*, 2006). Furthermore, the tar yield-temperature relationship also depends on the type of reactor used. Slight increases in tar yields at low temperatures and subsequent decreases at higher temperatures are characteristic of fixed-bed reactors systems. Furthermore, it was established that no significant change in tar yield occurred with an increase in temperature during rapid devolatilization studies performed in fixed-bed reactor systems (Khan, 1989). According to Khan (1989), primary devolatilization products undergo additional cracking reactions within fixed-beds which subsequently produce lower molecular weight compounds. Accordingly, tar quality increases at the expense of tar yield. The significant shift in product distribution (increased gas yield) at 750°C indicates that the formation of gaseous species is favoured, mainly due to the presence of secondary gas-phase

degradation reactions (Kandiyoti *et al.*, 2006; Ladner, 1988; Nelson *et al.*, 1988). The expectation of a higher or lower tar yield at 750°C indicates that tar production was either significantly affected by the exposure of tar pre-cursors to particles in the bed as well as the hot reactor wall, or that the introduction of high flow rate inert gas ensured short product residence time in the reactor. For this particular investigation the fixed-bed depth was ensured to be representative of monolayer coverage in the reactor. The latter therefore suggest that tar degradation on the reactor walls and coal particles could have been minimised by the high flow rate of N₂ through the system. The use of carrier gases at high flow rates have been shown to effectively diminish the occurrence of secondary gas-solid reactions (Kandiyoti *et al.*, 2006).

6.5.2.3 Effect of particle size

Particle size is another important parameter dictating the behaviour of coals during devolatilization. A comparison of the results obtained for the two different particle sizes at a reaction temperature of 450°C is provided in Table 6.9 (a comparison of the 750°C results is given in Appendix C.1). Furthermore, the effect of particle size on product yield is illustrated graphically for both particle sizes and reaction temperatures in Figure 6.7. Mass transfer and secondary reactions become evidently more important with an increase in particle size, and therefore dictate the composition and yield of products evolved.

Table 6.9 Effect of particle size on the product distribution during devolatilization at 450°C.

Particle size	Products	Unit	Inertinite-rich coals		Vitrinite-rich coals	
			UMZ	INY	TSH	G#5
5 mm	Tar ^a	wt. %	4.8 ± 0.20	6.0 ± 0.70	5.5 ± 0.10	10.3 ± 0.35
	Gas ^{a,b}	wt. %	3.0 ± 0.10	3.1 ± 0.25	3.5 ± 0.10	5.1 ± 0.28
	Char ^a	wt. %	92.2 ± 0.13	90.9 ± 0.35	90.9 ± 1.00	84.7 ± 0.32
	Total	wt. %	100	100	100	100
20 mm	Tar ^a	wt. %	3.6 ± 0.38	4.1 ± 0.43	5.0 ± 0.40	10.1 ± 0.42
	Gas ^{a,b}	wt. %	3.6 ± 0.31	3.1 ± 0.20	3.7 ± 0.42	5.6 ± 0.12
	Char ^a	wt. %	92.8 ± 1.12	92.9 ± 0.76	91.4 ± 1.22	84.3 ± 0.71
	Total	wt. %	100	100	100	100

^a Values reported on a water and loss free basis. ^b Values estimated from species detected by gas chromatography.

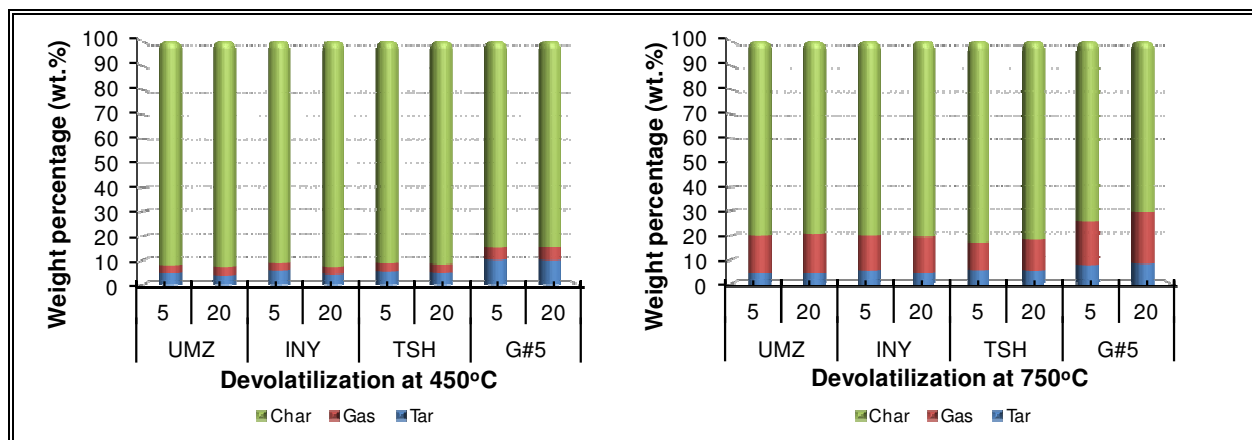


Figure 6.7 Effect of particle size on product yield.

Tar yields for the 5 mm particles of coals UMZ and INY were respectively 33.3% and 46.5% higher than the values obtained for the 20 mm particles. This provides evidence that secondary reactions were promoted more extensively in these coals due to their non-swelling nature. In contrast, however, no significant increase in tar yield could be observed for the 5 mm particles of the vitrinite-rich coals. Comparable values in tar yield from coal TSH at the two different particle sizes could be attributed to the formation of a solid agglomerated bulk (irrespective of particle size) due to its strong swelling nature. Mass transfer properties would then be similar due to a re-condensed, bulk char structure similar in size but larger in comparison to the original particle sizes, explaining similar yields of tar.

Slight increases in the amount of gas were observed for increasing particle size, while slightly lower char yields were obtained for coals INY and TSH. Although a decreasing volatile yield with increasing particle size has been the general consensus of numerous authors (Anthony *et al.*, 1976; Devanathan & Saxena, 1987; Kandiyoti *et al.*, 2006), no conclusive evidence of a significant decrease in total volatile yield with increasing particle size could be observed (Table 6.9). A similar observation was made by Seebauer *et al.* (1997) during a devolatilization study on particles ranging in size from 0.1 mm to 2.0 mm. Suuberg (1977) has also stressed the difficulty of quantitatively assessing the effect of particle size on devolatilization at high heating rates. Accordingly, the propagation of the temperature distribution towards the centre of a coal particle would be limited by the thermal conductivity of the coal. This provides some evidence towards the observation that no significant increase in total volatile yield was observed between the different particle sizes, as both samples (5 mm and 20 mm) are introduced after the reactor reached isothermal temperature.

6.5.3 Product composition and quality

6.5.3.1 Gas composition

Qualitative assessment of gas composition by online mass spectrometry:

Online gas MS was employed in order to qualitatively evaluate the evolution of gas species during the devolatilization of the four coal samples. Molecular masses higher than 100 m/z were not considered due to the uncertainty of the chemical structure of these species. Ion curves close to the noise level and showing no significant trend were neglected. Only the intensities of fifteen selected ions (m/z of 2, 12, 15, 16, 26, 27, 30, 31, 34, 41, 42, 43, 44, 56 and 64) were monitored, based on observations made during previous investigations on devolatilization of coals and biomasses (Arenillas *et al.*, 1999; Tihay & Gillard, 2010). An overview of typical molecular species representing the different ion masses is presented in Table 6.10 (Silverstein *et al.*, 2005).

Table 6.10 Molecular formulas for selected ion masses (Silverstein *et al.*, 2005).

Ion mass (m/z)	Probable molecular ion, molecule or fraction
2	H ₂ ⁺
12	C ⁺
15	HN ⁺ and/or CH ₃ ⁺
16	O ⁺ , H ₂ N ⁺ and/or CH ₄ ⁺
26	CN ⁺ and/or C ₂ H ₂ ⁺
27	CHN ⁺ and/or C ₂ H ₃ ⁺
30	NO ⁺ , H ₂ N ₂ ⁺ , CH ₂ O ⁺ , CH ₄ N ⁺ and/or C ₂ H ₆ ⁺
31	HNO ⁺ , H ₃ N ₂ ⁺ , CH ₃ O ⁺ and/or CH ₅ N ⁺
34	H ₂ O ₂ ⁺ and/or H ₂ S ⁺
41	CHN ₂ ⁺ , C ₂ H ₃ N ⁺ and/or C ₃ H ₅ ⁺
42	N ₃ ⁺ , CNO ⁺ , CH ₂ N ₂ ⁺ , C ₂ H ₂ O ⁺ , C ₂ H ₄ N ⁺ and/or C ₃ H ₆ ⁺
43	HN ₃ ⁺ , CHNO ⁺ , CH ₃ N ₂ ⁺ , C ₂ H ₃ O ⁺ , C ₂ H ₅ N ⁺ and/or C ₃ H ₇ ⁺
44	N ₂ O ⁺ , CO ₂ ⁺ , CH ₂ NO ⁺ , CH ₄ N ₂ ⁺ , C ₂ H ₄ O ⁺ , C ₂ H ₆ N ⁺ and/or C ₃ H ₈ ⁺
56	C ₂ O ₂ ⁺ , C ₂ H ₂ NO ⁺ , C ₂ H ₄ N ₂ ⁺ , C ₃ H ₄ O ⁺ , C ₃ H ₆ N ⁺ and/or C ₄ H ₈ ⁺
64	SO ₂ ⁺ , S ₂ ⁺ and/or C ₅ H ₄ ⁺

The table above represents the vast complexity of the structure and probability of molecular species/fragments at higher ion masses. For this reason, semi-quantitative or quantitative determinations were not conducted on the observed mass spectrometric results. For comparative purposes between the different experimental conditions, ion intensities for the selected ions were normalised to dimensionless relative intensity values, based on the sum of the total evolution area of these ion species. Only the results obtained from the devolatilization of the 20 mm particles at 450°C and 750°C are shown in Figures 6.8 and 6.9, respectively. A full account of the ion curves obtained for the 5 mm particles are not included, due to the similarity in observations made with respect to the results for the 20 mm particles. Detailed evolution curves of the 5 mm particle results are provided in Appendix C.2. The results presented in Figures 6.8 and 6.9 were obtained from averaged values of all the repeatable measurements of each particular ion species.

Experimental reproducibility was established for each coal and a comparison between subsequent evolution curves for the different coal samples can be found in Appendix C.3. From the figures below it can be seen that for both temperatures the ion signals of 2, 15, 16, 26, 27 and 44 m/z showed the highest relative intensities. A comparison between evolution rates at 450°C revealed that the ion signal at 44 m/z (most probably attributed to CO₂ and propane formation) showed the fastest rate of evolution and is characterised by the occurrence of the co-elution of two overlapping evolution peaks for the different coals.

The first peak can be observed in the range of 2 to 7 minutes for all four coals and can most probably be attributed to the evolution of occluded CO₂ driven off at temperatures close to 200°C during the heating up of the coal particle (Smith *et al.*, 1994). In contrast, however, the evolution of CO₂ (second peak) at longer residence times (where the coal particle has a uniform temperature distribution) could be attributed to the scission of weak aliphatic-ether linkages present in the coal structures (Smith *et al.*, 1994). It should, however, be kept in mind that the occurrence of an ion signal at mass 44 m/z could also be attributed to the production of possible propane (C₃H₈).

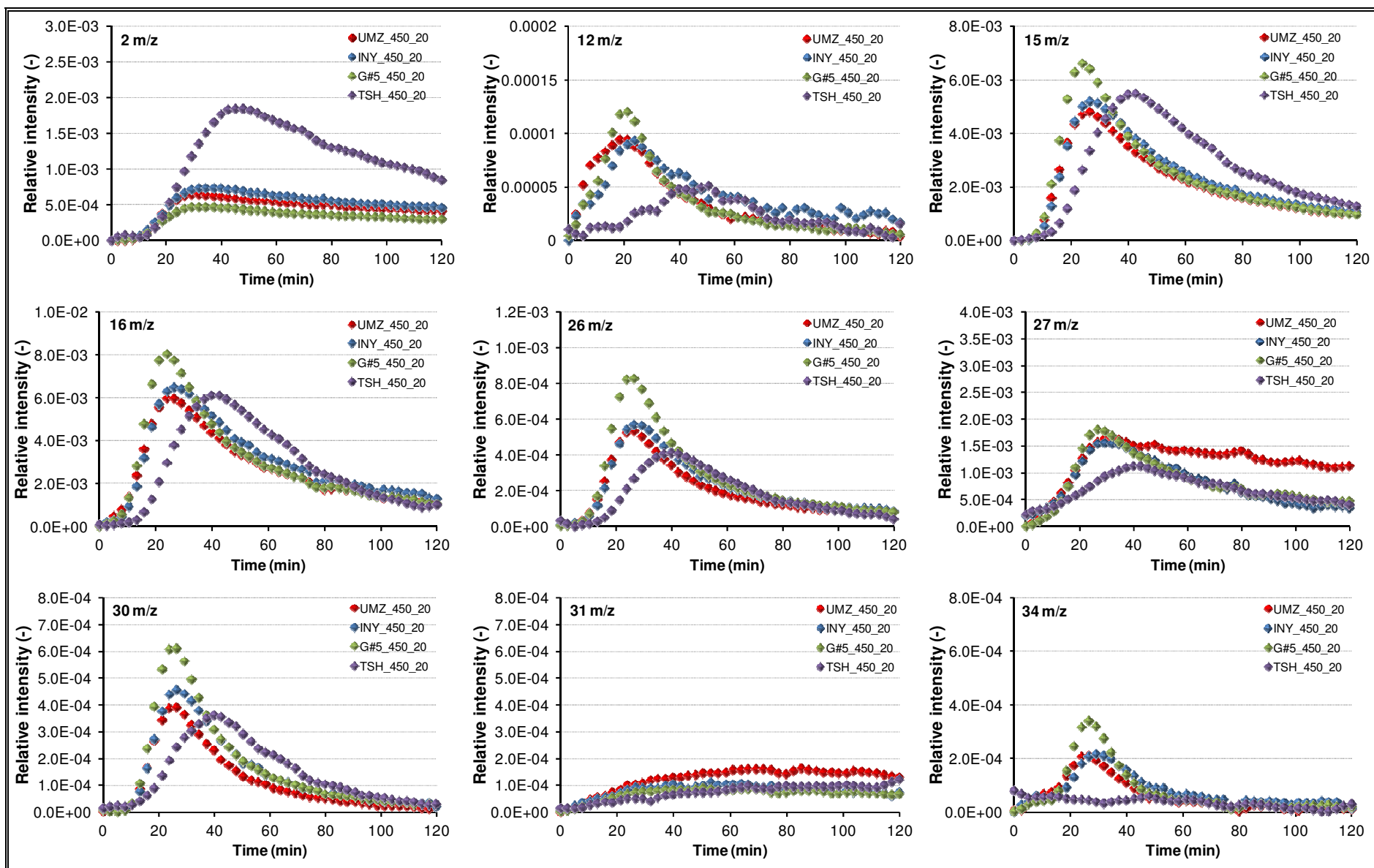


Figure 6.8 Evolution curves of selected ion species obtained from 20 mm particles at 450°C.

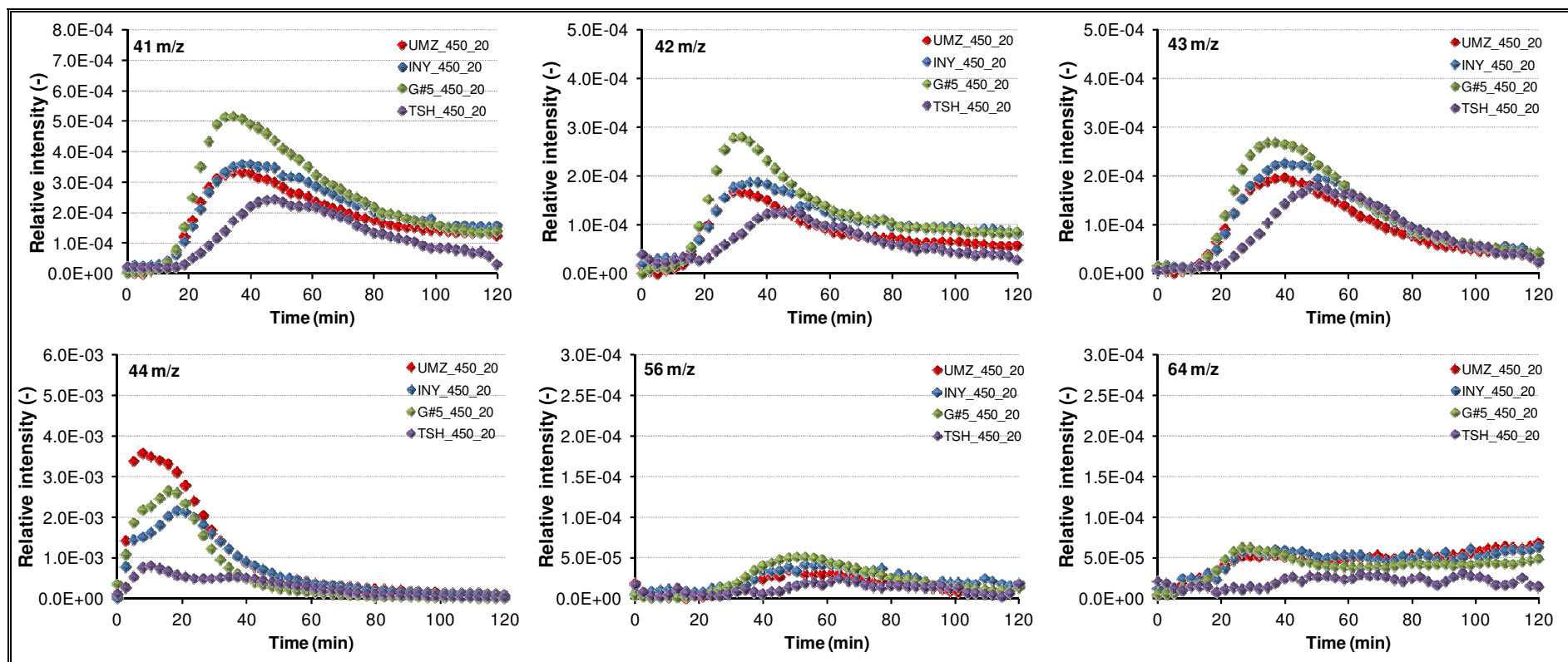


Figure 6.8 Evolution curves of selected ion species obtained from 20 mm particles at 450 °C (continued).

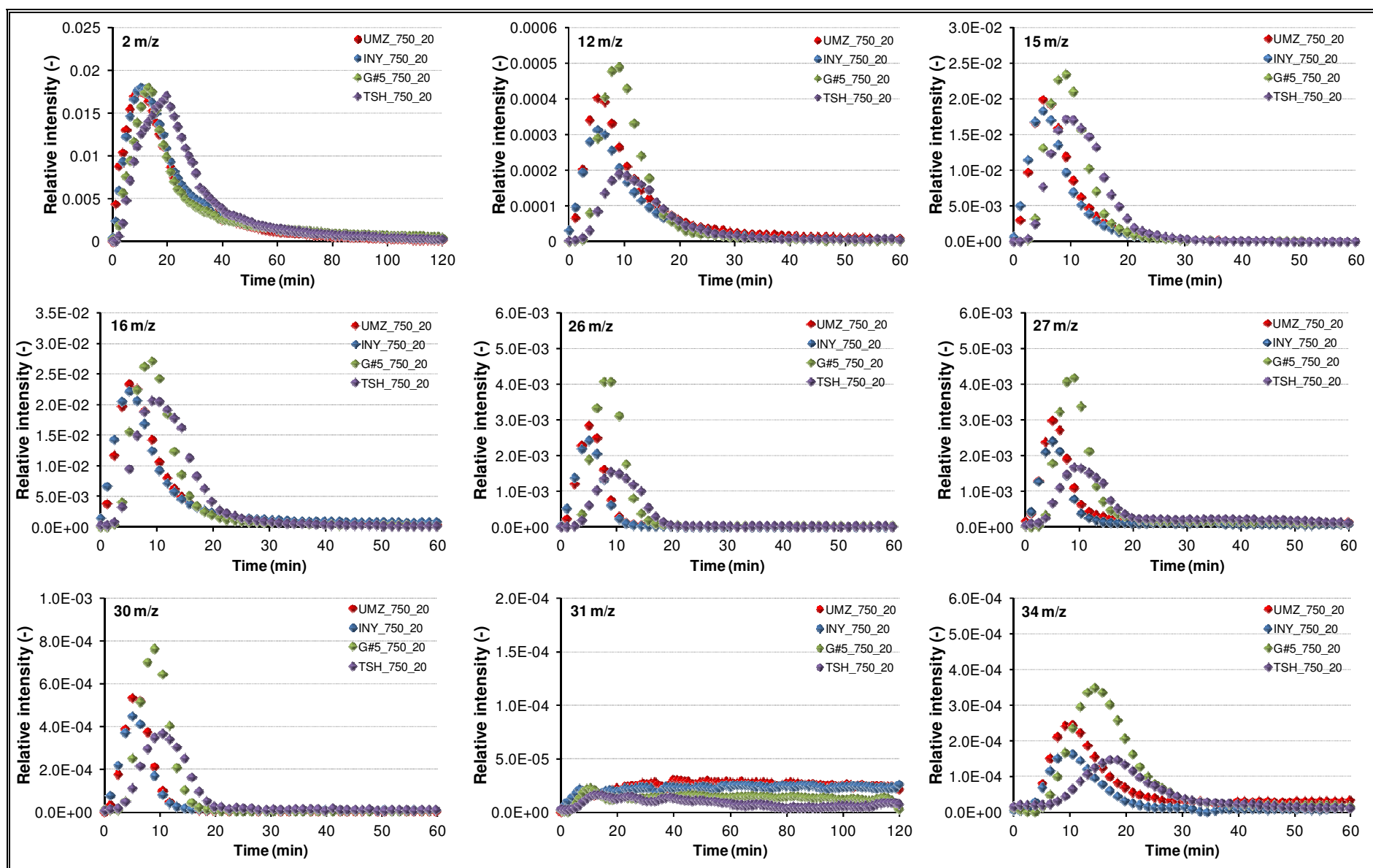


Figure 6.9 Evolution curves of selected ion species obtained from 20 mm particles at 750°C.

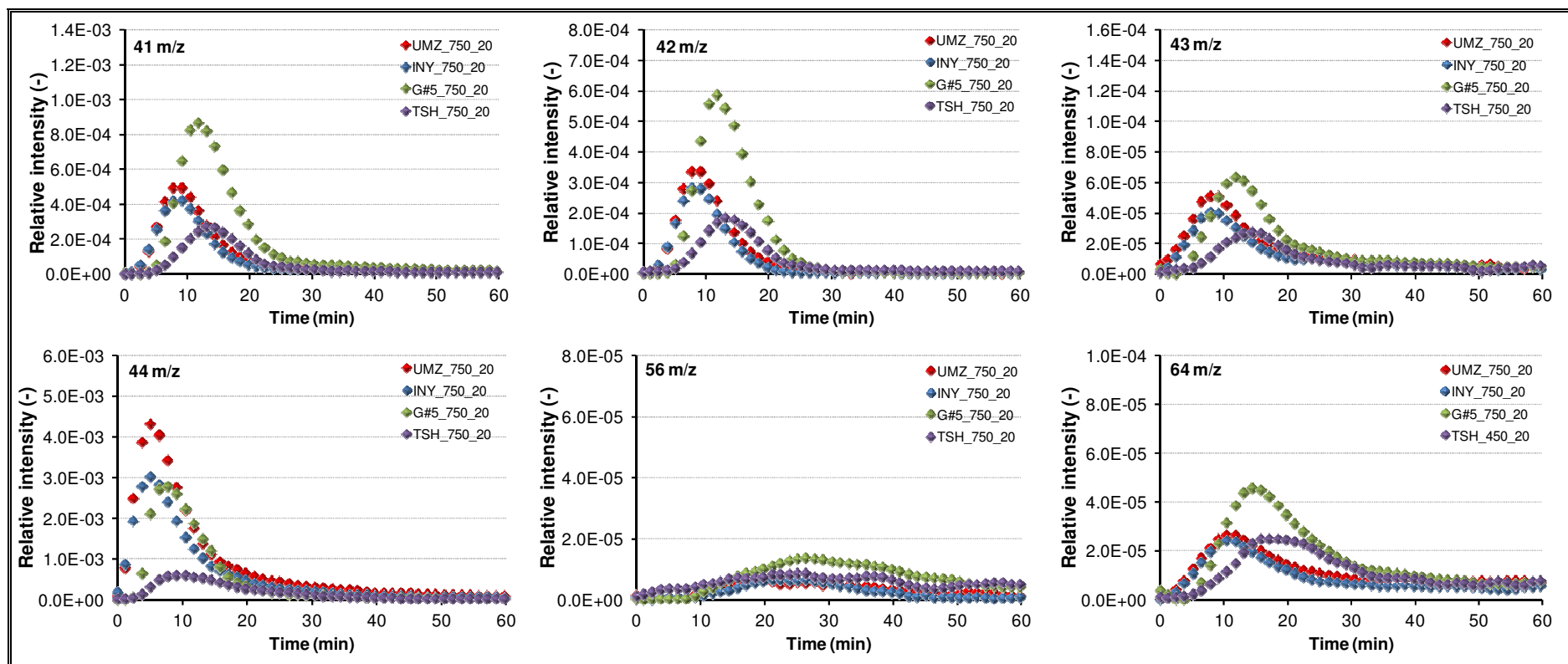


Figure 6.9 Evolution curves of selected ion species obtained from 20 mm particles at 750 °C (continued).

This can be supported by the evolution of $C_3H_7^+$ ions at a mass signal of 43 m/z, although low in intensity values as compared at the intensity signals at mass 44 m/z. In addition, coal TSH showed a delay in the occurrence of the second peak in the mass 44 m/z signal in comparison to the other coals. The separation of two peaks at mass 44 m/z was not observed for the 5 mm experiments (Appendix C.2) and could be the results of shorter heating times needed for 5 mm particles as compared to 20 mm particles. At 750°C, a single peak for all four coals was observed at shorter residence times (faster evolution rate) for the evolution curve of the ion signal at 44 m/z. Furthermore, devolatilization of coal UMZ displayed a larger intensity of the mass 44 m/z signal for both temperatures, whereas coal TSH contained the least amount of this species. In all cases a significant increase in maximum intensity (yield) was observed for ion signals 2, 12, 15, 16, 26 and 27 m/z (corresponding to typical devolatilization species such as H_2 , CH_4 , ethylene, ethane etc.) with an increase in temperature, while slight increases or decreases in maximum evolution intensities were found for the other selected ions. The increase in intensities (yields) of H_2 (2 m/z), CH_4 (15 and 16 m/z) and short-chain aliphatic gases (15, 16, 26 and 27 m/z) are in agreement with results generated from temperature related effects on gas yields as obtained by numerous authors (Arenillas *et al.*, 1999; Chen *et al.*, 2010; Das, 2001; Nelson *et al.*, 1988; Hu *et al.*, 2004; Song *et al.*, 2001). For all cases, coal G#5 displayed the highest evolution intensity (largest yield) for all gaseous species, with the exception of the mass 2 m/z, 31 m/z and 44 m/z ion curves. This can be attributed to either the less condensed structure of this coal (low aromaticity and high fraction of disordered carbon) (Okolo, 2010), or the presence of significant amounts of liptinite in comparison to the other three coals (Cloke & Lester, 1994; Du Cann, 2010; Tsai, 1982). In contrast, however, a significant amount of H_2 and CH_4 (masses 2, 15 and 16 m/z) were produced from the devolatilization of coal TSH, while the evolution of the other molecular fragments were found to have occurred to a lesser degree. No significant difference was observed in the intensity of H_2 evolution (m/z of 2) for coals UMZ, INY and G#5 for both experimental temperatures. Similar evolution profiles were observed for the selected ions of coals UMZ and INY at both 450°C and 750°C. From a kinetic perspective, a comparison between Figures 6.8 and 6.9 revealed the subsequent effect of devolatilization temperature on the evolution rate of gaseous species. For all ion species, evolution rate increased with an increase in experimental temperature, therefore indicating an increase in total devolatilization rate. This can be seen from the shorter total evolution times observed for the 750°C experiments compared to the 450°C results. An increase in devolatilization rate with temperature is consistent with work conducted by Solomon and Hamblen (1985) and Yeasmin *et al.* (1999). Similar characteristic trends in ion signals were

observed for the 5 mm experiments, although relatively shorter evolution times (higher evolution rates) were recorded for all mass signals at 450°C when compared to the 20 mm experiments. This can be explained by the difference in the subsequent transient nature of both heat- and mass transfer resistances of different coal particles sizes (Devanathan and Saxena, 1987). A significant difference in evolution times was however not observed for the higher temperature experiments on the two different particles sizes.

Quantitative assessment of gas composition by gas chromatography

Quantitative gas measurements were conducted on a GC due to the lack in sensitivity of quantification by mass spectrometry (Tihay & Gillard, 2010). Retention time estimates were based on pre-calibration of the GC with a refinery gas standard similar in composition to typical gaseous components observed from coal devolatilization. Calibration was not performed for other coal conversion gases such as NO_x, H₂S, SO_x etc. Sampling and analyses of gas samples were conducted according to the method outlined in Section 6.4.4.2. Only peaks detected in the specified retention times were considered for quantification. Quantification of the detected species was done for all coals on both particle sizes (5 mm and 20 mm) and temperature experiments (450°C and 750°C). The effect of these conditions on the subsequent distribution of gaseous species is attended to in the following text. Gas measurements with the GC system were found to be reproducible for all cases and the variance in experimental repeatability for each coal is shown separately in different figures confined to Appendix C.4. The experimental error was found to be close to 10% for the inertinite-rich coals, while lower experimental errors were achieved for the vitrinite-rich coals (typically in the order of 5%). The obtained errors were therefore found to be acceptable if the uncertainty in large particle homogeneity is kept in mind.

Effect of coal type and temperature:

A detailed account of time-resolved measurements of gas composition during coal devolatilization of 20 mm particles at 450°C and 750°C is provided in Figures 6.10 and 6.11, respectively. The total amount of each gas species evolved was estimated using the method described in Section 6.4.4.2. Gas samples were collected at fixed intervals, with shorter intervals used for the 5 mm experiments during the first few minutes of gas evolution. The total amount of each gas species (mass and molar basis) as calculated for the different coal samples is summarised in Tables 6.11 and 6.12 for the two temperatures respectively.

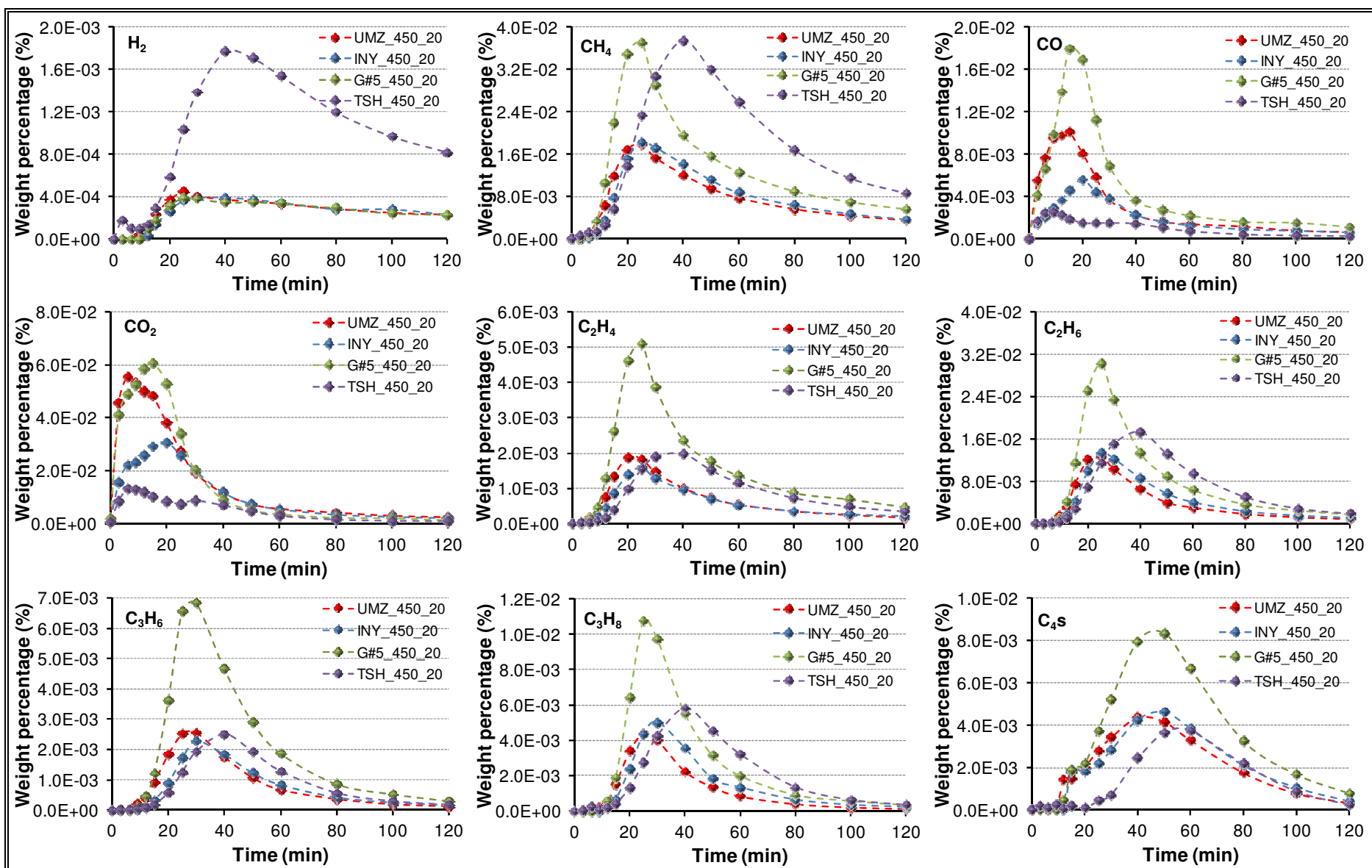


Figure 6.10 Gas evolution profiles determined at 450°C for 20 mm coal particles.

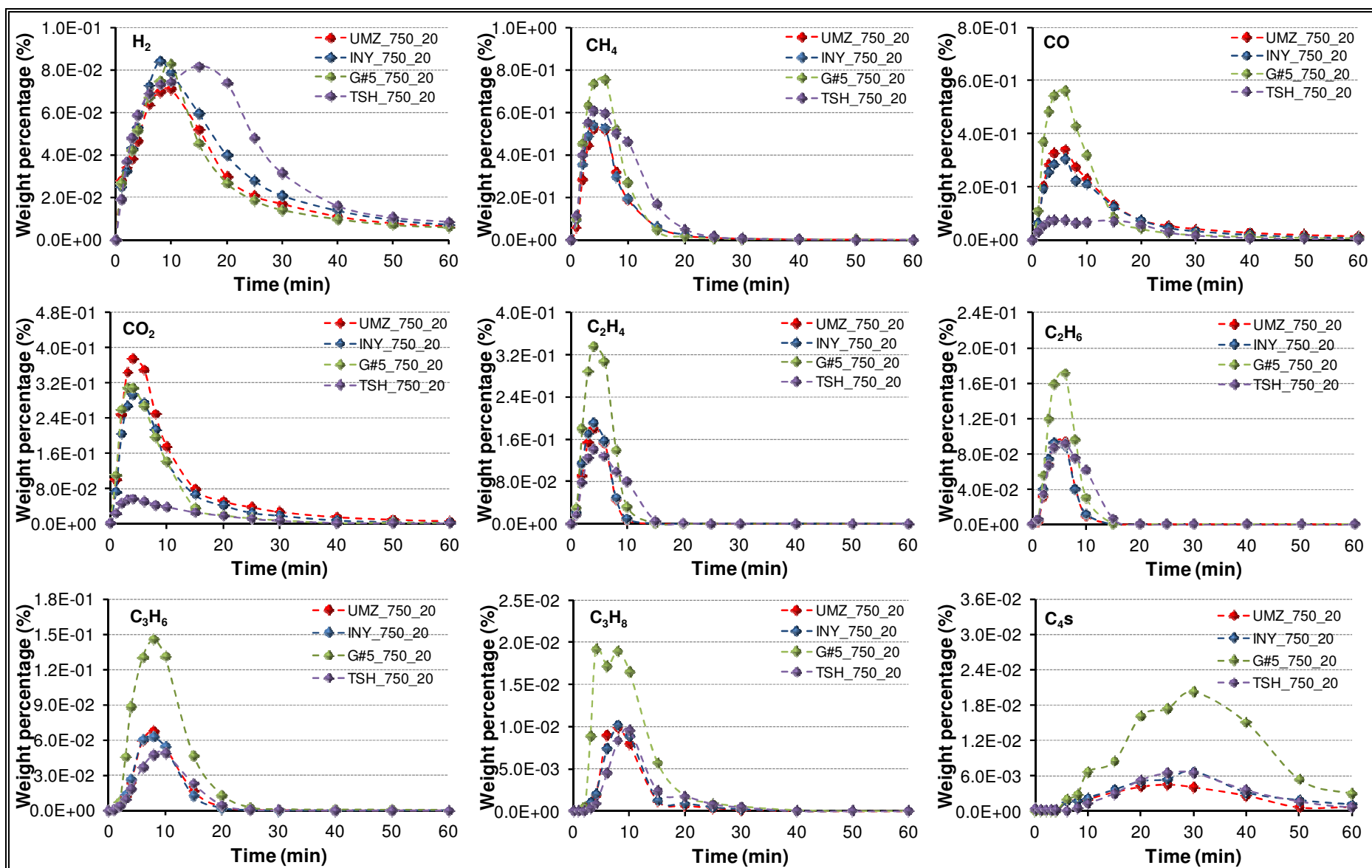


Figure 6.11 Gas evolution profiles determined at 750°C for 20 mm coal particles.

Table 6.11 Mass composition of gas species evolved at both temperatures for 20 mm particles.

Gas species (wt.% ^a)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		TSH		G#5	
	450 °C	750 °C	450 °C	750 °C	450 °C	750 °C	450 °C	750 °C
H ₂	0.03	1.77	0.03	2.08	0.13	2.58	0.03	1.71
CH ₄	0.91	4.47	1.00	4.66	2.18	7.02	1.63	6.20
CO	0.35	5.71	0.23	4.87	0.11	1.95	0.54	6.22
CO ₂	1.81	4.56	1.24	3.49	0.54	0.92	1.75	3.10
C ₂ H ₄	0.08	0.95	0.07	1.02	0.11	1.18	0.19	2.01
C ₂ H ₆	0.45	0.55	0.54	0.56	0.85	0.82	0.97	1.06
C ₃ H ₆	0.10	0.60	0.09	0.57	0.11	0.52	0.24	1.52
C ₃ H ₈	0.13	0.08	0.17	0.09	0.25	0.09	0.32	0.22
C ₄ S ^c	0.24	0.16	0.27	0.21	0.19	0.20	0.45	0.67
Total	4.10	18.86	3.65	17.55	4.48	15.28	6.12	22.70
Error %	11.6	10.5	10.2	11.1	15.1	12.9	4.1	8.9

^a Values reported on dry ash free basis of initial coal mass. ^c Butane (C₄H₁₀) chemical structure assumed for average structure of C₄s.

Table 6.12 Molar composition of gas species evolved at both temperatures for 20 mm particles.

Gas species (mol.% ^b)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		TSH		G#5	
	450 °C	750 °C	450 °C	750 °C	450 °C	750 °C	450 °C	750 °C
H ₂	10.8	57.33	11.3	62.73	24.9	67.63	6.9	50.50
CH ₄	36.9	18.11	42.7	17.54	52.1	23.02	42.9	22.84
CO	8.1	13.22	5.6	10.49	1.5	3.66	8.2	13.09
CO ₂	26.6	6.73	19.2	4.78	4.7	1.10	16.8	4.16
C ₂ H ₄	1.8	2.21	1.8	2.19	1.5	2.22	2.9	4.23
C ₂ H ₆	9.8	1.18	12.1	1.13	10.8	1.44	13.7	2.08
C ₃ H ₆	1.5	0.92	1.5	0.81	1.00	0.65	2.4	2.13
C ₃ H ₈	2.0	0.12	2.7	0.12	2.2	0.11	3.0	0.29
C ₄ S ^c	2.7	0.18	3.1	0.22	1.3	0.18	3.3	0.68
Total	100	100	100	100	100	100	100	100

^b Values reported on mole basis of total devolatilization gas evolved. ^c Butane (C₄H₁₀) chemical structure assumed for average structure of C₄s.

Values in these tables are expressed on a dry ash free weight basis (wt.%) of the initial mass of the coal sample as well as a molar basis (mol.%) of the total gas evolved. Values shown in Figures 6.10 and 6.11 for the two different temperatures were converted to a dry ash free weight basis of the initial coal sample. Line graphs have been included to guide the reader's eye through the experimental data points.

From the above results it is evident that the major devolatilization gases (H_2 , CH_4 , CO , CO_2 , C_2S and C_3S) (Nelson *et al.*, 1988; Wen *et al.*, 2009; Xiong *et al.*, 2010) were observed for all four coal samples. In general, gaseous species evolution rate increased with increasing temperature for all four coals. CH_4 , CO and CO_2 (on a wt.% basis) were found to be the dominant gaseous species evolved at the lower temperature, while the total amount of H_2 evolved became predominantly more important at 750 °C. Low proportions of hydrogen were detected at 450 °C for all four coals (0.03 wt.% to 0.13 wt.%), while H_2 yield increased significantly with an increase in temperature (1.71 wt.% to 2.58 wt.%). This is in agreement with what was observed by a number of other authors (Arenillas *et al.*, 1999; Chen *et al.*, 2010; Cui *et al.*, 2006; Khan, 1989; Smith *et al.*, 1994; Wen *et al.*, 2009; Xiong *et al.*, 2010). According to Khan (1989), a significant increase in H_2 evolution at higher temperatures can be attributed to the thermodynamically favoured cracking of heavier hydrocarbons. This increase in H_2 concentration could also have been the result of re-arrangement and condensing of aromatic structures and the direct dehydrogenation of the formed chars (Uzun *et al.*, 2007). On a molar basis, H_2 represents more than 50 mol.% of the total amount of gas evolved at 750 °C for each coal. The production of H_2 at temperatures as low as 450 °C could, however, have originated from the scission of very weak aliphatic (C-H) bonds during bond stabilization of the formed char (Smith *et al.*, 1994). For both temperatures, coal TSH produced the highest amount of H_2 (0.13 wt.% and 2.58 wt.% respectively) in comparison to the other coals. The higher yield and slower evolution rate of H_2 from coal TSH indicate that cracking was more extensive in this coal, which could have been a direct consequence of its extensive coking properties delaying the transport of hydrocarbon species within the solid matrix.

The amount of methane (CH_4) increased extensively with an increase in temperature, while the highest yields were obtained from the devolatilization of the two vitrinite-rich coals (G#5 and TSH). On a molar basis, CH_4 represents the largest fraction of the devolatilization gas at 450 °C (36.9 mol.% to 52.1 mol.%), while its predominance is overruled by the sharp increase of H_2 at 750 °C. A substantial amount of CH_4 was obtained at both temperatures from coal TSH (2.18 wt.% and 7.02 wt.% respectively) in comparison to the other three coals. Slightly higher CH_4

yields were obtained for the inertinite-rich INY coal, while the lowest amount of CH₄ was generated from coal UMZ. CH₄ formation during devolatilization is mainly attributed to the decomposition of hydro-aromatic and/or aryl methyl groups (Charpenay *et al.*, 1996). The presence of CH₄ at low temperatures (such as 450°C) in the product gas can therefore be attributed to the decomposition and/or hydrogenation of the methyl side chains on the parent coal or evolved tars (Cui *et al.*, 2006). Furthermore, occluded methane retained in the porous structure of coal is also evolved at lower temperatures and has been found to be a dangerous hazard during coal mining (Al-Muhareb *et al.*, 2006; ICS Reference Library, 1920). In contrast however, it has been proposed that the formation of CH₄ at moderate to high temperatures is the direct result of cross-linking reactions of coal macromolecules and/or the cracking of saturated hydrocarbons (Cui *et al.*, 2006). In addition, CH₄ itself becomes unstable at temperatures exceeding 725°C and cracks to form additional H₂ (Khan, 1989). This provides additional evidence for the sharp increase in H₂ experienced for all four coals at the higher temperature.

Oxygen-containing molecular structures within coal have been found to be extremely important during coal devolatilization (Smith *et al.*, 1994). CO and CO₂ are therefore well known contributors to devolatilization product gas and constituted large fractions of the product gas evolved for all four coals at both temperatures. From a molecular bond perspective, aliphatic ether linkages have been found to be among the weakest bonds to break during devolatilization (Smith *et al.*, 1994). Work conducted by Brendenberg *et al.* (1987) has shown the relative order of reactivity of oxygen-containing entities in coal to increase in the order: furans < phenols < ketones < aldehydes < open ethers. Cleavage of these bonds via decarbonylation and dehydration therefore leads to the formation of not only carbon-oxides, but also water during coal devolatilization (Smith *et al.*, 1994). At 450°C the amount of CO evolved ranged between 0.11 wt.% and 0.54 wt.%, while CO₂ production was found to be close to 0.54 wt.%-1.81 wt.%. For the higher temperature CO and CO₂ yields were in the order of 3.10 wt.% to 6.22 wt.% for coals UMZ, INY and G#5, while yields below 1.75 wt.% were detected for coal TSH. The evolution of CO₂ during the devolatilization of the four different coals can therefore be attributed to the decomposition of carboxyl functionalities within the coal molecular structure (Cui *et al.*, 2006; Murakami *et al.*, 1997; Wang *et al.*, 2005; Xiong *et al.*, 2010; Zhu *et al.*, 2000) as well as a number of minerals, especially carbonates (Campbell & Stephens, 1976). This process is believed to occur at temperatures ranging between 300°C and 700°C (Chen *et al.*, 2010). In addition, the existence of intermolecular carboxylic acid anhydrides in bituminous coals has also been shown to contribute to the production of CO₂ during devolatilization (van Heek & Hodek,

1994). The detection of carbonyl and aliphatic oxygen moieties by ^{13}C NMR (although low in concentration $< 0.01\%$) (Section 5.4.1.2) in the molecular structure of coals UMZ, G#5 and INY tends to support the high concentrations of CO_2 observed for these coals in comparison to coal TSH. Only minute amounts of phenolic and aliphatic functionalities were detected for coal TSH, thus providing evidence for the very low yield of CO_2 .

In contrast, however, various routes could have contributed to the formation of CO which include: the decomposition of carbonyl groups at temperatures lower than 400°C (Zhu *et al.*, 1998), the rupture of oxygen heterocycles at temperatures exceeding 500°C , the dehydrogenation of hydroxyl groups (Zhu *et al.*, 2000), as well as the initiation of CO_2 gasification of C for temperatures exceeding 700°C (Smith *et al.*, 1994; Wang *et al.*, 2005; Xiong *et al.*, 2010). The significant shift of the molar ratio of CO to CO_2 from approximately 1:3 at 450°C to 3:1 at 750°C suggests that, apart from the normal mechanisms of CO formation, CO_2 gasification of C (either in the char or in tar-precursors) could have played a significant role. This observable shift in CO versus CO_2 yield at higher temperatures has also been confirmed by Ciu *et al.* (2006) and Xiong *et al.* (2010). As is the case for CO_2 evolution, the lower CO yield obtained from coal TSH is in accordance with the low amount of oxygen functionalities present in this coal. Furthermore, lower ranked coals are characterised by loosely bound carbonyl and ether functionalities, which are prone to rupture under extensive devolatilization conditions (Chen *et al.*, 2010). The slightly higher rank of coal TSH could therefore attribute to low evolution potential of this coal with respect to CO_2 and CO. At 750°C , a larger proportion of coal G#5's oxygen content fractionates in the form of CO compared to the other three coals, which suggests a different mechanism of oxygen decomposition from the coal structure. Light olefin ($\text{C}_2\text{-C}_4$) gases, although only minor constituents of devolatilization gas, was also observed for all four coal samples with yields normally not exceeding 1 wt.% for 450°C and 2 wt.% for 750°C . Although only small amounts of these gases were observed in the product gas, they do however form an integral part of the devolatilization process. The heats of reaction/combustion of these low molecular weight olefin species far exceed that of H_2 , CH_4 , CO and CO_2 and therefore have a significant effect on the heating value of the product gas, which in turn plays an important role in ignitability during a coal conversion process such as combustion (Campbell & Stephens, 1976).

From Table 6.11 it can be seen that the yield of the non-saturated alkene gases, C_2H_4 and C_3H_6 , increase significantly for all four coals with an increase in temperature, whereas, the comparative yields of the saturated alkane species, C_2H_6 and C_3H_8 , show slight increases or

decreases, respectively. This corresponds with what was obtained by Cui *et al.* (2006), who found that the yield of the short-chain alkene gases increased monotonously with temperature, while a maximum yield occurred at 650°C for the alkane species. It is evident from Table 6.12 that a significant shift in the molar ratio of the different olefin species occurs with an increase in temperature. The molar ratio of ethylene (C_2H_4) to ethane (C_2H_6) shifts from a ratio of 1 to between 4 and 7 at 450°C to a ratio of between 1.5 and 2 to 1 at 750°C. This is also observed for the molar ratio of propylene (C_3H_6) to propane (C_3H_8), where a shift from a ratio of 1 to between 1.2 and 1.8 at 450°C to between 5.9 and 7.7 to 1 at 750°C occurs. This substantial shift in molar ratio suggests that, apart from cracking of tars and long-chain aliphatic hydrocarbons to produce short chain alkenes, the corresponding alkanes additionally decompose to form alkenes and H_2 due to the thermal stability of olefins at higher temperatures (Cui *et al.*, 2006; Gavalas, 1982). The evolution of C_4 s from the different coals ranged between 0.16 wt.% and 0.67 wt.% and could also be attributed to the cracking of long-chain aliphatic hydrocarbons (Cui *et al.*, 2006). From the GC analysis no distinct structure could be provided for these 4-carbon atom species and therefore they were lumped together as C_4 s. Butane was assumed to be an average structure for the C_4 s in order to perform gas yield estimations. From the results it was evident that the largest amount of light olefin gases was evolved from coal G#5. This can be explained by the high aliphatic nature (fraction aliphatics = 0.34) and large liptinite content (9 vol.% m.m.f.b.) of this coal in comparison to what was obtained for the other three coals. Similar observations were made for the gas evolution curves of the 5 mm particles. The GC results confirm expected trends as observed from the MS measurements performed online.

Effect of coal particle size:

The effect of particle size on the gas evolution characteristics of coal UMZ can be seen in Figures 6.12 and 6.13 for the two different temperatures, respectively. Figures of the other three coals can be found in Appendix C.5. A detailed comparison of the amount of gaseous species evolved for the two different particle sizes at the different temperatures is summarised in Tables 6.13 and 6.14. From the figures it is clear that evolution rate increased, while the time to maximum evolution of each individual gas species decreased with decreasing particle size, similar to what was found with MS measurements. A decrease in maximum evolution time of between 4 to 7 minutes was found for the 450°C experiments, while shorter time differences were observed at the higher temperature. This difference can be attributed to the shorter heating period required to heat up smaller particles (Cui *et al.*, 2006; Incropera *et al.*, 2007).

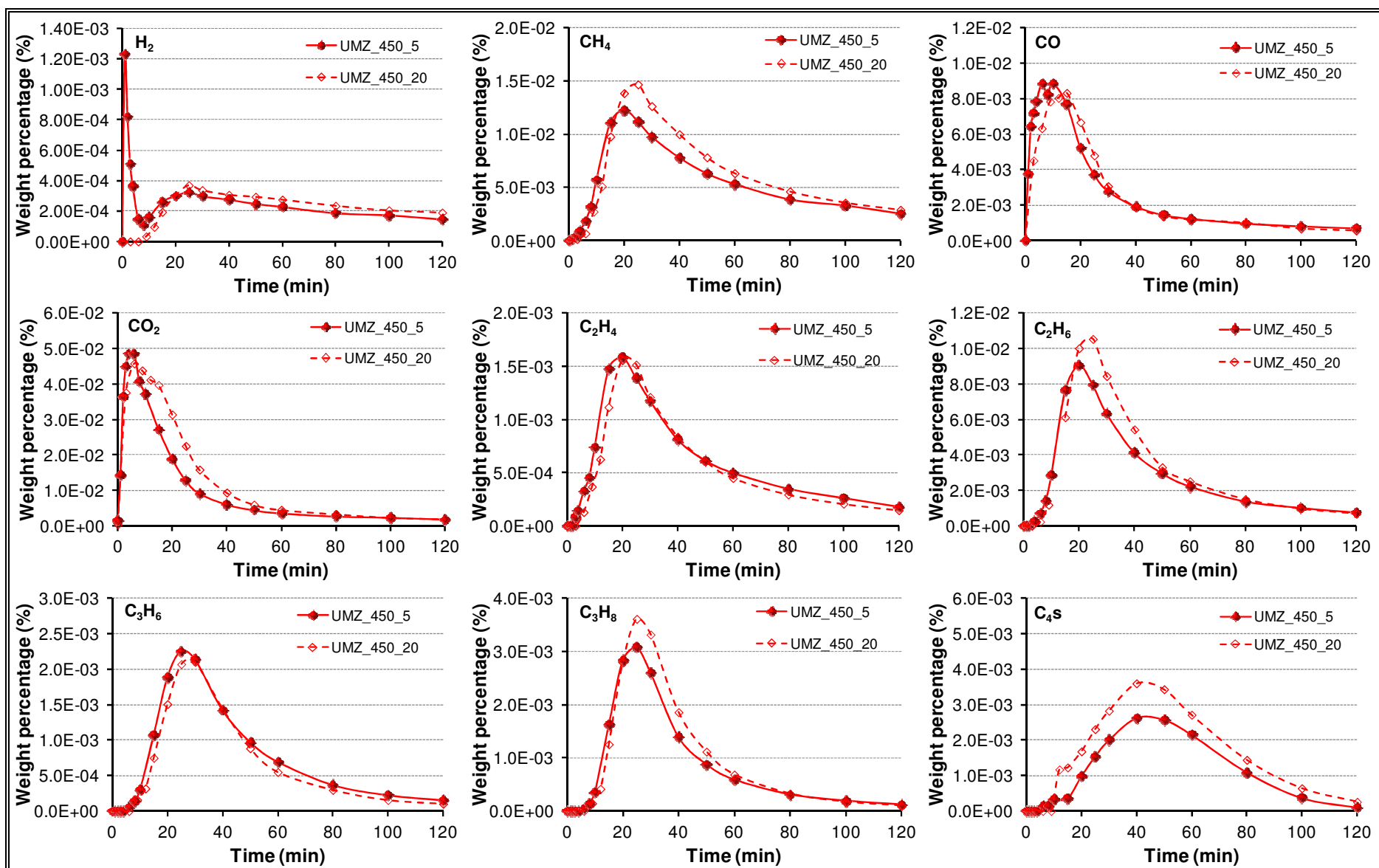


Figure 6.12 Gas evolution profiles determined at 450°C for both particle sizes of coal UMZ.

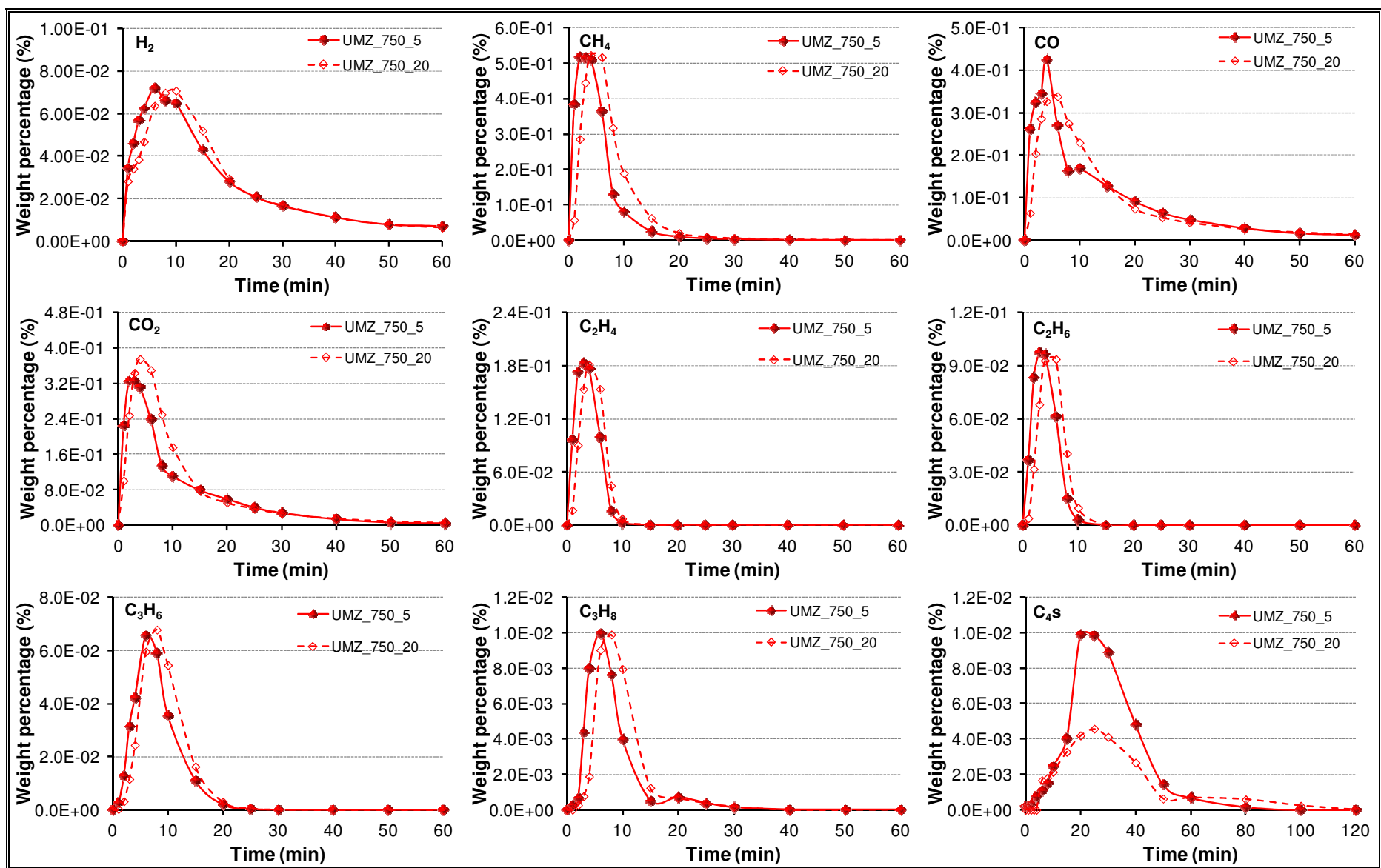


Figure 6.13 Gas evolution profiles determined at 750°C for both particle sizes of coal UMZ.

Table 6.13 Summary of amount of gas species evolved at 450 °C for both particle sizes.

Gas species (wt.% ^a)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		TSH		G#5	
	5 mm	20 mm	5 mm	20 mm	5 mm	20 mm	5 mm	20 mm
H ₂	0.03	0.03	0.04	0.03	0.10	0.13	0.03	0.03
CH ₄	0.81	0.91	1.10	1.00	2.03	2.18	1.37	1.63
CO	0.35	0.35	0.31	0.23	0.07	0.11	0.63	0.54
CO ₂	1.35	1.81	1.10	1.24	0.39	0.54	1.72	1.75
C ₂ H ₄	0.09	0.08	0.10	0.07	0.12	0.11	0.18	0.19
C ₂ H ₆	0.42	0.45	0.56	0.54	0.84	0.85	0.81	0.97
C ₃ H ₆	0.11	0.10	0.13	0.09	0.13	0.11	0.23	0.24
C ₃ H ₈	0.12	0.13	0.17	0.17	0.26	0.25	0.26	0.32
C ₄ S ^c	0.18	0.24	0.22	0.27	0.22	0.19	0.35	0.45
Total	3.46	4.10	3.73	3.65	4.17	4.48	5.59	6.12
Error %	3.9	11.6	8.0	10.2	3.0	15.1	5.7	4.1

^a Values reported on dry ash free basis of initial coal mass. ^c Butane (C₄H₁₀) chemical structure assumed for average structure of C₄s.

Table 6.14 Summary of amount of gas species evolved at 750 °C for both particle sizes.

Gas species (wt.% ^a)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		TSH		G#5	
	5 mm	20 mm	5 mm	20 mm	5 mm	20 mm	5 mm	20 mm
H ₂	1.77	1.77	1.75	2.08	2.20	2.58	1.58	1.71
CH ₄	3.72	4.47	4.07	4.66	6.19	7.02	4.70	6.20
CO	5.68	5.71	4.79	4.87	1.97	1.95	5.36	6.22
CO ₂	3.93	4.56	3.02	3.49	0.82	0.92	2.23	3.10
C ₂ H ₄	0.96	0.95	1.12	1.02	1.09	1.18	1.95	2.01
C ₂ H ₆	0.53	0.55	0.62	0.56	0.72	0.82	0.88	1.06
C ₃ H ₆	0.55	0.60	0.69	0.57	0.50	0.52	1.43	1.52
C ₃ H ₈	0.08	0.08	0.11	0.09	0.09	0.09	0.18	0.22
C ₄ S ^c	0.28	0.16	0.34	0.21	0.20	0.20	0.82	0.67
Total	17.48	18.86	16.49	17.55	13.77	15.28	19.15	22.70
Error %	7.7	10.5	4.1	11.1	4.9	12.9	6.5	8.9

^a Values reported on dry ash free basis of initial coal mass. ^c Butane (C₄H₁₀) chemical structure assumed for average structure of C₄s.

Although large evolution rates and time differences were expected for the smaller particles, the discrepancy in heating could therefore be attributed to the fact that the transient nature of the monolayer packed bed (due to the use of 60 g of sample) cannot be neglected. Only slight differences in gas composition were detected at 450 °C between the two particle sizes, while differences became much more pronounced at the higher temperature. For both temperatures, the total amount of gas increased with an increase in particle size due to the increased effect of secondary reactions as propagated by heat and mass transfer limitations in larger coal particles. This is consistent with what was observed by Cui *et al.* (2006).

A comparison between the values listed in Tables 6.13 and 6.14 showed that the largest differences in yields were observed for H₂, CH₄ and CO₂, with differences especially significant at 750 °C. At 450 °C the H₂ evolution curves of the 5 mm particle runs (Figures 6.12 and C.11-C.13) were characterised by a sharp peak occurring in the first few minutes of gas evolution that was not observed for the 20 mm particles. This could have been the result of the rupture of weak hydrogen bonds during the fast heating period of the smaller particles. The increased yield of H₂, CO₂ and CH₄ at higher temperatures and for a larger particle size indicates the possibility of the occurrence of more extensive hydrocarbon cracking (either from aliphatic hydrocarbons or aromatic moieties containing aliphatic or oxygenated functional groups in the tars). The increase in these gas species has also been observed by Cui *et al.* (2006) and Ibrahim (1997). No direct conclusion could, however, be inferred for the other species.

6.5.3.2 Tar composition and quality

Tar composition and quality were assessed with the aid of SIMDIST, GC-MS/FID, SEC and NMR analyses. SIMDIST and SEC analyses were conducted to determine the boiling point- and molecular mass distributions of the generated tars. The amount of low-boiling point (<300 °C) molecular species within the tar was evaluated by GC-MS/FID analyses. The assessment of hydrogen and carbon functionalities within the tars, necessitated the use of ¹H- and ¹³C NMR, which are valuable techniques that can be globally applied to the whole tar sample and is not restricted to a certain fraction as GC-MS/FID is. The results obtained and evaluated trends for the different analyses are discussed in the text below. Analyses were only performed on the tar fraction retained after water and toluene removal via Dean-Stark distillation and rotary vaporization. Most of the low boiling point compounds such as benzene, toluene, xylene, etc. possibly reporting to the distilled fraction could therefore not be analysed.

Boiling point distribution of tars with the aid of SIMDIST analysis

Boiling point distributions for the tars generated at different experimental conditions are provided in Figure 6.14. The distillation curves reported in Figure 6.14 have been determined on a solvent free basis (CH_2Cl_2 free basis). From the Figure it is evident that for all cases, the tar boiling point distributions were confined between approximately 112°C-114°C and 540°C-543°C. In addition, a 100% recovery of tar mass was obtained with no residue being formed at temperatures exceeding 550°C.

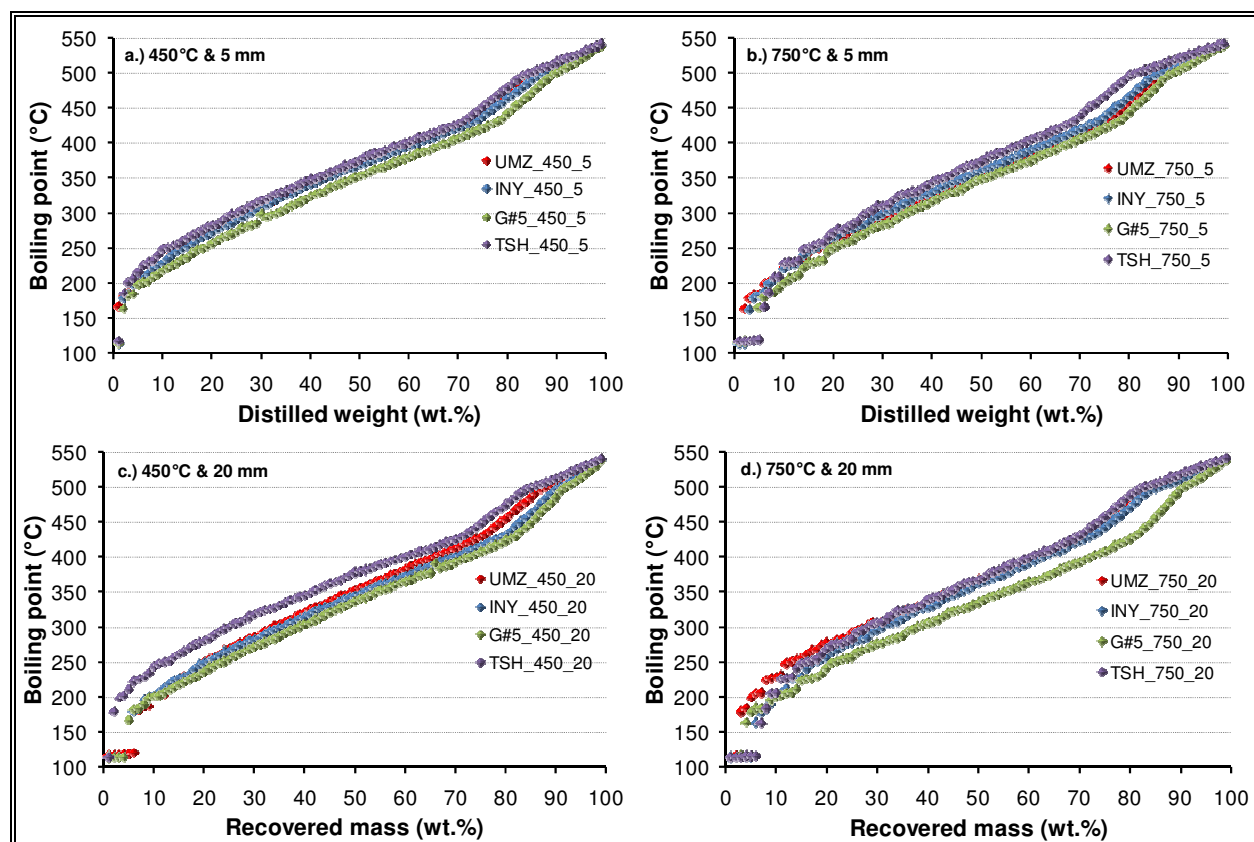


Figure 6.14 Distillation curves of the generated tars as determined from SIMDIST analysis for 450°C (a.) & (c.) and 750°C (b.) & (d.).

No material with a boiling point less than 100°C was observed due to the fact that the tars were already constrained to water and toluene removal prior to analysis. For both temperatures and particle sizes (Figure 6.14) it was found that the tars generated from coal TSH yielded the highest boiling point distribution with respect to constant recovered mass, while tars from coal G#5 displayed the lowest boiling range. Boiling point distributions for coals UMZ and INY were found to be quite similar. The determined boiling distributions are in accordance with what was

observed for typical fossil fuel and waste-derived tars and oils (Bunger, 1976; Karayildirim *et al.*, 2006; Lee, 2009; Li *et al.*, 2001; Shie *et al.*, 2003). For the purpose of comparison between the different tars, the boiling range distributions were fractionated into several distinct sections. A typical cut fraction classification system developed for crude oil refining was employed to compare between the different generated tars (Rand, 2003). As another comparative measure the weight average boiling point (*WABP*) of each tar was estimated using the method outlined by Kegler (Escallon, 2008):

$$WABP = \frac{T_{10 \text{ wt.\%}} + T_{30 \text{ wt.\%}} + T_{50 \text{ wt.\%}} + T_{70 \text{ wt.\%}} + T_{90 \text{ wt.\%}}}{5} \quad \text{Equation (6.6)}$$

Where each temperature in Equation (6.6) corresponds to 10, 30, 50, 70 and 90 wt.% recovered mass. The respective calculated values are summarised in Table 6.15 for both experimental temperatures and particle sizes. The initial and final boiling points for each tar sample have also been included.

Table 6.15 Boiling point distributions for the different tars based on crude oil fractions

Experimental temperature	Boiling fraction/ definition	Boiling Range ^a (°C)	Unit	Inertinite-rich coals				Vitrinite-rich coals			
				UMZ		INY		TSH		G#5	
				5 mm	20 mm	5 mm	20 mm	5 mm	20 mm	5 mm	20 mm
450 °C	Medium naphtha ^a	79-121	wt. %	0.15	6.02	0.26	4.13	1.06	1.11	0.31	4.13
	Heavy naphtha ^a	121-191	wt. %	3.34	3.32	3.28	3.50	1.29	1.51	4.19	4.06
	Kerosene ^a	191-277	wt. %	17.21	17.66	17.47	20.30	16.08	16.10	21.27	22.80
	Distillate fuel oil ^a	277-343	wt. %	19.81	19.80	19.79	21.40	19.90	20.29	21.01	21.40
	Light vacuum gas oil ^a	343-455	wt. %	36.54	33.23	37.59	34.47	37.17	37.41	35.83	33.49
	Heavy vacuum gas oil ^a	455-566	wt. %	21.96	18.97	20.63	15.20	23.50	22.59	16.40	13.11
	Initial boiling point	-	°C	113.2	116.4	112.6	113.2	116.0	113.6	113.2	113.2
	Average boiling point ^b	100-550	°C	368.4	351.4	366.8	345.2	376.8	375.2	355.3	337.3
	Final boiling point	-	°C	542.4	542.2	542.2	541.6	543.2	543.0	541.8	540.8
750 °C	Medium naphtha ^a	79-121	wt. %	0.33	2.10	0.51	5.14	5.07	6.13	2.31	3.13
	Heavy naphtha ^a	121-191	wt. %	5.50	2.39	5.99	3.94	2.16	2.21	6.45	5.47
	Kerosene ^a	191-277	wt. %	19.31	16.01	17.11	15.92	13.73	13.66	19.19	22.06
	Distillate fuel oil ^a	277-343	wt. %	20.83	20.77	19.80	18.88	18.80	19.33	20.27	21.67
	Light vacuum gas oil ^a	343-455	wt. %	33.80	35.69	34.63	33.56	33.07	33.20	33.50	32.55
	Heavy vacuum gas oil ^a	455-566	wt. %	19.23	22.04	20.97	21.56	26.17	24.47	17.28	14.11
	Initial boiling point	-	°C	112.6	113.6	112.6	113.2	116.4	113.6	115.4	113.6
	Average boiling point ^b	100-550	°C	360.2	367.6	362.6	358.8	374.2	365.8	348.2	339.6
	Final boiling point	-	°C	542.4	543.0	543.0	543.0	543.4	543.4	542.2	541.6

^a Crude oil fractions as reported by Rand (2003). ^b Average boiling point as estimated by the method outlined in Escallon (2008).

From Table 6.15 it can be seen that all tars contained considerable amounts of material confined to the higher boiling ranges annotated by kerosene, distillate fuel oil, light- and heavy vacuum gas oil. Of these fractions the largest proportion of boiling constituents reported to the light vacuum gas oil fraction (32.55 wt.%-37.17 wt.%). A comparison between the tars produced at the two different temperatures revealed that a reduction in the higher boiling ends with the subsequent favouring (increase in mass recovered) of the lower boiling fractions (i.e.; naphthas and kerosenes) was observed for the higher temperature. This indicates that extensive thermal cracking occurred at the higher temperature causing a subsequent increase in the amount of lower distillation cuts (Bunger, 1976; King *et al.*, 1978). A similar observation was made for increasing particle size at a fixed temperature. As a comparison, the characterisation of typical commercial oils and fuels (as adapted from Lee (2012a & b) and Villalanti *et al.* (2000)) is given in Table 6.16.

Table 6.16 Boiling range distributions for commercial petrochemical products (adapted from Lee (2012a & b) and Villalanti *et al.* (2000)).

Boiling fraction/ definition	Boiling Range^a (°C)	Unit	Gasoline^b	Diesel^b	Wax^c	Crude Oil^d
Light naphtha	< 79	wt. %	72.50	0.00	0.00	2.40
Medium naphtha ^a	79-121	wt. %	24.38	2.25	0.00	4.09
Heavy naphtha ^a	121-191	wt. %	3.12	12.75	2.25	10.00
Kerosene ^a	191-277	wt. %	0.00	30.00	2.75	15.12
Distillate fuel oil ^a	277-343	wt. %	0.00	35.00	7.75	13.24
Light vacuum gas oil ^a	343-455	wt. %	0.00	20.00	44.13	21.66
Heavy vacuum gas oil ^a	455-566	wt. %	0.00	0.00	43.12	33.49

^a Crude oil fractions as reported by Rand (2003). Values for commercial oils and products taken from Lee (2012a)^b, Lee (2012b)^c and Villalanti *et al.* (2000)^d.

The boiling fraction distribution of the different tars therefore closely resembles that of diesel, wax and crude oil. A comparison of descriptive boiling points revealed that the tars from coal TSH were characterized by the highest *WABP* (365.8-376.8°C), while tar generated from coal G#5 had the lowest *WABP* (337.3-355.3°C) for all experimental conditions. The boiling range of the light vacuum gas oil fraction is therefore the dictating factor in the overall *WABP* of the different tars. This discrepancy in the *WABP* between tars generated from coal TSH and G#5 can be ascribed to a difference in intermolecular forces of the confined tar species due to either

the presence of higher molecular weight molecules, polar and/or non-branched hydrocarbon species; or a larger amount of aromatic constituents within the tars of coal TSH (Kotz & Treichel, 2003; McMurry, 2004). The subsequent lowering of *WABP* for the higher temperature and large particle size tars is directly proportional to the increase in the amount of lower boiling constituents as observed from Table 6.15.

Composition of low molecular mass compounds in tar with GC-MS and GC-FID

Tar samples were subjected to GC-MS and GC-FID analyses in order to obtain information regarding the types of hydrocarbon species present in the low molecular weight fraction of the tars. The samples, dissolved in dichloromethane, were analysed according to the method outlined in Section 6.4.4.3. From the SIMDIST results it is clear that due to the temperature constraint of GC columns (~300°C) only 40-55 wt.% of the original tar sample can be analysed, therefore confining the GC results to the low molecular weight range of compounds. Total ion chromatograms (TIC) for tars generated from coals UMZ and G#5 at 450°C and 750°C, respectively, are provided in Figures 6.15-6.18. The results shown are only of tars produced from 5 mm particles, while the chromatograms for the other coals and 20 mm experiments can be found in Appendix C.6. Semi-quantitative measurements on detected peaks were performed via FID and only peaks with a relative abundance exceeding 0.005 wt.% were considered. Composition results were normalised to a 100 wt.% of the sample analysed.

A summary of the results for both particle sizes and temperatures is given in Tables 6.17 and 6.18. For comparative purposes and the sake of simplicity, detected species were classified into molecular families which included: aliphatics, alkyl-benzenes, alkyl-phenols, aromatic ethers and esters, alkyl-indenes, alkyl-naphthalenes, poly-aromatic hydrocarbons, mixed aliphatics and aromatics, nitrogen heteroatoms and sulphur heteroatoms. Subsequent species representative of each molecular family has also been included in both tables. A detailed list of the detected compounds/species and their relative abundance (in wt.%) for each tar can be found in Appendix C.6.

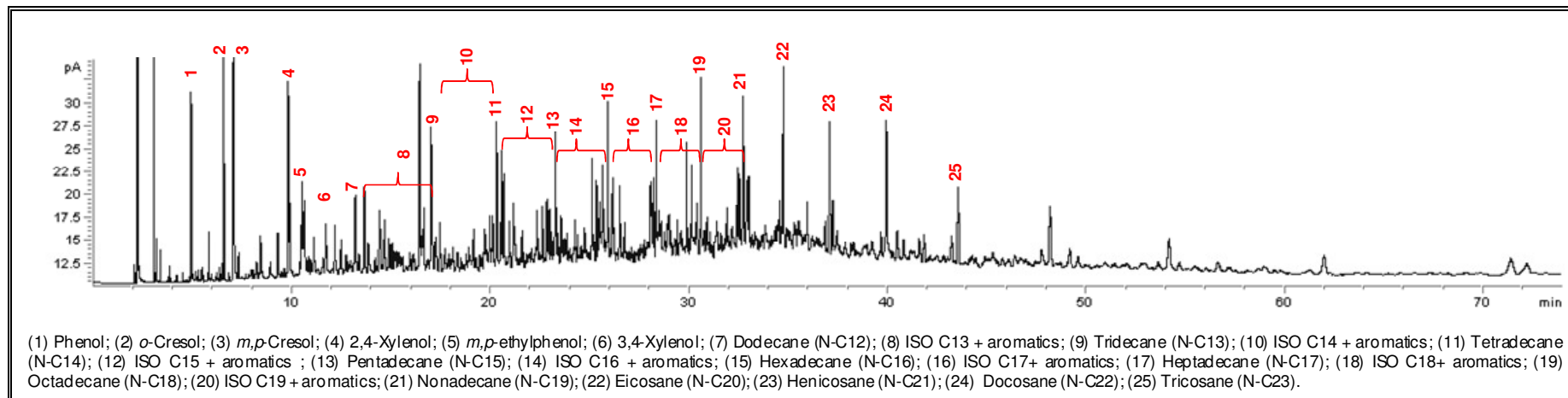


Figure 6.15 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal UMZ at 450 °C.

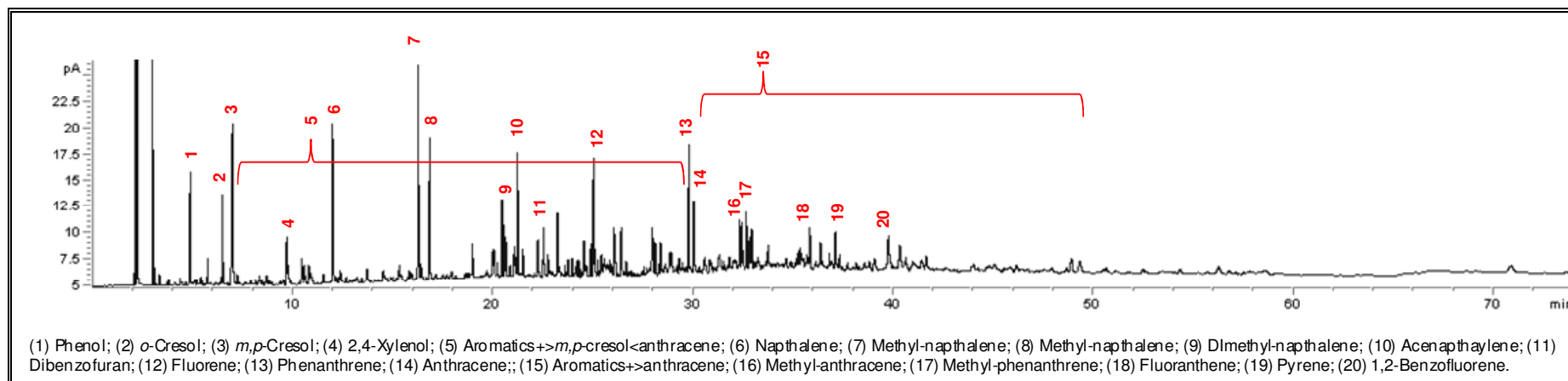


Figure 6.16 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal UMZ at 750 °C.

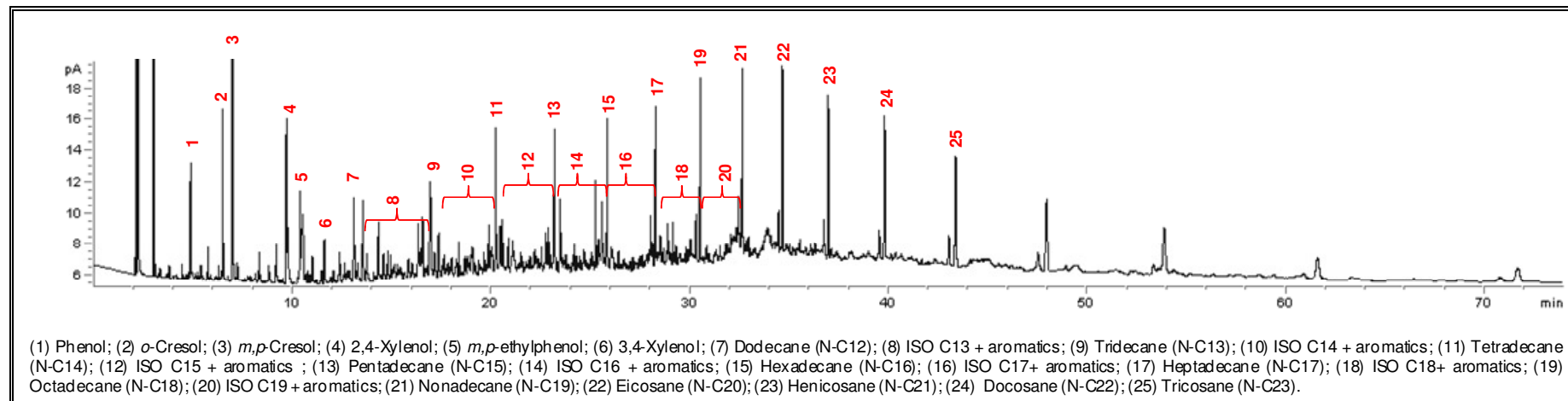


Figure 6.17 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal G#5 at 450°C.

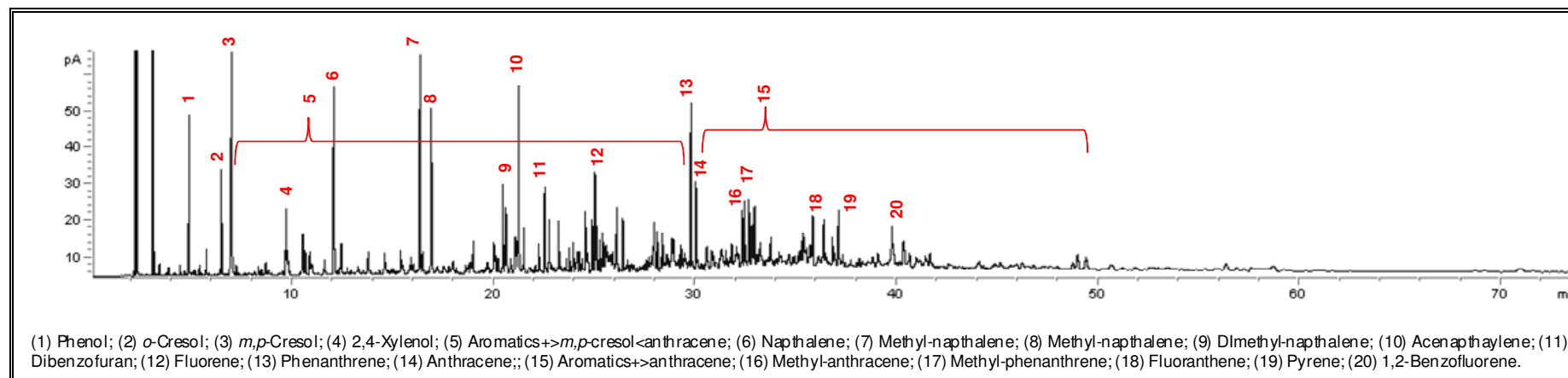


Figure 6.18 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal G#5 at 750°C.

Table 6.17 GC-MS/FID results obtained for tars generated from 5 mm coal particles.

Analysis of tars obtained from 5 mm particles		Unit	Inertinite-rich coals				Vitrinite-rich coals			
Molecular family	Typical compounds		UMZ		INY		TSH		G#5	
			450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Aliphatic compounds	Normal- and iso-paraffins, olefins and acetylenes. Acyclic compounds.	wt.%	14.21	0.22	12.23	0.18	0.00	0.00	24.25	0.16
Alkyl-benzenes	Benzene and its derivatives, i.e.; toluene, xylene, higher substituted benzenes	wt.%	0.24	0.52	0.25	0.94	0.38	1.36	0.33	0.89
Alkyl-phenols	Phenol, cresol, xlenol	wt.%	12.03	11.59	9.60	8.11	5.70	2.14	24.56	10.22
Aromatic ethers and esters	Dibenzofuran	wt.%	0.00	1.24	0.00	0.95	0.57	0.67	0.00	1.20
Alkyl-indenes	Indene, methyl-indene	wt.%	0.03	0.76	0.47	0.49	0.13	0.27	0.19	0.56
Alkyl-naphthalenes	Naphthalene, methyl-naphthalene and acenaphthylene	wt.%	0.43	13.94	0.78	10.13	6.50	14.60	0.22	10.11
Poly-aromatic hydrocarbons	Fluorene, anthracene, phenanthrene, fluoranthene and other aromatics	wt.%	0.00	71.52	0.00	78.96	86.62	80.72	3.63	76.61
Mixed aliphatic and aromatic compounds ^a	Co-elution of iso-aliphatics and aromatics	wt.%	72.98	0.00	76.55	0.00	0.00	0.00	46.53	0.00
Nitrogen heteroatoms	Pyridene, aniline, benzene-amine, etc.	wt.%	0.02	0.23	0.09	0.10	0.11	0.13	0.29	0.23
Sulphur heteroatoms	Methyl-thiophene, mercaptan, etc.	wt.%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Other	Not classified in the above	wt.%	0.03	0.07	0.04	0.02	0.00	0.00	0.00	0.01
Total		wt.%	100.0	100.1	100.0	99.9	100.0	99.9	100.0	100.0

^a Mixed aliphatic and aromatic compounds refer to compounds that cannot be distinguished due to co-elution of peaks.

Table 6.18 GC-MS/FID results obtained for tars generated from 20 mm coal particles.

Analysis of tars obtained from 20 mm particles		Unit	Inertinite-rich coals				Vitrinite-rich coals			
Molecular family	Typical compounds		UMZ		INY		TSH		G#5	
			450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Aliphatic compounds	Normal- and iso-paraffins, olefins and acetylenes. Acyclic compounds.	wt.%	11.01	0.69	13.52	0.47	0.25	0.33	19.40	0.25
Alkyl-benzenes	Benzene and its derivatives, i.e.; toluene, xylene, higher substituted benzenes	wt.%	0.79	0.31	0.25	1.26	0.59	1.09	2.37	1.82
Alkyl-phenols	Phenol, cresol, xlenol	wt.%	12.98	11.33	9.42	7.16	3.82	2.11	19.02	11.22
Aromatic ethers and esters	Dibenzofuran	wt.%	0.47	1.14	0.00	0.81	0.64	0.62	0.00	1.06
Alkyl-indenes	Indene, methyl-indene	wt.%	0.03	0.53	0.00	0.29	0.10	0.21	1.31	0.55
Alkyl-naphthalenes	Naphthalene, methyl-naphthalene and acenaphthylene	wt.%	4.92	13.86	0.53	10.94	5.73	12.03	0.08	9.73
Poly-aromatic hydrocarbons	Fluorene, anthracene, phenanthrene, fluoranthene and other aromatics	wt.%	4.37	71.82	0.00	78.71	88.66	83.36	4.43	75.05
Mixed aliphatic and aromatic compounds ^a	Co-elution of iso-aliphatics and aromatics	wt.%	64.58	0.00	76.15	0.00	0.00	0.00	52.99	0.00
Nitrogen heteroatoms	Pyridene, aniline, benzene-amine, etc.	wt.%	0.08	0.32	0.12	0.34	0.19	0.23	0.39	0.30
Sulphur heteroatoms	Methyl-thiophene, mercaptan, etc.	wt.%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Other	Not classified in the above	wt.%	0.66	0.00	0.01	0.03	0.03	0.02	0.00	0.03
Total		wt.%	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^a Mixed aliphatic and aromatic compounds refer to compounds that cannot be distinguished due to co-elution of peaks.

Effect of coal type and temperature

For the 450°C experiments the main compounds identified included: phenol, *o*-cresol, *m,p*-cresol, 2,4-xyleneol, a series of aliphatic hydrocarbons ranging from C₁₁ to C₁₈; and some co-eluting iso-aliphatics and aromatics. In contrast however, tars generated at 750°C contained numerous amounts of aromatic species of which the most important were: phenol, *o*-cresol, *m,p*-cresol, aromatic derivatives larger than cresol but smaller than anthracene, naphthalene and its derivatives, dibenzofuran, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, 1,2-benzofluoranthene and aromatics larger in molecular size than anthracene. The fact that aliphatic compounds were not detected for the higher temperature does not imply their non-existence but only that they could be present in negligible quantities.

For a comparison between coal synergistic effects, only the 450°C experiments are considered due to the fact that primary devolatilization predominantly governs volatile evolution at lower temperatures, while secondary reactions become more favourable at higher temperatures (Kandiyoti *et al.*, 2006; Ladner, 1988; Nelson *et al.*, 1988). Tar derived at 450°C (for both particle sizes) from coal TSH showed a profound similarity in composition to tars obtained for the other three coals at 750°C. According to Casal *et al.* (2008), the predominance of aromatics and their oxygenated derived compounds (phenols and cresols) are characteristic of tars generated from high-rank coals, while tars from lower rank coals also display a clear series of n-alkane homologues ranging from C₁₁ to C₂₈. This can be clearly seen from the chromatograms of coals UMZ, INY and G#5 at 450°C. In addition, Nip and Leeuw (1992) established that the devolatilization of the liptinite maceral produces a homologue series of n-alkanes and that coals with high liptinite contents present the clearest series of these aliphatic compounds (Casal *et al.*, 2008). From the 450°C chromatograms it is evident that the homologue series of n-alkanes is predominantly visible for the tars generated from coal G#5, while it is apparently missing for coal TSH. From Tables 6.17 and 6.18 it is evident that the amount of aliphatic compounds generated increases in the order TSH < INY < UMZ < G#5 for the 5 mm particles and TSH < UMZ < INY < G#5 for the 20 mm particles. This can therefore be attributed to the higher liptinite- and aliphatic content of coal G#5 (9.7 vol.%, m.m.f.b. and 34%, respectively), while the obscurity of any alkane (aliphatic) homologues in the tars of coal TSH can be ascribed to its higher rank or higher aromaticity (Medium Rank B / 81 % aromatic) and its lower liptinite content (1.1. vol.%, m.m.f.b.) (Casal *et al.*, 2005 & 2008; Freihaut *et al.*, 1989). Furthermore, the phenolic and alkyl-phenolic compounds constitute a substantial fraction (2.11 wt.% and 24.56

wt.%) of the lower temperature tars, while little to no higher order poly-aromatic hydrocarbons are observed for both particle sizes of coals UMZ, INY and G#5. According to Casal *et al.* (2008) the amount of phenolic compounds (alkyl-phenols) decrease with an increase in coal rank, while Given *et al.* (1960) showed that the amount of phenolics present is a strong function of liptinite content. This is in agreement with what was obtained for this investigation, where the higher rank, lower liptinite coal (TSH) contained the lowest amount of total alkyl-phenols as opposed to coal G#5 with the highest liptinite and lowest random vitrinite reflectance (lower aromaticity). The observed effect of liptinite content (vol.%, m.m.f.b.) on the amount of aliphatic- and alkyl-phenol content generated (wt.%) is depicted in Figure 6.19 a.) and b.) for the 450°C tars. A comparison with *DOI* and the amount of elemental oxygen has also been included in Figure 6.19 c.) and d.). Line graphs shown in the respective figures are to guide the reader's eye through the experimental data points.

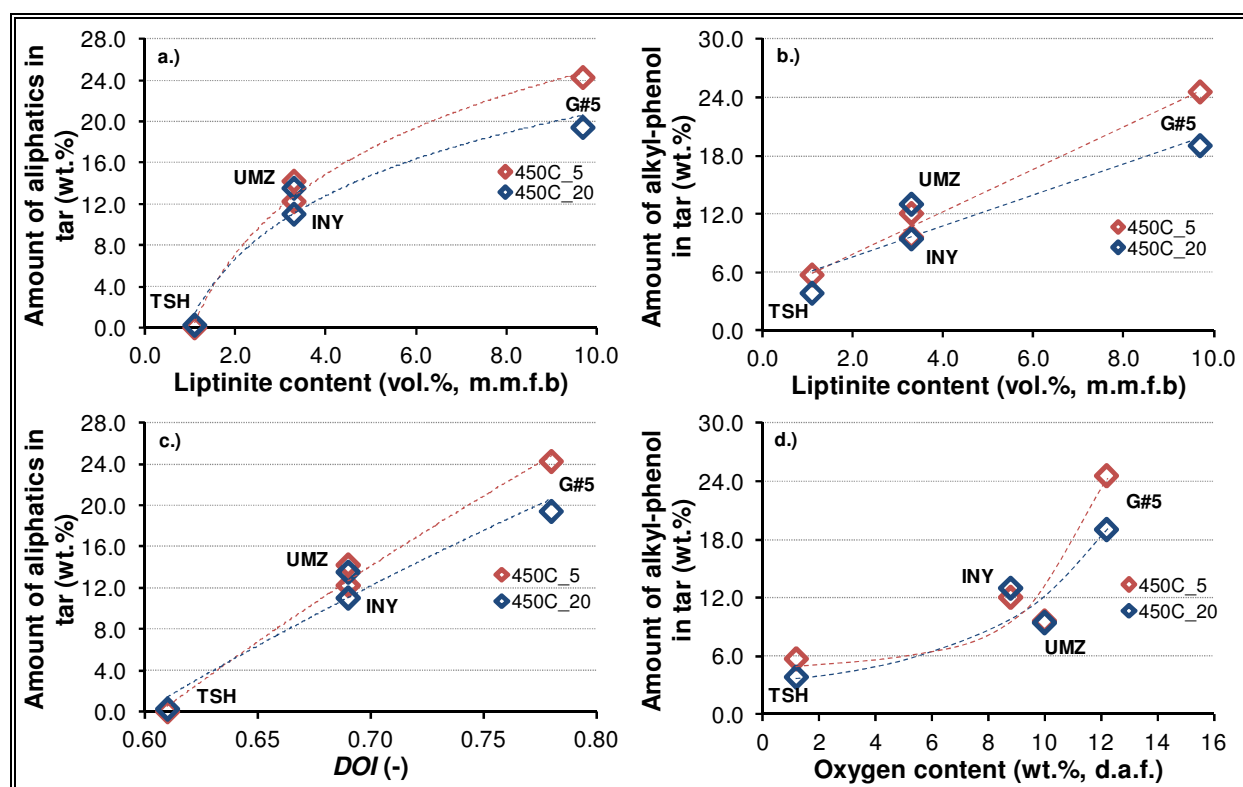


Figure 6.19 Correlation of aliphatic- and phenolic content in tars with coal liptinite content, *DOI* and elemental oxygen content..

From the above Figure it could therefore be concluded that alkyl-phenolic content increased for both an increase in parent coal liptinite- (b.) and -elemental oxygen content (d.). In addition, tar aliphatic content was also found to be related to the degree of disorder (*DOI*) within each coal;

therefore supporting the higher expected aliphatic tar yield from coal G#5 (Figure 6.19 c.). Tars derived at 450°C from coal TSH were however characterised by a substantial amount of poly-aromatic compounds in comparison to the other tars. This could also be attributed to the rank effect dominating the behaviour of coal TSH. Accordingly, it has been shown that aromaticity as well as the degree of methylation of aromatic compounds within the tar increases with an increase in coal aromaticity or rank (Casal *et al.*, 2008; Zoller & Johnston, 1999). This explains the presence of compounds such as naphthalene, fluorene, anthracene, phenanthrene etc. in tar from coal TSH even at a temperature as low as 450°C.

Furthermore, only small to negligible amounts of alkyl-benzenes (between 0.24 wt.% and 2.37 wt.%), alkyl-indenes (between 0.03 wt.% and 1.31 wt.%), aromatic ethers and esters (between 0.00 wt.% and 1.24 wt.%), alkyl-naphthalenes (between 0.22 wt.% and 4.92 wt.% for coals UMZ, INY and G#5); and heteroatoms (between 0 wt.% and 0.39 wt.%) were observed for both particle sizes at 450°C. This is in agreement with what was observed by Nelson *et al.* (1988). No definite conclusions or trends could be drawn for the mixed aliphatic- and aromatic compounds. For future investigations it is proposed to conduct GC-GC-MS analyses in order to prevent the co-elution of these molecular compounds. This will evidently not only improve the resolution of the required data but also provide better insight into the type and amount of aromatic- and/or aliphatic compounds present in the mixed molecular compound family. From Tables 6.17 and 6.18 it can be observed that an increase in devolatilization temperature leads to a significant decrease in aliphatics and mixed compounds with the subsequent increase in aromatic species. The significant decrease in the amount of polymethylenes (n-alkanes) within the coal tar is consistent with the findings of Nelson and Tyler (1988), who observed an increase in polymethylenes with increasing temperature up to 500°C, followed by the rapid decrease to near zero at 750°C.

The apparent absence of polymethylenes at temperatures as high as 750°C has also been observed by Wang *et al.* (2010). Furthermore, a decrease in the average chain length of both paraffins and olefins with increasing temperature was also observed by Nelson and Tyler (1988). This behaviour was attributed to gas-phase cracking reactions cleaving the long-chain aliphatics with the subsequent production of more short chain olefins such as ethylene, propylene and 1-butene (Doolan & Mackie, 1983; Rebick, 1983). This is in agreement with what was observed from the gas analyses results in this investigation, where a significant increase in ethylene (C₂H₄) and propylene (C₃H₆) was observed with increasing temperature. In addition,

the apparent absence of polymethylene compounds in the tars of coal TSH, as well as the evolution of light paraffinic and olefinic species in the gas phase, indicates the possibility of the long chain aliphatic hydrocarbons being cracked extensively due to the swelling nature of the coal.

A noticeable change also occurs in the amount of alkyl-benzenes (2 to 4 times larger at 750 °C) and alkyl-indenes produced with temperature, while the yield of naphthalene and its derivatives increases significantly (as high as 32 times larger than at 450 °C) due to the severity of devolatilization at higher temperatures and the cleavage of more aromatic bridge structures. According to Nelson *et al.* (1988), yields for substituted aromatic species reach a maximum around 850 °C, whereafter the yields significantly decrease with an increase in temperature. A significant increase in alkyl-naphthalenes was also observed by Nelson *et al.* (1988). Larger yields of alkyl-substituted benzenes and naphthalenes could have occurred, but could have been subjected to decomposition to methane and the parent aromatics, i.e.; benzene and naphthalene due to transport limitations in larger coal particles. This decomposition mechanism has been proposed for powdered coal samples at higher temperatures (Gräber & Hüttinger, 1982). This decomposition could also have attributed to the subsequent increase in methane yield as observed from the gas analyses results presented in Section 6.5.3.1.

Oxygen-containing tar species, especially phenol and its derivatives, were observed to decrease with temperature for all four coals. This was also observed during the investigation conducted by Nelson *et al.* (1988), where phenolic compounds were found to increase up to a certain temperature, whereafter yields substantially decreased. Accordingly, it has been shown that phenol and cresol species can be decomposed via decarbonylation to produce CO and either cyclopentadiene (C₅H₆) at temperatures ranging between 665 °C and 865 °C (Cyprens & Bettens, 1974 & 1975; Nelson *et al.*, 1988). In addition, yields of alkyl-phenols decreased significantly by 14.34 wt.% and 7.80 wt.%, respectively for the 5 mm and 20 mm particles of coal G#5. Reduction in the amount of alkyl-phenols could therefore be attributed to enhanced secondary decomposition reactions occurring at higher temperatures and is in accordance with the elevated levels of CO species observed at 750 °C.

The largest increase in tar component yields was observed for poly-cyclic aromatic hydrocarbons (PAHs). The amount of PAHs increased from near zero to between 71.52 wt.% to 78.96 wt.% for high temperature tars generated from coals UMZ, INY and G#5, while a slight

decrease in PAH yield was observed for coal TSH as a result of possible secondary cracking. Similar observations were made by Nelson and Tyler (1988) and Nelson *et al.* (1988). The mechanism of PAH formation is however not clear, but independent studies have shown that PAHs can be produced from the devolatilization of simple aromatic species such as toluene (Badger, 1965; Smith, 1979), flames of acetylene and benzene (Homann & Wagner, 1967); ethylene and acetylene (Crittenden & Long; 1973); benzene (Bittner & Howard, 1981); and butadiene (Cole *et al.*, 1984). Other proposed mechanisms include PAH formation from reaction intermediates such as phenylacetylene, styrene and indene generated from ethylene and acetylene flames (Crittenden & Long; 1973). The preceding developments do however not overrule the possibility for PAH production as a direct result of the evolution of low molecular weight PAHs present in the parent coal structure.

Furthermore, only small amounts of nitrogen functionalities, which consisted mainly of pyridines, anilines and benzene amines, were identified for both particle sizes. No detectable sulphur containing species were identified, although they could have been present in very small amounts. The fact that detectable amounts of nitrogen heteroatoms were observed in comparison to sulphur functionalities can be explained by the fact that nitrogen atoms are normally confined to the aromatic structures such as pyridenes and pyrroles and report predominantly to the tar fraction during devolatilization (Chen *et al.*, 1990; Smith *et al.*, 1994). Sulphur can be found in some organic structures but also forms a major part of the sulphide minerals such as pyrite, FeS_2 . The main shuttle of sulphur released during devolatilization is generally in gaseous form as H_2S (Smith *et al.*, 1994), although some sulphur functionalities such as thiols and thiophenes can report to the tar fraction. Other analytical techniques such as specialised GC-MS and XPS (X-ray photoelectron spectroscopy) are therefore recommended for a better understanding of the evolution of sulphur functionalities.

Effect of particle size

A comparison between the quantitative GC results obtained for the different particle sizes is provided in Figure 6.20. From the Figure and the accompanying Tables (6.17 and 6.18), no direct conclusions could be drawn on the variance of tar composition with particle size, although differences could be observed in some molecular families. For the 450 °C experiments, aliphatic yield decreased with an increase in particle size for coals UMZ and G#5, while the opposite was true for coals INY and TSH. Although the complete mechanism is not clear, differences in

composition could have been the result of more severe cracking reactions due to higher transport resistances in the 20 mm particles (Howard, 1981).

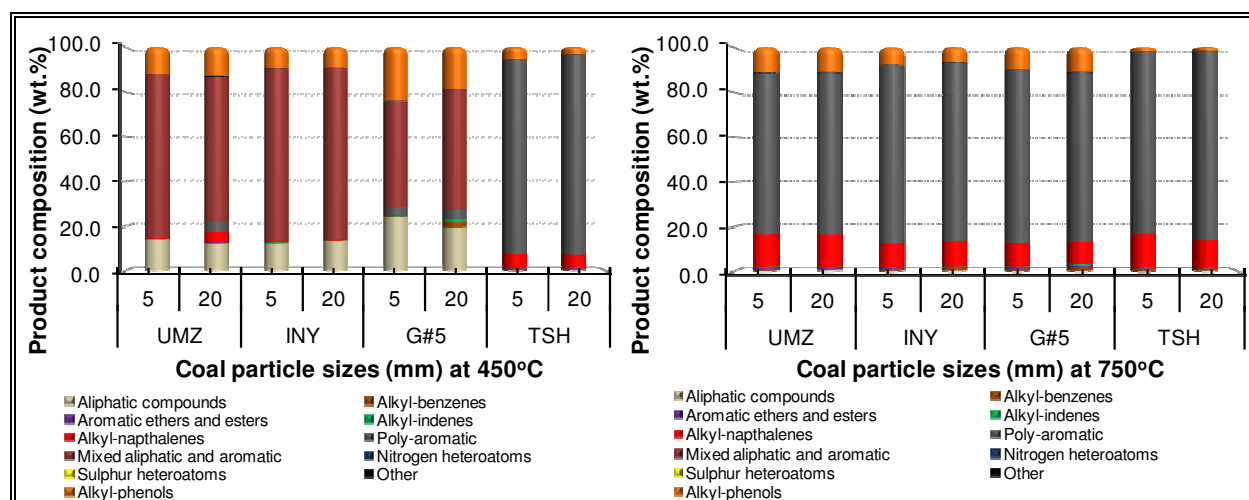


Figure 6.20 Comparison of GC results between particle sizes.

Molecular mass distribution with the aid of SEC

Currently no single, independent method is available for unambiguously accessing the molecular mass distribution or chemical properties of coal-derived species with molecular masses exceeding the ~450-500 Da mass range (Herod *et al.*, 2007). This requirement places new emphasis on the need for understanding the processing of higher mass material in especially oil refineries (Herod *et al.*, 2007). SEC analysis has proven to be a valuable technique for determining a broader range of molecular masses compared to techniques such as GC-MS and GC-FID. The determination of mass estimates for complex fuel-derived mixtures does, however, require the calibration of the SEC columns with appropriate polymer standards. In this investigation this was conducted with the aid of 10 polystyrene standards with polydispersities ($M_{w,p}/M_n$) close to 1. The results obtained for the ten different calibration standards are reflected in Figure 6.21a, while the derived calibration curve is shown in Figure 6.21b.

Elution times at maximum peak intensity were used respectively for each polystyrene standard in derivation of the calibration curve for conversion of SEC elution times to molecular mass (M_p) estimates (Herod *et al.*, 2007; Kandiyoti *et al.*, 2006; Karaca *et al.*, 2004; Morgan *et al.*, 2005). A

plot of the logarithm of polymer molecular mass versus elution time (t_E) provided a calibration curve that could be adequately described by a linear model ($R^2 = 0.987$). Accordingly, polymer standards with a narrow poly-diversity ($M_p/M_n < 1.1$) have been shown to provide strong linear relationships in the calibration of SEC results.

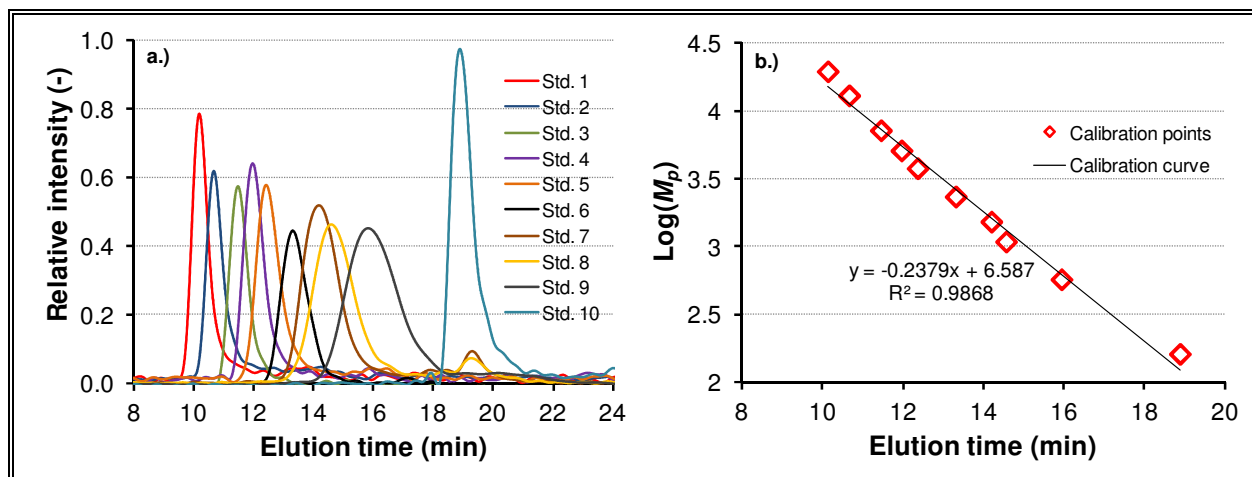


Figure 6.21 SEC chromatogram of the 10 calibration standards used a.) and b.) calibration curve determined from the elution times of the different calibration standards.

The equation derived for this purpose is therefore defined as:

$$\log(M_p) = -0.2379 \cdot t_E + 6.587 \quad \text{Equation (6.7)}$$

Elution times obtained from the SEC analyses of the different coal tar samples were therefore converted to molecular mass with the aid of Equation (6.7). The conversion of elution time (SEC results obtained at 370 nm UV detection) to molecular mass distribution is illustrated graphically for tar generated at 450 °C from 5 mm UMZ particles in Figure 6.22a and 6.22b. For both graphs intensity results have been normalised and reported on a relative basis with respect to the total peak area (Adegoroye *et al.*, 2004; Herod *et al.*, 2003). Raw chromatograms (relative intensity versus elution time) for the different tars can be found in Appendix C.7. All chromatograms (Appendix C.7) were characterised by the occurrence of an excluded peak in the range of 9 to 12 minutes as well as a retained peak confined to elution times between 12 and 27 minutes. The presence of an excluded peak in SEC chromatograms has also been confirmed by numerous authors (Deelchand *et al.*, 1999; Herod *et al.*, 1996; Herod *et al.*, 2000; Herod *et al.*, 2003; Herod *et al.*, 2007; Islas *et al.*, 2003; Mokoena *et al.*, 2008; Morgan *et al.*, 2008b) and is normally defined as material excluded from the column porosity.

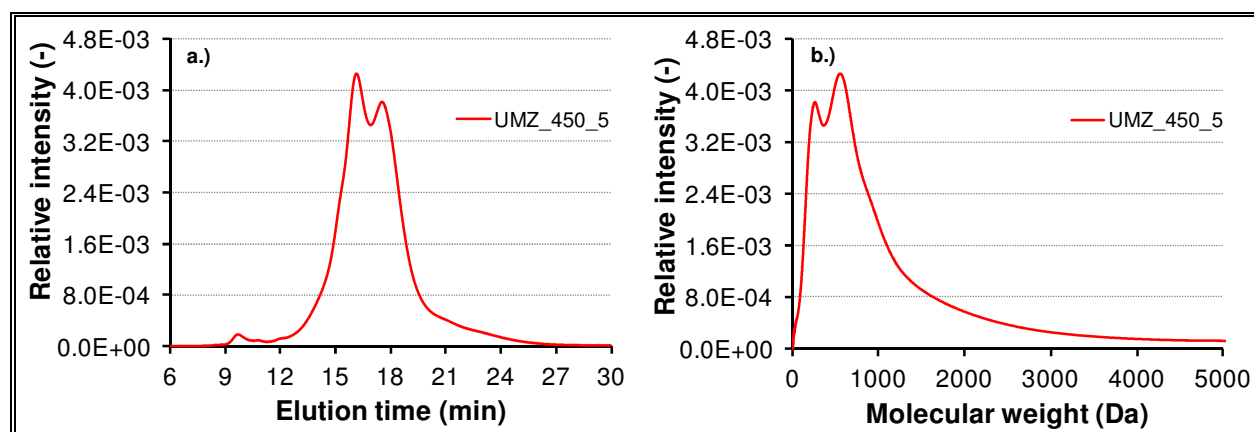


Figure 6.22 SEC chromatogram (370 nm) for tar generated from coal UMZ at 450°C and 5 mm shown as a function of a.) elution time and b.) molecular mass (Da) estimate.

For characterisation purposes the excluded material is not included in the calculation of molecular mass estimates due to the uncertain nature of this apparently high mass material. It has, however, been proposed that material excluded from the column porosity is possibly of non-planar and/or three-dimensional conformation, where the relationship between molecular size and molecular mass deviates significantly from what is expected based on the polystyrene calibration (Berrueco *et al.*, 2008; Herod *et al.*, 2007; Kandiyoti *et al.*, 2006; Karaca *et al.*, 2004). For this purpose, SEC characteristic comparisons were confined to the molecular material retained by the column porosity. An increase in UV absorbance detector wavelength showed a respective decrease in the intensity of the retained peaks for all tar samples (not shown here). This is consistent with what was found by Herod *et al.* (1996), Islas *et al.* (2003) and Lazaro *et al.* (2001); and indicates structural changes with molecular size. No significant increase in the intensity of the excluded peak was observed for wavelengths exceeding 350 nm, thus indicating no significant increase in the concentrations of possible larger poly-nuclear aromatic ring systems as well as greater heteroatom content (Begon *et al.*, 2000; Herod *et al.*, 1996; Lazaro *et al.*, 2001). Furthermore, comparisons between the different coals and operating conditions will only be discussed for SEC results obtained at 370 nm.

Effect of coal type and temperature

The influence of operating temperature on the molecular mass distribution of each coal is shown graphically in Figure 6.23. Only the results for the 5 mm particles are shown. The results for the 20 mm particles can be found in Appendix C.8.

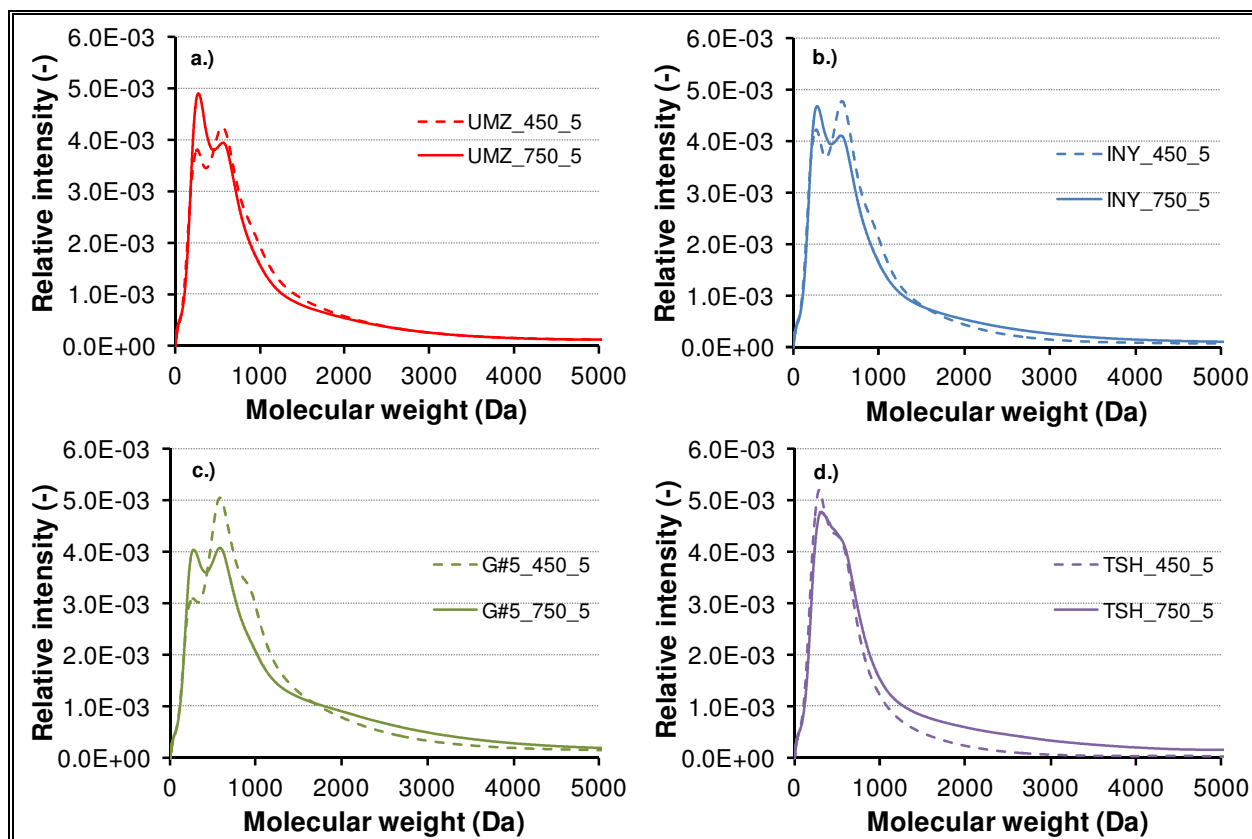


Figure 6.23 SEC chromatograms (370 nm) for tars generated at 450°C and 750°C from 5 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH.

A comparison (not shown here) between the excluded peak regions of tars generated at 450°C and 750°C revealed a slight shift in maximum intensity to shorter elution times, strongly suggesting an increase in the colloidal particle sizes with increasing temperature. This is in agreement with results obtained on tars generated from gasification processes as outlined in the work of Adegoroye *et al.* (2004) and Mokoena *et al.* (2008).

From Figure 6.23 it is evident that for both experimental temperatures and particle sizes the molecular weight distributions of the tars generated are characterised by bimodal behaviour (to a lesser extent for tar from coal TSH), with the exception of the tar obtained at 450°C from coal G#5, which shows trimodal type behaviour. For coals UMZ, INY and G#5 it can be clearly observed that an increase in devolatilization temperature leads to a subsequent shift in the molecular weight distribution (intensity increase at longer elution times), favouring the formation of lower molecular weight entities. A slight increase in higher molecular mass species (> 1500 Da) can also be observed with an increase in temperature. In addition, these trends are remarkably significant for tar generated from coal G#5, where the molecular mass distribution

changes from tri-modal to bi-modal behaviour, therefore suggesting a significant change in product distribution for this coal. In contrast, however, a slight reduction in relative intensity was observed for the lower molecular distribution (< 500 Da) of tar obtained at 750°C from coal TSH, while large increases in intensity were observed for molecular species exceeding a mass of close to 800 Da.

Furthermore, molecular masses as large as 5000 Da were observed for all the tar samples. Similar observations of the temperature effect on the molecular mass distribution were made by Adegoroye *et al.* (2004), Li *et al.* (1993a) and Mokoena *et al.* (2008). Accordingly, the subsequent shift to lower molecular weight can be attributed to the cracking of the formed tars due to a higher probability and rate of secondary reactions observed for higher temperatures and larger particle sizes (Adegoroye *et al.*, 2004; Li *et al.*, 1993a; Mokoena *et al.*, 2008). It should, however, be noted that the contribution of aliphatic species are not included due to the fact that pure NMP was used as eluent. This can be ascribed to the low solubility of aliphatics in NMP and therefore eluents such as heptane are normally suggested for the detection of aliphatic compounds (Herod *et al.*, 2007).

Furthermore, the observation of aliphatic species could have been limited by the use of a UV detector during the SEC analyses. The use of other detection methods such as RID (refractive index detection/detector) are therefore proposed for investigating the presence of aliphatic compounds. For semi-quantitative comparisons, the molecular mass estimate results were divided according to the amount of peaks detected in the chromatogram. The contribution of each peak to the total molecular mass distribution as well as the regions of interest are summarised in Table 6.19. Area contributions were estimated with the aid of the Origin 8.0 software.

Table 6.19 Summary of SEC results obtained on different tars generated from 5 mm particles.

Coal tar (5 mm experiments)	Temperature				
	450 °C			750 °C	
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2
UMZ					
Elution time range (min)	> 16.90	< 16.90	-	> 16.58	< 16.58
Molecular mass range (Da)	< 369	> 369	-	< 440	> 440
Elution time / peak max. (min)	17.53	16.16	-	17.45	16.12
Molecular mass / peak max. (Da)	260	553	-	272	565
Area contribution (%)^a	17.4	82.6	-	26.6	73.4
INY					
Elution time range (min)	> 16.81	< 16.81	-	> 16.57	< 16.57
Molecular mass range (Da)	< 387	> 387	-	< 441	> 441
Elution time / peak max. (min)	17.48	16.11	-	17.39	16.16
Molecular mass / peak max. (Da)	268	568	-	282	553
Area contribution (%)^a	20.7	79.3	-	25.9	74.1
G#5					
Elution time range (min)	> 17.39	15.53- 17.39	< 15.53	> 16.65	< 16.65
Molecular mass range (Da)	< 282	282-779	> 779	< 424	> 424
Elution time / peak max. (min)	17.50	16.07	15.47	17.43	16.07
Molecular mass / peak max. (Da)	266	579	808	276	582
Area contribution (%)^a	10.2	30.0	59.8	17.5	82.5
TSH					
Elution time range (min)	> 16.65	< 16.65		> 16.58	< 16.58
Molecular mass range (Da)	< 424	> 424	-	< 438	> 438
Elution time / peak max. (min)	17.35	16.65	-	17.22	16.58
Molecular mass / peak max. (Da)	288	424	-	310	438
Area contribution (%)^a	34.9	65.1	-	24.8	75.2

^a Percentage contribution of peak area to total area.

From the table it can be seen that for both temperatures, tars derived from coal UMZ, INY and G#5 exhibited two peaks with maxima confined to ranges of 260 Da-288 Da and 553 Da-582 Da, respectively. These molecular mass ranges are in accordance with molecular weight estimates proposed for average structural entities of the parent coals determined by ^{13}C NMR, MALDI-TOF MS and HRTEM (Chapter 5). A third peak with a maximum occurring at 808 Da is also observed for the low temperature tar derived from coal G#5. Tars generated from coal TSH did however exhibit two co-eluting peaks of which local maxima were confined to a narrower distribution range of 288 Da-310 Da and 424 Da-438 Da, respectively for the two temperatures. The contribution of the low molecular mass peaks (peak 1) increased in the order $\text{G\#5} < \text{UMZ} < \text{INY} < \text{TSH}$ for both temperatures. As previously described, contributions of peak 1 for coals INY, UMZ and G#5 increased by between 5% and 10% with increasing temperature, while the subsequent high mass contribution (peak 2) decreased. The opposite was, however, true for the tars of coal TSH, where a significant decrease in peak 1 was observed. Similar tendencies were observed for the 20 mm experiments. A summary of the SEC results for the 20 mm experiments is provided in Table C.4 of Appendix C.8. A comparison between the molecular mass distributions of the different coals at the two experimental temperatures (450°C and 750°C) is provided in Figure 6.24.

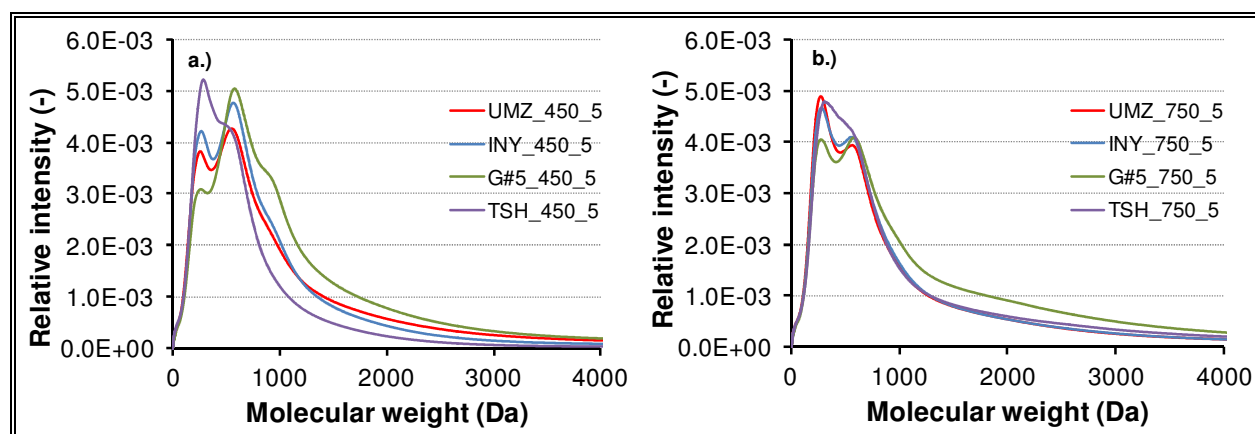


Figure 6.24 Comparison between SEC results (370 nm) obtained on tars generated from the different coals at a.) 450°C and b.) 750°C.

In co-juncture with the results presented in Table 6.19 it is evident that, for both temperatures, larger intensities (a larger amount) of higher molecular species (> 800 Da), were observed for tars generated from coal G#5. For the 450°C experiments this is clearly represented by the shift of peak 2 and the shoulder peak (peak 3) to higher molecular masses. This shift to higher molecular masses has also been observed by Li *et al.* (1993a) for tars generated from a liptinite-

rich maceral concentrate. The shrinkage of this shoulder peak as well as the shift to lower molecular masses with increasing devolatilization temperature is in accordance to what was observed by Li *et al.* (1993a). Although tar generated from liptinite macerals has been found to be more thermally sensitive, the possibility exists that the major difference in molecular mass distribution for tar generated at 450 °C from coal G#5 could be attributed to either this coal's lower aromaticity or the generation of a more open structure (porosity) during devolatilization.

The subsequent lower aromaticity (higher aliphaticity) indicates the presence of a larger amount of aliphatic structural features (such as side chains and bridges), which upon heating can be cleaved to release aromatic structures of possibly larger molecular weight in comparison to the higher aromatic coals, where some of the released aromatic structures re-polymerise to form char. This is supported by the fact that hydro-aromatic and aliphatic structures play an important role during devolatilization, where transferable hydrogen forms an important step for capping free radicals (Smith *et al.*, 1994). A reduction in this transferable hydrogen can therefore lead to the favouring of re-condensation and char-forming reactions (Neavel, 1982). In addition, it has been shown that coals characterised by larger H/C ratios and liptinite contents show greater affinity for fluidity during devolatilization (Lynch *et al.*, 1988). The second postulation involves the generation of larger porosity which can reduce the available resistance to mass transfer and subsequently decrease the probability of secondary reactions affecting the species evolved from this coal. This tends to explain the lower amount of smaller molecular mass estimates (< 300 Da) and larger proportions of higher mass material (> 800 Da) at the lower temperature, compared to the other three coals. At higher temperatures the characteristics of the tar are, however, governed by the thermally sensitive nature of liptinite with increasing temperature as proposed by Li *et al.* (1993a). This postulation also holds true for the high swelling coal, TSH, of which tars displayed a higher proportion of low mass material (< 300 Da), indicating that secondary cracking was more severe in comparison to the other coals.

Effect of particle size

Molecular mass distributions of tars derived from coals UMZ (inertinite-rich coal) and G#5 (vitritinite-rich coal) from the two different particle sizes are shown in Figure 6.25 for both experimental temperatures.

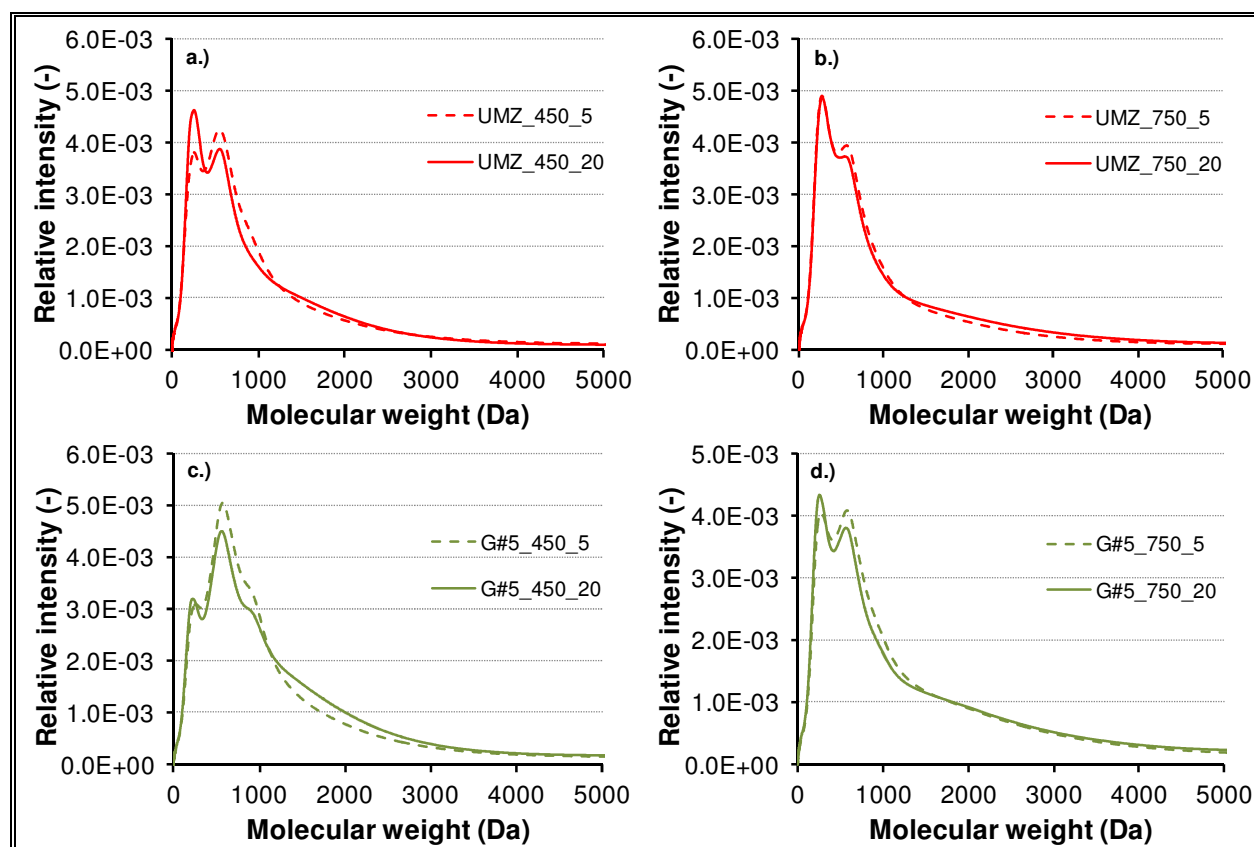


Figure 6.25 Comparison between SEC results (370 nm) obtained on tars generated from coals UMZ (a.) and (b.) and G#5 (c.) and (d.) for the different particle sizes.

From the Figure it can be seen that a substantial shift in relative intensity was observed for an increase in particle size at the lower temperature, therefore favouring the formation of smaller molecular masses. This shift was, however, not so extensive for the higher temperature tars. The apparent shift in molecular mass distribution with increasing particle size for the lower temperature (450°C) tars therefore suggests that secondary reactions were favoured more due to the larger mass transfer resistance experienced by tar-precursors in larger coal particles. The general consensus from the latter was that the formation of lower molecular masses increased for increasing bed height, therefore indicating the strong effect of mass transfer resistance on the increased probability of cracking reactions. For the 750°C experiments, the small differences in tar molecular masses due to particle size can possibly be ascribed to an increased rate of cracking governing the decomposition of tars at higher temperatures in comparison to mass transfer resistances. Similar observations, to those indicated above, were found for the tars generated from the other two coals (Appendix C.9.).

Structural features of tars as determined from ^1H - and ^{13}C NMR

Solution state NMR was performed on all tar samples in order to obtain a holistic overview of the proton- and carbon functionalities present in the different tars. For quantitative purposes the limits of integration for each hydrogen- and carbon type were confined to a combination of spectral regions defined by Díaz and Blanco (2003), Guillén *et al.* (1998), Morgan *et al.*, (2008), López *et al.*, 2010 and Wang *et al.* (2010). For illustrative purposes the different proton- and carbon spectral assignments are shown in Figure 6.26 for two hypothetical molecules.

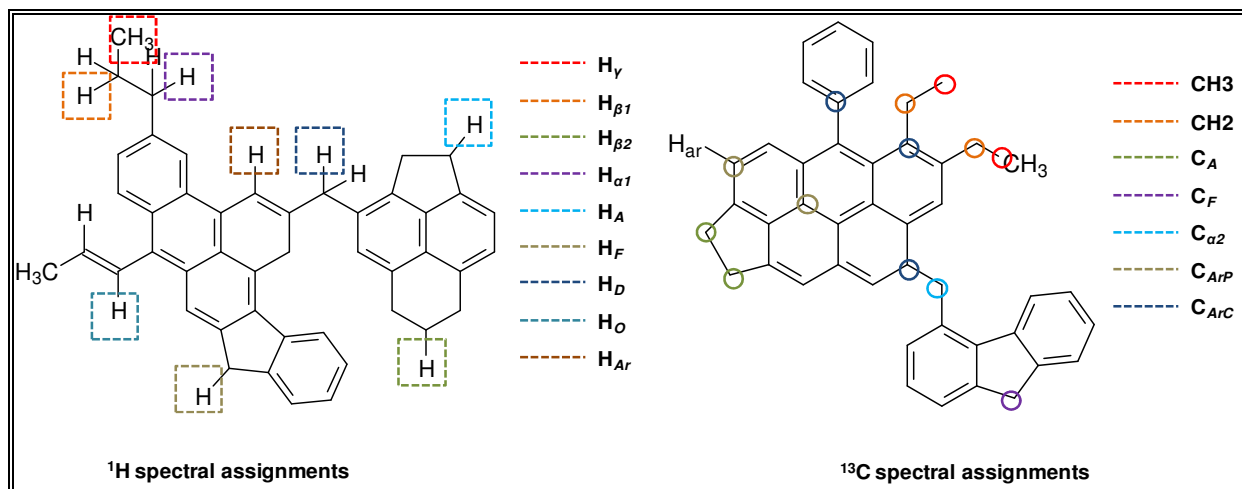


Figure 6.26 NMR spectral assignments as adapted from Diaz *et al.* (2003), Guillen *et al.* (1998), Morgan *et al.* (2008) and Wang *et al.* (2010).

The definition and chemical shift range for proton- and carbon spectral assignments are provided respectively in Tables 6.20 and 6.21. Results obtained from ^1H - and ^{13}C NMR analyses are presented and discussed separately in the text to follow.

Effect of coal type and temperature

 ^1H NMR study

A qualitative comparison of the ^1H NMR spectra of tars generated at both temperatures from the 5 mm particles of the four coals is given in Figure 6.26. The corresponding quantitative results, expressed as a percentage of the total amount of hydrogen types observed, are provided in Table 6.20.

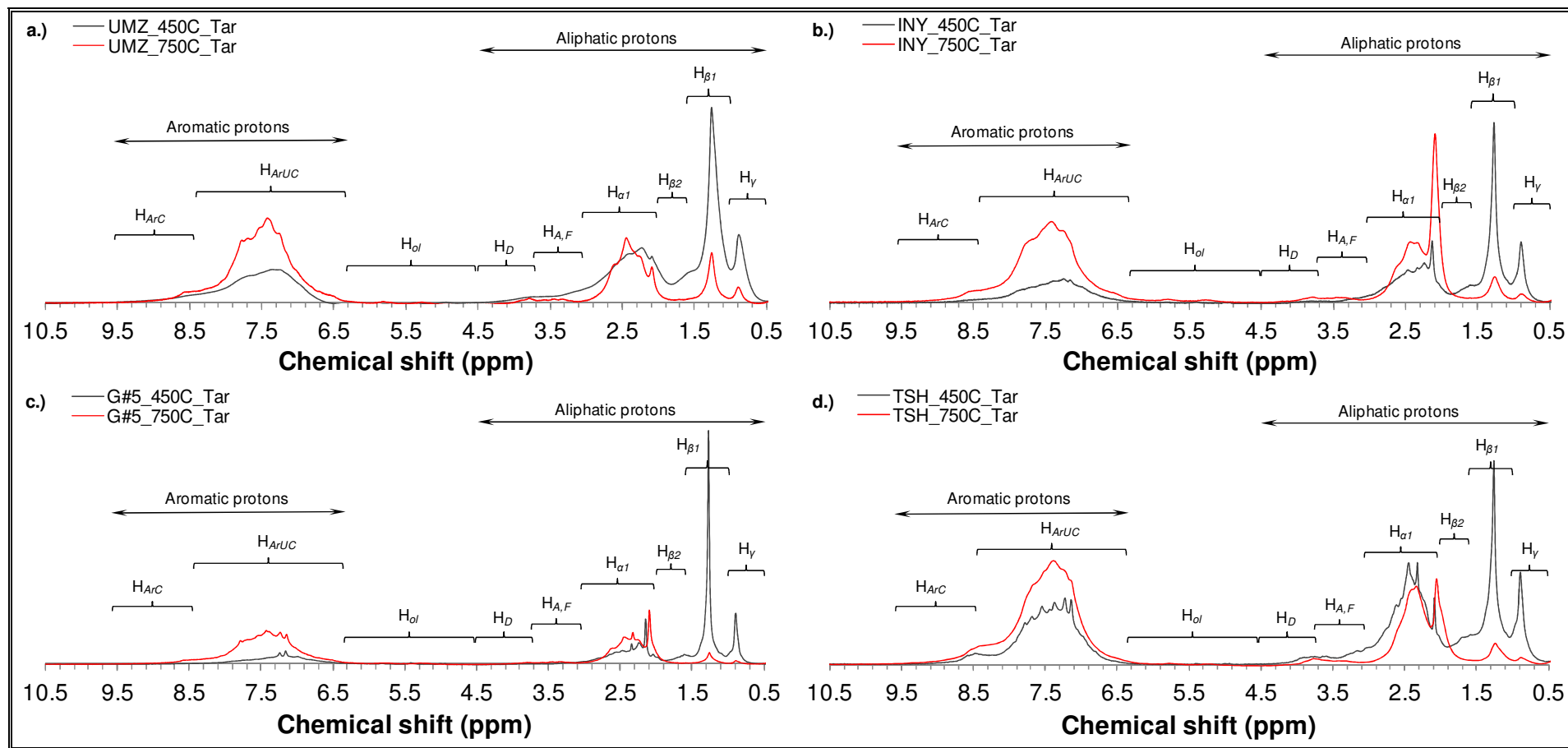


Figure 6.27 ^1H NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (5 mm particles).

Table 6.20 ^1H NMR distribution of tars derived at two different temperatures from 5 mm coal particles.

Proton type (5 mm experiments)	Symbol	Relative abundance expressed in area % of spectra							
		UMZ		INY		TSH		G#5	
		450 °C	750 °C	450 °C	750 °C	450 °C	750 °C	450 °C	750 °C
Aliphatic protons (0.5-4.5 ppm)	H_{Al}	73.74	36.36	72.80	43.43	66.19	36.10	79.25	39.50
Aliphatic H in methyl or methylene γ to an aromatic ^a	H_{γ}	8.89	1.60	8.79	1.01	7.19	1.08	10.11	0.98
Aliphatic H in methyl or methylene β to an aromatic ^a	$H_{\beta 1}$	28.71	6.86	28.74	3.98	18.62	3.53	36.95	3.50
Alicyclic H β to two aromatics (naphtenic, methylenes) ^a	$H_{\beta 2}$	6.12	1.32	5.23	2.89	5.10	4.57	5.13	2.28
Aliphatic H in methyl or methylene α to an aromatic and possible attachment in γ to another or same ring ^a	$H_{\alpha 1}$	24.53	25.01	27.27	32.76	29.94	24.79	25.29	29.58
Aliphatic H in methylene α to an aromatic ring and β to another or two rings (acenaphthene and fluorene type) ^a	$H_{A,F}$	3.93	1.39	2.42	1.74	3.83	1.52	1.69	2.29
Aliphatic H in methyl or methylene α to two aromatic rings (diphenylmethane type) ^a	H_D	1.56	0.18	0.34	1.05	1.51	0.61	0.08	0.88
Olefinic protons (4.5-6.3 ppm)	H_O	1.02	0.95	0.16	1.68	0.02	0.32	0.89	1.89
Aromatic protons (6.3-9.5 ppm)	H_{Ar}	25.24	62.69	27.04	54.89	33.79	63.58	19.86	58.60
Aromatic hydrogen ^a	H_{ArUC}	22.33	58.61	25.45	51.22	31.62	58.80	19.02	54.81
Sterically hindered aromatic hydrogen, in angular PAH's, in very peri-condensed PAH's or next to heteroatoms ^a	H_{ArC}	2.91	4.08	1.60	3.67	2.17	4.78	0.84	3.79
TOTAL		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Chemical shift ranges (δ , ppm): Aliphatic protons; H_{γ} (0.5-1.0), $H_{\beta 1}$ (1.0-1.6), $H_{\beta 2}$ (1.6-2.0), $H_{\alpha 1}$ (2.0-3.0), $H_{A,F}$ (3.0-3.69) and H_D (3.69-4.5). Olefinic protons: H_O (4.5-6.3). Aromatic protons; H_{ArUC} (6.3-8.36) and H_{ArC} (8.36-9.5) as adapted from Guillén et al. (1998). ^a Expressed in percentage of total observed protons (area %)

Results for the tars generated from the 20 mm particles have been included in Appendix C.10. Integration limits were combined from chemical shift values (δ , ppm) specified in literature (López *et al.*, 2010; Guillén *et al.*, 1998; Morgan *et al.*, 2008a) and have been included in Figure 6.27 for illustrative purposes. Calculated integrals were area normalised according to the detected TKS signal (~ 0.2338 ppm relative to TMS) within the ^1H NMR spectrum. The reader is therefore referred to Figure 6.26 for additional information regarding the structural assignments of the different protons. Selected tar samples were subjected to analytical repeatability in which experimental errors of no more than 4% were obtained.

From Figure 6.27 it is evident that, in accordance to published results (Guillén *et al.*, 1998; Iglesias *et al.*, 2001; Khan *et al.*, 2003; Morgan *et al.*, 2008a; Wang *et al.*, 2010), the spectra of the different tars display signals due to both aliphatic (0.5 ppm-4.5 ppm) and aromatic (6.3 ppm-9.5 ppm) protons present in the samples. The aliphatic region of the ^1H NMR spectrum was characterised by the presence of several signals, with certain sharp and well-defined signals specifically confined to the 0.5 to 3 ppm range. Accordingly, signals ranging from 0.5 to 1.0 ppm could be attributed to methyl or methylene protons bonded in γ coordination, 1.0 to 2.0 ppm to methylene or methane protons in β coordination, while signals observed in the range from 2.0 to 3.0 ppm could be attributed to typical de-shielded aliphatic protons such as those bonded in α position to an aromatic ring (Cyr & Selucky, 1985; Khan *et al.*, 2003).

From both Figure 6.27 and Table 6.20 it is clear that an increase in devolatilization temperature led to a significant decrease of more than 50% in the amount of aliphatic protons. A comparison between the quantitative ^1H NMR results (Table 6.20) of the different tars revealed that the amount of aliphatic protons decreased in the order G#5 > UMZ > INY > TSH for the 450°C experiments, while aliphatic proton contents reached values between 36.4% and 43.4% for the higher temperature tars. Furthermore, aliphatic protons of the low temperature tars were predominantly distributed in proton functionalities confined to α ($H_{\alpha 1}$) and β ($H_{\beta 1}$) positions of straight chain aliphatics (methyls or methylenes) on aromatic rings, with the latter accounting for up to 79% of the total amount of aliphatic protons. The latter therefore suggests that aliphatic chains bonded to aromatic structures are not too long, which is in accordance with observations made by López *et al.* (2010). In addition, the high proportion of β -substituted aliphatic protons (1.0 ppm-1.6 ppm) observed for tars generated at the lower temperature correlates with results obtained on coal-derived extracts and –pyrolysates (Calkins & Tyler, 1984, Iglesias *et al.*, 2001;

Thiel & Wachowska, 1989), and has been more generally associated with the presence of long chain polymethylene chains found in the respective coals (Iglesias *et al.*, 2001).

It is clear from Figure 6.27 that some signals in the 0.5 to 2 ppm range display either narrow or broad features, which reflects the extent of branching of the alkyl-substituents on aromatic rings (Khan *et al.*, 2003). It can be observed from the spectra that the tars generated at 450 °C from coal INY are likely to be more branched, while the degree of branching would be less extensive for tars produced from coal G#5. An increase in temperature saw the significant reduction in the amounts of H_γ and $H_{\beta 1}$, while the fraction of $H_{\alpha 1}$ showed no remarkable change (less than 5%) for tars generated from coals UMZ, G#5 and TSH. A substantial increase in the amount of α -substituted aliphatic protons was, however, noted for tars generated from coal INY. These findings indicate that devolatilization at 750 °C was characterised by increased covalent bond cleavage of the polymethylene functionalities in the coal structure as well as secondary cracking reactions of tar in the gas phase, which subsequently led to the formation of more and larger aromatic compounds with lower degrees of aliphatic substitution. This is supported by the increased amounts of simple aromatics, PAHs, short chain olefins and paraffins observed respectively from GC-MS, GC-FID and GC (Section 6.5.3.1 and 6.5.3.2).

Lower abundances (smaller than 4%) of acenaphthene ($H_{A,F}$)-, fluorene ($H_{A,F}$)- and diphenylmethane (H_D) type protons were detected in all tar samples. In general the amount of $H_{A,F}$ decreased with increasing temperature for tars generated from the Witbank coals, while the opposite was observed for the amount of H_D present in the tars of coals INY, G#5 and TSH. Relatively low signal intensities were recorded for olefinic hydrogen functionalities as observed in the chemical shift range from 4.5 ppm to 6.3 ppm. Furthermore, the amount of H_O increased with increasing temperature which is in disaccord with what was observed from GC-MS and GC-FID. According to the GC-MS and GC-FID results, the amount of aliphatic compounds (alkanes, alkenes, alicyclics etc.) decreases with increasing temperature. This discrepancy can be attributed to the mass detection limit of GC analyses, which typically favours only the detection of compounds boiling below 300 °C and therefore does not detect the whole spectrum of species within the tar. It is therefore possible that the increased levels of olefinic hydrogen observed could be ascribed to olefinic side chains present on the larger aromatic components within the coal tar. The chemical shift range of 4.9 ppm-5.1 ppm has also been assigned to the presence of protons connected to oxygen or nitrogen hetero-atomic molecules, or protons bonded in α -position to ketone carbonyl groups (Khan *et al.*, 2003; Netzel *et al.*, 1990). For all tar samples no

signals could be detected in this range. Aliphatic proton content was correlated with structural parent coal properties in order to elucidate any visible trends. Figure 6.28, 6.29 and 6.30 provide comparisons of the degree of disorder index (*DOI*) (measure of coal poly-condensation), liptinite content and coal rank with different proton functionalities. From the figures it is evident that a strong linear correlation of aliphatic proton content (total and protons confined to the 0.5 ppm-3.0 ppm range) with *DOI*, liptinite content and coal rank can be inferred for the tars generated at 450°C. A decrease in *DOI* (more disordered structure) or coal rank therefore leads to the presence of a higher abundance of aliphatic protons, and in particular methylene protons confined to the 0.5 ppm-3.0 ppm range.

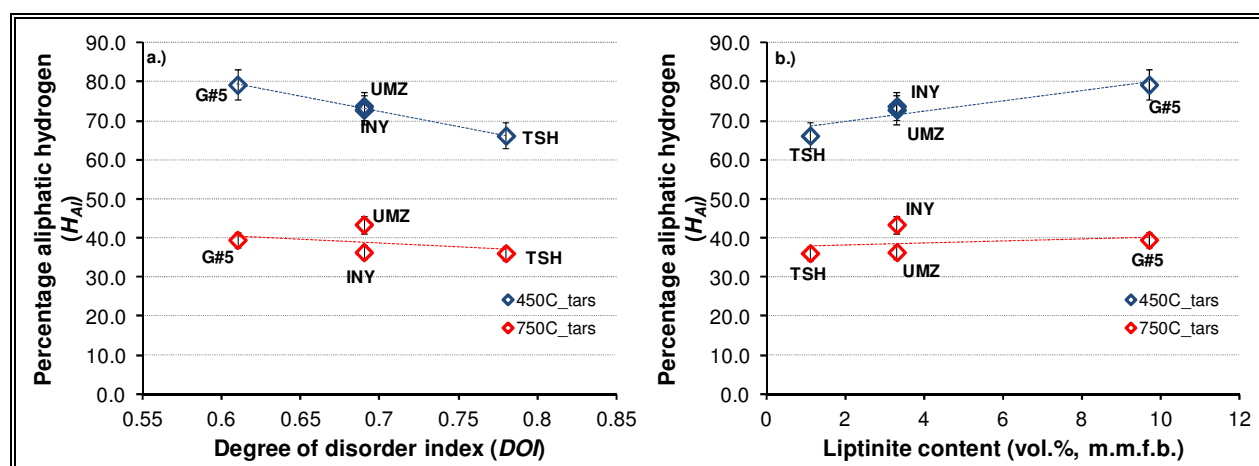


Figure 6.28 Comparison of the relative abundance of aliphatic proton with a.) *DOI* and b.) total liptinite content (m.m.f.b.).

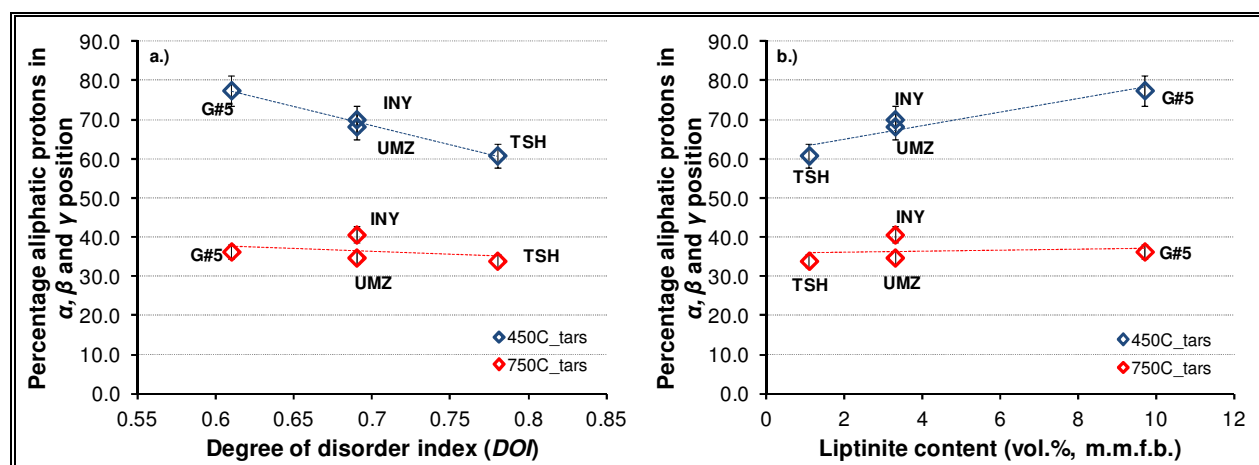


Figure 6.29 Comparison of the relative abundance of aliphatic proton confined to 0.5 to 3.0 ppm with a.) *DOI* and b.) total liptinite content (m.m.f.b.).

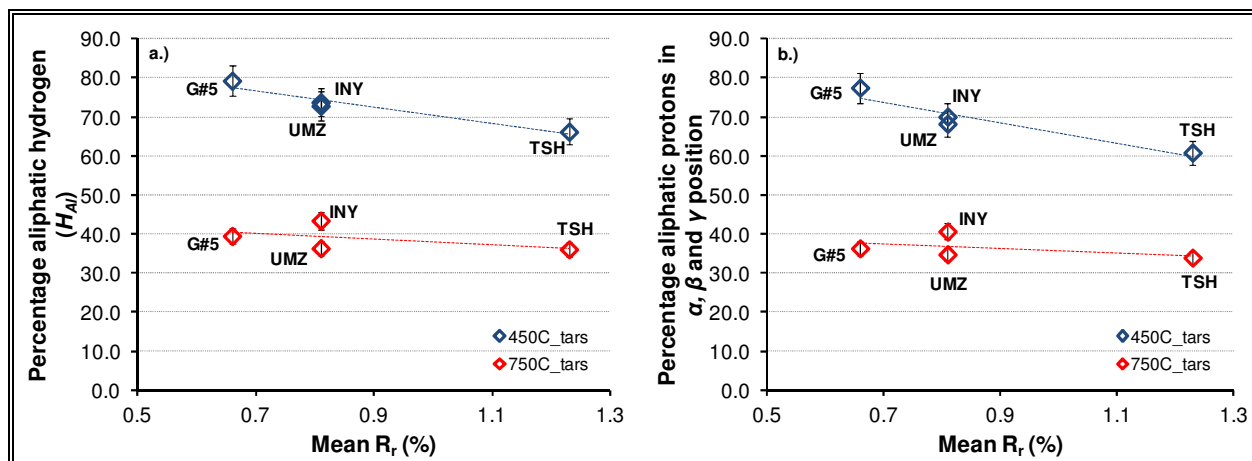


Figure 6.30 Comparison of mean random vitrinite reflectance (coal rank) with the relative abundance of a.) total aliphatic protons and b.) aliphatic protons confined to 0.5 to 3.0 ppm.

In addition, the hydrogen-rich liptinite maceral produces the highest amount of volatile matter upon heating, containing a significant amount of aliphatic homologues (Casal *et al.*, 2008; Cloke & Lester, 1994; Du Cann, 2010; Nip & Leeuw, 1992; Tsai, 1982). No concrete trends or conclusions could be drawn for the values obtained at the higher temperature due to the sensitivity and susceptibility to secondary reactions of tars generated at 750°C.

The range of aromatic protons (6.3 ppm-9.5 ppm) was characterised by prominent peaks representing a vast array of different aromatic conformations. The spectra of tars generated at 450°C from coals G#5 and TSH showed several sharp singlet peaks centred in the regions of 7.0 ppm-7.4 ppm and 6.9 ppm-7.0 ppm. According to Haw *et al.* (1981), these peaks are suggestive of the presence of biphenyl structures. In all four cases, the relative abundance of aromatic protons (H_{Ar}) was found to increase by a factor of between 2 and 3 for an increase in devolatilization temperature (Table 6.20). For the low temperature tars the low proportion of aromatic protons (19%-31%) is in accordance with the low abundance of alkyl-benzenes, alkyl-phenols and alkyl-naphthalenes detected in GC-FID and GC-MS analyses. It should, however, be noted that components confined to the mixed aliphatic and aromatic molecular class (as defined for the GC-MS and GC-FID results) could also have contributed to the amount of aromatic protons observed. This is, however, not true for tars generated from coal TSH which contained a significant amount of PAHs (86.62 wt.%) even at the lowest devolatilization temperature. Furthermore, the higher proportions of aromatic protons observed at 750°C show good correlation with increased amounts of aromatic components (PAHs and alkyl-naphthalenes) present in the tars from the different coals. Results obtained for the 20 mm particle experiments, presented in Appendix C.10, displayed similar trends to what was observed for the influence of

temperature and coal type on the 5 mm particles, although no direct conclusions could be drawn from the effect of particle size. Conclusions made in this investigation correspond to what was obtained from other investigations regarding NMR analyses performed on coal-derived tars and pitches (Guillén *et al.*, 1998; Iglesias *et al.*, 2001; Khan *et al.*, 2003; López *et al.*, 2010; Morgan *et al.*, 2008a; Wang *et al.*, 2010).

¹³C-NMR study

Solution state ¹³C NMR spectra (shown in Figure 6.31 for the 5 mm experiments) revealed similar structural features to those observed from the ¹H NMR and allowed the distinction of two main regions i.e.; an aliphatic/saturated carbon region (13 ppm-49.3 ppm) and an aromatic carbon region (110 ppm-160 ppm). The integral reset points for subsets of different types of carbon functionalities were based on chemical shift ranges proposed by Díaz and Blanco (2003), Morgan *et al.* (2008a) and Wang *et al.* (2010). The occurrence of a large triplet peak between 77 ppm-80 ppm was attributed to the resonance signal of the solvent (CDCl₃) and is in accordance with what was obtained by Fulmer *et al.* (2010), Iglesias *et al.* (2001) and Wang *et al.* (2010). Calculated integrals were area normalised according to the detected TKS signal (~2.9519 ppm relative to TMS) within the ¹³C NMR spectrum. The reader is referred to Figure 6.26 for additional information regarding the structural assignments of the different carbon types. Selected tar samples were subjected to analytical repeatability in which experimental errors of no more than 4% were obtained. Results for the tars generated from the 20 mm particles have been included in Appendix C.10. An overview of the quantitative results obtained is provided in Table 6.21.

Aliphatic carbons (Table 6.21) were confined to methyl, methylene and methine groups, although the possibility of the presence of any quaternary aliphatic carbons could not be ruled out. This could, however, not be confirmed due to the fact that a DEPT (Distortionless Enhancement by Polarization) NMR sequence was not performed. Closer inspection of the spectra confined to the chemical shift range 13 ppm to 49.3 ppm revealed the occurrence of a few sharply defined resonance signals centred at 14-15, 20, 22-23, 32 and 33 ppm.

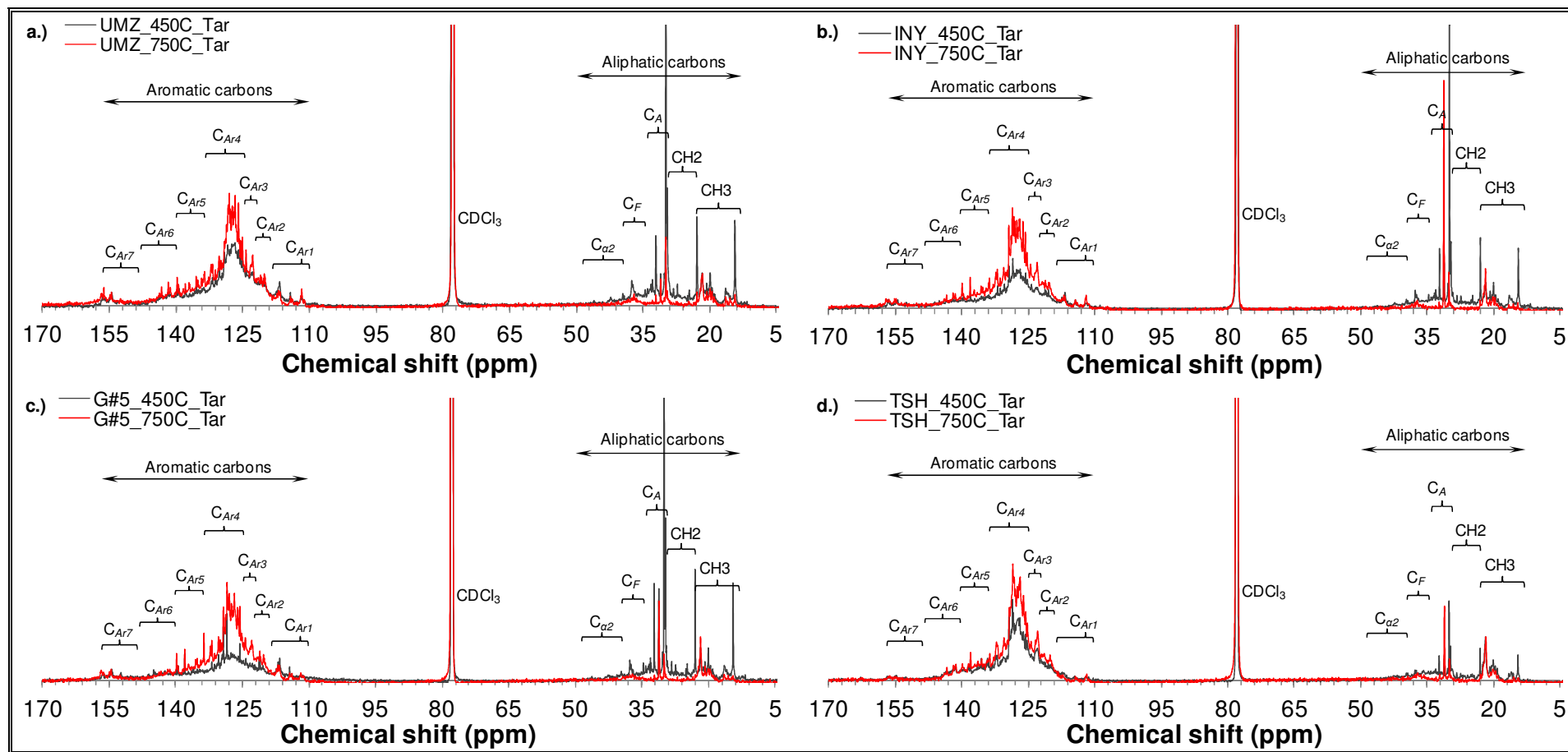


Figure 6.31 ^{13}C NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (5 mm particles).

Table 6.21 ^{13}C NMR distribution of tars derived at two different temperatures from 5 mm coal particles.

Carbon type (5 mm experiments)	Symbol	Relative abundance expressed in area % of spectra							
		UMZ		INY		TSH		G#5	
		450 °C	750 °C	450 °C	750 °C	450 °C	750 °C	450 °C	750 °C
Aliphatic carbons (13 ppm-49.3 ppm)	C_{Al}	38.31	12.65	39.04	9.29	14.77	9.44	47.05	11.74
Methyl carbons ^a	CH_3	10.72	5.25	11.28	3.29	5.05	3.74	12.49	5.14
Methylene (CH_2) and methine (CH) carbons α or further from an aromatic ring (i.e.; ethyl and propyl groups) ^a	CH_2	5.88	1.06	6.00	0.20	1.95	0.26	7.16	0.79
Methylene (CH_2) and methine (CH) carbons α to an aromatic ring and β to another (acenaphthene type) ^a	C_A	13.97	2.74	13.31	4.00	3.58	2.52	19.69	2.80
Methylene (CH_2) and methine (CH) carbons α to two aromatic rings (fluorene type) ^a	C_F	4.97	2.26	5.27	1.29	2.52	1.65	4.98	1.81
Methylene (CH_2) and methine (CH) carbons α to two aromatic rings (diphenylmethane type) ^a	$C_{\alpha 2}$	2.77	1.34	3.16	0.51	1.67	1.27	2.73	1.21
Aromatic carbons (110 ppm-160 ppm)	C_{Ar}	61.69	87.35	60.96	90.71	85.23	90.56	52.95	88.26
Pericondensed aromatic- or protonated aromatic carbons ^b	C_{ArP}	46.79	64.62	42.47	68.04	63.04	71.56	35.75	66.78
$C_{ar}\text{-H}$ ortho to $C_{ar}\text{-OH}^a$	C_{Ar1}	4.77	3.27	4.69	4.11	3.21	0.97	6.06	4.01
$C_{ar}\text{-H}$ para to $C_{ar}\text{-OH}$; $C_{ar}\text{-CH}_3$ ortho to $C_{ar}\text{-OH}^a$	C_{Ar2}	6.18	7.03	5.50	7.82	7.28	7.67	4.96	7.47
$C_{ar}\text{-CH}_3$ para to $C_{ar}\text{-OH}^a$	C_{Ar3}	4.93	6.47	4.34	7.12	7.17	7.59	3.52	6.66
Quaternary aromatic carbons; $C_{ar}\text{-H}$ meta to $C_{ar}\text{-OH}^a$	C_{Ar4}	30.91	47.84	27.95	48.98	45.36	55.33	21.22	48.63
Catacondensed aromatic carbons, aromatic carbons both with heteroatomic or aromatic substituents ^b	C_{ArC}	14.90	22.74	18.49	22.68	22.20	19.00	17.19	21.48
$C_{ar}\text{-CH}_3$; CH_2 or CH para to $C_{ar}\text{-OH}^a$	C_{Ar5}	7.52	11.93	8.27	11.88	12.62	12.33	7.13	11.93
CH_2 or CH meta to $C_{ar}\text{-OH}^a$	C_{Ar6}	4.29	5.91	5.49	5.71	6.63	4.88	5.14	5.04
$C_{ar}\text{-OH}^a$	C_{Ar7}	3.09	4.90	4.73	5.08	2.95	1.78	4.92	4.52
TOTAL		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Chemical shift ranges (δ , ppm): Aliphatic carbons; CH_3 (13-23), CH_2 (23-29.5), C_A (29.5-34), C_F (34-39.5), $C_{\alpha 2}$ (39.5-49.3) as adapted from Díaz & Blanco (2003) and Morgan et al. (2008a). Aromatic carbons: C_{Ar1} (110-118), C_{Ar2} (118-122), C_{Ar3} (122-124), C_{Ar4} (124-133), C_{Ar5} (133-140), C_{Ar6} (140-147), C_{Ar7} (147-167) as adapted from Wang et al. (2010).

^a Expressed in percentage of total observed carbons (area %). ^b Sum of respective aromatic regions.

Accordingly, Khan *et al.* (2003) have attributed the presence of these signals to a few defined carbon types, of which the signals observed at 14 ppm-15 ppm and 20 ppm can be ascribed to a terminal methyl bonded to a methylene carbon substituted at the end of an alkyl chain, and a branched methyl bonded to a methane carbon in an alkyl chain respectively.

Resonance signals observed at 22 ppm to 23 ppm were classified as methylene carbons attached to terminal methyl carbons in an alkyl chain, while the signal at 32 ppm was ascribed to the resonance of carbons situated three positions from the end of an alkyl chain and bonded β to an aromatic system (Khan *et al.*, 2003). Furthermore, Cyr *et al.* (1987) and Sklenar *et al.* (1980) have assigned the signal at 33 ppm to a methene carbon in a branched aliphatic chain. From the Table it is evident that the bulk of the aliphatic carbons were attributed to the resonance of CH₂ and CH groups (CH₂, C_A, CF, C _{α 2}) which accounted for between 56.21% and 72.02% of the total amount of aliphatic carbons present in tar samples obtained from both temperatures. A comparison between the aliphatic carbon (C_{Al}) values obtained for tars generated at 450 °C from the different coals revealed striking differences.

The amount of aliphatic carbon present in the low temperature tars decreased in the order G#5 > INY > UMZ > TSH, with the largest proportion of C_{Al} distributed amongst methyl groups (CH₃) and methylene and methine groups confined to α positions on one aromatic ring and β to another ring (acenaphthene type structures) (C_A). Tars generated at 450 °C from coal TSH were characterised by the lowest number of different aliphatic carbons, with relative abundances not exceeding 5.05%. This is in agreement with the low proportion of aliphatic species observed within the tar samples derived from both temperatures from coal TSH (Table 6.17 and 6.18). Andresén *et al.* (2001) have described the extent of paraffinic cracking as the ratio of the total amount of methylene and methine groups (23 ppm to 49.3 ppm) relative to the total amount of methyl groups confined to the chemical shift range of 13 ppm to 23 ppm. From this perspective it was established that this ratio varied between 1.92 and 2.73 for tars generated at 450 °C, while a reduction to ratios between 1.41 and 1.54 was achieved at the higher temperature, thus indicating an increase in the extent of paraffinic cracking as expected. Tars produced at the lower temperature are therefore characterised by the presence of longer aliphatic or alicyclic chains, while more, fairly branched aliphatics or alkyl-substituted aromatics are predominant within the tars generated at 750 °C (Andresén *et al.*, 2001). This is supported by similar trends observed from the GC-MS, GC-FID (Table 6.17 and 6.18) and ¹H NMR results (Table 6.20).

A comparison of ratios obtained for tars generated from the different coal sources, at the two different temperatures, revealed that more than a 50% reduction was induced during the devolatilization of coal G#5. Tars generated from coal G#5 were therefore subjected to more extensive paraffinic cracking reactions, which are in accordance with the significant increase in the amount of CH₄; and low molecular weight paraffins and -olefins observed in the gas phase with increasing temperature (Table 6.11). An examination of the aromatic section of the spectra shown in Figure 6.31 shows a subsequent broadening of the spectra in the region confined to 120 ppm-160 ppm with an increase in temperature. This is also reflected in the significant shift in carbon aromaticity values (C_{Ar}) observed in Table 6.21, where the amount of aromatic carbon increases from between 52.95% and 85.23% to between 87.35% and 90.71%. From the Table it is evident that for both temperatures, tars generated from coal TSH were highly aromatic (85.23% and 90.56%, respectively), followed by tars yielded from coals UMZ, INY and G#5. The significant increase in tar aromaticity can be ascribed to either de-alkylation and/or aromatisation of aliphatic structures during heating (Iglesias *et al.*, 2001), or the subsequent evolution of larger amounts of aromatic species from the parent coal structure.

Furthermore, an increase in the latter would imply a subsequent increase in the aromaticity of the solid chars, which is generally reflected in lower volatile yields and larger carbon contents of the formed solid residues (Jiménez *et al.*, 1998). A comparison with ¹H NMR results shows that hydrogen aromaticity values (19.86% to 63.58%) are generally lower than aromaticity values obtained from ¹³C NMR (52.95% to 90.71%). This can be explained by the fact that ¹³C NMR makes it possible to not only evaluate the periphery of a tar molecular structure (as is the case for ¹H NMR), but also the internal molecular frame (Díaz & Blanco, 2003). For both temperatures, aromatic carbons were predominantly peri-condensed and/or protonated aromatic carbons, with contents ranging between 42.47% and 71.56%.

From the spectra it is evident that several sharp features are noticeable in the aromatic region centred at 125 ppm to 131 ppm, which is attributed to substituted and/or polycyclic aromatic species present in the tar (Pugmire *et al.*, 1977). This is also evident from the large proportions of quaternary carbons (C_{Ar4}) (as shown in Table 6.21), which constituted in some cases more than 50% of the total aromatic carbons for both temperature experiments. The significant increase in C_{Ar4} with increasing temperature also supports the significant increase in the amount of short-chain substituted aromatics and/or PAHs observed from the GC-MS and GC-FID analyses. This is in accordance with findings of Nelson *et al.* (1988) and Smith *et al.* (1994), who

observed that high temperature tars contain progressively larger aromatic structures as well as increased amounts of un-substituted polycyclic aromatic hydrocarbons.

Furthermore, the presence of resolved signals observed in the chemical shift region of 155 ppm to 165 ppm also confirms the presence of carbonyl and/or phenolic compounds in the tars (Khan *et al.*, 2003), which showed slight increases with increasing temperature for tars generated from coals UMZ and INY (Table 6.21). Aliphatic/aromatic and methyl carbon content were correlated with structural parent coal properties in order to elucidate any visible trends. Figures 6.32, 6.33 and 6.34 provide comparisons of the degree of disorder index (*DOI*), liptinite content and coal rank (mean random vitrinite reflectance) with different carbon functionalities.

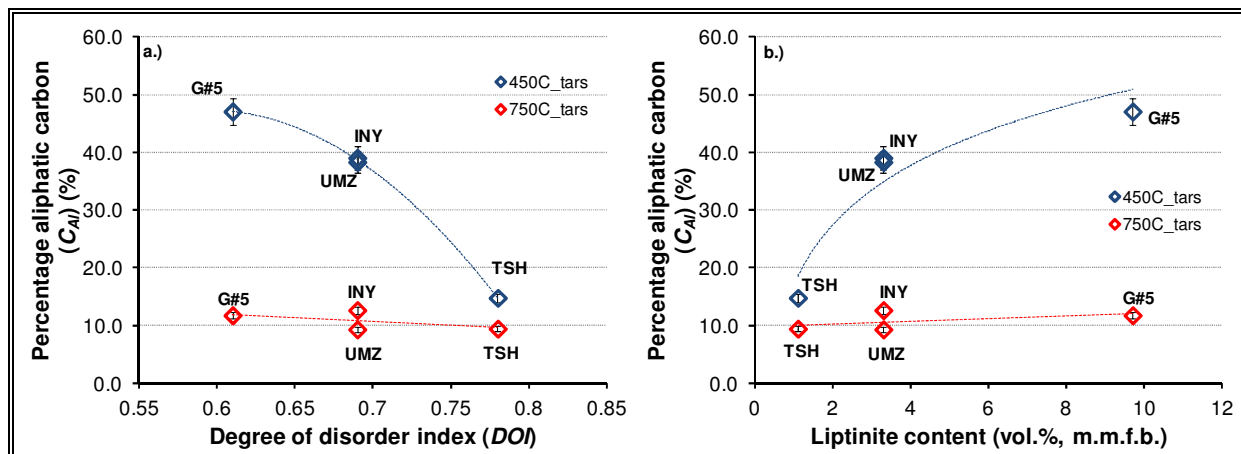


Figure 6.32 Comparison of the relative abundance of aliphatic carbon with a.) *DOI* and b.) total liptinite content (m.m.f.b.).

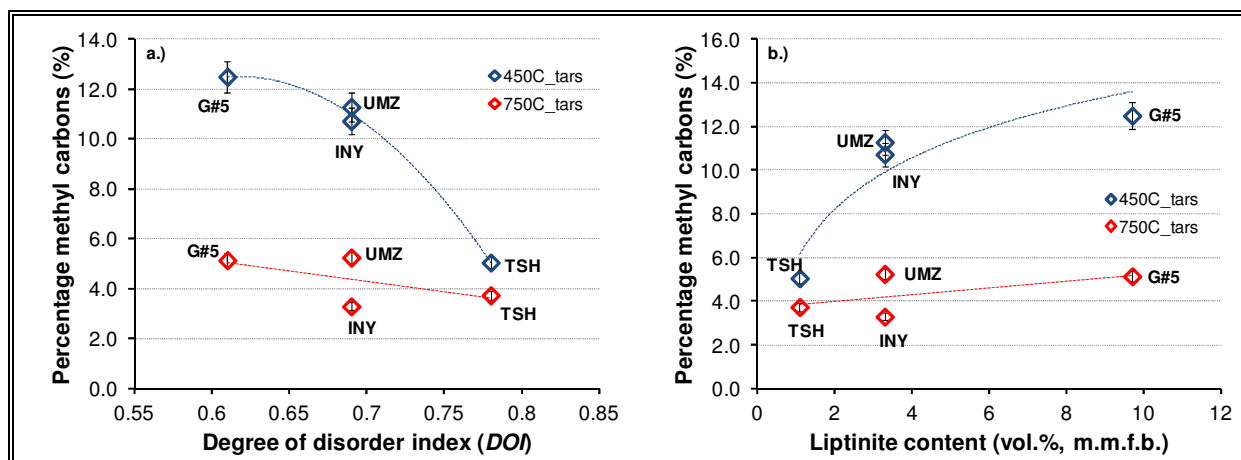


Figure 6.33 Comparison of the relative abundance of methyl carbon with a.) *DOI* and b.) total liptinite content (m.m.f.b.).

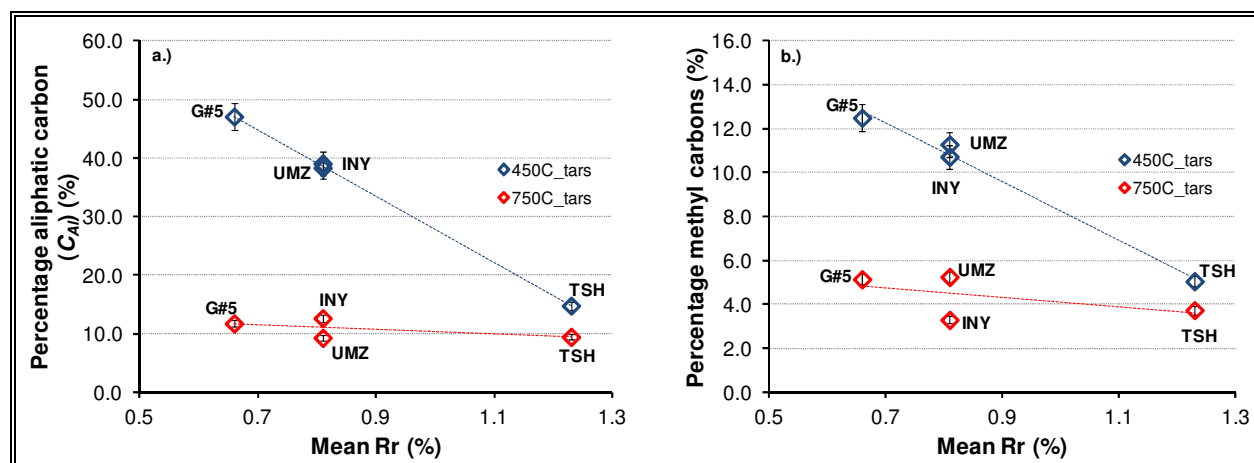


Figure 6.34 Comparison of mean random vitrinite reflectance (coal rank) with the relative abundance of a.) total aliphatic carbons and b.) methyl carbons.

From the figures it is evident that a decrease in *DOI* (more disordered structure) or coal rank therefore leads to the presence of a higher abundance of aliphatic carbons, and in particular methyl carbons. Inversely, the high aromatic nature of coal tars produced from coal TSH can be attributed to the higher aromaticity or higher rank of the parent coal. Only the correlations with coal rank showed a strong linear relationship for all cases, while the effect of liptinite content is in agreement with what was observed for the correlation with aliphatic proton content. No concrete trends or conclusions could be drawn for the values obtained at the higher temperature, due to the sensitivity and susceptibility to secondary reactions of tars generated at 750°C. Results obtained for the 20 mm particle experiments, presented in Appendix C.10, displayed similar trends to what was observed for the 5 mm particles, although no direct conclusions could be drawn from the effect of particle size.

6.5.3.3 Char structure and characterization

Char produced during devolatilization forms an important solid product for use in coal conversion processes such as combustion and gasification. The chemical and structural properties of char determine the reactivity of a coal and are therefore important for efficiently operating downstream processing units. The char produced from the devolatilization experiments were subjected to different conventional- and advanced characterisation techniques, similar to what was done for the four parent coals. Conventional analysis conducted on the chars included proximate-, ultimate- and char morphological (a petrographic method) analysis, while XRD carbon crystallite, HRTEM and ¹³C NMR were the advanced techniques employed for assessing char molecular structure.

The respective methods have been summarised in Section 6.4.4.4. The results obtained from the different analyses will be discussed in the following text.

Chemical analysis (proximate- and ultimate)

Proximate- and ultimate analyses were performed on chars generated at both temperatures and particles sizes. The results obtained from these analyses for the 20 mm experiments are summarised in Table 6.22. Results for the 5 mm particles were not included, due to their similarity, and can be found in Table C.7 of Appendix C.11. Important reactivity indices such as fuel ratio (FC/VM), atomic H/C and O/C ratio were also estimated from the results for the respective chars. Proximate- and ultimate results were reported on a dry, ash free basis (d.a.f.).

In addition, Figures 6.35 and 6.36 provide a graphical summary of the respective proximate- and ultimate results as compared to the results obtained for the parent coals. From the Table and respective figures it is evident that the systematic trends followed for coal devolatilization have been observed. As expected, volatile matter yield (d.a.f.) decreased for all coals/chars with an increase in devolatilization temperature, while volatile yields of up to 4.4 wt.% (d.a.f.) basis were still evident after exposure to 750°C. The opposite was true for the fixed carbon content remaining after devolatilization.

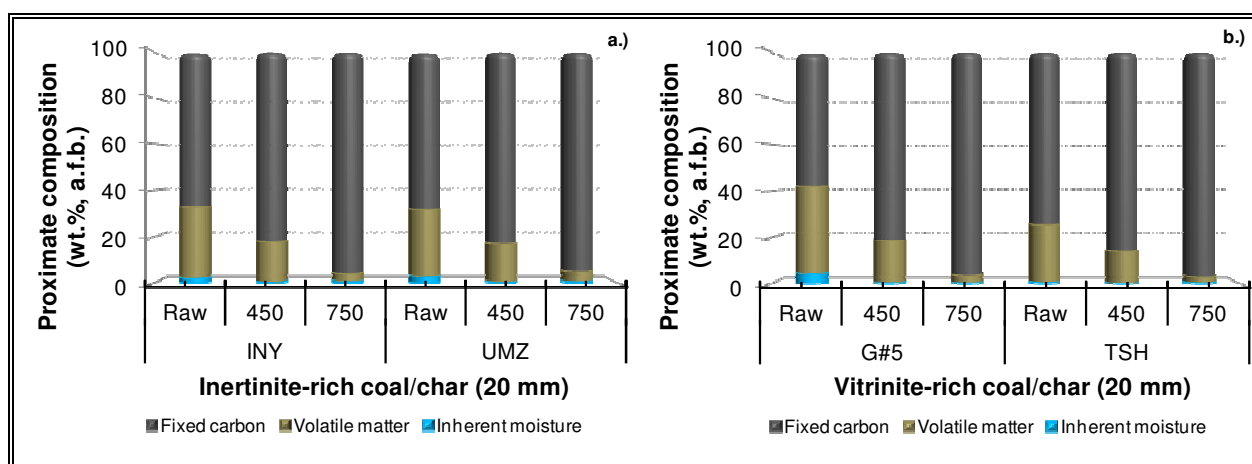


Figure 6.35 Comparison of proximate results for the transition from raw coal to char for a.) the inertinite-rich coals and b.) the vitrinite-rich coals.

The decreasing trend of volatile matter with devolatilization temperature is consistent with what was obtained by Chabalala *et al.* (2011).

Table 6.22 Chemical properties of chars produced at 450°C and 750°C.

Chars derived at 450°C and 750°C for 20 mm coal particles			Inertinite-rich coals				Vitrinite-rich coals			
			INY		UMZ		G#5		TSH	
			450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Proximate analysis (Dry basis)	Unit	Standard								
Ash	wt.%	SABS ISO 1171:1997	18.9	10.9	14.3	20.8	9.2	11.3	22.4	20.0
Volatiles matter (VM)	wt.%	SABS ISO 562:1998	14.1	2.7	14.2	3.5	16.6	2.8	10.6	2.0
Fixed Carbon (FC)	wt.%	By difference	67.0	86.4	71.6	75.7	74.2	85.8	67.0	78.0
TOTAL	wt.%		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Fuel ratio (FC/VM)			4.7	31.7	5.0	21.5	4.5	30.5	6.3	38.8
Proximate analysis (Ash free basis)										
Volatiles matter (VM)	wt.%	SABS ISO 562:1998	17.4	3.1	16.5	4.4	18.3	3.2	13.7	2.5
Fixed Carbon (FC)	wt.%	By difference	82.6	96.9	83.5	95.6	81.7	96.8	86.3	97.5
TOTAL	wt.%		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate analysis (Dry, ash free basis)		ISO 12902								
Carbon	wt.%		84.5	96.2	85.0	93.2	75.4	83.2	89.1	94.9
Hydrogen	wt.%		3.9	1.0	3.6	1.1	5.2	4.0	4.2	0.9
Nitrogen	wt.%		2.2	2.3	2.3	2.2	2.1	2.6	2.2	2.4
Oxygen	wt.%	By difference	9.2	0.1	8.4	2.6	11.5	9.9	3.9	0.6
Total sulphur (IR Spectroscopy)	wt.%	ISO 19759	0.3	0.3	0.6	0.9	0.9	0.3	0.7	1.1
TOTAL	wt.%		100.0	100.0	100.0	100.0	100.0	100.0	100.1	100.0
Atomic H/C ratio	-		0.55	0.13	0.51	0.14	0.58	0.13	0.57	0.11
Atomic O/C ratio	-		0.08	0.00	0.07	0.02	0.09	0.03	0.03	0.01

The higher fuel ratios (FC/VM) (6.3 and 38.8, respectively) calculated from the proximate results for the chars derived from coal TSH suggest that, for both temperatures, the energy obtained from a carbon conversion process such as gasification or combustion will be the highest from these chars. This also agrees with what was observed for the parent coal fuel ratio.

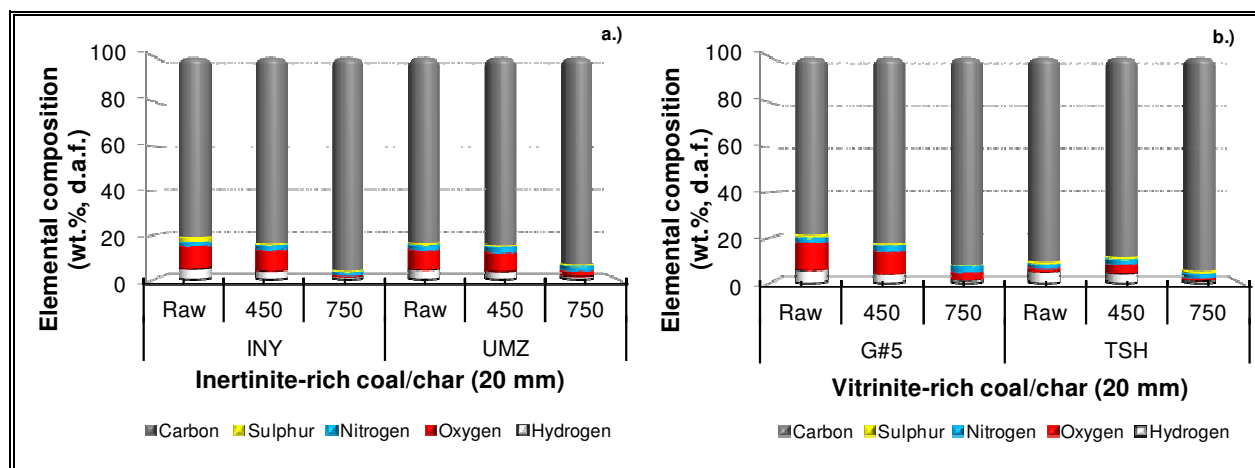


Figure 6.36 Comparison of ultimate results for the transition from raw coal to char for a.) the inertinite-rich coals and b.) the vitrinite-rich coals.

The lower amounts of volatile matter (13.7 wt.% and 2.5 wt.%, respectively, d.a.f) retained in the different chars of coal TSH could, however, imply some ignitability issues, whilst the chars obtained from coal G#5 at 450°C and UMZ at 750°C, respectively, will show the highest ignitability (Shen *et al.*, 2009; Su *et al.*, 2001b). For all chars it was evident that both hydrogen (wt.%, d.a.f.) and oxygen content (wt.%, d.a.f.) decreased, while carbon content (wt.%, d.a.f.) increased with increasing devolatilization temperature, analogous with what was observed for the amount of fixed carbon. These abrupt changes are also reflected in the atomic H/C and O/C ratios calculated from the ultimate results. At 750°C, hydrogen- and oxygen contents as low as 0.9 wt.% (d.a.f) and 0.1 wt.% (d.a.f.) were respectively observed, while carbon contents extended well above 90 wt.% (d.a.f.).

Oxygen content only started decreasing significantly at higher temperatures, which corresponds to the drastic increase in the amount of CO and CO₂ gas evolved at 750°C in comparison to 450°C. The subsequent decrease in the atomic ratios as observed for increasing devolatilization temperature indicates that the molecular structure of the chars progressively move to a more aromatic nature (Furimsky & Ripmeester, 1983). The lower atomic O/C and H/C ratios determined for char TSH at 750°C suggest that this char might have the highest aromaticity

compared to the other coals. No conclusive remarks could be made on the amount of nitrogen contained in the chars as no significant increases or decreases were observed for all chars. Sulphur contents were, however, significantly lower in the chars compared to the coals and the largest reduction in sulphur was observed for coal INY, where the amount decreased from 2.0 wt. % (d.a.f) to close to 0.3 wt.% (d.a.f). This removal of sulphur is in accordance with the mass 34 m/z peak observed in the MS results. The decreasing trend of sulphur was, however, not so obvious for the smaller particle sizes. This discrepancy could also be linked to the amount of mineral matter, especially in the form of sulphides such as pyrite, present in the coal prior to devolatilization. This is especially true for the larger particles where particle homogeneity with respect to mineral matter is not certain. Similar tendencies were reported for the smaller particle experiments (not shown here). No significant differences in chemical properties were observed between the two particle sizes.

Char morphological structure

Results obtained from petrographic, char morphological analyses are summarised in Table 6.23 for the char/cokes generated from all four coals at both temperatures. Examples of the different char structures have been included in Figure 6.37, while Figure 6.38 provides an example of differences observed in the optical texture (isotropic/anisotropic nature) of the derived chars. Maceral- and microlithotype information of the parent coals is provided in Chapter 4 (Table 4.10 and 4.13). Char morphological classification was conducted based on the methods developed and outlined by Bailey *et al.* (1990) and Wagner (1998).

Table 6.23 Summary of char morphological results as obtained for the different chars.

Char morphological analyses in vol.% m.m.b.			Inertinite-rich coals				Vitrinite-rich coals			
Class	Type/Classification	Optical texture	INY		UMZ		G#5		TSH	
			450°C	750°C	450°C	750°C	450°C	750°C	450°C ^a	750°C ^a
Organics	Coal	-	65.0	-	78.3	-	58.8	-	23.0	-
	Devolatilized coal	-	33.7	2.5	20.3	-	36.5	-	2.8	-
	Partial coke devolatilized ^{b,c}	-	-	-	-	-	-	-	46.3	-
	Partial coke massive ^d	-	-	-	-	-	-	-	25.8	-
	Coke	-	-	3.9	-	3.7	-	-	0	-
	Total organics	-	98.7	6.4	98.6	3.7	95.3	0	97.9	0
Chars	Cenosphere (<i>Tenuispheres and/or crassispheres</i> **)	Isotropic	-	-	-	-	-	-	-	-
		Anisotropic	-	-	-	-	-	-	-	-
	Honeycomb (<i>Tenuinetworks and/or mesospheres</i> **)	Isotropic	-	21.9	0.3	24.3	-	53.8	-	3.2
		Anisotropic	-	19.8	-	8.3	-	-	-	43.6
	Dense (<i>Inertoids and/or solids</i> **)	Massive (isotropic)	-	11.3	-	6.7	-	5	-	9.2
		Massive (anisotropic)	-	-	-	-	-	-	-	15.2
		Porous/cracked ^e	1.3	20.1	1	39.6	-	27.8	-	17.2
	Fusinoid	Isotropic	-	6.7	-	7.3	-	2.5	-	7.6
	Mixed (<i>porous and dense</i> **)	-	-	2.8	-	4.3	-	1.8	-	0.4
	Total char	-	1.3	82.6	1.3	90.5	0.0	90.9	0.0	96.4
Inorganic	Mineral	-	-	2.5	-	1.7	4.8	2.3	2.3	0.4
	Mineroid	-	-	8.5	-	4.0	-	7.0	-	3.2
	Total other	-	0.0	11.0	0.0	5.7	4.8	9.3	2.3	3.6
TOTAL			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Anisotropy	Isotropic features ^f			44.8		40.6		67.6		20.8
	Anisotropic features ^f			22.3		8.8		0.0		61.0

^a Please note that this sample consists of coke particles and not chars. The terminology used to define coke particles differs from that of chars. Char categories have been used for this research so that the results can be comparable to the char samples in terms of structure and not texture. Anisotropy therefore includes all mosaic, lenticular, ribbon coke structures..^b Partial coke is a term given to the TSH 450°C sample where the texture resembles early (pre) coke formation but the particles have not completely converted to coke..^c Partial coke devolatilized - pre-coke-like texture with devolatilization pores. ^d Partial coke massive - only pre-coke like structure, no pore development. ^e Dense porous / cracked is essentially inertodetrinite origin where there are signs of conversion. The next step would be anisotropic honeycomb structures. ^f Estimated from sum of anisotropic and isotropic structures respectively. **Classification system of Bailey et al. (1990) included for clarification.

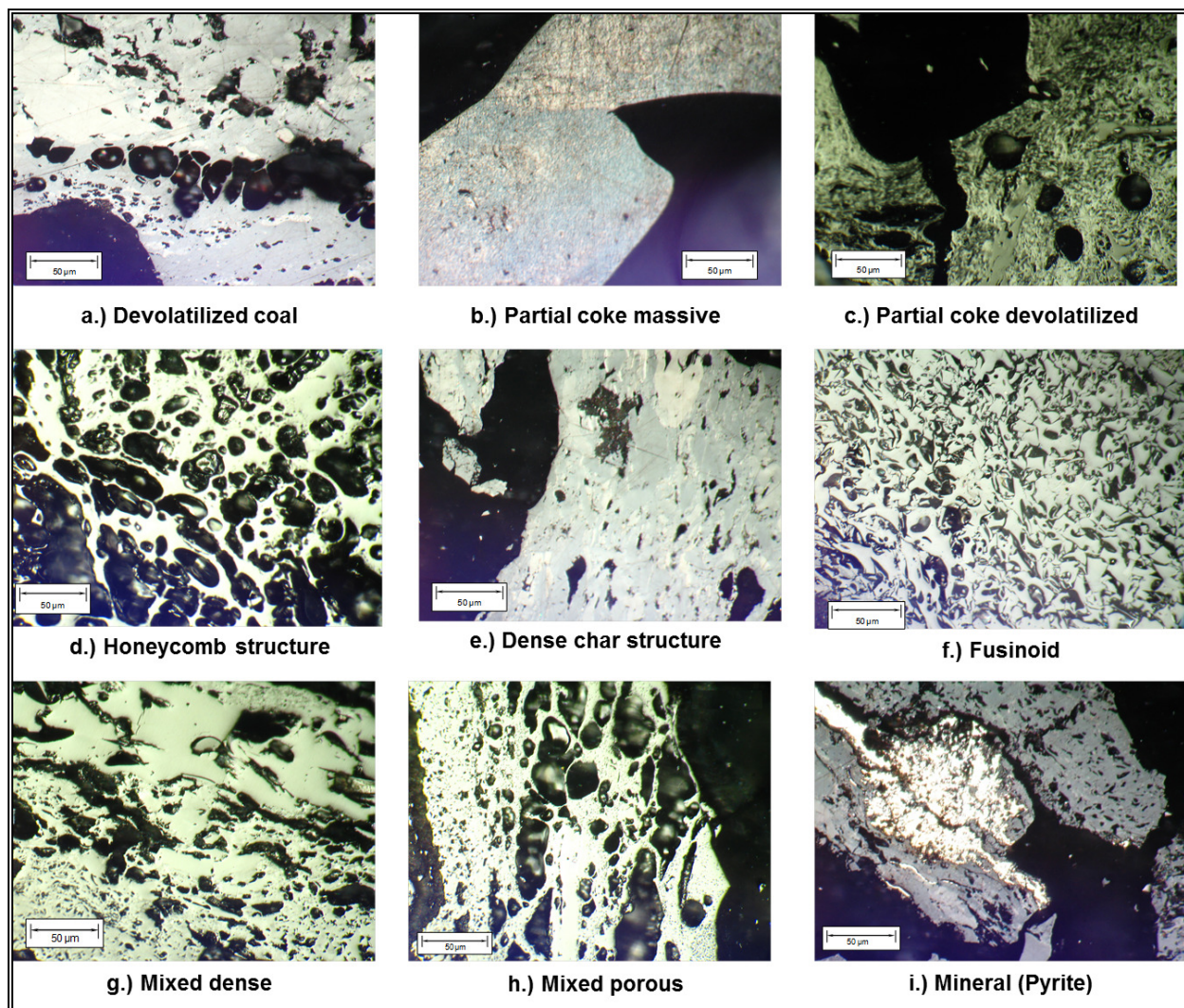


Figure 6.37 Specimens of char structures: a.) devolatilized coal, b.) partial coke massive (TSH), c.) partial coke devolatilized (TSH), d.) honeycomb (tenuinetwork) structures, e.) dense char, f.) fusinoid, g.) mixed dense structures, h.) mixed porous structures and i.) pyrite mineral.

Due to the characteristic coking nature of coal TSH additional classes had to be included for the low temperature char/coke, while the characteristic classifications for chars were used for the higher temperature chars/cokes in order to compare chars and cokes in terms of structure and not texture. Anisotropy was therefore defined to include all mosaic, lenticular and ribbon coke structures. Partial coke classifications were defined for both porous and non-porous pre-coke structures and textures observed for coal TSH. The devolatilization of coals UMZ, INY, and G#5 at 450 °C was characterised by the formation of small amounts of pores and cracks and the subsequent formation of devolatilized coal particles (Figure 6.37a) observed from the gray shade change, compared to raw coal. Similar observations were made for chars/cokes generated from coal TSH, with the development of pre-coke structures containing either

devolatilization pores (voids) (Figure 6.37b) or displaying no evidence of the development of any porous structure (Figure 6.37c). From Table 6.23 it is evident for the three Witbank coals that coal conversion to devolatilized particles increased in the order of UMZ < INY < G#5, while the highest devolatilization conversion was observed for coal TSH. This can be attributed to fact that devolatilized coal particles mainly evolve from vitrinite and reactive inertinites (reactive semifusinite and reactive inertodetrinite) (Bailey *et al.*, 1990) (Table 4.10). The higher proportion of devolatilized coke structures (total devolatilized structures) at 450°C for coal TSH can therefore be attributed to its higher sum of vitrinite and reactive inertinite constituents (76.9 vol.%, m.m.f.b.) as compared to the coals G#5 (68.8 vol.%, m.m.f.b.), INY (55.6 vol.%, m.m.f.b.) and UMZ (47.8 vol.%, m.m.f.b.) (as seen from Table 4.10).

No direct correlation could be drawn between the total amount of reactive macerals (sum of vitrinite, liptinite and reactive inertinite contents) and the extent of devolatilization at 450°C, due to the similarity in reactive maceral contents observed for coals G#5 and TSH. This discrepancy can possibly be ascribed to the high swelling nature and slightly higher rank of the latter coal. Higher temperatures (750°C) saw the development of well defined char/coke forms including tenuinetworks, dense chars, fusinoids and mixed (porous and dense) char/coke structures. Classic cenospheric (tenuispheres and crassispheres) char particles could not be quantified due to the fact that devolatilization was performed on large coal particles which were subsequently reduced in particle size in order to perform the morphology analyses.

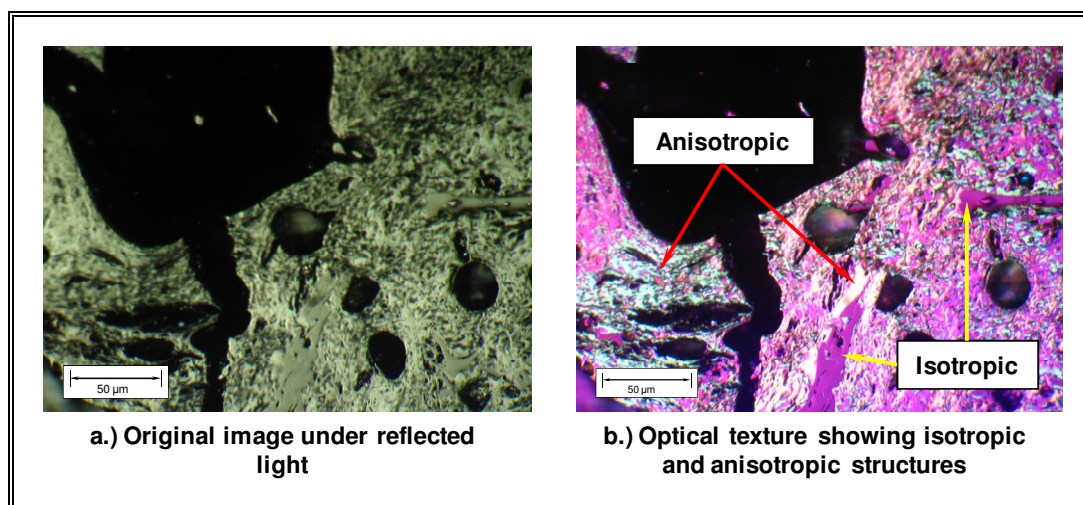


Figure 6.38 Comparison between the a.) original image obtained under reflected light and the occurrence of b.) isotropic/anisotropic structures within the chars using a retarder plate under crossed polars.

Chars produced from the vitrinite-rich coals contained a large fraction of honeycomb structures with contents of 46.8 vol.% (m.m.b.) and 53.8 vol.% (m.m.b.), respectively for coals TSH and G#5. In addition, dense chars (in the form of massive and porous/cracked structures) accounted for more than 30 vol.% (m.m.b.) of the total char forms, with char UMZ containing the largest amount (46.3 vol.%, m.m.b.). A physical breakdown of the different forms of dense chars is also included in Table 6.23.

Porous char structures, such as tenuinetworks, are normally derived from reactive maceral components such as vitrinite and liptinite, which tend to fluidize and experience large extents of devolatilization (Yu *et al.*, 2007). Furthermore, it has been found that vitrinite-rich microlithotypes such as vitrite and clarite produce low density chars resulting in tenuispheres and tenuinetworks (Bailey *et al.*, 1990; Cloke & Lester, 1994). This corresponds to the relatively higher yield of honeycomb structures reported for coals G#5 and TSH (large amount of vitrinite-rich microlithotype contents for both these coals) (Table 4.13), although only a slightly higher amount of honeycomb structures were encountered for coal TSH in comparison to the coals UMZ and INY. The higher rank (higher aromaticity) of coal TSH could, however, contribute to this behaviour.

Char types produced from vitrinite-rich microlithotypes have also been found to be more reactive during coal conversion processes (Chabalala *et al.*, 2011). In contrast, inertinite plays an important role in the formation of relatively dense- or solid chars, which are less reactive in comparison to their vitrinite counterparts (Bailey *et al.*, 1990; Chabalala *et al.*, 2011; Jones *et al.*, 1985; Yu *et al.*, 2007). It has, however, been established that inertinite is also capable of forming almost all of the known types of char, ranging from networks and tenuispheres to dense solids depending on its rank and plasticity (Cloke & Lester, 1994; Shibaoka, 1969). In order to include the effect of rank and variability of char type formation due to inertinite concentration, the formation of porous honeycomb chars were correlated with respect to the maceral index (*M*) defined in Chapter 4. The results obtained are illustrated graphically in Figure 6.39. A line has been included to guide the reader's eye through the experimental points.

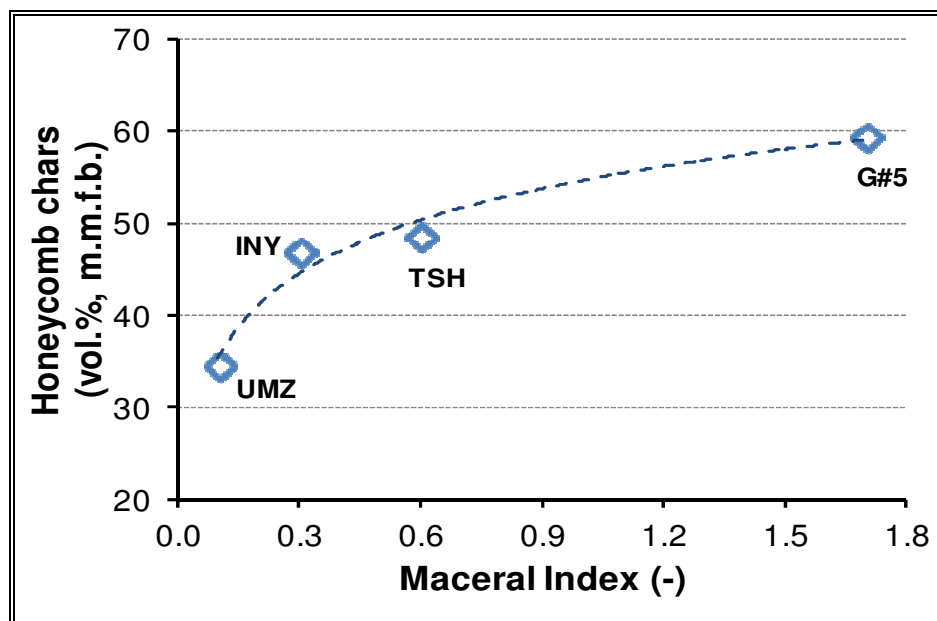


Figure 6.39 Correlation of number of honeycomb structures with maceral index (MI).

From this Figure it is evident that the number of honeycomb structures increases with increasing *MI*. It is therefore clear that rank played a major role with regard to honeycomb formation for coal TSH, which describes the discrepancy in the amount of these structures formed, although coal TSH contains relatively more reactive macerals compared to coal G#5. Relatively low amounts of mixed char types (mixed porous and mixed dense) were observed for all coals, with contents not exceeding 4.3 vol.% (m.m.b.). Isotropic fusinoid structures were also observed and showed distinct correspondence to the amount of fusinite determined for the parent coals. The low amount of fusinite for coal G#5 (3.0 vol.%, m.m.f.b.) therefore supports the low numbers of fusinoid structures (2.76 vol.%, m.m.f.b.) formed for chars from this coal. According to Pusz *et al.* (2009), the formation of non-reactive char structures which maintain their original morphological identity can be mainly attributed to the presence of fusinites and inert semifusinites.

A large variation in optical anisotropic or isotropic forms was also observed for the different chars derived at 750°C. It is generally proposed that, during thermal heat treatment of coal (normally in the range of 400°C to 600°C), the formation of cross-links between structural units can impede the improvement in structural order and preserve the random order of structural units present in the parent coal (Derbyshire, 1997). The resulting chars are therefore hard, porous, and highly isotropic, and are termed non-graphitizing in nature. In contrast, conditions with minimal cross-linking lead to the formation of an intermediate, carbonaceous, liquid crystal

mesophase, which forms anisotropic structures upon re-solidification (Burchell, 1999; Derbyshire, 1997). This is of importance for the carbonization of coking coals, which form valuable pre-cursors for the production of graphitic-like higher value carbons. In addition, it is known that an increase in coal rank (or aromaticity) subsequently leads to both an increase in reflectance and optical anisotropy (Borrego *et al.*, 2000; Yu *et al.*, 2007).

In order to validate the above-mentioned findings, the amount of isotropic and anisotropic features were semi-quantitatively estimated from the char morphological results by summing the amounts of isotropic and anisotropic structures observed for the 750°C chars. Anisotropic features were predominantly observed for char TSH (61.0 vol.%, m.m.f.b.), as shown in Figure 6.40, while the presence of anisotropy decreased in the order $INY > UMZ > G\#5$. A comparison between isotropic- or anisotropic structures, observed for the 750°C chars, and parent coal aromaticity (as determined from ^{13}C NMR) is shown in Figure 6.31. Lines have been included to guide the reader's eye through the experimental points.

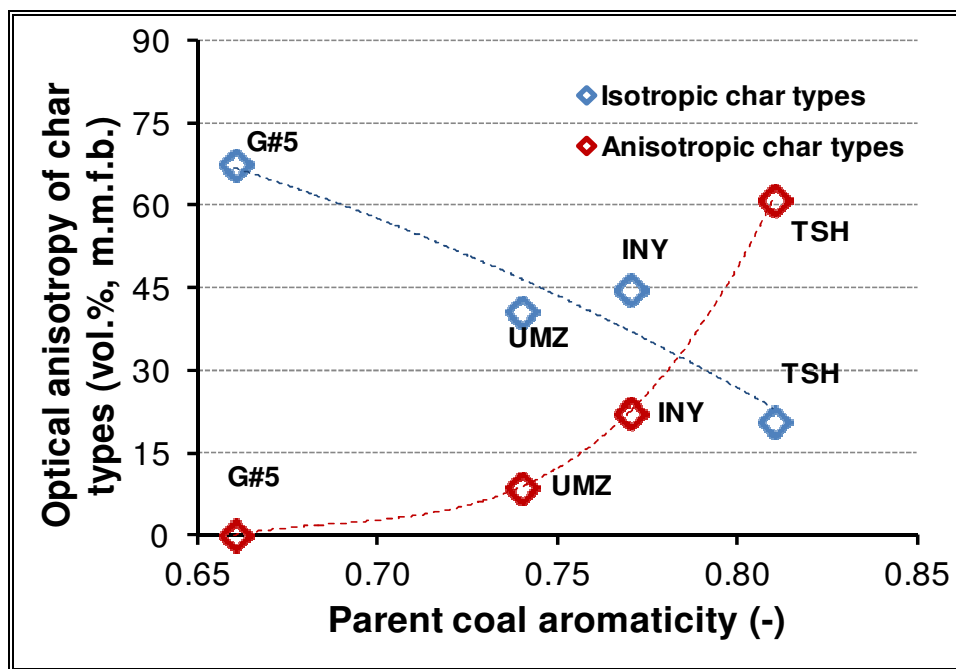


Figure 6.40 Comparison between the relative amounts of isotropic or anisotropic features with respect to parent coal aromaticity.

From the Figure it can be seen that the extent of anisotropy increases with an increase in parent coal aromaticity, while the opposite is true for the amount of isotropic features. The large numbers of anisotropic structures in the char/coke from coal TSH can therefore be attributed to

its higher apparent parent coal aromaticity (0.81). Furthermore, as described in Chapter 4, coal TSH was characterised as a strong coking coal (FSI = 9) which ensures the large probability of mesophase formation during thermal treatment.

Solid-state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR)

Molecular structure estimations of chars generated from 5 mm coal particles was done with the aid of ^{13}C NMR (CP-MAS and DD) measurements. An overview of the experimental methodology employed has been provided in Section 6.4.4.4. Longer acquisition times (12000 scans) were used for the high temperature chars in order to obtain adequate signal to noise for quantification purposes. A comparison of the ^{13}C CP-MAS spectra of each generated char is provided in the stack plots given in Figure 6.41. Results are shown in a.) and b.) for chars generated from the inertinite-rich coals, while the NMR spectra for chars generated from the vitrinite-rich coals are given in c.) and d.). The spectra of the parent coals have also been included for comparative purposes. From the Figure below it is clear that, similar to the results of the parent coals, the CP-MAS spectra of the generated chars exhibit three distinct peaks: a less prominent spinning sideband peak at 200-255 ppm, a peak confined to the aromatic region at 90-200 ppm and an aliphatic region at 0-90 ppm. It should be noted that a second spinning sideband overlaps with the aliphatic signal and is assumed to be of similar magnitude to the spinning sideband observed in the 200-255 ppm region.

A comparison between the CP-MAS spectra of the coals and the chars generated at different temperatures revealed that an increase in devolatilization temperature leads to a subsequent reduction in the intensity of the aliphatic signal (0-90 ppm); while a distinct, corresponding change in signal intensity of the aromatic signal was not observed. This is consistent with what was observed by Chou *et al.* (1983), Malumbazo *et al.* (2011), Perry *et al.* (2000), Solum *et al.* (1989b) and Timpe *et al.* (1987); therefore suggesting that aliphatic functionalities are progressively removed upon heating under an inert atmosphere, leading to the formation of a more aromatic solid residue. This does however not rule out the fact of the removal of aromatic functionalities from the coal structure. It can also be observed that the shoulder band (150-165 ppm) representing the phenolic- and carbonyl functionalities becomes much less prominent with increasing temperature for the inertinite-rich chars.

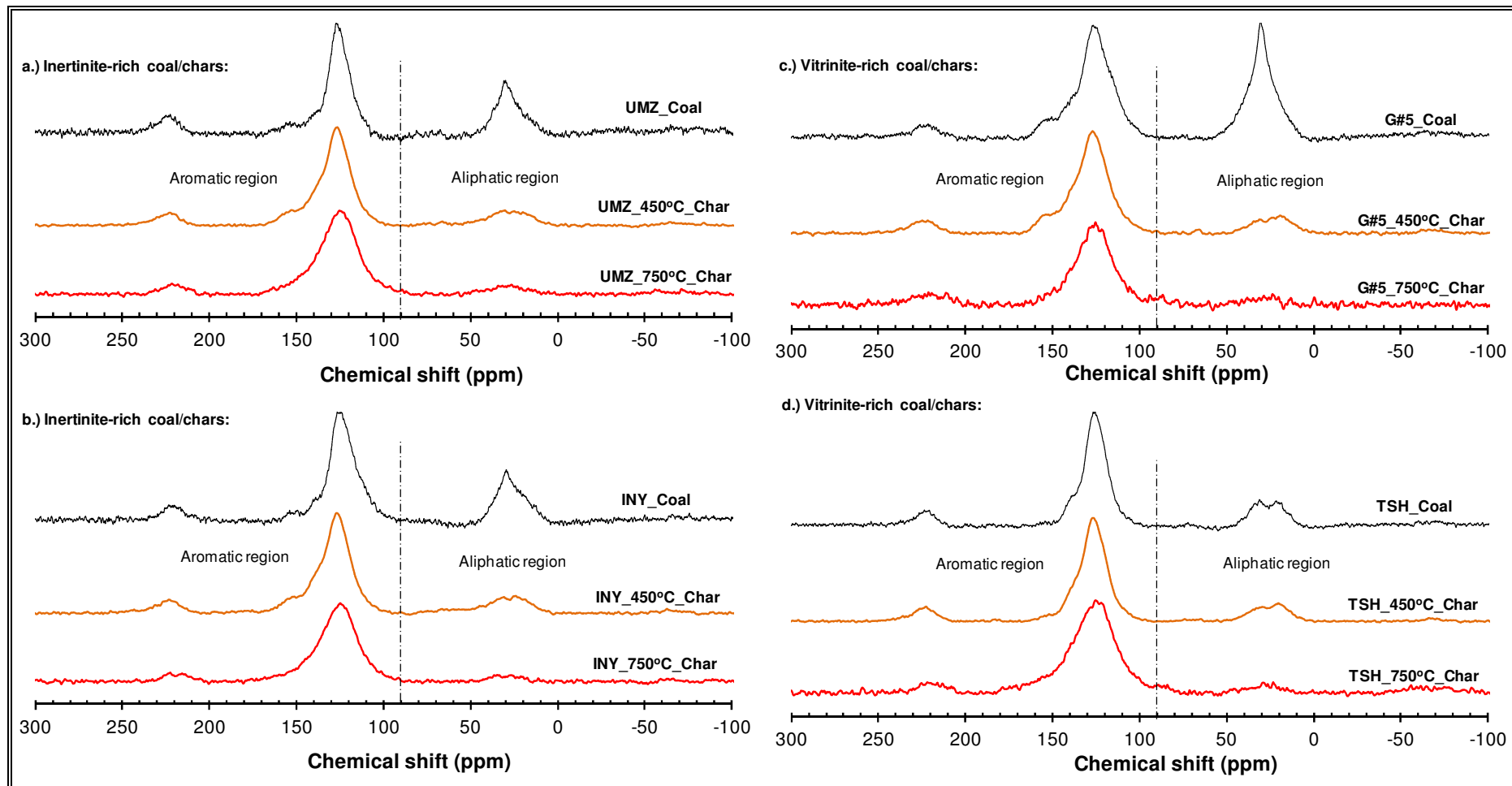


Figure 6.41 Comparison of CP-MAS acquired spectra for chars generated from coal a.) UMZ, b.) INY, c.) G#5 and d.) TSH respectively.

The removal of aliphatic, phenolic and carbonyl functionalities is therefore consistent with the subsequent generation of aliphatic homologues (predominantly at 450°C) and phenols observed from GC-MS and GC-FID analyses performed on the respective tars. Signal reduction in the 150-165 ppm range has also been observed in the work of Chou *et al.* (1983), Malumbazo *et al.* (2011) and Perry *et al.* (2000). From a structural perspective it can be seen from Figure 6.41 that broadening of the main aromatic peak tends to occur with increasing temperature, which can be ascribed to a change in the relaxation behaviour of the aromatic carbons due to the formation of large aromatic free radicals (Perry *et al.*, 2000). This change in the char structure can be associated with the transition from the evolution of light tar compounds, to the production of much larger aromatic molecules at the higher temperature, and is in agreement with what was observed from the tar analyses of Solum *et al.* (1989a).

The main spectral areas (aromatic and aliphatic) were further subdivided into smaller chemical shift regions, as was done for the parent coals, in order to obtain a more detailed estimation of the change in the different carbon functionalities with charring temperature. Annotations of the carbon specific species to different spectral regions were done according to the method outlined by Solum *et al.* (1989a) and Suggate and Dickinson (2004). The reader is referred to Chapter 5 (Figure 5.6 and Table 5.4) for a detailed description of the annotated spectral regions.

The structural parameter results (as described in Section 5.3.1.2) are provided in Table 6.24 for the chars generated at both temperatures from the 5 mm coal particles. Values obtained for the parent coal samples have also been included for reference and comparison. The influence of charring temperature on structural changes from coal to char is clearly reflected in the values provided in Table 6.24. A significant increase in the fraction of aromatics (f_a) with increasing temperature was observed for all four samples, with aromaticity values typically ranging between 0.91 and 0.94 for the 450°C chars, while values close to unity (0.98-1.00) were found for the chars generated at the highest temperature. This process was accompanied by a corresponding decrease in the fraction of aliphatics (f_{al}) as confirmed in the spectra of the respective chars. A similar temperature versus carbon aromaticity relationship was observed for the tars produced from the four coal samples. Dipolar dephasing experiments were also conducted in order to differentiate between the protonated and non-protonated aromatic- and aliphatic carbon entities, of which the spectra can be found in Appendix C.12.

Table 6.24 Structural parameters from ^{13}C NMR for chars generated from all four coals.

Sample	Structural parameters											
	f_a	f_a^{C}	$f_{a'}$	f_a^{H}	f_a^{N}	f_a^{P}	f_a^{S}	f_a^{B}	f_{al}	f_{al}^{H}	f_{al}^*	f_a^{O}
Coal INY	0.74	< 0.01	0.74	0.23	0.51	0.05	0.14	0.32	0.26	0.22	0.04	< 0.01
Char INY (450 °C)	0.91	0.02	0.89	0.11	0.79	0.07	0.19	0.54	0.09	0.09	0.00	0.01
Char INY (750 °C)	1.00	0.00	1.00	0.03	0.97	0.04	0.18	0.74	0.00	0.00	0.00	0.00
Coal UMZ	0.77	0.00	0.77	0.29	0.48	0.06	0.13	0.29	0.23	0.20	0.03	0.00
Char UMZ (450 °C)	0.92	0.00	0.92	0.13	0.73	0.06	0.18	0.49	0.08	0.08	0.00	0.01
Char UMZ (750 °C)	0.98	0.00	0.98	0.18	0.77	0.05	0.18	0.53	0.02	0.02	0.00	0.00
Coal G#5	0.66	< 0.01	0.66	0.24	0.42	0.04	0.11	0.26	0.34	0.28	0.06	0.00
Char G#5 (450 °C)	0.94	0.00	0.94	0.18	0.78	0.07	0.20	0.51	0.06	0.06	0.00	0.00
Char G#5 (750 °C)	1.00	0.01	0.99	0.31	0.69	0.05	0.20	0.44	0.00	0.00	0.00	0.00
Coal TSH	0.81	0.00	0.81	0.33	0.48	<< 0.01	0.08	0.40	0.19	0.12	0.07	<< 0.01
Char TSH (450 °C)	0.93	0.00	0.93	0.16	0.78	0.02	0.16	0.59	0.07	0.07	0.00	< 0.01
Char TSH (750 °C)	0.99	0.03	0.96	0.28	0.73	0.07	0.20	0.46	0.01	0.01	0.00	0.02
Ranges from Literature**	0.60-0.86	0.00-0.10	0.53-0.86	0.16-0.37	0.23-0.99	0.02-0.09	0.13-0.21	0.09-0.81	0.14-0.40	0.08-0.29	0.06-0.17	0.01-0.12

**Literature ranges taken from Malumbazo et al. (2011), Perry et al. (2000), Solum et al. (1989a,b & 2001), Van der Merwe (2010b), Van Niekerk (2008) and Watt et al. (1996.)

For the aliphatic functionalities, an increase in charring temperature favoured the complete removal of methyl and/or methoxy groups (f_{al}^*) even at temperatures as low as 450°C, while total removal of methylene and methine groups (f_{al}^H) were only achieved at the higher charring temperature. In all four cases, significant changes with temperature were observed in the amount of protonated (f_a^H), non-protonated (f_a^N) and bridge-head aromatic carbon (f_a^B) functionalities. A clear monotonic increase in the amount of f_a^N could be distinguished for the inertinite-rich coals (INY and UMZ), while slight decreases in the corresponding values were observed for the chars generated at 750°C from coals G#5 and TSH. No direct dependence of the amount of f_a^H on temperature was evident, although significant reductions were observed for chars produced at 450°C. At the higher charring temperature, values of f_a^H for chars produced from coals TSH and G#5 reported amounts close to (or even higher than) what was observed for the original unheated samples. The latter results therefore suggest the formation of more highly cross-linked and condensed aromatic structures with increasing charring temperature; and corresponds to what was observed by numerous other studies concerning the elucidation of char structures (Fletcher *et al.*, 1990; Malumbazo *et al.*, 2011; Perry *et al.*, 2000; Solum *et al.*, 1989a).

The higher poly-condensed structure of the formed chars has also been reflected in the decreasing trend observed for both the atomic H/C and -O/C ratios (a rank dependent parameter) obtained from the chemical analyses performed on the different chars (Table 6.22). The trade-off between f_a^N and f_a^H can be attributed to the fact that protonated carbons are weakly bonded and tend to break faster in comparison to non-protonated functionalities (Malumbazo *et al.*, 2011). Furthermore, an increase in temperature leads to the removal of aliphatic functionalities as volatiles from the cleavage of covalent bonds between bridge-head carbons. From this perspective, it is evident that char produced at 750°C from coal INY displayed the highest extent of cross-linking between aromatic structures due to the low amount of f_a^H (0.03) and elevated amounts of f_a^N and f_a^B (0.97 and 0.74, respectively) observed. No concrete conclusions could be drawn from the values presented in Table 6.24 for the fraction of carbonyl functionalities (f_a^C), as well as the fraction of carbons associated with phenolic groups (f_a^P). From Figure 6.39 a clear reduction in the phenolic shoulder peak at 154 ppm was observed for chars INY, UMZ and G#5, while the opposite was found for chars generated from coal TSH. This apparent anomaly has been ascribed by Solum *et al.* (1989a) to the decreasing aliphatic content, which is based on 100 total carbons. For comparative purposes Solum *et al.* (1989a) proposed expressing these values as relative amounts of aromatic functionalities. The

relative abundance of f_a^P with respect to the total amount of f_a^N (i.e.; f_a^P / f_a^N) therefore decreases with increasing charring temperature for the values obtained for INY (0.10, 0.08 and 0.04), UMZ (0.12, 0.08 and 0.06) and G#5 (0.11, 0.10 and 0.07). This has also been found to be true for the amount of alkylated aromatic compounds (f_a^S) and is in accordance with what was observed by Solum *et al.* (1989a). In contrast, however, the opposite trend was observed for the relative amounts of f_a^P and f_a^C for chars generated from coal TSH, while a subsequent increase was also evident for the amount of aliphatic carbons bonded to oxygen (f_{al}^O). This has also been observed for soots produced at different temperatures from model carbon compounds; and may not be the result of the formation of additional oxygen functional groups. Solum *et al.* (1989a and 2001) have attributed this increasing trend to the occurrence of a broad Lorentzian signal underlying the normal aromatic resonance signal, which was also evident from the spectra of chars produced from coal TSH. As a comparison, Table 6.24 also includes some specified values obtained for CP-MAS structural parameters from literature. Good agreement was obtained between the structural values obtained in this investigation and those presented in published results. It is, however, a well known fact that CP-MAS measurements of highly conductive materials, such as large PAH structures, are characterised by some systematic problems which include peak broadening as well as penetration limits of NMR radio frequency in order to observe internal carbons (Solum *et al.*, 2001). Lattice parameter estimations were therefore not performed on the obtained CP-MAS results in order to avoid large calculation errors due to the highly conductive nature of the respective char samples.

X-ray diffraction (XRD)-carbon crystallite analyses

XRD carbon crystallite analyses were employed to establish the crystalline structure of the formed chars. Figure 6.42 shows the processed and smoothened diffractograms of the respective low- and high temperature chars after the background, due to the presence of the amorphous carbon fraction, was removed (Maity & Mukherjee, 2006). Background subtraction and smoothening was accomplished with the aid of the HighScore Plus peak analysis tool. The diffractograms of the raw coals have also been included for comparison. The char diffractograms, as presented in Figure 6.40, display similar graphitic-like features as was observed for the raw coals and correspond to what was observed in other carbon crystallite studies conducted on coals and chars (Franklin, 1951; Lu *et al.*, 2001; Lu *et al.*, 2002b; Maity & Mukherjee, 2006; Okolo, 2010; Shiraishi & Kobayashi, 1973; Wu *et al.*, 2008).

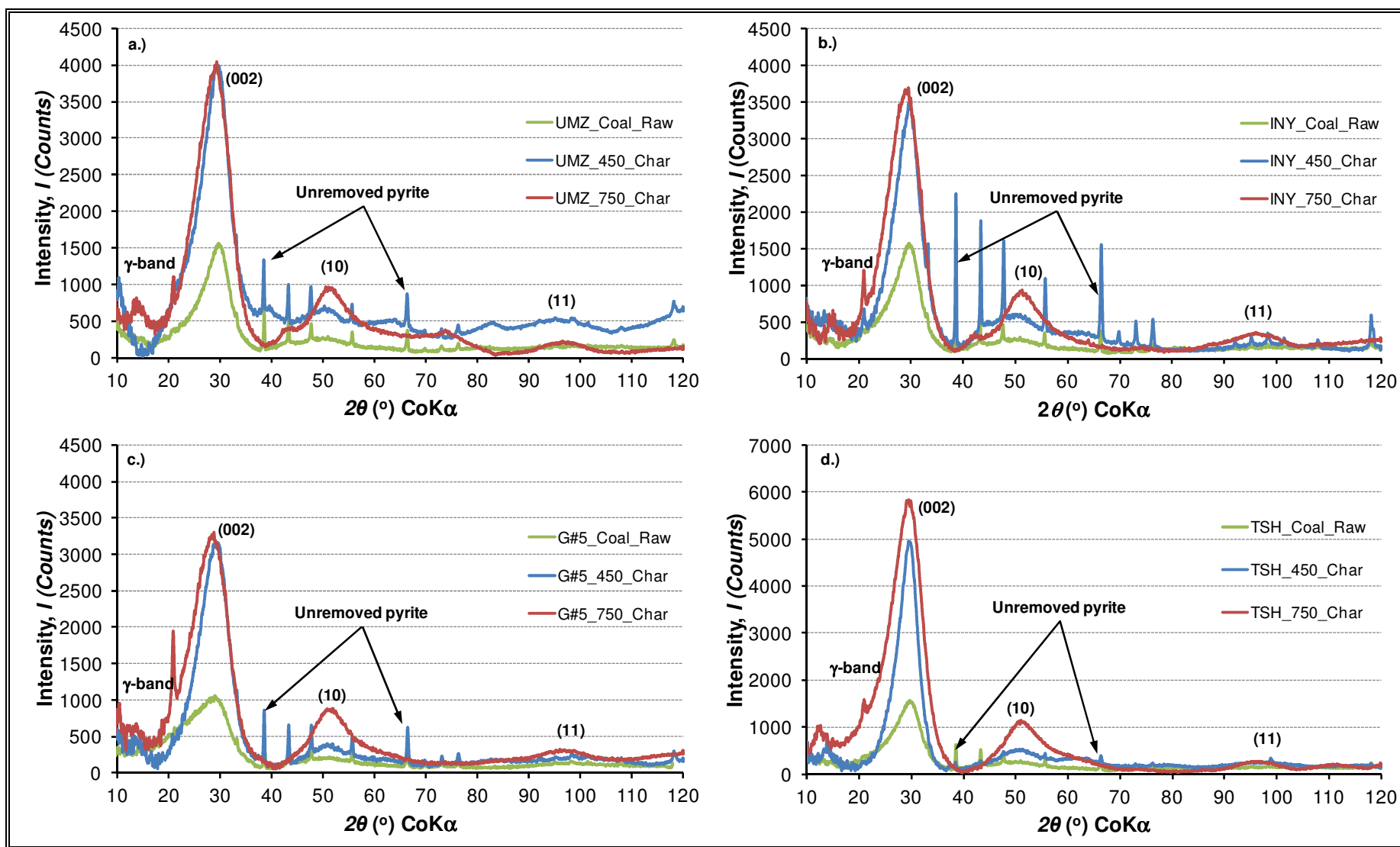


Figure 6.42 Smoothened and background corrected diffractograms of the parent coals and their respective chars.

All eight char samples were characterised by a distinct peak in the range of $27.6^\circ < 2\theta < 32^\circ$ which is related to the stacking of the graphitic basal planes in crystallite structures (Zhang *et al.*, 2008). This (002) reflection of carbonaceous matter, due to the layer stacking of aromatic structures, can therefore be related to the interlayer spacing of graphite (Okolo, 2010; Takagi *et al.*, 2004). Two lesser prominent peaks confined respectively to the ranges $38.8^\circ < 2\theta < 69.4^\circ$ and $89.5^\circ < 2\theta < 104.1^\circ$ (Okolo, 2010; Takagi *et al.*, 2004) were also observed and have been shown previously to correspond to hexagonal ring structures within the coal (Okolo, 2010; Zhang *et al.*, 2008).

From Figure 6.42 it is evident that a sharp increase in both intensity and broadening of the (002) and (10) peaks was observed for an increase in devolatilization temperature, while the amorphous γ -band was much more prominent in the coals when compared to the respective chars. The (002) peaks of the 450°C chars were, however, observed to be less broad than the parent coals, while peak broadening increased substantially for chars generated at 750°C. The descriptive sharp peaks for pyrite were also observed for the chars generated from coals UMZ, INY and G#5, which indicated the presence of un-removed pyrite within the demineralised char structures. This did, however, not affect the determinations of the crystallite parameters, due to the fact that these peaks did not interfere or obscure the intensities of the (002) and (10) bands of the three coals. In theory, the (002) band generally displays a symmetric profile (Lu *et al.*, 2001), but the apparent asymmetric nature of this peak as observed for both the coals and chars (although not so apparent in the higher temperature chars) in Figure 6.42 has necessitated the need to delineate this peak into the d_{002} peak and the γ -sideband (Ergun & Tiensuu, 1959; Franklin, 1951; Okolo, 2010). It has been shown that the existence of the γ -sideband can be associated with saturated organic structures such as aliphatic side chains, (Ergun & Tiensuu, 1959). The presence of this sideband is assumed not to contribute to the high angle side of the d_{002} peak due to its low intensity (Lu *et al.*, 2001).

Crystallite (lattice) parameters such as interlayer spacing was calculated from the (002) peak position with the aid of Bragg's law, while L_c was calculated from the peak position and full width at half maximum (FWHM) of the (002) band. According to Yen *et al.* (1961), the average crystallite diameter (L_a) can be either calculated from the (10) or (11) band. As was shown for the coal crystallite parameters (Chapter 4), the (11) band is normally not used for quantitative analyses, due to its diffuse and obscure nature (Okolo, 2010). From the work of Lu *et al.* (2001) it has been proposed that the (10) band may be significantly affected for quantification due to its

close proximity to the (002) band. As a comparison, L_a was therefore determined for both the (10) and (11) ($L_{a,(10)}$ and $L_{a,(11)}$) bands from the their respective peak positions and full widths at half maximum (FWHM), with the aid of Origin 8.0. In addition, the average number of stacks (N_{ave}) was determined according to Equation (5.12). The calculated crystallite parameters from the corrected and smoothened diffractograms of the different coals and chars are presented in Table 6.25.

Table 6.25 Summary of crystallite parameters for the different chars as derived from the XRD.

XRD carbon crystallite		Inertinite-rich coals					
XRD parameters	Symbol	INY			UMZ		
		Raw	450°C	750°C	Raw	450°C	750°C
Interlayer spacing (Å)	d_{002}	3.51	3.49	3.59	3.51	3.54	3.81
Stacking height (Å)	L_c	17.70	17.99	13.47	18.80	19.24	13.95
Stacking diameter (10) (Å)*	$L_{a,(10)}$	11.20	17.49	26.08	13.50	23.10	26.60
Stacking diameter (11) (Å)*	$L_{a,(11)}$	15.17	26.39	27.20	23.12	30.09	32.01
Average number of stacks	N_{ave}	6.05	6.15	4.75	6.36	6.44	4.66
XRD carbon crystallite		Vitrinite-rich coals					
XRD parameters	Symbol	G#5			TSH		
		Raw	450°C	750°C	Raw	450°C	750°C
Interlayer spacing (Å)	d_{002}	3.58	3.55	3.63	3.54	3.50	3.58
Stacking height (Å)	L_c	14.60	16.22	12.56	18.50	21.38	13.80
Stacking diameter (10) (Å)*	$L_{a,(10)}$	13.00	19.92	23.43	10.70	18.94	23.97
Stacking diameter (11) (Å)*	$L_{a,(11)}$	17.15	23.61	25.66	14.47	28.03	40.36
Average number of stacks	N_{ave}	5.07	5.57	4.46	6.23	7.11	4.85

* Calculated from the full width at half maximum with the aid of Origin 8.0.

All the chars displayed inter planar distances comparable to graphite (d_{002} for artificial graphite is 3.36 to 3.37 Å, while the d_{002} for true graphite is known to be 3.354 Å) (Franklin, 1951; Iwashita & Inagaki, 1993; Lu *et al.*, 2001). No concrete conclusions could be drawn from the interlayer spacing results, mainly due to the fact that all four parent coals were quite similar in rank (Okolo, 2010). Furthermore, a significant decrease in interlayer spacing, reaching values close to that of graphite, is only experienced at temperatures exceeding 900 °C (Zhang *et al.*, 2008). Significant differences could, however, be observed between the L_c and L_a values of the different chars. Narrowing and broadening of the (002) peak in the diffractograms of the chars can be ascribed to different mechanisms controlling the structural re-ordering and re-orientation of the aromatic carbon layer. Broadening of peaks gives rise to decreases in the crystallite size, while an increase in peak symmetry and -sharpness provides evidence of crystallite growth (Fu

et al., 2011; Kumar & Gupta, 1995; Kuroda & Akamatu, 1959; Lu *et al.*, 2002a & 2002b; Short & Walker, 1963; Wu *et al.*, 2008).

From Figure 6.42 and Table 6.25 it is therefore evident that crystallite height (L_c) first increases and then subsequently decreases at the higher temperature, whereas a monotonic increase in crystallite diameter (L_a) is observed with an increase in temperature. In addition, the average number of stacks for all chars seems to follow a similar trend as observed for L_c . These results suggest that structural ordering, in terms of stacking extent, is lower for the high temperature chars compared to the low temperature chars, and that crystallite growth due to coalescence of crystallites in the a direction was possibly favoured more during the higher temperature experiments, leading to a more aromatic structure (Fu *et al.*, 2011; Zhang *et al.*, 2008). The trend observed for L_c is, however, contradictory to the work of Wu *et al.* (2008) and Zhang *et al.* (2008) who observed an increase in L_c with temperature. From XRD investigations on different rank coals, Song *et al.* (2011) have, however, shown that L_c increases up to a certain coalification degree and then subsequently decreases thereafter, while L_a increases monotonically with increasing coal rank. Furthermore, independent investigations by Davis *et al.* (1995) and Wu *et al.* (2008) have also shown that crystallite diameter increases substantially with an increase in residence time and rapid heating, respectively. The observations made by Davis *et al.* (1995), Song *et al.* (2011) and Wu *et al.* (2008) therefore tend to support the findings made in this study (experiments were performed at “pseudo”-isothermal conditions (rapid heating) for close to 2 hours) when the close analogy that exists between coalification and thermal annealing is kept in mind. The discrepancy in L_c values could possibly be attributed to the large temperature differential experienced by the coal particles at 750 °C, causing an quite extensive cleavage of bonds and cross-linkage during the heating up stage. Furthermore, the more symmetric nature of the (002) band for chars generated at the higher temperature suggests that the degree of orientation of the aromatic lamellae becomes more prominent with an increase in temperature at the expense of crystal growth in the c direction (Fu *et al.*, 2011). The average number of crystallites in a stack was found to range between 4 and 7 for all the chars, which is in agreement with results obtained in numerous other studies concerning carbon crystallite analyses of coals and chars (Lu *et al.*, 2001; Okolo, 2010; Takagi *et al.*, 2004; Van Niekerk, 2008). As for the parent coals, estimation of the amount of amorphous carbon and the aromaticity was also conducted on the different chars following the methods and deconvolution strategies outlined in Section 5.3.1.3 and 5.4.1.3 (Lu *et al.*, 2001; Wu *et al.*, 2008; Wang *et al.*, 2001). The fraction of amorphous carbon could therefore be calculated with relative ease by using Equation (5.13). For illustrative purposes, the deconvoluted Gaussian curves as obtained

from Origin 8.0 software, as well as the original diffractograms of the chars generated from coal G#5 at 450 °C and 750 °C, respectively, are provided in Figure 6.43. The deconvolution results of the other chars are provided in Appendix C.13. The determination of the aromaticity of the different char samples followed a similar deconvolution strategy by delineation of the (002) band into a symmetric Gaussian curve describing the high angle side of the peak. Once this peak was resolved, a second Gaussian curve was fitted to the remaining intensity in the low angle side of the peak and was therefore attributed to the γ band.

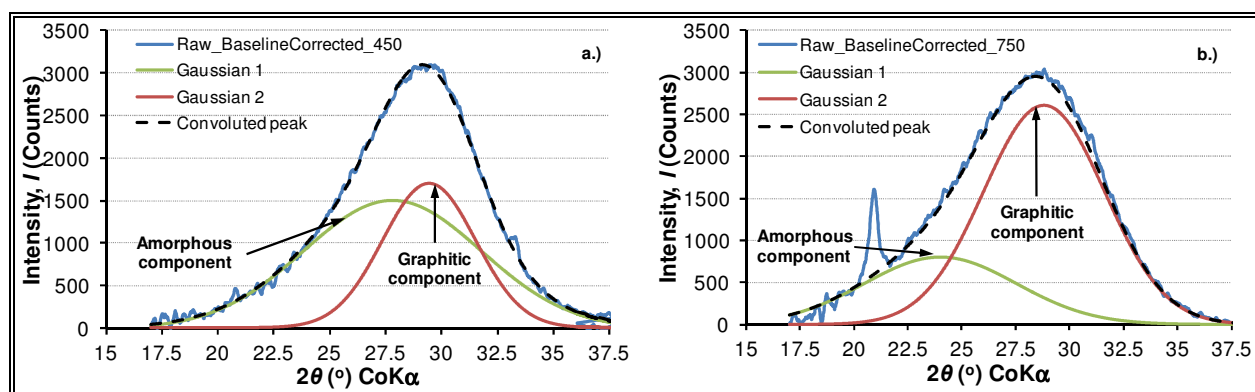


Figure 6.43 Estimation of the fraction of amorphous carbon for chars generated at a.) 450 °C and b.) 750 °C from coal G#5.

The sum of the two Gaussian curves was calculated to obtain a convoluted peak that could describe the combined (002) and γ band. After peak deconvolution, the areas respectively under the (002) band and γ band was used to estimate the aromaticity of each coal with the use of Equation (5.14). The deconvolution of the diffractograms of chars generated from coal G#5 at 450 °C and 750 °C, respectively, are presented in Figure 6.44. Deconvolution results for the other chars can be found in Appendix C.14.

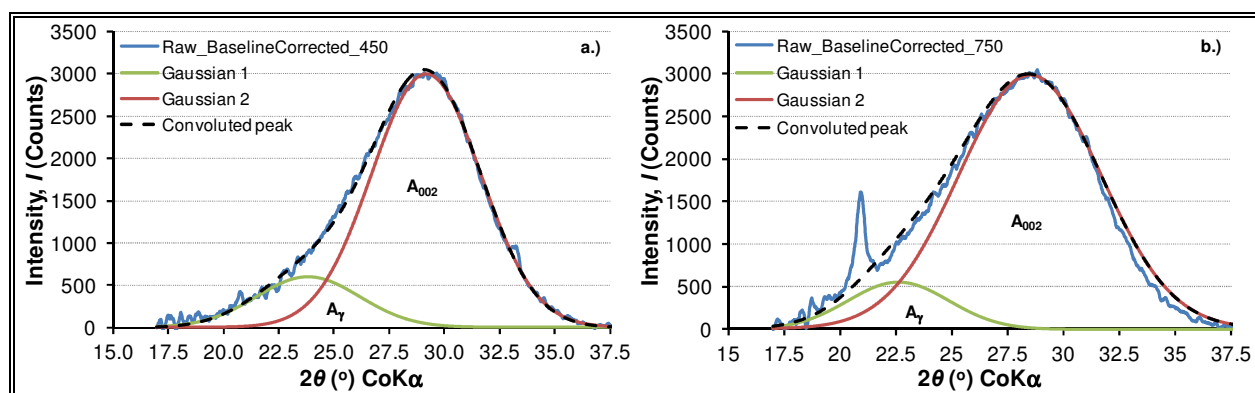


Figure 6.44 Estimation of the fraction aromatics for chars generated at a.) 450 °C and b.) 750 °C from coal G#5.

The degree of disorder index (*DOI*) was subsequently calculated from the obtained X_A and f_a values as discussed in Section 5.3.1.3. A comparison of the obtained results between the four different coals and their respective chars is provided in Table 6.26. The values obtained for the different coals have also been included in order to present respective trends.

Table 6.26 Summary of additional crystallite parameters.

<i>XRD carbon crystallite</i>		<i>Inertinite-rich coals</i>					
<i>XRD parameters</i>	<i>Symbol</i>	<i>INY</i>			<i>UMZ</i>		
		Raw	450°C	750°C	Raw	450°C	750°C
Fraction of amorphous carbon*	X_a	0.58	0.50	0.30	0.59	0.54	0.17
Aromaticity*	f_a	0.80	0.84	0.92	0.76	0.79	0.87
Degree of disorder index	<i>DOI</i>	0.66	0.58	0.36	0.69	0.64	0.27
Volatile matter (d.a.f.) ^a		31.4	19.5	3.9	29.7	18.5	5.2
Fixed Carbon (d.a.f.) ^a		68.6	80.5	96.1	70.3	81.5	94.8
Atomic H/C ratio ^a		0.69	0.55	0.12	0.62	0.53	0.13
Atomic O/C ratio ^a		0.09	0.07	0.02	0.08	0.08	0.03
<i>XRD carbon crystallite</i>		<i>Vitrinite-rich coals</i>					
<i>XRD parameters</i>	<i>Symbol</i>	<i>G#5</i>			<i>TSH</i>		
		Raw	450°C	750°C	Raw	450°C	750°C
Fraction of amorphous carbon*	X_a	0.67	0.63	0.28	0.52	0.50	0.20
Aromaticity*	f_a	0.70	0.84	0.88	0.84	0.86	0.91
Degree of disorder index	<i>DOI</i>	0.77	0.69	0.36	0.60	0.57	0.27
Volatile matter (d.a.f.) ^a		39.4	18.8	3.7	25.0	12.9	3.0
Fixed Carbon (d.a.f.) ^a		60.6	81.2	96.3	75.0	87.1	97.0
Atomic H/C ratio ^a		0.83	0.58	0.11	0.66	0.56	0.12
Atomic O/C ratio ^a		0.11	0.08	0.03	0.01	0.04	0.02

* Calculated through Gaussian curve fitting. ^a Inserted for comparative purposes with XRD results.

In addition, Table 6.26 also contains the results determined from proximate and ultimate analyses of both the coals and their respective chars. The obtained aromaticity results, although lower in numeric value, showed good agreement with what was obtained from solid state ¹³C NMR. From Table 6.26 it is clear that aromaticity increases with increasing devolatilization temperature, while a subsequent decrease in the fraction of amorphous carbon and *DOI* is experienced for all four cases.

The increase in aromaticity is a direct result of the loss of aliphatic side chains in the parent coal as the charring process became more extensive. This is supported by the obscurity and near-loss of the γ -band as seen in the diffractograms of the coals and chars; as well as the

generation of more CH_4 and short-chain aliphatics as quantified during GC analyses of the product gases. The decrease in the fraction of amorphous carbon, which is a quantitative measure of the amount of disorder carbon, with increasing devolatilization temperature can be attributed to the annealing of the turbostratic structure of the parent coals and the subsequent formation of more crystallites in the chars (Okolo, 2010). This finding is supported by a similar decreasing pattern observed for the degree of disorder index (DOI), which corroborates with the increase in aromaticity and gives a further indication of the compact, orderly structure of the generated chars. Furthermore, a correlation between aromaticity and DOI plotted against stacking diameter ($L_{a,(10)}$) (Figure 6.45) confirms the formation of larger condensed, aromatic structures. Similar observations were made by Kawakami *et al.* (2006), Lu *et al.* (2001, 2002a & 2002b), Maity and Mukherjee (2006), Okolo (2010) and Senneca *et al.* (1998).

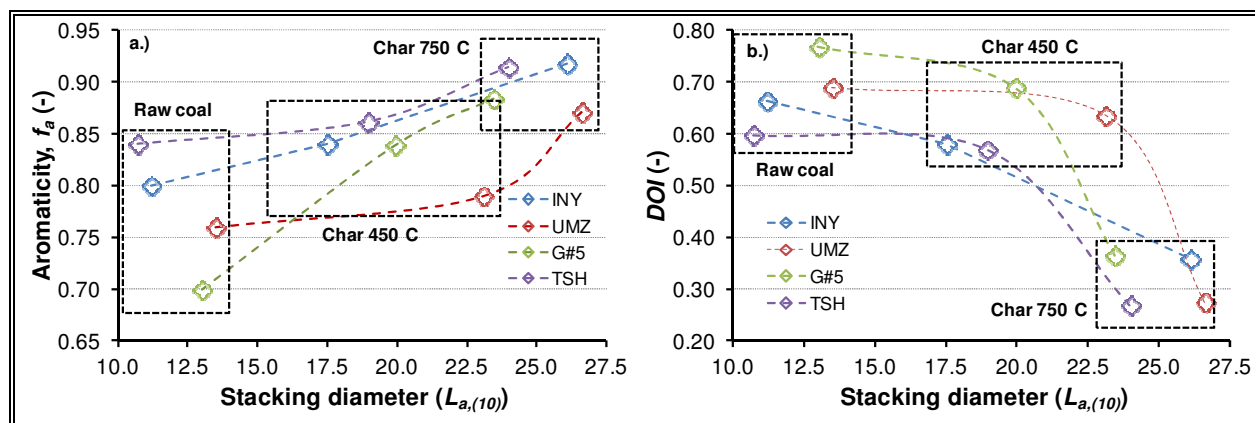


Figure 6.45 Correlation of a.) aromaticity and d.) DOI with crystallite stacking diameter.

A comparison of the XRD derived parameters with results obtained from proximate and ultimate analyses is provided in Figure 6.46 for the parent coals and their respective chars. The properties of the coals and different chars were colour coded for illustration. From Figure 6.46a it can be seen that aromaticity decreases linearly with increasing volatile matter (d.a.f.), thus providing evidence that the scission of hydrocarbon bonds and the subsequent removal of volatile matter lead to a more aromatic structure formation with increasing temperature. Similar behaviour is observed in Figure 6.46c for aromaticity versus hydrogen-carbon ratio. A decrease in the proportion of these groups due to devolatilization will therefore result in a lower volatile matter content and a subsequently higher aromaticity (Choi *et al.*, 1989; Okolo, 2010).

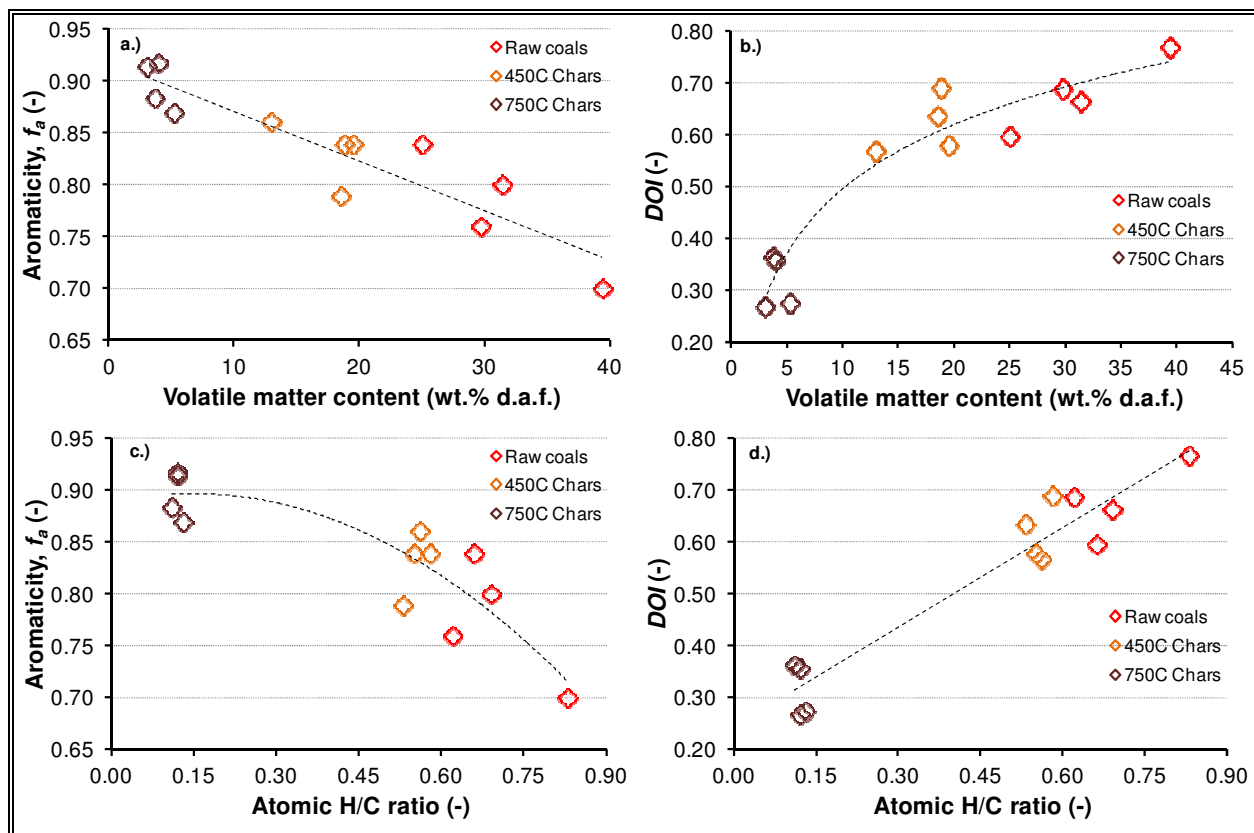


Figure 6.46 Comparison of aromaticity and DOI with volatile matter (a.) and, b.) and atomic H/C ratio (c.) and d.).

The effect of the degree of disorder index (DOI) on volatile matter content and atomic H/C ratio is displayed respectively in Figure 6.46 b.) and d.). The amount of volatile matter (wt.% d.b.) increases with an increase in DOI . Higher values of this parameter are indicative of a higher relative abundance of disordered carbon (Lu *et al.*, 2002b; Okolo, 2010), possibly in the form of low molecular weight aliphatics and/or saturated hydrocarbons. This contributes largely to the amount of volatile matter released during devolatilization.

A decrease in DOI therefore indicates a more ordered structure with less volatile matter that can be evolved. This is also supported by the linear increase in DOI with atomic H/C ratio, which suggests that the increase in crystallite order is described by a larger proportion of aromatic molecules tightly bonded and cross-linked to one another. In addition, it is important to note that the group scattering of coals and chars as presented in Figure 6.46 seems to decrease with increasing devolatilization temperature, which suggests that char properties become much more similar in nature, irrespective of coal origin, and that a temperature threshold exists above which char properties will not change significantly.

High-resolution transmission electron microscopy (HRTEM) and image analyses

A detailed discussion of the distribution of aromatic layers within the molecular structure of the four parent coals has been provided in Section 5.4.1.5. HRTEM has proven valuable for understanding the molecular structure of coals and coal-derived products and has widely received attention by authors such as Mathews *et al.* (2010), Sharma *et al.* (2000), Sharma *et al.* (2001), Van Niekerk (2008), Yang *et al.* (2006) and Yoshizawa *et al.* (1998). A similar lattice fringe extraction and image analysis methodology as proposed by Mathews *et al.* (2010) and Sharma *et al.* (1999) was followed for studying the respective chars, of which details can be found elsewhere (Section 5.3.1.5). As illustration, examples of processed images from the cropping step, through the binary conversion step, to the final lattice-fringe extracted image are provided respectively in Figure 6.47 for the chars generated at 450°C and 750°C from coal TSH. Similar figures for the other coals can be found in Appendix C.15.

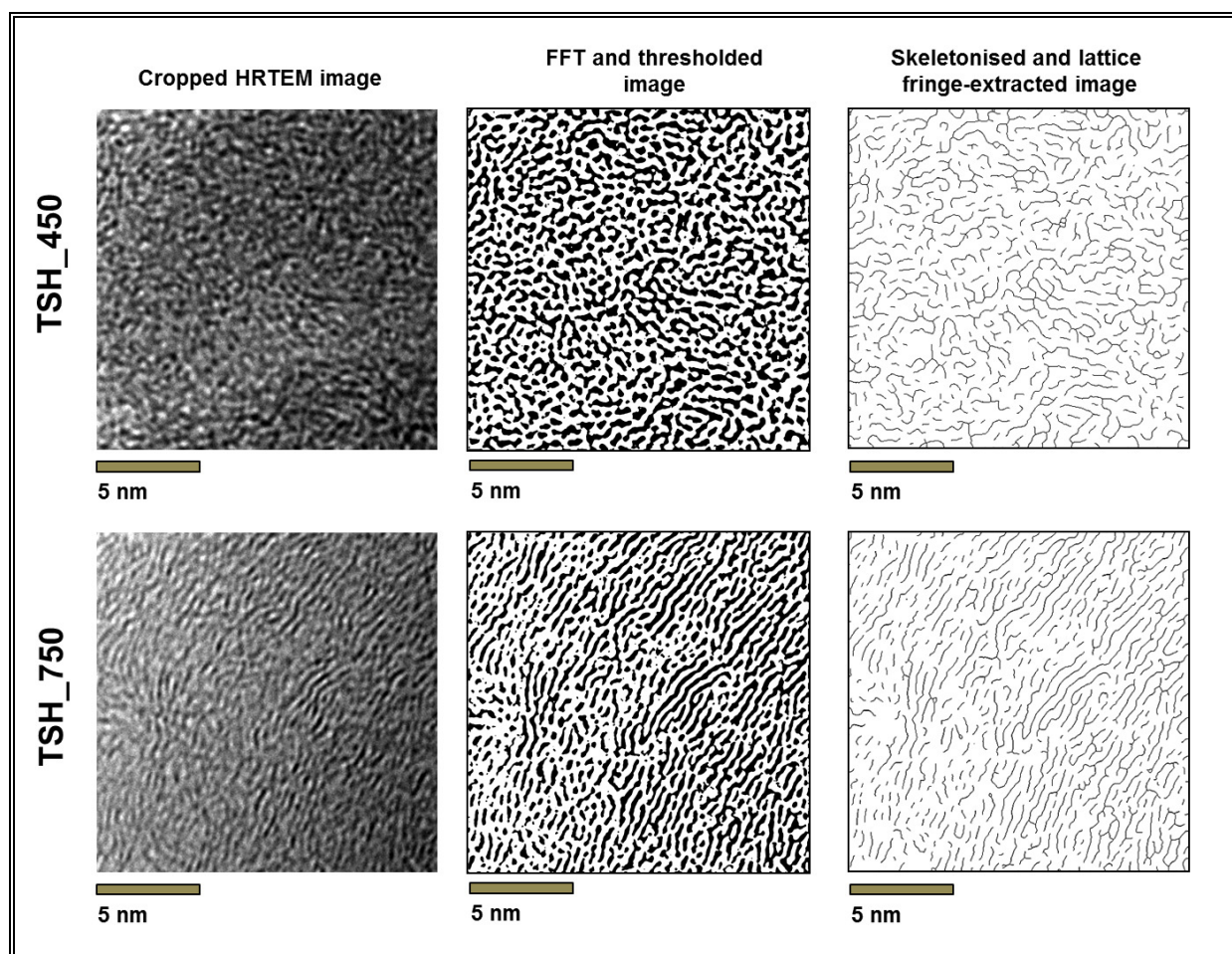


Figure 6.47 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal TSH.

The obtained micrographs displayed similar features to what was observed for both coals and chars by Roberts (2012), Fernandez-Alos *et al.* (2011), Mathews and Chaffee (2012), Mathews and Sharma (2012), Sharma *et al.* (1999 & 2000) and Van Niekerk (2008). Some micrographs were found to be slightly lower in quality compared to the micrographs published by Sharma *et al.* (2000), which could have been the result from possible system drift during the analyses (Van Niekerk, 2008). The image processing toolkit of Reindeer Graphics was further applied to determine the length (in Angstroms) of each extracted aromatic fringe in each of the micrographs of the respective chars. To compare the different chars, the segment selection and colour coding tool of the image processing toolkit was used to select and colour fringes in specified length ranges as illustrated for the small (red coloured), intermediate (regime I and II (green- and blue coloured)) and large size (black coloured) ranges of the lattice-fringe extracted HRTEM image of chars derived from coals UMZ and TSH respectively (Figures 6.48 and 6.49). Similar results were obtained for chars generated from coals INY and G#5, of which examples of the processed images can be found in Appendix C.15. Fringe length selection was done in the same range for both the 450 °C and 750 °C chars.

Visual inspection of the fringe-extracted micrographs (Figures 6.48 and 6.49) of the different chars showed striking differences in shape, size and orientation of the aromatic layers. For the 450 °C chars the highest abundance of fringes was confined to the small to intermediate I regime, whilst only small numbers of the relatively large fringes were observed. An increase in charring temperature did, however, lead to the production of greater quantities of the intermediate II- and large fringes, accompanied by the subsequent increase in the structural orientation and layer size of these higher temperature chars, compared to the more random orientation of the fringes observed for the 450 °C chars. This is in agreement with what was observed by Fernandez-Alos *et al.* (2011) and Sharma *et al.* (1999 & 2000). Furthermore, larger and more oriented layers could also be observed for the 750 °C char derived from coal TSH in comparison to the other chars, indicating that structural orientation was more extensive for the coking coal. The tendency of coal TSH to form chars with a higher degree of structural alignment can be attributed to its plastic properties. Accordingly, during devolatilization, aliphatic bridges are broken and the basic aromatic structural units become free to form an intermediate, carbonaceous, liquid crystal mesophase (or plastic stage). The formed structural units are therefore orientated into parallel sheets of molecular domains due to the metaplast that acts as a solvolizer (Rouzaud, 1990). As devolatilization progresses the molecular domains are extended and quenched due to volatilization of the formed metaplast (Rouzaud, 1990).

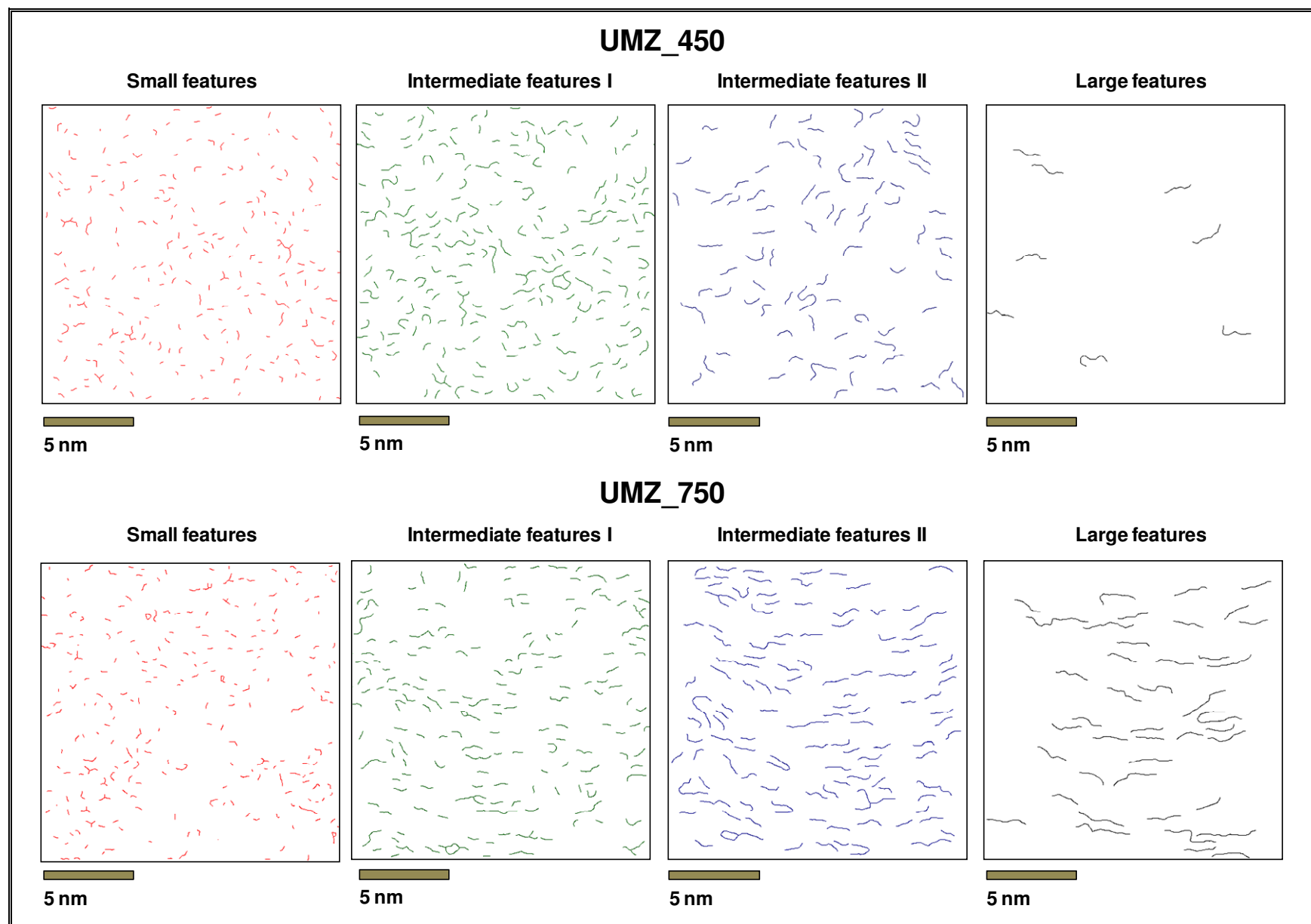


Figure 6.48 Selected fringes in different size-ranges for chars derived from coal UMZ at 450°C and 750°C.

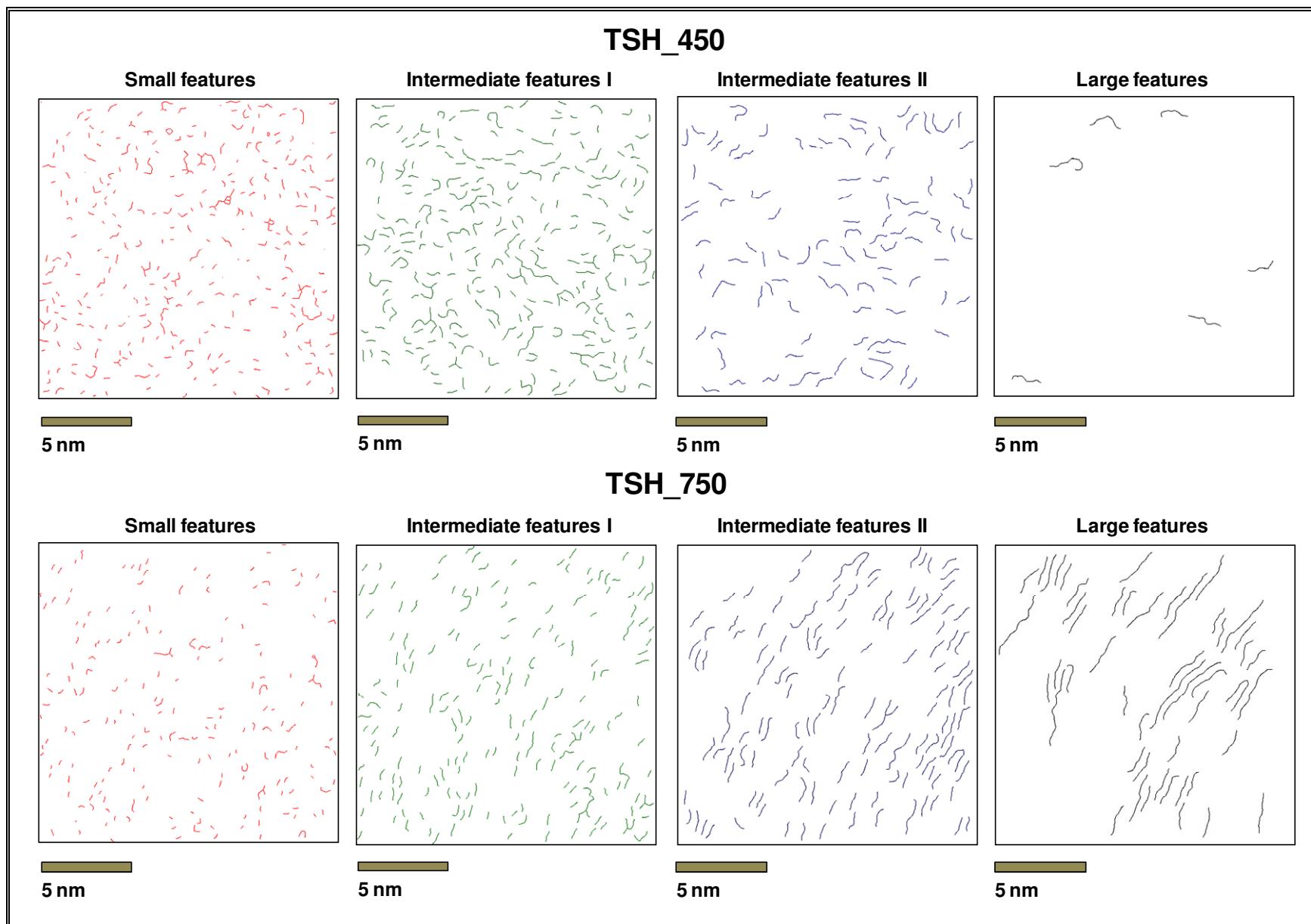


Figure 6.49 Selected fringes in different size-ranges for chars derived from coal TSH at 450°C and 750°C.

This corresponds to the conclusions drawn from XRD and supports the fact that coking coals provide valuable feed stocks for the production of graphitic-like, higher value carbons (Burchell, 1999; Derbyshire, 1997). Although crystallite growth was experienced for the lower temperature chars, the lower degree of structural orientation suggests that the energy needed for structural re-alignment was not sufficient to favour the formation of parallel-aligned aromatic layers. These observations tend to be consistent with what was observed with the *DOI* values obtained from XRD analyses. In addition, chars derived at both temperatures from coal G#5 displayed the formation of numerous amounts of aligned aromatic layers resembling “onion-like” structures as shown in Figure 6.50. This was, however, not found for chars generated from the other coals.

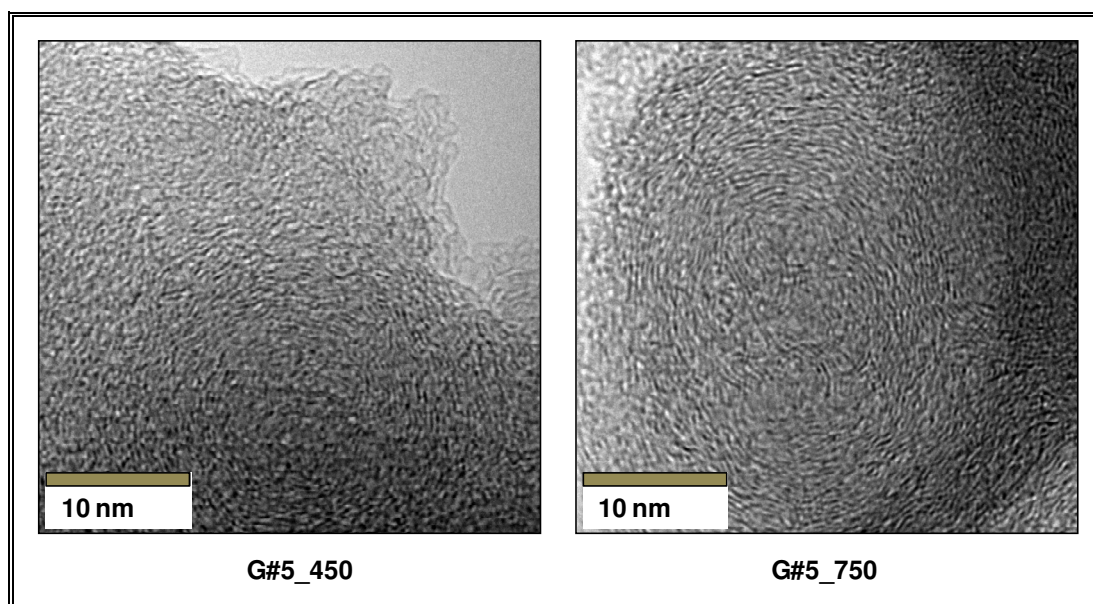


Figure 6.50 Onion-like structures observed for chars derived from coal G#5.

Similar observations were made by Sharma *et al.* (2001) with regard to the molecular structure of Pocahontas #3 coal (Kabe *et al.*, 2004). It has been suggested that these structures resemble HRTEM images observed by Iijima (1980) for spheroidal carbon particles and provide direct evidence of the presence of fullerene-like structures within coals and chars (Kabe *et al.*, 2004). The obtained skeletal char structures were further subjected to aromatic raft determinations by applying the methods developed in Section 5.3.1.5. Although these estimations are built on the assumption of symmetric, parallelogram catenations; they provide a reasonable starting point for qualitatively describing the diversity and distribution of the aromatic layers or rafts present in the chars and coals (Van Niekerk, 2008). The obtained fringes were therefore classified within the different parallelogram catenation groups and the relative frequency of each specific parallelogram raft size was expressed as a percentage of the total number of fringes. For each

cropped micrograph (100 mm x 100 mm) of each char more than 600 fringes were extracted and subjected to image analyses and aromatic raft size determination. The number of fringes extracted was, however, lower than that of the parent coals as the char structures contained a greater abundance of the larger aromatic fringes than parent coals. The method proposed by Mathews *et al.* (2010) was used to relate the fringe lengths of parallelogram shaped aromatic fringes to the average molecular weight of that particular fringe size (Equations (5.17)-(5.19)). The obtained aromatic raft size distributions, with respect to molecular weight, of chars generated from coals INY, UMZ, G#5 and TSH are shown respectively in Figure 6.51a.) to d.). Aromatic raft size distributions of all four coals have also been included for comparative purposes. From the Figure it is evident that the aromatic raft size distributions of the chars exhibited similar Lorentzian type behaviour to that found from the HRTEM results of the parent coals. It is, however, striking to notice that the molecular weight distributions tend to shift to higher molecular weights as the charring temperature is increased, with aromatic raft sizes significantly exceeding 20x20 for the highest temperature chars. This supports the fact that devolatilization releases volatile products from the coal matrix and subsequently forms larger, orientated, poly-condensed structures as temperature is increased, which is consistent with what was obtained from ^{13}C NMR and XRD performed on the chars. Average structural parameters have also been deducted from the aromatic raft size distributions and are summarised in Table 6.27.

Table 6.27 Average structural properties as derived from HRTEM.

HRTEM analyses		Inertinite-rich coals					
HRTEM parameters	Unit	INY			UMZ		
		Raw	450°C	750°C	Raw	450°C	750°C
Highest fringe distribution	-	2x2	3x3	4x4	2x2	3x3	4x4
Largest frequency*	%	16.5	20.4	17.1	18.1	18.6	14.1
Average molecular weight**	m/z	467.1	598.0	725.0	426.8	682.0	778.5
Average fringe length	Å	10.2	11.7	13.1	9.7	12.7	13.6
XRD carbon crystallite		Vitrinite-rich coals					
HRTEM parameters	Unit	G#5			TSH		
		Raw	450°C	750°C	Raw	450°C	750°C
Highest fringe distribution	-	2x2	3x3	3x3	3x3	5x5	5x5
Largest frequency*	%	18.9	17.2	21.9	15.3	14.9	11.3
Average molecular weight**	m/z	411.7	686.1	658.5	506.0	807.5	1192.2
Average fringe length	Å	9.5	12.7	12.4	10.7	13.9	17.4

*Corresponding to the fringe size with the highest frequency. **Estimated from the relative frequencies of the different fringes.

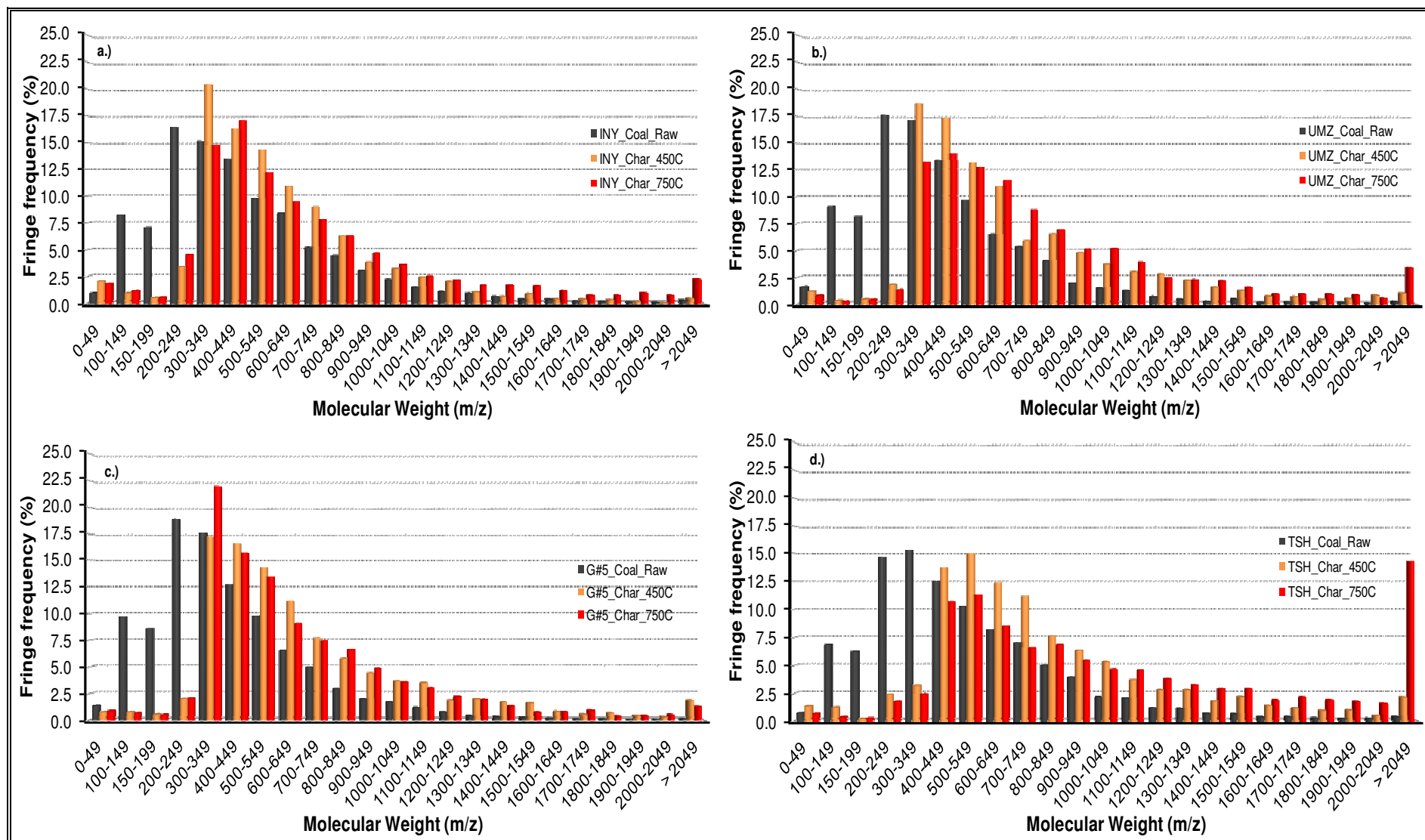


Figure 6.51 Molecular weight distributions from HRTEM for the parent coals and their respective chars.

From Figure 6.51 it is clear that a significant reduction in fringes below 2x2 was observed with an increase in temperature, and that a greater abundance of fringes were concentrated in the 3x3 to 5x5 region. The reduction in molecular fringes confined to smaller than 2x2 could be attributed to the evolution of aromatic species to the tar fraction (including benzene, naphthalene, anthracene, etc. as observed from the GC-MS analyses), or the subsequent re-polymerisation of these low molecular weight fringes to produce larger molecular entities. The low temperature chars derived from coals UMZ, INY and G#5 were characterised by high abundances of 3x3 structures with an accompanying increase in average molecular weight of up to 686.1 m/z. In contrast however, the low temperature chars derived from coal TSH showed slightly higher abundances of aromatic fringes in the range of 5x5, which can be related to the relatively large molecular weight fringes observed for the parent coal. A further increase in temperature led to a further reduction in fringe sizes below 5x5 favouring the formation of larger aromatic layers with significant increases in fringe sizes exceeding 20x20, as in the case of TSH. From Table 6.28 it can be seen that the average molecular weight increased significantly due to a shift in relative frequency of fringes to the high molecular sizes. Furthermore, average molecular weights for the 750 °C chars increased in the order G#5 < INY < UMZ < TSH up to 1192.2 m/z. As in the case of the parent coals, chars derived from coals UMZ and INY displayed similar structural features suggesting that the mechanism of devolatilization for these two coals are possibly similar in nature. A comparison with molecular mass estimates from SEC indicated that molecular masses for the heavy tar constituents (roughly between 400-800 m/z) are in the same order as observed for the respective chars, therefore suggesting that some heavier molecules were not retained in char re-polymerisation reactions and were able to escape to the tar fraction.

6.6 Summary

A product evolution study was conducted in order to assess the characteristics of products generated during the devolatilization of large coal particles (5 mm and 20 mm particles) on both a qualitative and quantitative basis. A self-fabricated reactor system (TCR facility), enabling the capturing of tars and the online measurement of evolved gases, was constructed in order to evaluate the devolatilization behaviour of each coal at two different isothermal reactor temperatures: 450 °C and 750 °C. Evolved gasses were monitored by both online MS and stand-alone GC measurements, while tar- and char yield was determined gravimetrically. Evaluation of

tar and char characteristic properties involved the use of various conventional- and advanced analytical techniques. In general, it was found that temperature was the dominating factor dictating the yield and quality of devolatilization products, while the influence of particle size was less significant. Tar yields ranged between 3.6 wt.% and 10.1 wt.% and increased in the order UMZ < INY < TSH < G#5 for both devolatilization temperatures. Tar yields were compared to parent coal properties and it was found that the large liptinite and vitrinite content of coal G#5 was primarily responsible for the high levels of tar obtained from this coal. The subsequent lower tar yield from the vitrinite-rich, coal TSH was attributed to its highest aromaticity and slightly higher rank. Gaseous products were found to be composed mainly of H₂, CH₄, CO, CO₂, light paraffins (ethane and propane), light olefins (ethylene and propylene) and C₄ homologues. An increase in experimental temperature subsequently led to not only an increase in the rate of gas species evolution, but also to significant increases in both volatile matter and gas species production (factor 3 to 4 increase), indicating the occurrence of extensive covalent bond cleavage and secondary gas reactions.

SIMDIST analyses performed on the retained tar samples indicated that the weight average boiling points of the different tars varied between 337.3°C and 376.8°C, with a higher proportion of distilled material reporting to the light- and heavy vacuum gas oil fractions. Furthermore, low temperature tars were characterised by the presence of appreciable amounts of aliphatic compounds (up to 24.45 wt.%), alkyl-phenols (3.82-24.56 wt.%) as well as mixed aliphatic- and aromatic compounds (up to 76.55 wt.%), while an increase in temperature saw the release of larger amounts of aromatic compounds such as alkyl-naphthalenes (10.13 wt.%-14.60 wt.%) and PAHs (71.52 wt.%-88.66 wt.%). Tars generated at 450°C from coal G#5 displayed a larger aliphatic character in comparison to tars generated from the other coals, while tar obtained from coal TSH was found to be more aromatic for both temperatures. From SEC measurements it could be concluded that all of the tars contained a large proportion of material confined to masses below 1000 Da, while heavier molecular compounds of up to 5000 Da were observed in smaller abundances. An increase in temperature led to a subsequent shift in mass distribution, favouring the formation of lower molecular weight compounds due to possible secondary cracking reactions at higher temperature. From ¹H and ¹³C NMR analyses it was evident that the tars generated at 750°C were characterised not only by smaller abundances of aliphatic proton and carbon functionalities (higher aromaticities), but also by less aromatic structures substituted with long aliphatic chain attachments. Liptinite content and aromaticity were found to be the dominating factors controlling tar quality.

Char characteristics were found to exhibit similar characteristics to the properties of tars yielded at corresponding temperatures. Char morphological petrography revealed that the chars were characterised by a vast array of morphological types ranging from devolatilized coal structures at 450°C, to more honeycomb and cracked dense structures at 750°C. From the ^{13}C NMR and XRD carbon crystallite results it was clear that an increase in temperature led to the formation of progressively more aromatic and poly-condensed carbon structures within each coal. This was also supported by the findings from HRTEM and image analyses, which indicated the growth of respective aromatic structures to form more orientated, aligned and larger molecular weight fringes.

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