

Pyrolysis product evaluation and prediction of coals of different rank

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DECLARATION

I, Gustav Nico Pretorius, hereby declare that the dissertation entitled: “***Pyrolysis product evaluation and prediction of coals of different rank***”, submitted in fulfilment of the requirements for the degree of Master in Chemical Engineering, is my own work except where acknowledged in text, it has been language edited as required and has not been submitted to any other tertiary institution in whole or in part.

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Signed at Potchefstroom on the _____ day of November 2016.

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University number

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Abstract

When coal is heated slowly ($<10\text{ }^{\circ}\text{C/min}$), as in the Lurgi Fixed Bed Dry Bottom (FBDB) gasification process, products formed in the pyrolysis region of the gasifier include gas liquor, condensable tars, oils and non-condensable gases. Knowledge of the temperature profile together with coal behaviour (partitioning into char, tar, gas and liquid) is therefore very important when designing a gasification plant. Extensive research on the effect of coal type on the flash pyrolysis at high heating rates of different coals has been reported, but only limited research on the tar, oil and naphtha composition produced by slow heating rates exists. When screening coals for suitability in Lurgi FBDB gasification, slow heating rate pyrolysis predictions and a total mass balance of elements (carbon, hydrogen, nitrogen, sulphur and oxygen) of the product yields obtained based on only raw coal information (proximate-and ultimate analysis) will be very advantageous and needed. With the support of validated existing pyrolysis models e.g. FLASHCHAIN[®] and statistical regression the determination of which coals are more amenable to chemicals and gas production can be ascertained in an uncomplicated fashion.

The aim of this study was to evaluate/develop models for five coals of different rank in order to predict the char, tar, water and gas yields, as well as the tar composition (naphtha, oils and tars) when heated at slow heating rates ($<10^{\circ}\text{C/min}$). A modified Fischer Assay setup, developed at the North-West University, was used in order to investigate pyrolysis at temperatures higher than that of the ISO 647 standard, for the pyrolysis experiments, i.e. final temperatures of $520\text{ }^{\circ}\text{C}$, $720\text{ }^{\circ}\text{C}$ and $920\text{ }^{\circ}\text{C}$.

The five coals studied (A-E) were characterised and classified as follows: Coal A, B and C were ranked as lignite B coals, coal D as rank C bituminous, and coal E as subbituminous. Anthracite was not included in this study, since the selection was based on coals which are conventionally used in Lurgi FBDB gasification.

The Fischer Assay pyrolysis experiments showed that temperature has a large effect on the pyrolysis product yield, i.e. the volatile matter released increased with an increase in pyrolysis temperature. Tar yields of all coals increased to a maximum at $720\text{ }^{\circ}\text{C}$, before decreasing or remaining the same at higher temperature, which means that a maximum tar yield has been reached by $720\text{ }^{\circ}\text{C}$. Only the char yield was found to be rank dependent with large variations being observed for the derived tar yields. Coal B had the highest tar yield ($8.8\text{ wt\%}$.) compared to that of coals A, C, D and E ($2.8\text{wt\%}$, $2.9\text{wt\%}$, $3.2\text{wt\%}$ and $4.9\text{wt\%}$ respectively). An elemental balance of the pyrolysis products derived from coal B, relative to the other coals, showed that more carbon and hydrogen partitioned into the gas phase than into the tar

fraction, where the opposite was seen. This partitioning therefore seems to correlate well with the tar yield observed.

The elemental carbon and oxygen contents of the tars formed at a final pyrolysis temperature of 920 °C have been found to correlate well with the elemental analysis of the raw coals. Carbon contents in the original coals are ranked as follows: coal A < coal C < coal B < coal D < coal E, whereas the carbon content in derived tars formed at a pyrolysis temperature of 920 °C are ranked as follows : coal A < coal B < coal C < coal D < coal E. Identical trends were found for oxygen. Coals of lower rank therefore form tars that are more oxygen rich than coals of higher rank. This was seen evident in the gas yield results, where lower rank coals formed more oxygen gas species than higher ranked coals. No rank dependence was observed for the results obtained using Simdis and SEC-UV. From the Simdis results, the only temperature dependence found was that the tar heavy residue fraction at 920 °C was higher than observed at 520 °C, which indicates that lighter tars cracked while being heated to 920 °C. From the GC-MS results it appears as if tars derived from higher rank coals form more phenolic compounds, and a similar trend is seen for furans, but no rank dependence is apparent for cresol and paracresol and long chain alcohols. For the gas species it was observed that the CO and CO₂ yields were rank dependent and closely related to the oxygen content in the original coal. Lower rank coals had higher oxygen contents and produced more oxygen containing gases (CO and CO₂). On the other hand, no rank dependence was found for the H₂ yields.

FLASHCHAIN[®] was able to provide accurate predictions of the char yield, and good trends of tar and gas yield for all 5 coals. Elemental carbon in the char was also accurately predicted at 720 °C and 920 °C, and elemental nitrogen in the char was accurately predicted at 520 °C and 720 °C. Elemental carbon content in tar formed at 920 °C was also accurately predicted. Statistical regression was applied in order to determine the relationship between raw coal properties and pyrolysis products and its compositions. A number of coal properties were found to have statistically significant relationships with some of the coal pyrolysis products, but no strong correlation was found for the gas yield. These properties include inherent moisture content, ash content, elemental carbon, oxygen and sulphur and Al₂O₃ for the char yield. The statistically significant properties that correlated well with the water yield include inherent moisture content, ash content, elemental carbon, nitrogen, oxygen and sulphur and Al₂O₃. Finally, XRF (x-ray fluorescence) ash constituents (MgO, CaO, TiO₂ and Fe₂O₃) seemed to have statistically significant correlations with the gas species and tar composition, which could indicate catalytic effects of the minerals occurring during heating.

Keywords: Coal rank, pyrolysis, FLASHCHAIN[®], devolatilisation, tar, char, gas

Table of Contents

Acknowledgements	ii
Abstract.....	iii
List of Figures	viii
List of Tables	x
Table of abbreviations.....	xii
Chapter 1 - Introduction	1
1.1 Background and motivation	1
1.2 Problem statement and objectives	2
1.3 Research methodology.....	3
1.4 Chapter layout	4
Chapter 2 - Literature review.....	5
2.1 Introduction.....	5
2.2 Coal overview.....	5
2.2.1 Coal utilisation.....	5
2.2.2 Coal rank	5
Medium rank D (Bituminous D)	8
2.2.3 Chemical and physical properties of coal	9
2.3 Coal pyrolysis	11
2.3.1 Introduction to coal pyrolysis	11
2.3.2 Valuable products from coal pyrolysis	13
2.3.3 Assessment of coal pyrolysis	15
2.4 Factors affecting coal pyrolysis products and efficiency.....	16
2.4.1 Effect of coal properties on coal pyrolysis.....	16
2.4.2 Effect of operating conditions on coal pyrolysis	18
2.5 Coal devolatilisation models	22
2.5.1 The FG-DVC model	22
2.5.2 The FLASHCHAIN® model	23
2.5.3 The CPD model	24

Chapter 3 - Coal characterisation.....	27
3.1 Introduction.....	27
3.2 Coal origin and sampling	27
3.2.1 Origin of coals	27
3.2.2 Coal Preparation	27
3.3 Analyses and results	28
3.3.1 Chemical and mineralogical analyses	29
3.3.2 Petrographic analyses.....	32
3.3.3 Structural analyses.....	34
3.3.4 Coal rank classification.....	38
Chapter 4 – Experimental and analytical procedures	40
4.1 Introduction.....	40
4.2 Thermogravimetric analysis	40
4.3 Fischer Assay pyrolysis	40
4.3.1 Fischer Assay operating procedure	40
4.3.2 Pyrolysis product yield.....	43
4.4 Pyrolysis product analyses	44
4.4.1 Char analyses	44
4.4.2 Tar analyses	45
4.4.3 Gas analyses	47
4.5 Experimental plan (Fischer Assay)	48
4.6 Modelling	48
4.6.1 FLASHCHAIN®	48
4.6.2 Statistical regression	50
Chapter 5 - Results and discussion.....	52
5.1 Introduction.....	52
5.2 Experimental results and discussion.....	52
5.2.1 Thermogravimetric analysis	52
5.2.2 Pyrolysis product yields.....	53

5.2.3 Char composition	59
5.2.4 Gas composition	63
5.2.5 Tar composition	65
5.2.6 Elemental partitioning.....	71
5.3 Application of FLASHCHAIN®	74
5.3.1 Pyrolysis product yields.....	74
5.3.2 Prediction of char composition	75
5.3.3 Prediction of tar composition	77
5.3.4 Prediction of H ₂ , CH ₄ , CO and CO ₂ yields	78
5.4 Statistical regression	78
5.4.1 Pyrolysis product yields.....	79
5.4.2 Tar and gas composition	80
Chapter 6 - Conclusions and recommendations.....	84
6.1 Introduction.....	84
6.2 Conclusions.....	84
6.3 Recommendations for future work	88
Reference list.....	90

List of Figures

Figure 2-1: Coalification and coal types (Adapted from Bell <i>et al.</i> , (2011))	6
Figure 2-2: Primary and secondary coal devolatilisation. (adapted from (Gönenç & Sunol, 1994))	13
Figure 2-3: Effect of coal rank on tar yield (taken from (Xu & Tomita, 1987a))	17
Figure 0-1: Effect of pyrolysis temperature on pyrolysis products (taken from Xu & Tomita, (1987b))	
Figure 2-5: Typical chemical structures (as seen on ¹³ C-NMR) used by the CPD for the description of the coal structure. Taken from (Fletcher <i>et al.</i> , 1992) 25	
Figure 3-1: DRIFT spectra of a) coal A b) coal B c) coal C d) coal D e) coal E	37
Figure 3-2: Five coals plotted on a Van Krevelen diagram	39
Figure 4-1: Schematic of Fischer Assay experimental setup	41
Figure 4-2: Fischer Assay temperature profile for final pyrolysis temperatures of 520 °C, 720 °C and 920 °C	42
Figure 4-3: Boiling point ranges for tar samples analysed by Simdis (After ASTM D2887) ..	46
Figure 4-4: Hydrocarbon gases output report example for Coal A: 520 °C	50
Figure 5-1: Weight loss curves as determined by thermogravimetric analysis for all five raw coals	52
Figure 5-2: Experimental Fischer-Assay yields of five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C	53
Figure 5-3: a) Char yields, b) Tar yields, c) Water yields and d) Gas yields for five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C	55
Figure 5-4: Volatile matter release distribution into tar and gas at final pyrolysis temperatures of a) 520 °C, b) 720 °C and c) 920 °C	59
Figure 5-5: Percentage of original volatile matter in raw coal released at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C	60
Figure 5-6: Gas yields of H ₂ , CH ₄ , CO and CO ₂ of five coals at final pyrolysis temperatures of 520°C. 720 °C and 920 °C	64
Figure 5-7: Size exclusion chromatography of tars formed at a) 520 °C, b) 720 °C and c) 920 °C	67
Figure 5-8: Elemental partitioning into char, tar, water and gas (dry basis) of a) carbon, b) hydrogen and c) oxygen	72
Figure 5-9: FLASHCHAIN® vs. experimental yields of a) char, b) tar, c) water and d) gas	75
Figure 5-10: FLASHCHAIN® predicted and experimental values for elemental a) carbon, b) hydrogen, c) oxygen d) nitrogen and e) sulphur in char	76

Figure 5-11: Comparison between FLASHCHAIN® predicted and experimental results of elemental a)carbon ,b)hydrogen, c)oxygen, d)nitrogen and e)sulphur in tar derived at 920 °C	77
Figure A-1:TGA flow calibration curve	107
Figure A-2: SEC-UV calibration curve	108
Figure B-1: Mass los curve of coal A.....	114
Figure B-2: Mass loss curve of coal B	114
Figure B-3: Mass loss curve of coal C	115
Figure B-4: Mass loss curve of coal D	115
Figure B-5: Mass loss curve of coal E	116
Figure B-6: Sample A - Char at 920 °C	117
Figure B-7: Sample C - Char at 720 °C	117
Figure B-8: Coal D raw coal	117
Figure B-9: Hydrogen gas yields	118
Figure B-10: Methane gas yields.....	118
Figure B-11: Carbon monoxide gas yields.....	119
Figure B-12: Carbon dioxide gas yields.....	119
Figure B-13: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal A.....	121
Figure B-14: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal B.....	122
Figure B-15: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal C	124
Figure B-16: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal D	125
Figure B-17: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal E.....	127
Figure C-1: FLASHCHAIN® predicted gas yields compared with experimentally determined gas yields for final pyrolysis temperatures of a) 520 °C, b) 720 °C and c) 920 °C	129

List of Tables

Table 2-1: Coal macerals (Adapted from ASTM D121-05 and ASTM D 2799-13)	6
Table 2-2: Classification of coals by rank (Adapted from ASTM D 388)	7
Table 2-3: Rank classification of coals according to ISO 11760:2005	8
Table 2-4: Coal pyrolysis temperature regions (Adapted from Ladner, 1988)	12
Table 2-5: Coal to chemical projects in China. After (Shaanxi Yanchang Petroleum Group, 2015)	15
Table 2-6: Mineral matter decomposition reactions (Adapted from Bryers, (1986))	18
Table 2-7: Quality of pyrolysis products (Adapted from Ladner, 1988)	20
Table 3-1: Initial sample quantities and particle size distribution	28
Table 3-2: Analyses conducted to characterise the raw coals	28
Table 3-3: Proximate-and ultimate analysis results of the 5 raw coals.....	30
Table 3-4: Maceral composition and reflectance of the five raw coal samples.....	33
Table 3-5: CO ₂ adsorption parameters.....	35
Table 3-6: Classification of five coals according to ISO 11760:2005	38
Table 4-1: Fischer-Assay operating specifications	42
Table 4-2: Standards used for analyses done on chars.....	45
Table 4-3: Laboratories responsible for tar analyses.....	45
Table 4-4: GC operating conditions and specifications.....	47
Table 4-5: Experimental plan for final Fischer Assay experiments	48
Table 4-6: Coal sample input	49
Table 4-7: Operating conditions input.....	49
Table 4-8: Output variables of FLASHCHAIN®	49
Table 4-9: Inputs and outputs of statistical regression.....	51
Table 5-1: Pyrolysis product yields of five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C. Yields in wt% of coal (ad).....	54
Table 5-2: Proximate- and ultimate analysis of five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C	62
Table 5-3: CO ₂ adsorption results for chars formed at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C	63
Table 5-4: Elemental analysis of tar formed at 920 °C as the final pyrolysis temperature....	66
Table 5-5: Molecular weight estimates from SEC data for tars created at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C.....	68
Table 5-6: Summary of GC-MS results of five coals	69
Table 5-7: Simdis results of tars formed at final pyrolysis product temperatures of 520 °C, 720 °C and 920 °C.....	71

Table 5-8: Mass balance on elemental carbon, hydrogen, oxygen, nitrogen and sulphur. Done on pyrolysis products at 920 °C.....	73
Table 5-9: Statistical correlation coefficients (R^2) for pyrolysis product yields.....	80
Table 5-10: Statistical regression parameters (R^2) for tar composition	81
Table 5-11: Statistical regression parameters (R^2) for gas composition.....	83
Table B-1: Full XRF analysis.....	109
Table B-2: Error calculations of repeatability done on coal D	109
Table B-3: Errors calculated (%) for gas compositions	110
Table B-4: Statistical report on repeatability done on determinations of elemental CHSNO of tar	111

Table of abbreviations

FBDB	Fixed bed dry bottom
TGA	Thermogravimetric analysis
FG-DVC	Functional group – depolymerisation, vapourisation, cross-linking
CPD	Chemical percolation devolatilisation
AFT	Ash fusion temperatures
XRD	X-ray diffraction
XRF	C-ray fluorescence
DRFIT	Diffuse reflectance Fourier transform spectroscopy
BET	Brunauer-Emmet-Teller

Chapter 1 - Introduction

1.1 Background and motivation

Coal is responsible for providing 30% of the world's energy needs and contributes to 40% and 70% of the world's electricity and steel production, respectively. Some of the top 10 coal producers relevant to this study include China, USA, India, South Africa and Germany, contributing to 71% of the total coal production in 2013 (WCA, 2014). A rapid increase in energy demand, stable coal prices and the need for countries to rely less on oil and/or gas because of varying and high prices make the need for coal as a chemical feedstock stronger (IEA, 2014). Coal liquefaction (the conversion of coal to liquid fuels) has been used in South Africa since 1955 for the production of coal-derived fuels, and supplied 30% of South Africa's gasoline and diesel products (WCI, 2009). Indirect liquefaction processes are grossly dependent on the gasification of coal (Hook & Aleklett, 2010; DTI, 1999), and the well-known Fisher-Tropsch (FT) process utilises the syngas (H_2 and CO) produced by gasification to form a coal-derived liquid product (Mondal *et al.*, 2011).

Coal pyrolysis is an important sub-process that occurs during coal conversion processes, not only for the application in the petrochemical feedstock industry, but also as the first step in combustion and gasification processes (Casal *et al.*, 2008; IEA, 2014; Schobert & Song, 2002). In-depth studies have therefore been done on the effect of pyrolysis conditions on pyrolysis products (Domínguez *et al.*, 1996; Juntgen, 1984; Khan, 1989; Larsen, 1988). An extensive study and critical review on coal pyrolysis experiments and product formation for heated grid experiments, entrained flow experiments, TGA (thermogravimetric analysis) and other slow heating experiments, fluidised beds, etc. have been reported by Solomon *et al.* (1992). A large number of products are formed during pyrolysis due to the intricate structure of coal and by the several chemical reactions that may occur (Porada, 2004; Casal *et al.*, 2008). Benzene, toluene, ethylbenzene, xylene and naphthalene (BTEXN) are devolatilisation products in either the gas or liquid phase and are used in industry for the production of synthetic fibres and plastic products (Li *et al.*, 2014; Schobert & Song, 2002).

The abovementioned pyrolysis products are largely determined by the coal rank, coal type and inorganic matter present in the coal (Xu & Tomita, 1987; Solomon *et al.*, 1993; Liu *et al.*, 2004). A few pyrolysis models, founded using analytical methods, have been proposed based on an understanding of coal structure, which is determined by the type of coal. These models include FG-DVC, FLASHCHAIN[®] and CPD, compiled by Solomon and co-workers (Solomon *et al.*, 1990b), Niksa and co-workers (Niksa & Kerstein, 1991) and the Grant- Fletcher group and co-workers (Fletcher *et al.*, 1992) respectively. With the knowledge of only raw coal properties, tar, char and gas yields can be estimated by the utilisation of these models (Li,

2004:205-210). Zhao *et al.* (1994) used and extended the FG-DVC model and validated the model for selected coals based on the elemental composition, and also reported that the model can be improved by implementing additional parameters such as sulphur content and/or maceral composition. Tar liquid products are also dependent on the chemical characteristics of the coal (Casal *et al.*, 2008), and due to consensus regarding the effect of the volatility of tar molecules on the molecular weight distributions of tar models, progress has been made for the quantitative description of tar formation during pyrolysis. These models correlate liquid fragments and the occurrence of the plastic phase of the coal when undergoing pyrolysis (Solomon *et al.*, 1993). Although literature reporting the characterisation of tar and the composition thereof exists, (Phuphuakrat *et al.*, 2010; Slaghuis & Raijmakers, 2004), there is limited literature available on the prediction of tar composition formed during slow pyrolysis, which is applicable to technologies such as fixed-bed gasification.

1.2 Problem statement and objectives

When coal is heated slowly ($<10\text{ }^{\circ}\text{C/min}$), as in the Lurgi FBDB gasification process, products formed in the pyrolysis region of the gasifier include gas liquor, condensable tars, oils and non-condensable gases. Temperature profiles together with coal behaviour are therefore important when designing a gasification plant. Extensive research on the effect of coal type on the flash pyrolysis at high heating rates of different coals has been published, but limited research on the tar, oil and naphtha composition produced by slow heating rates exists. Slow heating rate pyrolysis predictions and a total mass balance of elements (carbon, hydrogen, nitrogen, sulphur and oxygen) of the product yields based on only raw coal information (proximate-and ultimate analysis) and with the help of existing pyrolysis models i.e. FLASHCHAIN[®] and statistical regression can possibly be helpful to easily determine which coals are more amenable to chemicals and gas production.

The aim of this study is therefore to investigate temperature and coal rank effects and to ultimately predict the char, tar, water and gas yields as well as the tar composition (naphtha, oils and tars) when heated at slow heating rates ($<10^{\circ}\text{C/min}$) for coals of different rank (ranging from lignite B to bituminous C).

Objectives to be met in this study include:

- Characterisation of five coals of different rank using conventional and advanced methods;
- Investigate the effect of coal rank (ranging from lignite B to bituminous C) and final pyrolysis temperature on gas, tar, char and water yields;
- Analysing the tar liquid products using SEC, SimDis and GC/MS;
- Analysing the tar liquid products at $900\text{ }^{\circ}\text{C}$ on a CHSNO basis.

- Analysing the gas composition (H_2 , CO, CO_2 and CH_4) at three temperatures;
- Total elemental balancing of the overall process on a CHSNO basis;
- Exploring an existing analytical model, FLASHCHAIN[®], to predict liquid product yields and quality, as well as investigate statistical correlations between coal properties and pyrolysis products yields and compositions.

1.3 Research methodology

Coal feed stocks that was used in this study include coals of different rank, sourced from USA, India, China and South Africa.

Techniques used to characterise the coals include proximate analysis, ultimate analysis, calorific value, petrography (maceral analysis and reflectance of vitrinite), structural analysis (BET surface area), AFT (ash fusion temperatures), mineral XRD (x-ray powder diffraction) and ash XRF and DRIFT (diffuse reflectance Fourier transform spectroscopy).

A modified Fischer Assay setup (Roets *et al.*, 2014), with a heating rate of around 10 °C/min was used to determine the tar, char, water and gas yields at three temperatures (520 °C, 720 °C and 920 °C). The gas was collected and analysed, using GC (gas chromatograph), throughout the runs. Condensed tar liquid products were analysed using SEC (size exclusion chromatography), SimDis (simulated distillation), GC-MS (gas chromatography – mass spectrometry) and ultimate analysis. The char will be characterised by proximate analysis, ultimate analysis and BET (Brunauer-Emmet-Teller).

The FLASCHAIN model was evaluated to predict pyrolysis tar composition. If the modelling results are poor, a statistical model will be developed. This model should be capable of predicting tar and oil yields based on basic coal characteristics. Validation of the derived model is not part of the current study scope.

Expected benefits

- A detailed description of chemical, physical and structural properties, as well as a detailed description of pyrolysis products of five different coals to be used as chemical feedstock in chemicals / gas production.
- The liquid product yields and quality of five different coals will be known.
- Statistical regression, together with the implementation of the FLASHCHAIN[®] model, for yields and pyrolysis liquid products may prove to be of importance in the gasification industry for the identification of which coals are more amenable to chemical production than others.

1.4 Chapter layout

This dissertation layout includes the following 6 chapters:

- Chapter 1 provides the introduction of this dissertation by providing information regarding the background and motivation of the research before stating the aims and objectives of this study.
- A detailed literature survey on coal pyrolysis products and coal ranks is provided in Chapter 2.
- Coal selection, preparation and characterisation is reported in Chapter 3.
- Chapter 4 provides the experimental setup and equipment used, as well as experimental methods and modelling techniques.
- A detailed discussion of the results obtained from the experiments conducted using the Fischer Assay setup, as well as the modelling results is reported in Chapter 5.
- Chapter 6 provides the conclusions and recommendations based on findings of this research study.

Chapter 2 - Literature review

2.1 Introduction

This chapter provides the necessary background and review of relevant literature pertaining to coal and coal pyrolysis in order to investigate the study of pyrolysis product prediction based on coals of different rank. Coal utilisation, rank, fundamental structure and coal constituents are discussed in Section 2.2. An in-depth discussion on how coal pyrolysis works, products formed during coal pyrolysis, and current strategies used for studying coal pyrolysis is given in Section 2.3. Section 2.4 deals with coal properties and operating conditions as factors affecting the efficiency and products formed during coal pyrolysis. Lastly, the fundamentals of three devolatilisation models are discussed in Section 2.5.

2.2 Coal overview

2.2.1 Coal utilisation

Coal has uses in a wide range of industries including: electricity, steel, cement, coal combustion, coal to liquids and gasification (WCA, 2015). 76% of the total world coal use is dominated by China, USA, India, Russia and Japan (WCA, 2015). Coals of different rank mostly have different uses. Low rank coals, (47% of the world coal reserves), are largely used for power generation (lignite and sub-bituminous), cement manufacturing (sub-bituminous), and in industrial uses (sub-bituminous). Hard coal, (53% of the world coal reserves), is used for power generation, cement manufacturing and the manufacturing of iron and steel (bituminous). Anthracite, also a hard coal, is mostly used as a smokeless fuel (WCI, 2005). For efficient coal utilisation, various technologies can be integrated. The coal pyrolysis process produces solid char, gaseous and liquid products. Char can be used for power generation, gasification and in the metallurgical industry. A case study done on the Chinese market conditions show just how valuable the co-products of gasification can be. These products include clear tar and oil, naphtha, liquid ammonia and crude phenols, and can together with sulphur recovery account for as much as 25% of feedstock and utilities costs (Weiss & Schwinghammer, 2013). Recovered co-products can therefore have a significant positive impact on the plant economy.

2.2.2 Coal rank

Dead plant matter forms layers of years, which in turn form peat. Peat, exposed to high temperatures and pressures, form what is known as coal (process known as coalification). Over time the physical and chemical structure changes. Figure 2-1 shows types of coals as a function of age.

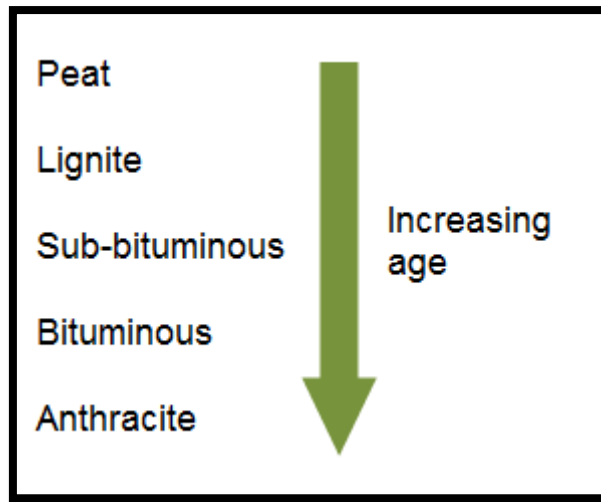


Figure 2-1: Coalification and coal types (Adapted from Bell *et al.*, (2011))

Morphologies of coal are used to describe the organic components of coal, called macerals. Three main maceral groups present in coal include (i) vitrinite (ii) liptinite; (iii) inertinite (Kandiyoti *et al.*, 2006). Table 2-1 shows the three main maceral groups and how they are derived from plant material.

Table 2-1: Coal macerals (Adapted from ASTM D121-05 and ASTM D 2799-13)

Maceral group	Maceral	Origin
Vitrinite/Huminite	Huminite	Woody tissue of plants (cellulose, lignin). Precursor of vitrinite
	Vitrinite	Woody tissue of plants (cellulose, lignin)
Liptinite	Alginite	Botryococcus algae
	Cutinite	Waxy coating (cuticle) of leaves, roots and stems
	Resinite	Plant resins
	Sporinite	Spores and pollen grains
Intertinite	Fusinite	Some structures of plant cell wall still visible
	Inertodentrinite	Fragments incorporated within other macerals
	Macranite	No plant cell wall structure, larger than 10 μm
	Micranite	No plant cell wall structure, less than 10 μm , and typically 1 to 5 μm
	Funginite	Fungi
	Secretinite	No obvious plant structure, sometimes containing fractures, slits or notch.
	Semifusinite	Like fusinite, but with less distinct evidence of cellular structure.

Coal rank classification

Coal rank ranges from lignite to anthracite. In Table 2-2 a summary of the classification of coal rank based on ASTM D 388-05 can be found. From the table it is evident that the rank of coal is dependent on the fixed carbon, volatile matter and calorific value of the coal (reported on a dry mineral matter free basis); these coal properties will be further discussed in Chapter 3.

Table 2-2: Classification of coals by rank (Adapted from ASTM D 388)

Rank	Fixed carbon limits (d.m.m.f.), %		Volatile matter limits (d.m.m.f.), %		Gross calorific value limits (m.m.f.), MJ/kg	
	Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than
Anthracitic:						
Meta-anthracite	98	-	-	2	-	-
Anthracite	92	98	2	8	-	-
Semianthracite	86	92	8	14	-	-
Bituminous:						
Low volatile bituminous coal	78	86	14	22	-	-
Medium volatile bituminous coal	69	78	22	31	-	-
High volatile A bituminous coal	-	69	31	-	32.6	-
High volatile B bituminous coal	-	-	-	-	30.2	32.6
High volatile C bituminous coal	-	-	-	-	26.7	30.2
Subbituminous:						
Subbituminous A coal	-	-	-	-	24.4	26.7
Subbituminous B coal	-	-	-	-	22.1	24.4
Subbituminous C coal	-	-	-	-	19.3	22.1
Lignitic:						
Lignite A	-	-	-	-	14.7	19.3
Lignite B	-	-	-	-	-	14.7

Another method for the classification of coals is stipulated in ISO 11750:2005. According to this standard coals are classified with three categories: rank, petrographic (maceral) composition and ash yield. Coals are firstly placed in a broad rank category, before being consigned into a rank sub category based on the random value of vitrinite reflectance and the bed moisture content, on an ash free basis. These categories can be seen in Table 2-3. Coals are then classified by the petrographic composition by using the vitrinite content (% by volume, mineral free) in four categories: (1) low vitrinite, (2), medium vitrinite, (3) moderately high vitrinite and (4) high vitrinite. Lastly, the ash contents (% by mass, dry basis) are used to classify the coals into five categories: (1) very low ash (<5), (2) low ash (≥ 5 and <10), (3) medium ash (≥ 10 and <20), (4) moderately high ash (≥ 20 and < 30) and (5) high ash (≥ 30 and < 50).

Table 2-3: Rank classification of coals according to ISO 11760:2005

Rank primary category	Rank sub category
Low rank (lignite and sub-bituminous coals)	Low rank C (lignite C)
	Low rank B (lignite B)
	Low rank A (Subbituminous)
Medium rank (Bituminous coals)	Medium rank D (Bituminous D)
	Medium rank C (Bituminous C)
	Medium rank B (Bituminous B)
	Medium rank A (Bituminous A)
High rank coals (Anthracites)	High rank C (Anthracite C)
	High rank B (Anthracite B)
	High rank A (Anthracite A)

Coal classification of coals from different origins of the world

The most abundant coals in the world include bituminous and sub-bituminous coals. In the USA, lignites are abundant with anthracites present in north-eastern Pennsylvania, while only a small amount of anthracites are available in the world (Bell *et al.*, 2011). 90% of China's coal fields can be found in the northern regions, (north of Kunlun Mountain-Qinling-Dabieshan line). China also has a wide range of coal rank, (lignite, sub-bituminous, bituminous and anthracite), with sub-bituminous coal accounting for a dominant share of 46.7%. 12.7% of China's coal resources are lignites, and 27.6% of coal resources are suitable for coking. Important characteristics, affecting coal technology choices, include high ash contents, high ash fusion

temperatures (AFT), high inertinite content and low sulphur content (Wenhua, 2003). South African coals are typically high in ash content and low in sulphur content (World Energy Council, 2007). Indian coals are broadly divided into two groups: Gondwana and Tertiary. The Gondwana type comprises of 90% of India's coal reserve and is predominantly high quality, old, bituminous coals (Kakkar, 2014). The younger coals are the Tertiary coals and include sub-bituminous and lignite coal types (Kakkar, 2014). High ash contents, usually between 20% and 30% by weight are common for Indian coals, and can have ash content of more than 40% (Jayanti *et al.*, 2007). A better understanding of the coal origins can ultimately be of assistance to explain differences in devolatilisation behaviour and the by-products formed in gasification.

2.2.3 Chemical and physical properties of coal

Coals, especially coals from different parts of the world, differ in various ways including: type of coal, grade of coal, coal rank, vitrinite reflectance, condition, tendency to gain / lose moisture and oxidation when exposed to the environment. These factors have an impact on the process of choosing a coal suitable for certain technologies (South African Coal Roadmap, 2011).

Proximate-, ultimate-, petrographic- and ash fusion temperature analyses are the most common techniques to characterise the fundamental structure of coal and to provide information regarding the maceral and elemental composition (South African Coal Roadmap, 2011; Gupta, 2007).

The standard test method of a proximate analysis provides information regarding the moisture-, ash-, volatile matter- and fixed carbon content (by difference) present in the coal (ASTM D-3172). The ultimate analysis of coal involves determining the elemental carbon, hydrogen, sulphur, nitrogen and oxygen (by difference) (ASTM D-3176).

As stated earlier the coal rank is predominantly determined by the fixed carbon content in the coal. The chemical structure and reactivity of a coal can however not only be explained by the carbon content (Gupta, 2007). The petrographic composition (macerals) gives a better indication of the conversion properties of the coal. Bituminous ranked coals have substantial differences in their maceral composition, whereas with higher ranked coals such as anthracite, it is difficult to distinguish between these macerals. The age of maturation therefore has an effect on the chemical composition of the coal (Falcon & Snyman, 1986; Van Krevelen, 1981). The physical structure of the coal is furthermore not only influenced by the quantities of C, H, N O and S in the organic component, but their spatial arrangement also influences the physical structure. The helium density or skeletal density refers to this spatial arrangement of the atoms (Gan *et al.*, 1972), and it is known that the helium density of macerals is rank dependent, increasing in the order: liptinite < vitrinite < inertinite (Falcon & Snyman, 1986).

Dry bottom fixed bed coal gasification temperature limits are determined by the melting temperature of the minerals, which is determined by the ash composition. Normally, coal gasifiers are operated at the initial deformation temperature (the point where the ash starts to sinter to clinkers) in order to achieve maximum conversion without causing slagging within the gasifier. Slagging needs to be prevented in non-slagging gasifiers, especially fluidised bed gasifiers and dry-bottom moving bed gasifiers such as the Lurgi gasifier, as these gasifiers require free-flowing ash (Bell *et al.*, 2011). The complex mixture of minerals, present in the coal determines over what temperature range the ash will start to melt. These melting temperatures are determined by ASTM D-1857-04 where a coal ash is used to determine the *initial deformation temperature* (IDT), the *softening temperature* (ST), the *hemispherical temperature* (HT) and the *fluid temperature* (FT). These temperatures are called the ash fusion temperatures.

These abovementioned methods however only give an overall description of the coal and allow classification. Advanced analytical methods have been developed in recent years in order to better describe the organic and inorganic parts of the coal as well as the molecular constituents. ^{13}C NMR (^{13}C Nuclear Magnetic Resonance), FTIR (Fourier transform infrared spectroscopy), XRD (X-ray diffraction) and XRF (X-ray Fluorescence) are some of these methods (Gupta, 2007; Smith *et al.*, 1994; Speight, 1994). Understanding the organic constituents of the coal gives more insight to the understanding of the thermal behaviour of coal.

One analytical tool that can be used to understand the organic constituents of the coal (in terms of chemical-structural features) is solid state ^{13}C Nuclear Magnetic Resonance spectroscopy (^{13}C NMR) (Suggate & Dickinson, 2004; Gupta, 2007; Smith *et al.*, 1994; Speight, 1994). Cross-polarization with magic-angle-spinning (CP-MAS), dipolar dephasing (DD), single pulse excitation (SPE), MAS with block decay (BD) and chemical shielding anisotropy (CSA) measurements are all ^{13}C NMR analyses that can be done to determine the chemical structure of coal and macerals (Smith *et al.*, 1994; Van Niekerk, 2008; Alemany *et al.*, 1984; Pugmire *et al.*, 1982). The number of aromatic and non-aromatic carbons are determined by CP-MAS, and DD measurements determine information about protonated and non-protonated carbon species. The combination of DD and CP-MAS provides twelve values relating to structural parameters of the coal. Some of these parameters include: the aromaticity of the coal, the number of bridgehead carbons, the aromatic cluster size, the number of side chains, bridges and loops and the theoretical molecular weight of a cluster (Smith *et al.*, 1994; Van Niekerk, 2008). Fourier transform infrared spectroscopy (FTIR) is another method of determining information regarding the functional groups of coal, which uses infrared radiation absorption to identify the molecules by assigning wavelengths to molecular

functionalities (C, H and O) (Smith *et al.*, 1994). X-ray diffraction (XRD) is another way of investigating the organic matrix of the coal (Gupta, 2007; Speight, 1994). Aromaticity and fraction of amorphous carbon are two structural parameters that can, as with ^{13}C NMR, be determined by XRD and these values have been shown to compare well when these techniques were compared (Lin & Guet, 1990; Van Niekerk, 2008).

2.3 Coal pyrolysis

2.3.1 Introduction to coal pyrolysis

When coal is heated in an inert atmosphere (absence of oxygen), water vapourisation and devolatilisation takes place (Bell *et al.*, 2011). This is the initial step in any coal conversion process, where up to 70% of the initial coal weight can be lost (Solomon & Hamblen, 1985). At temperatures lower than 350 °C, mostly vapourisation takes place (Ladner, 1988). When coal reaches temperatures above 320°C, bonds between carbon and oxygen/nitrogen/sulphur break, and fragmentation occurs. This process is called pyrolysis, and the four main products formed during pyrolysis are water, gas, char and tar (Fuchs & Sandhoff, 1942; Solomon & Hamblen, 1985). Fragments are caused by the breaking of labile bonds between aromatic clusters (Shadle *et al.*, 2002). These fragments are unstable, but pyrolyse further to stable compounds (Ahmad *et al.*, 2009; Bell *et al.*, 2011; Liu *et al.*, 2004). Low molecular weight components vapourise and escape the coal particle into tar and gas. The high molecular weight components do not vapourise and re-attach to the coal lattice (Fletcher *et al.*, 1992). All the components with a molecular weight higher than C_6 are defined as tars, whereas the components lighter than C_6 (of which CO , CO_2 , CH_4 , C_2H_6 and H_2O are the most significant) are defined as the gas. Both tar and gas are in the vapour phase during pyrolysis (Chen & Wen, 1979). Table 2-4 gives a summary of the products formed in certain temperature ranges during coal devolatilisation.

Table 2-4: Coal pyrolysis temperature regions (Adapted from Ladner, 1988)

Temperature range (°C)	Types of reactions	Products formed	Industrial application
< 350	Mostly evaporation	Volatile organics and water	Fundamental studies
400 – 750	Primary reactions/ degradation	Gas, tar and liquor	Smokeless fuels and chemicals
750 – 900	Secondary reactions	Gas, tar, liquor and hydrogen	Smokeless fuels and chemicals
900 - 1100	Secondary reactions	Gas, tar, liquor and hydrogen	Metallurgical coke and chemicals
> 1650	Tar cracking	Acetylene and carbon black	Electric arc pyrolysis

The mechanistic modelling of tar formation has been developed over the years and consensus has been achieved on the following steps regarding the formation of tar (Solomon *et al.*, 1993):

- Metaplast is formed by small fragments released when the weak bridges in the macromolecule break (depolymerisation).
- The metaplast formed during depolymerisation cross-links (repolymerisation) in order to prevent the vapourisation of the high molecular weight molecules.
- Lighter molecules leave the surface of the coal particle via vapourisation, convection and gas phase diffusion (Kristiansen, 1996).
- The molecules are transported internally towards the surface of the coal particle. For non-softening coals this occurs by convection and diffusion. For softening coal this occurs by liquid-phase or bubble transport (Gavalas, 1982; Smith *et al.*, 1994).

As seen in Table 2-4, primary and secondary devolatilisation reactions occur when devolatilising at high temperatures (Ladner, 1988). A schematic of a mechanistic approach can be seen in Figure 2-2. During primary devolatilisation the weak bridges break to form the fragments (as discussed above). A further consumption of hydrogen from hydroaromatic- or aliphatic functionalities will increase the hydrogen content in the aromatics. Alkyl aromatics, alkyl radicals and aromatic ring structures are subsequently formed, due to the breakage of hydrocarbon linkages (Wanzl, 1988). These molecules have a low molecular weight and vapourise to light oils and low molecular weight tars (Smith *et al.*, 1994).

It has been found that secondary tar reactions during pyrolysis result in polycyclic aromatic hydrocarbons (PAH) (Nelson *et al.*, 1988; Smith *et al.*, 1994). The aromaticity of formed tar is greatly affected by the amount of mono- and polyaromatic units, which is formed by phenols

and aliphatic molecules present in the tar. C_3 and C_4 olefins undergo Diels-Alder cyclisation reactions for the formation of cyclo-olefins (Cypres & Soudan-Moinet, 1980). Further reactions during secondary stages cause the formation of CH_4 (from methyl groups), HCN (from nitrogen species), CO (from ethers) and H_2 (ring structures condensation reactions) (Kristiansen, 1996). Operating conditions have a large effect on the tar formation in terms of molecular weight distribution. These operating conditions have an impact on the volatility of the tar, and progress has been made in recent years in the quantitative prediction of tar and char yields. In some cases, the plastic phase of the coal is linked with the liquid fragments formed in order to execute these predictions (Solomon *et al.*, 1993).

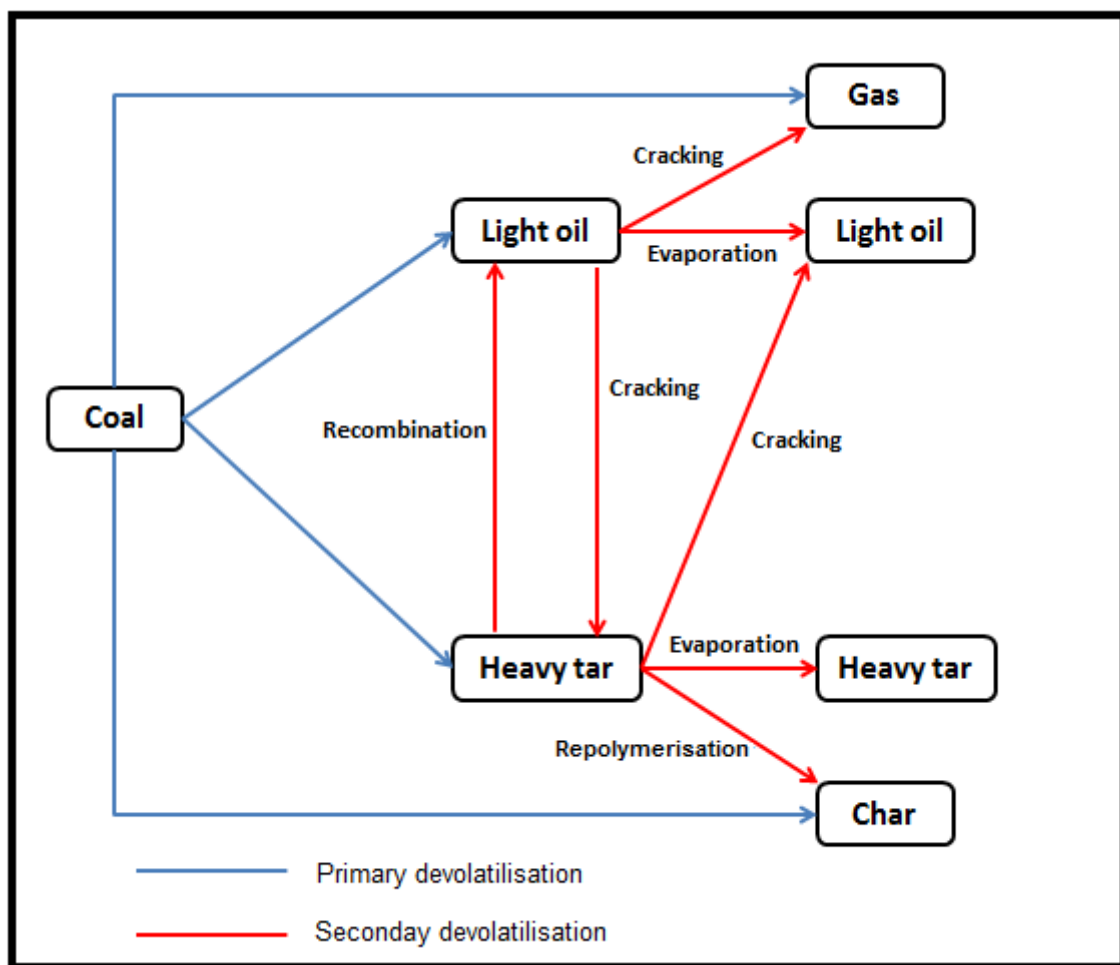


Figure 2-2: Primary and secondary coal devolatilisation (adapted from (Gönenç & Sunol, 1994))

2.3.2 Valuable products from coal pyrolysis

The main products formed and studied during coal pyrolysis are char, gas and tar/liquor. In the early work of Solomon (1977), yields of tar, water, CO_2 , CO , H_2 and hydrocarbon gases (CH_4 , C_2H_2 , C_2H_4 etc.) were considered the most important when investigating pyrolysis

behaviour. A large range of pyrolysis products can be formed, due to the intricate structure of coal. Coal pyrolysis and gasification processes are used for the development of thermally stable jet fuels, such as hydrogen based and hydrogen donor based (Schobert & Song, 2002).

Typical constituents of the light oil, recovered by steam stripping of the liquid tar product from devolatilisation, include BTX (benzene, toluene and xylene), alkanes, cycloalkanes, olefins and aromatic species (Speight, 1994). Benzol can be further produced by the fractional distillation of this oil. After a few washing stages, important BTX products, as well as naphtha, can be retrieved by distillation. Benzene, extracted from the BTX can further be converted into cumene, which can be used to produce synthetic phenol and acetone (Schobert & Song, 2002; Speight, 1994).

Valuable compounds obtainable from the tar of coal pyrolysis include many one- to four-ring aromatic and polar compounds. Some of these include phenol, naphthalene, phenanthrene, pyrene, biphenyl, cresol and pyridine (Schobert & Song, 2002; Speight, 1994). The synthesis of many compounds such as phenolic resins, adipic acid, alkyl-phenols, caprolactam, catechol and monomers (biphenol A and 2,6-xyleneol) are dependent on phenol. An application of 2,6-xyleneol is the synthesis of polyphenylene oxide (Schobert & Song, 2002). Chemicals, specialty chemicals and solvents can be produced with naphthalene (Song & Moffat, 1994). A monomer feedstock, 2,6-dialkyl substituted naphthalene, of advanced polyester materials can be produced by alkylation of naphthalene over a molecular sieve. The hydrogenation of naphthalene on the other hand produces commercial decalins which can be used as a thermally stable jet fuel (Song & Schobert, 1993; Schobert & Song, 1995).

China is now the largest coal derived chemical industry in the world. The chemical industry produces a wide range of products such as synthetic ammonia, methanol, hydrogen, coke calcium carbide and derivative products (e.g. fertilisers and soda ash) (Shaanxi Yanchang Petroleum Group, 2015). Table 2-5 shows some of China's large coal to chemical projects and includes technologies such as coal to methanol, coal to SNG (synthetic natural gas) and coal to olefins. For the coal to SNG process, fixed bed dry bottom (FBDB) pressurized gasification technology is widely applied. (Shaanxi Yanchang Petroleum Group, 2015).

Table 2-5: Coal to chemical projects in China. After Shaanxi Yanchang Petroleum Group (2015)

Project category	Description
Coal based fertiliser	73.42 million tons coal per year consumption
Coking coal	87% consumption by the steel industry (2008) 7.5% consumption by the chemical industry
Coal to methanol	31 million tons coal per year to produce 26.4 million tons methanol per year (2012)
Coal to SNG	Production capacity of 15.1 billion cubic meters per year by the four major projects.
Coal to oil	Direct and indirect coal to oil technologies to reach a potential of 20 million tons per year.

Gasification based coal conversion is an important aspect in the manufacturing of synthetic oil and gas and various other chemical products as described above (Minchener, 2011). Furthermore, for the coal to SNG process, fixed bed dry bottom (FBDB) pressurized gasification technology is widely applied in China (Shaanxi Yanchang Petroleum Group, 2015). The Ministry of Industry & Information Technology, in 2012, has also made suggestions to utilise coal to olefins in order to achieve at least 20% market penetration and to increase advanced gasification technologies for nitro-fertilisers to reach 30% (Asiachem, 2013).

2.3.3 Assessment of coal pyrolysis

The study of devolatilisation kinetics is commonly done by the use of thermogravimetric (TG) systems, and the literature contains many studies with the use of TG systems (Alonso *et al.*, 1999; Sun, 2010; Zhang, 2011). Other apparatus used to determine devolatilisation kinetics include entrained flow and fixed-bed reactors, as well as drop tube furnaces (Adesanya & Pham, 1995; Lee *et al.*, 1991; Ulloa *et al.*, 2004). The development of devolatilisation models are also commonly done with the use of drop tubes and wire-mesh reactors (Niksa, 1991b). These last mentioned types of reactors are commonly used to remove the effect of intra-particle reactions and minimises the effect of sample and reactor configuration (Kandiyoti *et al.*, 2006).

Product yield studies are not only sensitive to operating conditions, but also the design and configuration of experiments (Kandiyoti *et al.*, 2006). Systems to investigate product yields, especially tar formation and behaviour, are entrained flow/drop tube reactors and wire-mesh reactors (Kandiyoti *et al.*, 2006). Flash pyrolysis are normally performed using the drop tube reactors and can reach temperatures up to 2200 °C (Fletcher *et al.*, 1990; Kimber & Gray,

1967). A disadvantage of this method is the carry-over of solids into the quench zone (Kyotani *et al.*, 1993). Wire-mesh apparatus, where coal is heated with electrodes, can handle a large range of heating rates (1 - 20000°C/s), and example studies of pyrolysis using the wire-mesh can be found in Kandiyoti *et al.*, (2006) and Anthony *et al.*, (1974). The North-West University have also developed an alternative method to the Fischer Assay ISO 647 standard to quantitatively determine water, gas, tar and char yields during pyrolysis. This new method, referred to as the automated Fischer Assay method, was developed to overcome a few limitations, including limitations caused by thermal properties of the aluminum and the risk of operator error due to the manual manipulation of temperature control (Roets *et al.*, 2014).

2.4 Factors affecting coal pyrolysis products and efficiency

Devolatilisation efficiency and pyrolysis product formation is a function of both the parent coal properties (coal rank, mineral matter composition and catalytic species present) and the operating conditions (temperature, pressure, particle size, type of gas atmosphere and heating rate) (Solomon & Hamblen, 1985).

2.4.1 Effect of coal properties on coal pyrolysis

Coal properties, which include particle size, morphology, chemical-, petrographic- and mineral composition have a significant influence on coal conversion processes such as gasification and devolatilisation (Bailey *et al.*, 1990; Cloke & Lester, 1994; Estough & Smoot, 1996; Matthews *et al.*, 1997; Méndez *et al.*, 2003; Wang & Wen, 1972). Other properties regarding the minerals (mineral transformation) and physical structure, which determine particle density (Strezov *et al.*, 2005), also play a role in coal conversion processes (Méndez *et al.*, 2003; Shannon *et al.*, 2009).

2.4.1.1 Effect of coal rank/characteristic properties

It is known from the classification of coals by rank, ASTM D388, that high rank coals have a lower volatile matter content (Borrego *et al.*, 2000), and that devolatilisation and char conversion has been shown to be greatly affected by the maceral composition (Gupta, 2007). Coals with higher fixed carbon contents also indicate higher ranks. A decrease in coal rank will generally result in higher gas yields, and tar yields will increase to a maximum before it decreases (Fletcher *et al.*, 1992; Smith *et al.*, 1994; Solum *et al.*, 2001).

An increase in coal rank will generally cause an increase in the degree of aromatisation of tars during devolatilisation (Gupta, 2007). Coals with higher carbon contents usually have lower tar yield than lower rank coals (lignites) with lower carbon contents. Figure 2-33 shows the

rank dependence of tar formed during devolatilisation (Xu & Tomita, 1987a), and it has also been determined that the molecular weight of tars are strongly rank dependent when coal undergoes pyrolysis at slow heating rates (Solomon & Hamblen, 1985).

Other notable statements regarding the behaviour of coal during devolatilisation as a function of coal characteristics include:

- Coals with high ash contents will decrease the efficiency of combustion, gasification and direct liquefaction (Sun, 2010).
- Endothermic phase transformations of the present minerals are influenced by the fuel ratio and calorific values of the coal (Everson *et al.*, 2015).
- The decomposition and melting behaviour determines the structural changes a certain coal will undergo when heated (Gupta, 2007).
- The main volatile pyrolysis product of bituminous coals is tar (Gönenç & Sunol, 1994).
- Caking, the process of coals, when heated, stick together due to partial melting occurs with some coals, especially bituminous coals. In the gasification application, especially fluidised bed gasification, non-caking coals are preferred (Bell *et al.*, 2011).

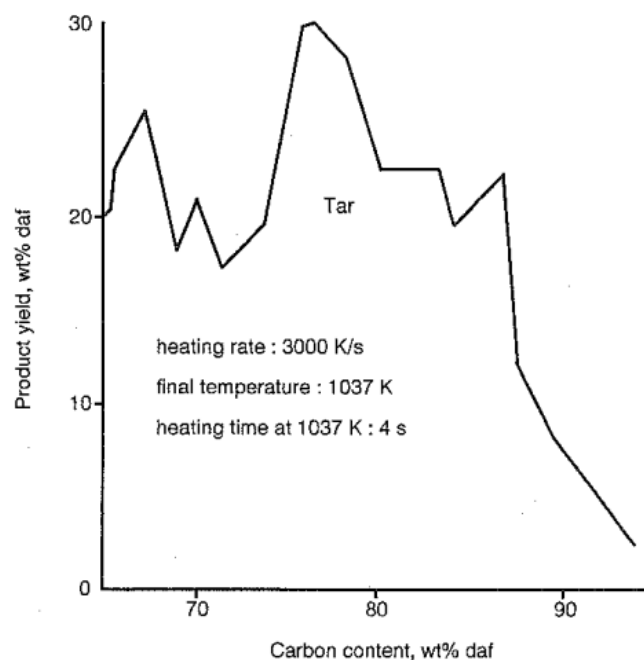


Figure 2-3: Effect of coal rank on tar yield (taken from Xu & Tomita, (1987a))

2.4.1.2 Effect of mineral matter

Inorganic components in coal have been shown to have a significant effect on coal reactivity (Jenkins *et al.*, 1973; Miura *et al.*, 1989; Mühlen *et al.*, 1993; Nishiyama, 1991). Differences in the maceral composition, thermoplastic properties and char morphology limit the study of the

effect of mineral matter on coal pyrolysis. It has been reported that mineral matter has an effect on many variables related to pyrolysis/gasification :

- final product distribution (Ahmad *et al.*, 2009; Liu *et al.*, 2004; Slaghuis *et al.*, 1991);
- coal reactivity (Miura *et al.*, 1989; Ye *et al.*, 1998);
- technological problems such as fouling and slagging (Pusz *et al.*, 1997).

By demineralising the coal with acid the individual effects of minerals can be studied (Hashimoto *et al.*, 1986; Kyotani *et al.*, 1993; Miura *et al.*, 1989).

Mineral matter decomposition reactions can be seen in Table 2-6, which can contribute significantly to CO₂ and H₂O released during pyrolysis.

Table 2-6: Mineral matter decomposition reactions (Gräbner & Lester, 2016)

Species	Decomposition reaction			Mass loss	Temperature
Muscovite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	$\rightarrow$	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 + 2H_2O$	-4.5%	450-700°C
Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	$\rightarrow$	$Al_2O_3 \cdot 2SiO_2 + 2H_2O$	-14.0%	400-600°C
Quartz	SiO_2	$\rightarrow$	SiO_2	0.0%	none
Hematite	Fe_2O_3	$\rightarrow$	Fe_2O_3	0.0%	none
Pyrite	$2FeS_2 + 7.5O_2$	$\rightarrow$	$Fe_2O_3 + 4SO_3$	-33.5%*	oxidation
Calcite	$CaCO_3$	$\rightarrow$	$CaO + CO_2$	-44.0%	920°C**
Siderite	$2FeCO_3 + 0.5O_2$	$\rightarrow$	$Fe_2O_3 + 2CO_2$	-31.1%	580°C + oxidation
Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	$\rightarrow$	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	0.0%	none
Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	$\rightarrow$	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	0.0%	none
Dolomite	$CaCO_3 \cdot MgCO_3$	$\rightarrow$	$CaO \cdot MgO + 2CO_2$	-47.7%	780 and 920°C
Ankerite	$2CaCO_3 \cdot FeCO_3 + 0.5O_2$	$\rightarrow$	$2CaO + Fe_2O_3 + 4CO_2$	-37.1%	700°C

* Without SO₃ capture in ash (otherwise +37.1%), **does not apply to proximate analysis conditions

2.4.2 Effect of operating conditions on coal pyrolysis

In addition to coal properties, operating conditions also have an impact on the yield and quality of products formed during coal pyrolysis, of which the most significant are: (i) temperature; (ii) heating rate and holding time; (iii) particle size, and (iv) pressure (Alonso *et al.*, 1999; Kandiyoti

et al., 2006; Kristiansen, 1996; Ladner, 1988; Solomon & Hamblen, 1985). The effect of these operating conditions on the yield and quality of pyrolysis products will be further discussed.

2.4.2.1 Operating temperature

The devolatilisation behaviour has been shown to be most affected by the operating temperature (Hu *et al.*, 2004), where an increase in operating temperature will result in an increase in volatile yield; but a large range of product compositions can occur (Hu *et al.*, 2004; Kandiyoti *et al.*, 2006; Kristiansen, 1996; Ladner, 1988). Coal properties are firstly greatly affected by the pyrolysis temperature, giving an indication of the severity of the pyrolysis process (Haykiri-Acma *et al.*, 2012). The reactivity of the chars formed during the pyrolysis step has been found to decrease with an increase in final pyrolysis temperature (Haykiri-Acma *et al.*, 2012). For heating rates of 5-10 °C/min, certain maximum tar and liquor values are observed in a range of 525-575°C (Öztaş & Yürüm, 2000; Yaw *et al.*, 1980). Temperatures above this range yields a decrease in tar and liquor yield, while gaseous species formation is starting to be favoured more (Speight, 1994). This phenomena, and the influence on the quality and quantity of products, can be observed in a review study done by Ladner (1988), comparing high temperature (900-1000°C) and low temperature (400-750°C) pyrolysis. Liquor, light oils, and tar yields were found to be lower for the high temperature pyrolysis, whereas gas and char yields were higher. The compositional differences can be seen in Table 2-7. At temperatures above 800 °C, the most predominant tars formed are PAH with up to five rings (Nelson *et al.*, 1988). This can also be observed (in Table 2-7) by the higher aromatic/phenol ratio observed at high temperature pyrolysis.

Table 2-7: Quality of pyrolysis products (Adapted from Ladner, 1988)

Low temperature pyrolysis (400-750°C)					
Gas	wt %	Light oil	wt %	Tar	wt %
H ₂	10	Paraffins	46	BTX	1.5
Hydrocarbons	65	Olefins	16	Phenol	1.5
CO	5	Cyclo-paraffins	8	Cresols	4.5
CO ₂	9	Cyclo-olefins	9	Xylenols	7.0
Other	11	Aromatics	16	Other phenols	16.0
		Other	5	Tar bases	2.0
				Naphthalene	3.5
				Other aromatics	38.0
				Pitch	26.0
High temperature pyrolysis (900-1100°C)					
Gas	wt %	Light oil	wt %	Tar	wt %
H ₂	50	BTX	89	BTX	0.6
Hydrocarbons	34	Alicyclics	5	Phenols and cresols	1.6
CO	8	Aliphatics	6	Xylenols	0.5
CO ₂	3			Other phenols	1.0
Other	5			Naphthalene	8.9
				Anthracene	1.0
				Other aromatics	24.6
				Tar bases	1.8
				Pitch	60.0

From Table 2-7 it can be seen that the lower molecular weight species are formed during high temperature pyrolysis and can be attributed to the secondary gas-phase degradation reactions taking place at higher temperatures. The tar is also more aromatic in nature, with unsubstituted polycyclic aromatic hydrocarbons present at the higher pyrolysis temperatures. (Nelson *et al.*, 1988). Xu & Tomita (1987b) also did a study on 7 various coals in order to determine the effect of pyrolysis on the yields of tar liquids, hydrocarbon gases and inorganic gases. A summary of their findings can be seen in Figure 2-4.

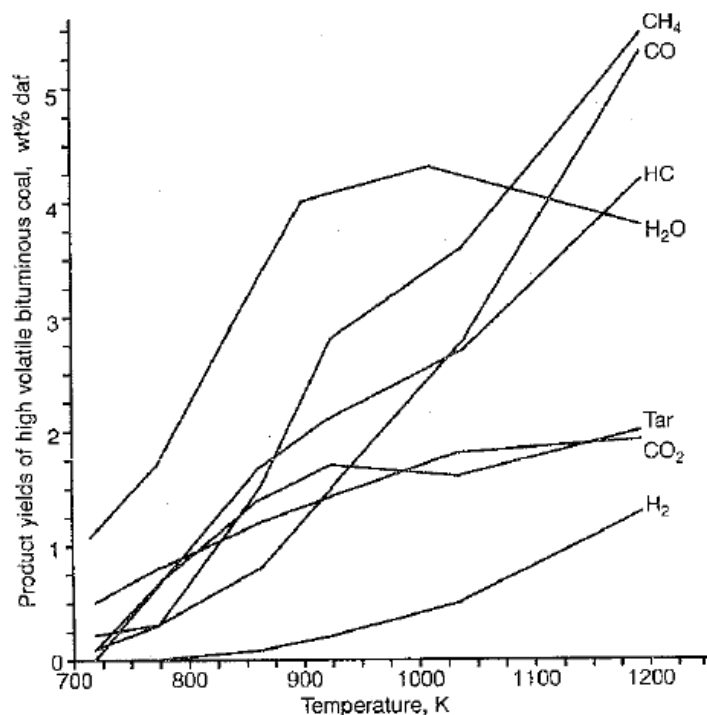


Figure 2-4: Effect of pyrolysis temperature on pyrolysis products (taken from Xu & Tomita, (1987b))

2.4.2.2 Heating rate and holding time

A decrease in heating rate will result in a decrease in tar yield (Shadle *et al.*, 2002). It has also been shown that a maximum tar yield for fast heating rates ($\sim 1000^{\circ}\text{C}/\text{min}$) is achieved at higher temperatures ($600\text{--}700^{\circ}\text{C}$), where maximum tar yields obtained by slow pyrolysis ($\sim 1^{\circ}\text{C}/\text{min}$) is achieved at lower temperatures ($550\text{--}600^{\circ}\text{C}$). At high heating rates, however, secondary reactions do not play a big role and consequently the tar quality will decrease (explained by H/C ratio), although higher yields are achieved (Kahn, 1989). Volatile yields are around 6-8% higher for fast heating rates than for lower heating rates (Gibbens-Matham & Kandiyoti, 1988; Kandiyoti *et al.*, 2006) and is directly related to the increase in tar yield (Kandiyoti *et al.*, 2006; Ladner, 1988). There are two possible explanations for this phenomenon (Kandiyoti *et al.*, 2006): (i) tar is forced out because of pressure building up internally; (ii) re-polymerisation reactions are limited due to the breaking of covalent bonds together with hydrogen release.

2.4.2.3 Particle size

Thermal conductivity plays a big role in the devolatilisation process. It is therefore definite that particle size will have an effect on the amount of volatiles produced during pyrolysis (Kandiyoti *et al.*, 2006). Lower volatile yields, as well as a decrease in weight loss, will therefore be achieved for larger coal particles (Anthony *et al.*, 1974; Franklin, 1980).

2.4.2.4 Pressure

An increase in operating pressure will result in a decrease in tar yield. This phenomenon is due to the fact that when operating at atmospheric pressure, that the tar will re-condense (Shadle *et al.*, 2002; Kandiyoti *et al.*, 2006). Pressures higher than atmospheric pressure will work against tar formation, decreasing flow and diffusion of volatiles to the surface, and to the atmosphere (Anthony *et al.*, 1974; Franklin, 1980; Kandiyoti *et al.*, 2006). The gas composition is also influenced by pressure. It has been found in a study that an increase in pressure increased the yields of CH₄ and C₂H₆, whereas no significant influences was observed for C₂H₄ (Arendt & Van Heek, 1981).

2.5 Coal devolatilisation models

Substantially different characteristics are found for coals of different origins and these variations have an impact on the design of coal gasification and combustion systems and operating conditions (Zhao *et al.*, 1994). It is therefore of great importance to characterise coals well before the utilisation thereof. This characterisation using standard and advanced methods can however be expensive and makes the prediction of coal devolatilisation behaviour an important method of application (Zhao *et al.*, 1994). Early devolatilisation models were simple, assuming single stage reactions, and later two-step models incorporating bridge-scission and cross-linking were developed. These models did however not rely on the chemical structure of the coal and results were of an empirical nature (Smith *et al.*, 1994). More complex coal devolatilisation models have recently been developed with the main focus on the prediction of coal thermal decomposition under certain operating conditions. These models include FG-DVC, FLASHCHAIN[®] and CPD, compiled by Solomon and co-workers (Solomon *et al.*, 1990b), Niksa and co-workers (Niksa & Kerstein, 1991a) and the Grant-Fletcher group and co-workers (Fletcher *et al.*, 1992).

2.5.1 The FG-DVC model

The main focus of the FG-DVC (functional group-depolymerization, vapourisation, cross-linking) model is the prediction of coal thermal decomposition into light gases, char and tar (Solomon *et al.*, 1988). Property changes such as coal fluidity and swelling, during pyrolysis can also be predicted with this model. A brief description of this model, summarizing detailed discussions in literature follows: (Solomon *et al.*, 1988; Solomon *et al.*, 1990; Solomon *et al.*, 1993; Zhao *et al.*, 1994).

An aromatic matrix, side chain components and loose fragments all form part of the intricate structure of coal, and the thermal decomposition thereof are led by many competitive

processes. Two sub-models are used by the FG-DVC to model these mentioned processes: The simulation of the thermal evolution of functional groups with the FG model; and the prediction of depolymerization, vapourisation and cross-linking processes with the DVC model. A network of nodes, representing polymer clusters, and connections between the nodes is used to model the thermal evolution of the coal polymer matrix. Two types of connections are defined: bonds and crosslinks. The FG-DVC model is particularly applicable to devolatilisation, as competition occurs between bond breaking and cross-linking when at elevated temperatures. Percolation theory, together with these two competing processes, is then used to determine the properties of the network, of which the molecular weight distribution of the clusters is the most important property of the network. Char will consist of the heavy molecules in the condensed phase, while the tar is formed by the evaporation of the light molecules. Fletcher *et al.*, (1992) proposed a mechanism which is used for the vapourisation calculations, focusing on the pressure variation of tar yield.

The model was validated for a large range of pressures, temperatures and heating rates by using the general input parameters and elemental compositions (C, H, N, O, S) of eight Argonne Premium coals and some PSOC DOE Sample Bank coals. Initially North American coals were used to validate this model; where after more international coals were used (Solomon *et al.*, 1993; Serio *et al.*, 1999).

Input parameters for FG-DVC includes advanced techniques such as TG-FTIR, NMR, solvent swelling and extraction, FIMS (field ionisation mass spectrometry), fluidity etc., but for many coals these data are not available (Zhao *et al.*, 1994). A technique based on coal rank was developed by (Zhao *et al.*, 1994) where these input parameters of unknown coals are interpolated. Well defined coals are used to form a triangular mesh in the van Krevelen diagram (H/C vs. O/C coalification diagram) (Genetti, 1999). If the unknown coal falls within this triangle formed by three known coals, the abovementioned input parameters can be interpolated by only using the elemental composition of the unknown coal (Zhao *et al.*, 1994; Serio *et al.*, 1999). This method was also validated by Zhao *et al.*, (1994) by devolatilising 27 coals at wide operating ranges (pressure and heating rates).

2.5.2 The FLASHCHAIN[®] model

Chain fragments, consisting of aromatic nuclei, labile bridges, char links and peripheral groups, constructed by monomers ranging to infinite chains are used to model coal. Aromatic nuclei is a unit that has the same characteristics as aromatic clusters (seen on ¹³C-NMR analyses), and all the nitrogen in the coal is seen as being present in the aromatic nuclei. Labile bridges and char links are types of links that can connect these nuclei. Aliphatic, alicyclic

and heteroatomic functionalities are represented by the labile bridges and all the oxygen, sulphur and aliphatic carbon are found in these bridges. All the aromatic functionalities are present in the char links, and not the bridges. A part left from a broken bond is called a peripheral group. FLASHCHAIN® then uses proportions of links and broken bridges to determine the initial configuration of the coal.

Devolatilisation of coal is explained by the FLASHCHAIN® model by the following: Chemical constitution, a 4-step reaction mechanism, chain statistics, and a flash distillation analogy. The main focus of this theory is the determination of various coals' devolatilisation behaviour, which is done with the knowledge of three element constituents in the coal: aliphatic, heteroatomic and aromatic. Predictions are therefore mostly focused on distinguishing between these constituents of various coals. In a later study Niksa (1994a) has shown that for accurate devolatilisation predictions of ultimate tar and total yields (char, tar, gas and water), that the only known characteristic needed to be known is the ultimate analysis.

With the FLASHCHAIN® coal devolatilisation model Niksa & Kerstein, (1991) predicted tar and total volatile yield when coal undergoes pyrolysis. The constitutions of the coal is determined by elemental analysis, carbon aromaticities (f'_a), hydrogen aromaticities (^Hf_a), number of aromatic carbons per cluster, pyridine's solvent extract yield (T_{PYR}) and the average molecular weight of the non-condensable gases. The carbon and hydrogen aromaticities used in FLASHCHAIN® is correlated by the following equations (Equation 1 and 2) produced by Gerstein & Ryan (1982):

$$f'_a = 0.0159(\%C, daf) - 0.564 \quad (\text{Eq. 2-1})$$

$$^Hf_a = 1.1 \times (\%C, daf) - 0.554 \quad (\text{Eq. 2-2})$$

These predictions can be done only based on the ultimate analysis of the coal (Niksa, 1991b). FLASHCHAIN®'s applicability comes from the fact that it can predict devolatilisation behaviour for a wide range of coals (Niksa, 1994a; Niksa, 1994b).

2.5.3 The CPD model

The CPD (chemical percolation devolatilisation) model sees coal as a macromolecular network consisting of various sized aromatic clusters, where nitrogen and oxygen are attached to heteroatomic systems (Fletcher *et al.*, 1990; Fletcher *et al.*, 1992). Side chains, including aliphatic ($-CH_n$) and carbonyl groups, are attached to these aromatic clusters (Fletcher *et al.*, 1992). Connections between these clusters are called bridges, which are aliphatic of nature, and can have different bond strengths (Fletcher *et al.*, 1990). A two-dimensional Bethe lattice is used to describe these connections and the breaking process of the bridges are

mathematically described. These connections can break during pyrolysis and are then called labile bonds; bridges that are stable during pyrolysis are called charred bridges (Fletcher *et al.*, 1992). A representation of the clusters, bridges and side chains can be seen in Figure 2-5.

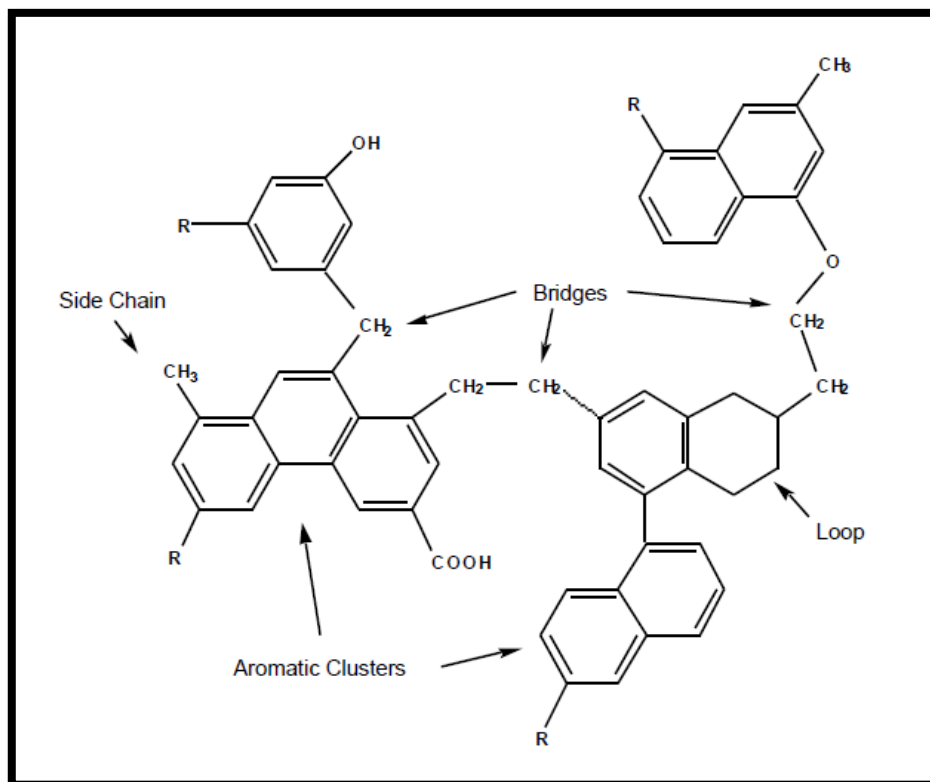


Figure 2-5: Typical chemical structures (as determined by ^{13}C -NMR) used by the CPD for the description of the coal structure. Taken from Fletcher *et al.* (1992)

This model uses the chemical structure of the coal (clusters, bridges and side chains) to explain the pyrolysis process, producing tar, char and light gases. The model, however, focuses on the total yield and the tar distribution of tar species. Five key features are used in the working of this model: (i) ^{13}C -NMR analyses is used to describe the parent coal's chemical structure, (ii) the use of a reaction mechanism based on the bridges; (iii) determination of tar formation based on the relationship between detached fragments and bridge breaks, which form tars; (iv) the use of vapour-liquid equilibrium correlations on coal liquids in order to predict the yields and molecular weight distribution of tars; (v) the use of a mechanism to describe the reattachment of high molecular weight tars to the char.

Input parameters to the CPD model include parameters (coal-dependent chemical structure) obtained from ^{13}C -NMR analysis: M_{cl} (average molecular weight per aromatic cluster), M_b (average side chain molecular weight), $\sigma + I$ (average number of attachments per cluster) and

p_0 (fraction of intact bridges). The use of NMR directly as an input makes this model more mechanistic of nature, as these parameters are not used as empirical fitting coefficients as in the other models (Fletcher *et al.*, 1992). CPD model predictions include tar and total volatile yields, and have been shown to compare well with existing experimental data by Fletcher *et al.* (1992). These predictions are as a result of the above discussion and given as a function of coal type, temperature, heating rate and pressure (Fletcher *et al.*, 1992). Predicted tar molecular weights have been compared to the results of SEC (size exclusion chromatography) and FIMS, and have fitted well (Fletcher *et al.*, 1992). In more recent years, this model was improved to predict light gas compositions by the use of a kinetic model, describing the release of these gases from their functional groups in the coal.

Selection of model

Each of these models require specific software developed in order to process data. The selection of model to be used in this study is based on the fact that the software for FLASHCHAIN[®] is available to the researchers at North-West University.

Chapter 3 - Coal characterisation

3.1 Introduction

This chapter provides the coal characterisation results obtained for the 5 coals studied. Characterisation was conducted using both conventional as well as some advanced analytical techniques. Section 3.2 describes the origin of the coal samples along with the sampling and coal preparation methods followed prior to analysis. The analytical techniques and the results thereof are discussed in detail in Section 3.3.

3.2 Coal origin and sampling

3.2.1 Origin of coals

A wide range of coal samples were chosen in order to represent a suite of coals typically considered for use in fixed bed dry bottom gasification. The following basis was therefore used for the coal selection:

- 1) The potential use of the coal in commercial fixed bed dry bottom gasifiers.
- 2) The coals should be of different rank ranging from lignite to bituminous.
- 3) The coals should be from different parts of the world.

Five coals (labelled A-E) were selected as a result of the criteria and have different countries of origin, including USA, China, India and South Africa. These were labelled:

Coal A;

Coal B;

Coal C - blend;

Coal D and

Coal E.

3.2.2 Coal Preparation

Table 3-1 shows the mass of the coal sample received as well as the particle size distribution of each sample. It can be observed that 4 of the 5 samples are relatively coarse, with the exception of coal D which is a filter cake sample obtained from an industrial process. The reduction in particle size of the coarse samples (coal A, B, C and E) was achieved by employing a jaw crusher (Samuel Osborne (SA) LTD, Model: 66YROLL) as the primary crusher to crush the entire sample to a particle size of <10mm. Secondary crushing was achieved using a hammer mill (Usborn Coalequip Engineering (PTY) LTD; Speed: 425 rpm;

Size: 4x6 macro crusher; Model no.: 46-126), before a rotary mill (Wenman Williams & Co. (PTY) LTD. 503A) was used to crush all of the coals (samples A-E) to the desired particle size for Fischer Assay experimentation as stipulated by ISO 647, i.e. 90 wt% of the coal sample should pass a 1mm sieve and not more than 50 wt% should pass a 0.5mm sieve. The crushed samples were sieved and homogenised using a riffle splitter and stored in a sealed container under an inert atmosphere in a fridge.

Table 3-1: Initial sample quantities and particle size distribution

	Coal A	Coal B	Coal C	Coal D	Coal E
	Sample mass, kg				
	6.01	4.07	3.86	4.17	6.77
Particle size (mm)	Fraction, % (retained)				
+19	0	9	9	-	27
+13.2-19	6	36	31	-	12
+6.7-13.2	35	28	31	-	17
+4.74-6.7	19	7	8	-	8
+4.74-2.36	20	9	9	-	13
-2.36	20	10	13	100	24

3.3 Analyses and results

Coal characterisation of the 5 coals studied included chemical, mineralogical, petrographic and structural analyses. Table 3-2 shows the details of the analyses conducted, the standard methods applied, as well as the laboratories used for the characterization.

Table 3-2: Analyses conducted to characterise the raw coals

Analysis	Details	Standard	Laboratory
Chemical and mineralogical	Proximate analysis		
	Inherent moisture content, %	ISO 11722, (1999)	Bureau Veritas
	Volatile matter content, %	ISO 562, (2010)	
	Ash content, %	ISO 1171, (2010)	
	Fixed carbon content, %	By difference	
	Ultimate analysis		
	Carbon, %	ISO 29541, (2010) (Not SANAS Accredited)	Bureau Veritas
	Hydrogen, %		
	Nitrogen, %		
	Oxygen, %		
Sulphur, %	ISO 19579, (2006)		

Petrographic	Calorific value	ISO 1928, (2009)	North-West University
	Ash XRF	ASTM D4326 (1997)	
	Mineral XRD	Rietveld method	Bureau Veritas
	Maceral composition	ISO 7404 Part 3, (1994)	
	Vitrinite reflectance	ISO 7404 Part 5, (1994)	
Structural	BET adsorption DRIFT	See Section 3.3.3	North-West University

3.3.1 Chemical and mineralogical analyses

Conventional coal analyses

The proximate analysis results of the five raw coals can be seen in Table 3-3. It can be seen that there is a significant difference between these coals' characteristics. Coal A has a high inherent moisture content (30%) and low ash content (6.6%) when compared to the other coals. The volatile matter contents, on an air dried basis, of all coals fall in a narrow region of 24-30%. From the dry, ash free reported basis (daf), it can be seen that coal A and B have almost the same volatile matter content (c.a. 46%), while coals C, D and E have lower volatile matter contents ranging between 35.4 and 37.3%. Coal C, D and E are therefore of a higher rank than coal A and B (ASTM, 1998). Table 3-3 also shows the ultimate analysis results of the five raw coals. It is noted that coal A has ± 10 wt % (daf) of carbon less than coal B, which also indicates that coal A is of a lower rank than that of the other coals; and has around the same low carbon value as some low-rank South Australian coals (Ye *et al.*, 1998). This coal also has the highest oxygen content value of all the coals. Finally, it is noted that all coals contain low sulphur contents, with coal D containing the highest value (1.1%).

Ash elemental analysis and crystalline mineral matter analyses (XRF and XRD)

All samples were characterised by XRF (X-ray fluorescence) and XRD (mineral X-ray diffraction) in order to determine the ash composition and crystalline minerals present in the coal. A better understanding of this is important as it was shown by Roets (2014) that mineral matter has catalytic effects during slow pyrolysis. The major components of the XRF analyses were performed in accordance with ASTM D4326 (1997) and results are reported on a loss of ignition (L.O.I.) free basis in Table 3-4. The full analysis can be found in Appendix B-1. A large variation in the ash composition is firstly observed and is expected due to the wide range of countries of origin of these samples. Acidic components, which include Al_2O_3 and SiO_2 , ranges between 21 and 76% and base/alkali components, which include Na_2O , MgO , CaO , K_2O and

Fe₂O₃, range between 9 and 56%. The effects of the ratio between the acidic and base components on the ash fusion temperature will be discussed later. It is further observed that coal B and coal D ash contains mostly Al₂O₃ and SiO₂. This corresponds to the high values of kaolinite (27.0% and 22.8% respectively for coal B and coal D) and quartz (15.7% and 7.9% respectively for coal B and coal D) observed in the mineral XRD results (Table 3-5). These two coals also show the lowest amorphous carbon content (55 and 65% respectively for coal B and coal D) compared to the other coals (100, 86 and 80% respectively for coal A, coal C and coal E).

Table 3-3: Proximate-and ultimate analysis results of the 5 raw coals

Sample identification	Coal A	Coal B	Coal C	Coal D	Coal E
Proximate analysis (air dried)					
% Inherent moisture content	30.1	8.5	12.8	5.2	7.3
% Ash content	6.6	26.0	10.7	27.9	15.2
% Volatile matter content	29.4	30.0	28.5	24.5	27.5
% Fixed carbon (<i>by difference</i>)	33.9	35.5	48.0	42.4	50.1
% Total sulphur	0.58	0.61	0.33	1.09	0.75
Gross Calorific value (MJ/kg)	17.13	20.51	22.25	19.98	23.71
Proximate analysis (dry, ash free)					
% Volatile matter	46.6	45.8	37.3	36.6	35.4
% Fixed carbon	53.6	54.3	62.7	63.4	64.6
Ultimate analyses (dry, ash free)					
% Carbon content	66.55	74.18	74.06	75.40	76.80
% Hydrogen content	4.79	5.10	3.92	4.13	4.33
% Nitrogen content	1.04	1.80	0.83	1.96	1.29
% Sulphur content	0.92	0.93	0.43	1.63	0.97
% Oxygen content (difference)	26.72	18.01	20.77	16.91	16.62

High values of CaO and Fe₂O₃ are observed for coal A and coal C when compared to the other coals. These two coals consist of approximately the same ash components with the SO₃ showing a large difference. The resulting observation of the XRF and XRD results are that the ash compositions differ by large margins, resulting in coals that can have different pyrolysis behaviours in terms of mineral effects.

Table 3-4: Ash XRF of raw coal samples, wt%, inorganic oxide percentages

Compound Name	Coal A	Coal B	Coal C	Coal D	Coal E
Na ₂ O	5.5	0.1	0.7	0.5	0.1
MgO	3.3	0.5	3.3	1.7	0.2
Al ₂ O ₃	8.4	25.3	12.7	26.5	28.0
SiO ₂	12.6	50.9	26.3	40.1	26.2
P ₂ O ₅	0.1	1.3	0.4	1.0	0.5
SO ₃	19.5	8.3	4.9	9.8	11.1
Cl	0.2	0.1	0.1	0.1	0.4
K ₂ O	0.5	1.3	1.1	1.2	0.2
CaO	24.0	2.4	32.0	8.3	4.1
TiO ₂	0.7	2.8	1.4	2.3	2.4
Fe ₂ O ₃	22.2	6.2	13.9	6.7	2.2
Br	0.0	0.0	-	-	16.3
SrO	1.9	0.1	1.9	1.1	1.5

Table 3-5: Crystalline mineral XRD results of all raw coal samples, wt%

Mineral Identification	Sample identification				
	Coal A	Coal B	Coal C	Coal D	Coal E
Quartz		15.7	5.5	7.9	
Kaolinite		27.0	6.0	22.8	12.6
Muscovite		1.5	0.7		0.7
Microcline				0.5	1.0
Dolomite				1.2	0.1
Anatase		0.3	0.3	0.8	0.2
Rutile			0.1	0.1	
Graphite			0.3		
Gypsum			0.2	0.9	
Fluorapatite		0.5			
Portlandite				0.1	
Periclase		0.1			
Calcite			0.8	0.8	0.3
Boehmite					4.7
Amorphous carbon content	100.0	55.0	86.1	64.9	80.4

Ash fusibility

The ash fusion temperatures (Table 3-6) can best be explained by observing the mineral composition results of the coal ash as given in Table 3-4, showing the XRF results. Mineral transformations and reactions of ash explain the melting temperatures and can also be a measure of predicted slagging in furnaces, although AFTs cannot accurately predict fouling and slagging (Gupta *et al.*, 1998; Hatt, 1996). Coals with lower rank usually have lower AFTs compared to that of coals of higher rank with increased Si, Al and Ti contents (Vassilev *et al.*, 1995). From the results it can be seen that coal A and coal C are of a lower rank than coal D and coal E. Coal B, however, together with coal D and E has low CaO concentrations (2.4, 8.3 and 4.1% respectively) compared to that of coal A and C (24 and 32% respectively) and explains the high AFT values obtained (Liu *et al.*, 2013; Song *et al.*, 2009). Reduced fluxing materials such as Fe₂O₃, CaO, MgO, K₂O and Na₂O increases the AFTs of coal ashes, and therefore the high Fe₂O₃ content of coal A (22%) can also explain the low AFTs obtained. Another indicator of low AFTs is an increased base/alkali content (Kong *et al.*, 2014; Liu *et al.*, 2013). Coal A and C, with the lowest AFTs has a base/alkali content of 55.5% and 51.0% respectively, which is much higher than the base/alkali content of coal B, D and E (10.5, 18.4 and 6.5% respectively).

Table 3-6: Ash fusion temperatures of the 5 coals studied

Sample identification	Coal A	Coal B	Coal C	Coal D	Coal E
Reducing					
Initial deformation temperature, °C	1162	1531	1159	1313	>1550
Softening temperature, °C	1182	>1550	1170	1331	>1550
Hemispherical temperature, °C	1203	>1550	1191	1359	>1550
Fluid temperature, °C	1225	>1550	1224	1377	>1550
Oxidising					
Initial deformation temperature, °C	1251	1531	1197	1361	>1550
Softening temperature, °C	1256	1540	1206	1383	>1550
Hemispherical temperature, °C	1271	>1550	1220	1402	>1550
Fluid temperature, °C	1321	>1550	1231	1415	>1550

3.3.2 Petrographic analyses

Bureau Veritas Testing and Inspections South Africa conducted the petrographic analyses according to ISO 7404. This microscopic evaluation aids in the evaluation of coal properties,

especially the parameters such as the maceral components and mineral matter (Falcon and Snyman, 1986; Falcon, 1978). Oil immersion objectives were used to identify and quantify different macerals present by taking 500 point readings on every specimen.

The random value of vitrinite reflectance (RoV random) can be seen in Table 3-7. According to the standard for the classification of coals (ISO 11760) coal B, C and E are of similar rank, while coal A is of a lower rank and coal D of a higher rank. A detailed discussion on rank, based on the petrographic analysis and the proximate analysis will be presented in Section 3.3.4.

Table 3-7 also shows the maceral composition of the five coals, which shows a significant difference in especially the huminite contents. Coal A and B are both high in huminite concentration and low in inertinite concentration compared to the other coals. It should be noted that the maceral present in coal A is huminite as opposed to vitrinite in coal B due to its low vitrinite reflectance value (0.27%). For values below 0.4% the tissue remnants are referred to as huminite and as the rank increases (reflectance values above 0.4%) it is referred to as vitrinite (Sýkorová *et al.*, 1994). Coal E is inertinite rich, while coal C and D are coals with similar vitrinite and inertinite contents. It can also be seen that all coals have low liptinite contents and significant differences in the type classifications can be seen for these coals; large differences in vitrinite and inertinite contents exist between the coals. Coals with the same RoV random (coal B and C) differ greatly in terms of the maceral composition and it confirms that there is a difference between coal type as reviewed by O'Keefe *et al.* (2013); i.e. coals of the same rank in terms of RoV can have a significant difference in the maceral content. It should be noted that because coal C is a blend of two coals of different rank, the RoV of coal C should be interpreted with care.

Table 3-4: Maceral composition and reflectance of the five raw coal samples

Sample identification	Coal A	Coal B	Coal C	Coal D	Coal E
Vitrinite/huminite	75.2	69.6	49.2	53.2	40
Liptinite	17.6	8.8	3.6	1.6	10.4
Inertinite	7.2	21.6	48.0	45.2	49.6
- Reactive Semifusinite	1.2	9.6	26.4	8.8	16.8
- Inert Semifusinite	6.0	11.2	18.8	36.4	31.2
- Fusinite + Secretinite	0.0	0.4	2.8	0.0	0.8
- Micrinite	0.0	0.4	0.0	0.0	0.8
RoV random	0.27	0.39	0.36	0.63	0.47

*Values are reported on a mineral matter free basis (as volume %)

3.3.3 Structural analyses

Surface area (CO₂ adsorption)

To better understand the behaviour of coal during utilisation processes it is important to have an understanding of the porosity and surface area of the coals (Şenel *et al.*, 2001; Mahajan, 1991; Rao, 1991). Micro porous properties (pore sizes smaller than 12 Å) were determined using BET CO₂ adsorption and these structural parameters are summarised in Table 3-5. The determination of these parameters was conducted using a Micromeritics ASAP 2020 surface area and porosity analyser. Sample preparation entailed degassing of a sample (0.20 g) under vacuum (10 µm Hg) at 90 °C for 2280 min. Adsorption analysis at 0 °C were then performed and data was automatically collected by ASAP 2020 v4.0 software. The micropore surface area was determined from this collected CO₂ adsorption data using the Dubinin-Radushkevich method (Şenel *et al.*, 2001).

The Dubinin-Radushkevich micropore surface areas of all the coals are seen to have larger values than the BET specific surface areas. This can be explained by the fact that micropores are the main contributor to specific surface area (Zou, 2013); the same trends are observed for all coals, i.e.-coals with a high BET surface area have a high Dubinin- Radushkevich micropore surface area.

The surface areas of coal are known to be closely related to coal rank and coal rank parameters such as elemental carbon and vitrinite reflectance (Zou, 2013). The inherent moisture content has also proved to correlate well with the internal surface area of coals (Thomas & Damberger, 1976). As metamorphism of coal is enhanced for medium and low ranking coals; the specific area of coal decreases gradually while it begins to increase towards anthracite (Zou, 2013). Bustin and Clarkson (1998) however showed in their CO₂ isothermal adsorption experiments that the micropore surface area decreases as coal rank rose and increased once it has reached a minimum for bituminous coal (Zou, 2013). An opposite trend has been seen for coal samples from China undergoing nitrogen surface area tests (Zou, 2013). As discussed in Section 3.3.4 coal B and C appear to be of similar rank, but in Table 3-8 it can be seen that coal B has the lowest value of surface area (75 m²/g), whereas coal C has the highest value of surface area (109 m²/g). No correlation between the surface area and coal rank has therefore been observed for these five coals from different parts of the world and supports literature (Zou, 2013). For coals of a medium rank and carbon content less than 85%, pore volume and surface area have an effect on the gasification reactivity; i.e. an increase in pore volume and surface area will increase the reactivity in these coals (NETL, 2016). The surface area of all five coals will therefore affect the reactivity as these coals are

all of low and medium rank. Lastly, the porosity of coals with elemental carbon contents lower than 75% (coal A, B and C) is attributed to macropores, whereas for coals with elemental carbon $76\% \leq \text{elemental carbon} \leq 84\%$ (coal D and E) the porosity is attributed to secondary porosity (micro- and meso-porosity) (Rodrigues & Lemos de Sousa, 2002; Gan *et al.*, 1972). For all five of these coals, macroporosity is therefore significant.

Table 3-5: CO₂ adsorption parameters

Samples	BET surface area (m ² /g)	Dubinin-Radushkevich micropore surface area (m ² /g)
Coal A	80	122
Coal B	75	111
Coal C	109	163
Coal D	77	118
Coal E	94	143

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)

The study of coal structures and identification of functional groups in coal is done by many researchers with the use of diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) (Xin *et al.*, 2014; Van Niekerk *et al.*, 2008; Li *et al.*, 2003; Miura *et al.*, 2001; Chen *et al.*, 1998a; Chen *et al.*, 1998b; Christy *et al.*, 1995; Sobkowiak & Painter, 1995; Cai & Smart, 1994, Painter *et al.*, 1987). All five raw coal samples (A-E) were prepared for DRIFT analysis according to studies done by Bona & Andrés, 2008; Van Niekerk *et al.*, 2008; Sobkowiak & Painter, (1995) . 20 mg of raw coal sample was mixed with 200 mg of KBr and stored under vacuum at 80 °C overnight. A Bruker alpha-P FTIR (Vertex 70) was used in the wavenumber range 370-4000 cm⁻¹ (Onwudiwe *et al.*, 2013). The KBr spectrum used as background and the spectra of the coal samples was obtained by using 400 scans at 4 cm⁻¹ resolution. Processing of the spectra was done using the Kubelka-Munk method (Van Niekerk *et al.*, 2008; Christy *et al.*, 1995) and a baseline correction was done by subtracting the background in order to obtain a useful background (Machnikowka *et al.*, 2002).

Three different spectra ranges were analysed and includes the ranges of 4000 – 2600 cm⁻¹, 1900 – 900 cm⁻¹ and 900 – 400 cm⁻¹. It was found that the absorption intensities differ a significant amount for the coals of different rank (Sobkowiak & Painter, 1995). The first peaks observed in the spectra are the peaks related to the mineral matter vibrations in the coal (Bona & Andrés; 2008b; Li *et al.*, 2004; Cai & Smart, 1994) and can be seen in the range 3800 – 3600 cm⁻¹. Peaks in all five coals can be seen in the range of 3653 – 3595 cm⁻¹ and the peaks in this range can be attributed to the free hydroxyl groups in the coal (Xin *et al.*, 2014; Van Niekerk *et al.*, 2008; Li *et al.*, 2004; Li *et al.*, 2003; Machnikowska *et al.*, 2002; Miura *et*

al., 2001; Chen *et al.*, 1998b; Painter *et al.*, 1987; Painter *et al.*, 1985). The aromatic and aliphatic CH stretching modes can be observed in the ranges 3100 – 3000 cm^{-1} and 3000 – 2800 cm^{-1} respectively (Sobkowiak & Painter, 1995). The strong peak observed for coal A at around 3500 cm^{-1} is attributed to the high moisture content of the coal, giving a strong O-H stretch. A strong aliphatic peak was also observed for coal A as well as a weak aromatic stretch, and therefore it can be concluded that coal A is more aliphatic than the other coals as indicated by the maceral analysis. Strong C=C aromatic stretches were however seen (1590 cm^{-1}) for all coals except for coal B. Coal A, D and E show strong C=O functionality (shoulder peak observed on the side of the C=C stretching vibration). Hydrogen bonding in coal C and D seem to be weak due to the weak O-H stretching vibrations at wavenumbers between 3700 cm^{-1} and 3100 cm^{-1} .

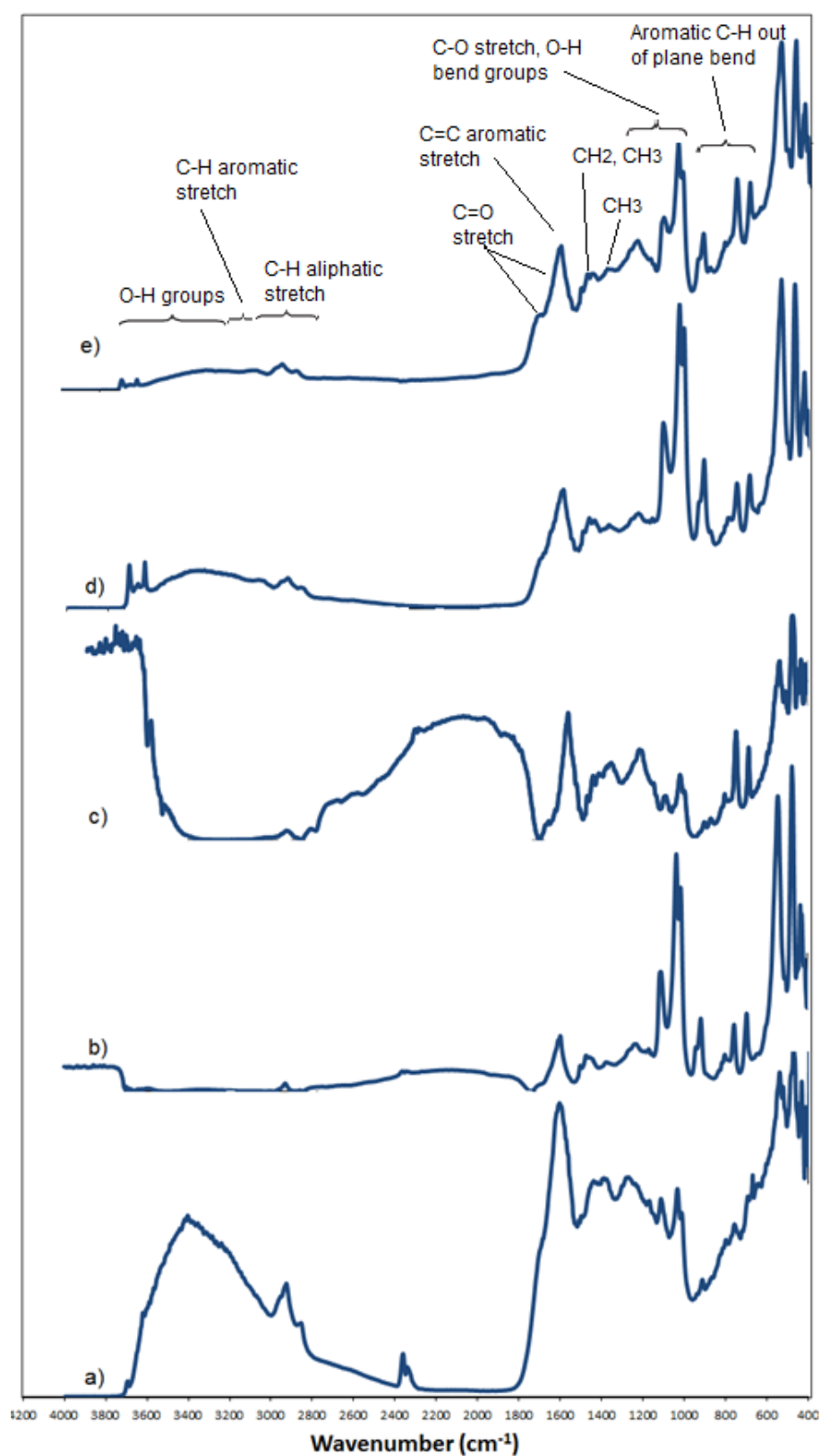


Figure 3-1: DRIFT spectra of a) coal A b) coal B c) coal C d) coal D e) coal E

3.3.4 Coal rank classification

The coal rank classification of the coals was done according to ISO 11760:2005 with the use of three characterisation parameters: random value of vitrinite reflectance, vitrinite content and ash yield (dry basis). The coals were firstly placed into broad range categories before being refined into sub-categories based on the random value of vitrinite reflectance. It can be seen from the results in Table 3-9 that coal A, B and C are of a lignite B rank. From Section 3.2.1, it should be noted that coal C is a blend of two coals of different rank (lignite and subbituminous), but is classified here as a lignite. Despite the fact that these three coals are of the same rank, the vitrinite ranges from medium to moderately high and the ash yield from low to moderately high. Coal D and coal E are of bituminous C and subbituminous rank respectively. The rank of coals used in this study therefore ranges between lignite B and bituminous C. A Van Krevelen diagram can also be used to classify coals into ranks according to their atomic H/C and O/C ratios (Van Krevlen, 1950) as seen in Figure 3-3. From this it is evident that coal A is a lignite rank coal. Coal B and C are in the subbituminous range and coal D and E are in the bituminous range. Conclusively, from the results in Table 3-9 and Figure 3-3 the coals can be grouped in three groups in terms of coal maturity and rank; with coal A being the youngest coal, coal B and C more mature than coal A, and lastly coal D and E the most mature coals.

Table 3-6: Classification of five coals according to ISO 11760:2005

	Coal A	Coal B	Coal C	Coal D	Coal E
Rank category	Lignite B	Lignite B	Lignite B	Bituminous C	Subbitmuminous
Vitrinite	Moderately high	Moderately high	Medium	Medium	Medium
Ash	Low	Moderately high	Medium	Moderately high	Medium

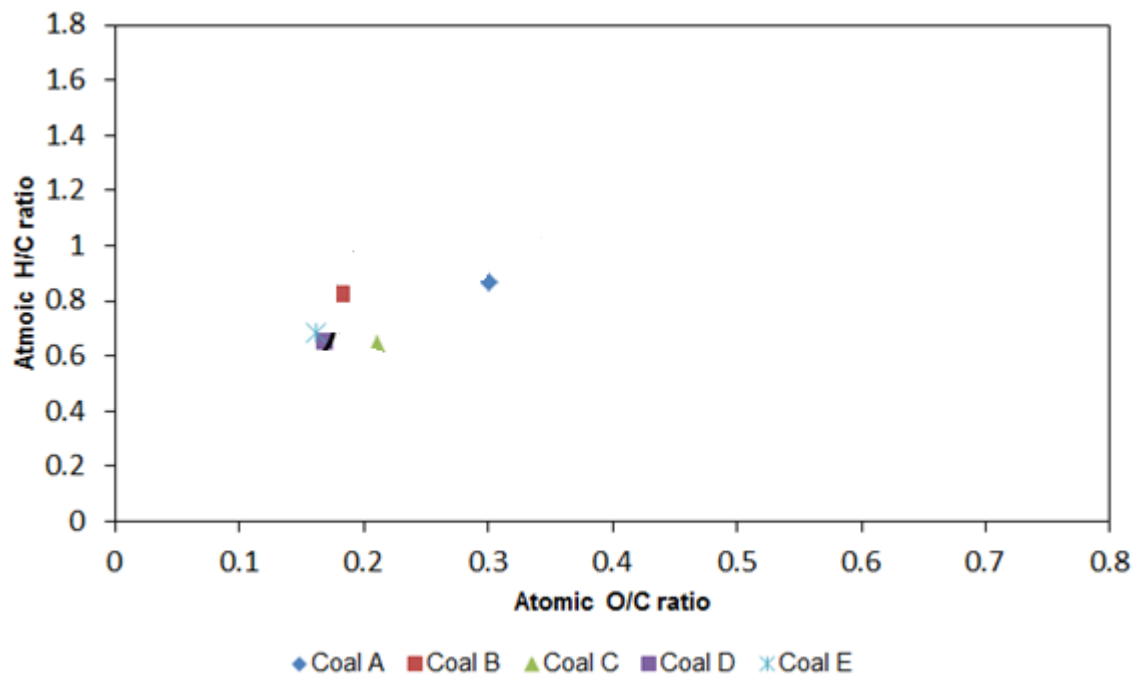


Figure 3-2: Five coals plotted on a Van Krevelen diagram - based on the coal ultimate analysis without inorganic volatile matter correction.

Chapter 4 – Experimental and analytical procedures

4.1 Introduction

This chapter provides detailed information regarding the experimental procedures used and analyses conducted which pertain to this study. Preliminary screening of the mass loss distributions by thermogravimetric analyses of the five coals was firstly needed to identify the temperatures at which the pyrolysis experiments should be conducted in a modified Fischer Assay setup, and the procedure used is given in Section 4.2. Section 4.3 contains the operating procedure and experimental conditions of the modified Fischer Assay setup. The pyrolysis product analyses undertaken are discussed in Section 4.4 and the experimental plan is given in Section 4.5. Finally, the FLASHCHAIN® modelling and statistical regression is explained in Section 4.6.

4.2 Thermogravimetric analysis

Mass loss curves as a function of temperature are fundamental and cost effective in the optimisation of coal conversion technologies such as pyrolysis and gasification (Magdziarz & Wilk, 2013; Zhang *et al.*, 2015), and to investigate the devolatilisation behaviour of coals (Bibrzycki *et al.*, 2016). These curves were obtained for all five coals (A-E) by thermogravimetric analysis in order to choose the final pyrolysis temperatures prior to pyrolysis experiments using the modified Fischer Assay setup. In the TGA work, a vertical tube furnace, with inner diameter of 50 mm supplied the necessary heat, containing a K-type thermocouple to measure the temperature inside the furnace. The inert atmosphere was obtained with a constant flow of N₂, controlled by a Brooks model 0254 mass flow controller (see Appendix A-2 for flow calibration). A sample holder (aluminium stand and quartz holder) was placed on a Radwag PS 750/C/2 balance in order to give continuous mass measurements as the temperature is increased. A heating rate of 10 °C/min was used, starting at room temperature and ending at 1000 °C, as devolatilisation occurs at temperatures below 1000 °C in fixed-bed dry bottom gasifiers (Krishnudu *et al.*, 1989).

4.3 Fischer Assay pyrolysis

4.3.1 Fischer Assay operating procedure

A modified Fischer Assay setup (Roets *et al.*, 2014) was used (Figure 4.1) for the pyrolysis product preparation at the 3 different temperatures determined by TGA. This setup was developed in order to perform Fischer Assay experiments at elevated temperatures above the ISO 647 temperature of 520 °C. Alterations made include the use of stainless steel retorts instead of aluminium in order to operate at temperatures close to 1 000 °C and the capture of non-condensable gases in gas sampling bags.

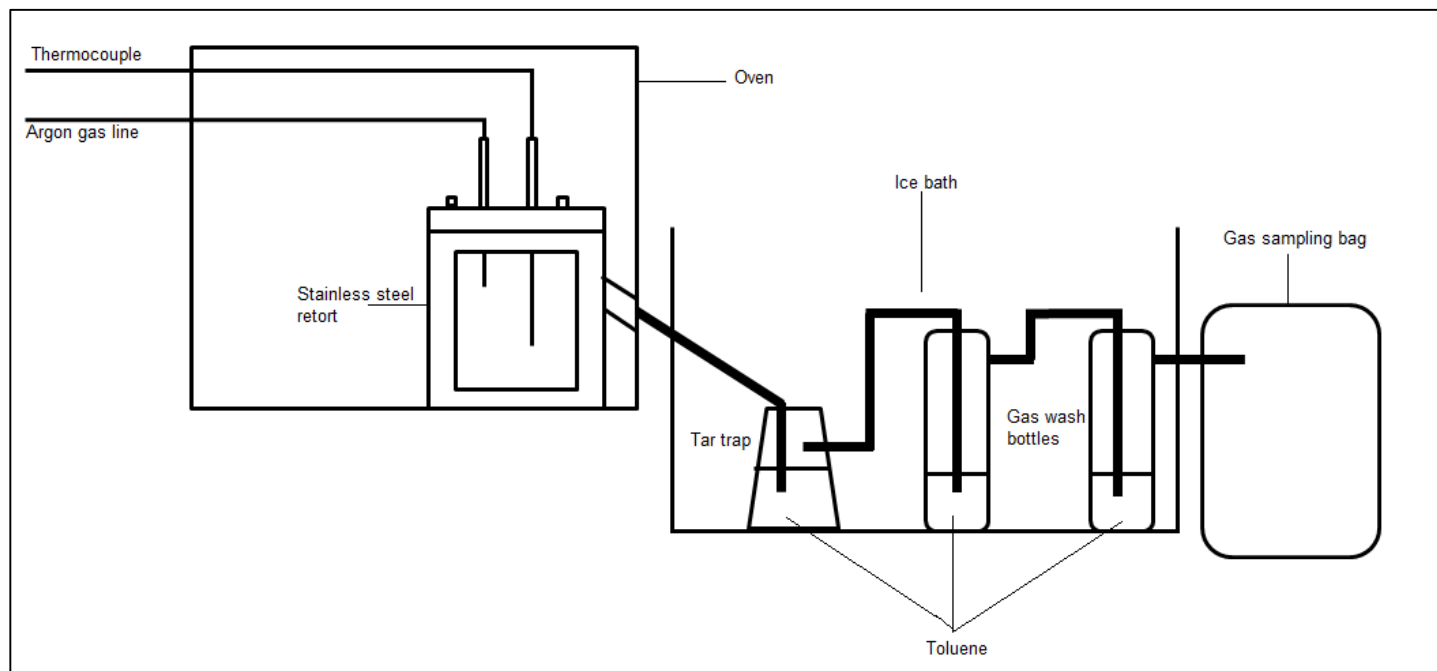


Figure 4-1: Schematic of Fischer Assay experimental setup

Two stainless steel retorts, built according to ISO 647 dimensions are used to load the 50 g coal samples with particle size as indicated in Table 4-1. Argon is used to create an inert atmosphere before the coal is heated in order to prevent combustion of the coal. The retorts are heated in a Lenton oven (22amp-48kW rating over 220V) fitted with a TOHO TTM-P4 temperature controller and a Shinko LMD-100 Console/Data Logger. Two K-type thermocouples are fitted within each of the two retorts, one measuring the bed temperature and the other the environment temperature inside the oven chamber. A lag in temperature increase between the oven chamber temperature and the bed temperature exists; therefore the bed temperature was used for temperature control. The heating rate ranges between 8.5 °C/min and 9.5 °C/min, depending on the final pyrolysis temperature. Heating curves can be seen in Figure 4-2.

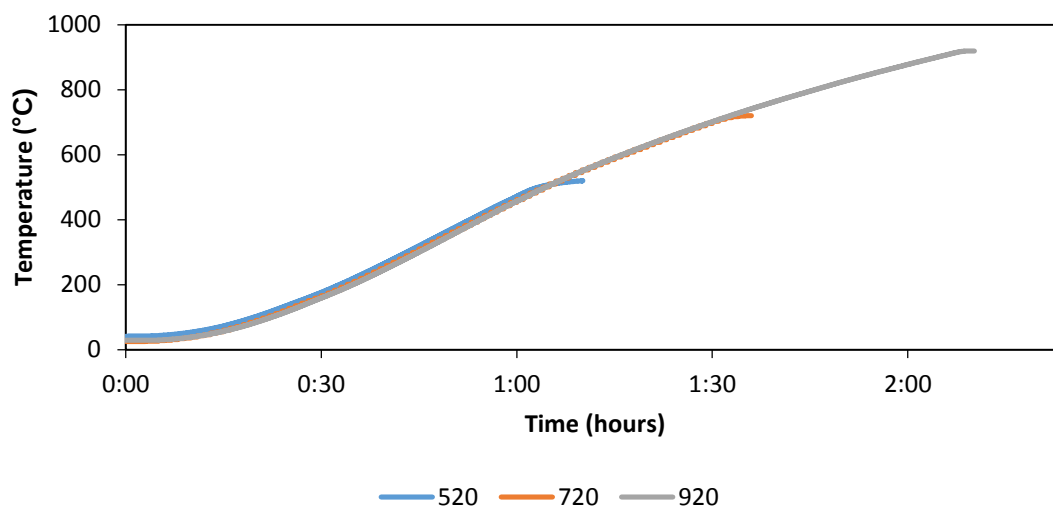


Figure 4-2: Fischer Assay temperature profile for final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

Other operating specifications can also be seen in Table 4-1. The gas formed during the heating of the coal and pyrolysis flows through stainless steel pipes and was bubbled through a tar trap and two gas wash bottles. This was done in order to capture the condensable gases (tar and water) before the non-condensable gases were captured in 10 L Tedlar gas sampling bags. Toluene was used as solvent in the tar trap and gas wash bottles, and was kept at 0 °C by immersion in an ice bath.

Table 4-1: Fischer-Assay operating specifications

Variable	Specification
Coal samples	5 coals of different origin ranging from lignite to bituminous
Load weight (g)	50 ± 0.1
Particle size	90% <1mm, not more than 50%<0.2mm According to ISO 647
Final pyrolysis temperature (°C)	520, 720 and 920
Heating rate (°C/min)	See Figure 4-2, 7 °C/min
Pressure	Atmospheric (87.5 kPa)
Inert gas	Argon

4.3.2 Pyrolysis product yield

Fischer Assay product mass yields derived from coal include char, tar, water and gas. All these products are captured in the closed system as explained in Section 4.3.1. The mass yields (on an “as analysed” basis) are determined by the following equations:

$$\text{Char yield (wt \%)} = \frac{m_4 \times 100}{m_0} \quad (\text{Eq. 4-1})$$

$$\text{Tar yield (wt \%)} = \frac{(m_2 - m_1 - m_3) \times 100}{m_0} \quad (\text{Eq. 4-2})$$

$$\text{Water yield (decomposition), wt \%} = \frac{m_3 \times 100}{m_0} - M \quad (\text{Eq. 4-3})$$

$$\text{Gas yield, wt \%} = \frac{(m_0 + m_1 - m_2 - m_4) \times 100}{m_0} \quad (\text{Eq. 4-4})$$

Where

m_0 is the sample mass;

m_1 is the mass of empty receiver and stopper;

m_2 is the mass of m_1 plus tar plus total water;

m_3 is the mass of total water determined;

m_4 is the mass of char

M is the inherent moisture content of the coal sample.

Yields on a dry basis can be determined by multiplication of the above equations (Eq. 4-1, 4-2, 4-3 and 4-4) with:

$$\frac{100}{100 - M} \quad (\text{Eq. 4-5})$$

Char yield

The char yield was determined by placing the residue retained in the retorts, (after it was left to cool to room temperature), on a mass balance and with the use of Eq. 4-1. Obtained chars were stored in air tight containers after purging with argon in order to prevent oxidation before characterisation was done.

Water yield

Dean-Stark distillation was used in order to determine the total water yield. Liquid obtained from the tar trap and two gas wash bottles, containing toluene, water and tar, was placed in a round bottomed flask inside a Seta MTop 5 heating mantle. This mixture was heated and evaporated components were condensed using a reflux condenser and captured in a reflux reservoir. The condensed liquid contained the water, toluene and light tar components. The higher density (998 kg/m^3) polar liquid (water) separated from the lower density (865 kg/m^3) non-polar liquid (toluene) could easily be decanted and weighed (Wiberg, 1960).

Tar yield

The mixture of toluene and tar, after the water has been removed using the Dean-Stark distillation method was then transferred into a round bottomed flask connected to a Büchi Rotavapor R II. The pressure inside the system is gradually decreased from atmospheric to 27 mbar (Hattingh, 2012), while the toluene-tar mixture is kept at 60°C . A Büchi V-850 vacuum controller and V700 vacuum pump is used to obtain this pressure. The pressure is kept at 60°C for at least 5 minutes in order to ensure that all the toluene is removed from the flask. The mass of the flask is determined after evaporation and the tar yield is determined using Eq. 4-2.

Gas yield

The gas yield is determined by difference using Equation 4-4.

4.4 Pyrolysis product analyses

A deeper understanding of the respective pyrolysis products can be achieved with qualitative analytical techniques. The char, tar and gas compositions were analysed using techniques discussed in the following section.

4.4.1 Char analyses

The char formed during pyrolysis was kept in an inert atmosphere and in cool conditions before it was analysed by Bureau Veritas Testing and Inspections South Africa. The proximate analysis, ultimate analysis and calorific value of all the obtained chars were conducted in order

to compare the properties with the original properties of the raw coal. Table 4-2 shows the standards used for these analyses and results will be discussed in Chapter 5.

Table 4-2: Standards used for analyses done on chars

Analysis	Standard
Sample preparation	ISO 13909-4: 2001
Moisture content (%)	ISO11722: 1999
Ash content (%)	ISO 1171: 2010
Volatile matter content (%)	ISO 562: 2010
Total sulphur (%)	ISO 19579: 2006
Gross calorific value (MJ/kg)	ISO 1928: 2009
Ultimate analysis	ISO 12902 - CHN Instrumental method

4.4.2 Tar analyses

Tars obtained from separation (as documented previously in this section) were kept in air tight glass bottles and in cool conditions prior to analyses. Analyses done on the tar samples include simulated distillation (Simdis), gas chromatography – mass spectrometry (GC-MS), size exclusion chromatography (SEC) and the determination of elemental C, H, O, N and S. These analyses were performed by various laboratories as seen in Table 4-3.

Table 4-3: Laboratories responsible for tar analyses

Analysis	Laboratory responsible
Simdis	Imperial College – London
GC-MS*	Imperial College – London
SEC	Imperial College – London
CHONS	Elementar Application Laboratory - Germany

* qualitative

Simulated distillation (Simdis)

Petrochemical products can be categorised into boiling point ranges using simulated distillation, a standard used for fractions with a boiling range between 55.5 °C and 538 °C (Ukwuoma, 2002). This analysis was done for all experimentally generated tars as explained in the experimental plan given in Section 4.5. A Perkinelmer Clarus 500 HT5 aluminium clad fused silica capillary column with 25 m length and an ID of 0.32 mm was used for this analysis. An FID detector was used and helium was applied as the carrier gas at a flow rate of 10

mL/min. The program was set to an injection temperature of 350 °C and the detector temperature at 370 °C. The first ramp was at 15 °C/min from 35 °C to 350 °C and was held for 2 min. A second ramp was introduced at a heating rate of 25 °C/min to 380°C and was held for 10 min. Fractions of samples of coal derived tar with boiling points higher than 450 °C were not analysed; the fractions with boiling points lower than 450 °C were analysed as seen in Figure 4-3.

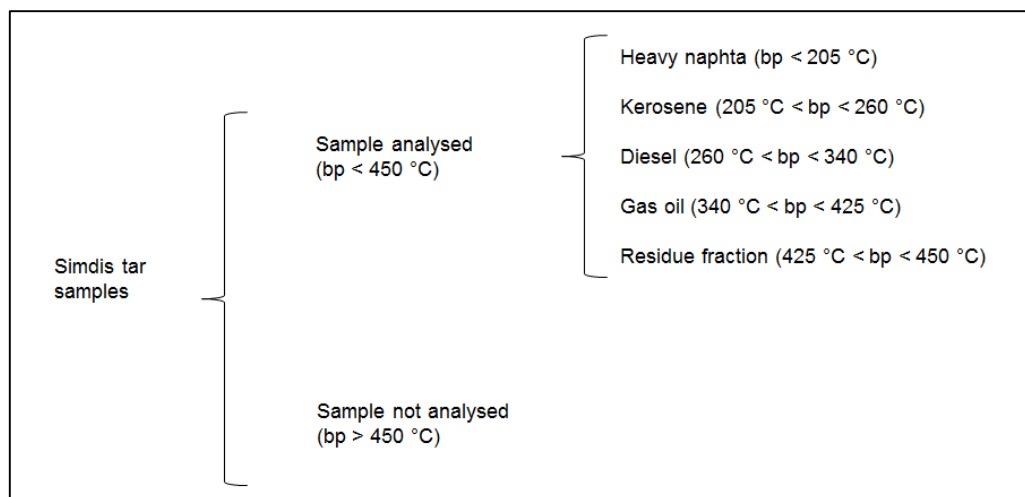


Figure 4-3: Boiling point ranges for tar samples analysed by Simdis (After ASTM D2887)

Size exclusion chromatography (SEC-UV)

The same tar samples used for previously mentioned Simdis analysis was used in the SEC analysis in order to estimate the molecular weight distributions of the liquid tar samples. A polystyrene/polydivinylbenzene mixed D packed column fitted with a Knauer 2600 UV detector was used. N-methyl pyrrolidone was used as carrier and analyses were done at 80 °C (Leyva *et al.*, 2013). The calibration curve of the mixed D packed column can be seen in Appendix A-2.

Gas chromatography mass spectrometry (GC-MS)

The analysis was performed using Varian star 2400 equipment fitted with an HT5 aluminium clad fused silica capillary column with 25 m length and an ID of 0.32 mm. A Saturn 2000 MS detector was used with helium as carrier gas at a flow rate of 10 mL/min. The program was set to an injection temperature of 350 °C and the detector temperature at 370 °C. The first ramp was at 15 °C/min from 35 °C to 350 °C and was held for 2 min. A second ramp was introduced with a heating rate of 25 °C/min to 380°C and was held for 10 min. The individual products were reported in order of appearance according to its retention times. The products were classified into the following chemical families:

- Alkyl benzenes
- Phenols
- Cresol and paracresol
- Furans
- Alkanes
- Polycyclic aromatic hydrocarbons (PAH)
- Long chain alcohols

CHNOS determination

The ultimate analysis of coal tars can easily be measured and used in predictive models (Shoko *et al.*, 2015) and is crucial in order to close an overall CHNOS mass balance for the Fischer Assay derived products. The analyser used for this was a varioEL cube run in a CHNS + O mode with a balance and a capsule press as peripherals. Area peaks were measured for C, H, N, S and O and converted into mass percentage present in the tar sample. The statistical report can be seen in Appendix B-4.

4.4.3 Gas analyses

The pyrolysis gas was analysed for its main components (H_2 , CO, CO_2 and CH_4) using an SRI 8610C multiple gas chromatograph (Hattingh, 2012; Roets, 2014). The gaseous species were first separated with a 6' Hayestep D packed column, 6' 13X molecular sieve and a 3' 5Å molecular sieve before being analysed with a flame ionisation detector (FID) and two thermal conductivity detectors (TCDs). A refinery gas and a $CO/CO_2/N_2$ mixture gas was used to calibrate the GC in order to measure hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethane, ethylene C_3S , C_4S and C_5S . Operating specifications can be seen in Table 4-4.

Table 4-4: GC operating conditions and specifications

Condition	Specification
Sample loop volume	0.5 μ L
TCD temperatures	TCD1: 300 TCD2: 150
FID carrier gas	He (25 psi and 20 mL/min)
Methaniser carrier gas	H_2 (20 psi and 25 mL/min) and Air (5 psi and 250 mL/min)
TCD carrier gases	TCD1: He (25 psi and 20 mL/min) TCD2: Ar (7psi and 10 mL/min)
Heating programme	Hold for 7 min at 60 °C, ramp from 60°C to 280 °C at 15 °C/min, hold for 20min at 280°C.

4.5 Experimental plan (Fischer Assay)

Repeatability was determined at all temperatures using Coal D where 10 experiments were conducted at each final pyrolysis temperature (520 °C, 720 °C and 920 °C). After the repeatability (see Section 5.2) was determined, pyrolysis experiments were conducted according to Table 4-5. Four repeat runs (two repeats of duplicate experiments as discussed in Section 4.3.1) were done for each sample to ensure sufficient tar production for analyses.

Table 4-5: Experimental plan for final Fischer Assay experiments

Coal sample	Temperature	Repeats
Coal A	520 °C	4
Coal B	520 °C	4
Coal C	520 °C	4
Coal D	520 °C	4
Coal E	520 °C	4
Coal A	720 °C	4
Coal B	720 °C	4
Coal C	720 °C	4
Coal D	720 °C	4
Coal E	720 °C	4
Coal A	920 °C	4
Coal B	920 °C	4
Coal C	920 °C	4
Coal D	920 °C	4
Coal E	920 °C	4

4.6 Modelling

4.6.1 FLASHCHAIN®

Modelling was applied with the assistance of PC Coal Lab®, which incorporates Niksa Energy Association's FLASHCHAIN® model. This is the first network depolymerisation theory created to do coal decomposition based only on proximate and ultimate analysis. The input for this model, therefore, is the proximate and ultimate analysis of coal and operating conditions. Table 4-6 and 4-7 show a summary of what inputs are needed by using Coal A as an example. As discussed in Section 2.5.2 the model was created for fast heating rates (~1-1000 K/s) and therefore a limitation exists in terms of the heating rate input. The slowest heating rate that executes the model without any errors was found to be 0.211 K/s (12.7 K/min).

Table 4-6: Coal sample input

Parameter	Proximate analysis (as determined basis)				Ultimate analysis (dry, ash free basis)				
	Fixed carbon %	Inherent moisture content %	Volatile matter %	Ash content %	% C	%H	%N	%S	%O
Coal A Value	33.9	30.1	29.4	6.6	66.6	4.8	1.0	0.9	27.7

Table 4-7: Operating conditions input

Parameter	Pressure	Gas flow	Starting temperature	Heating rate	Final temperature	O ₂ flow
Coal A Value	87 kPa	N ₂	25 °C	0.2 °C/s	520 °C 720 °C 920 °C	0%

Various reports are generated for a particular coal pyrolysed to a specific temperature and are shown in Table 4-8, together with more specifics of what can be found in the reports. It should be noted that the module 7 package of simulating tar decomposition at moderate temperatures was also applied. This package was developed in order to include tar composition chemistry due to the knowledge of tar cracking at moderate temperatures. A limitation of this package is the omission of non-condensable volatiles chemistry which means that the conversion of volatiles cannot be quantitatively simulated. The thermal time and temperature history is noted in all reports and only the last point in the thermal history was used as the value related to the final pyrolysis product. Figure 4-5 shows an example of an output report; this example is for Coal A with a final pyrolysis temperature of 520 °C.

Table 4-8: Output variables of FLASHCHAIN®

Outputs	Dependent variables obtained
Char composition	%C, %H, %N, %S, %O
Hydrocarbon gases	CH ₄ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ , H ₂ , H ₂ S
Non-condensable gases	Gas yield, CO ₂ , CO
Pyrolysis products	Gas, tar and char yield (dry, ash free)
Tar composition	%C, %H, %N, %S, %O, average molecular weight (g/mol)

WIRE GRID SIMULATION WITH PC COAL LAB

FULL DYNAMICS

COAL CHARACTERISTICS: A

Ultimate, daf wt. %	Proximate, as rec wt. %
%C 66.6	Moisture 30.1
%H 4.8	Vol. Mat. 29.4
%O 26.7	Ash 6.6
%N 1.0	Fixed C 33.9
%S 0.9	

OPERATING CONDITIONS:

Coal at 25. C is heated in N2 with 0.0 % O2 to
520. C at 0.2 C/s, then held for .100E+01 s.
The ambient pressure is 0.09 MPa.

Thermal History	Time,s	Tmp,C	wt.Loss daf wt. %	HCS	CH4	C2H4	C2H6	C3H6	C3H8	H2	H2S
.000E+00	25.	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00	0.00
.241E+03	76.	1.3	0.5	0.3	0.09	0.03	0.08	0.00	0.00	0.00	0.02
.541E+03	139.	3.4	1.3	0.7	0.23	0.08	0.19	0.00	0.00	0.00	0.05
.842E+03	203.	6.9	2.5	1.5	0.44	0.16	0.37	0.00	0.00	0.00	0.10
.114E+04	266.	12.7	4.2	2.4	0.73	0.27	0.61	0.00	0.00	0.01	0.17
.144E+04	330.	19.0	6.1	3.5	1.06	0.39	0.89	0.00	0.00	0.02	0.26
.174E+04	393.	28.0	8.6	4.9	1.49	0.55	1.25	0.00	0.00	0.03	0.37
.205E+04	457.	39.0	12.0	6.9	2.08	0.77	1.75	0.00	0.00	0.06	0.53
.235E+04	520.	45.0	12.0	6.9	2.08	0.77	1.75	0.00	0.00	0.06	0.62
.235E+04	520.	45.0	12.0	6.9	2.08	0.77	1.75	0.00	0.00	0.06	0.62

Figure 4-4: Hydrocarbon gases output report example for Coal A: 520 °C

4.6.2 Statistical regression

Due to the complexity of coal pyrolysis reactions and the assumption of equilibrium conditions, a mechanistic approach, chemical equilibrium model or kinetic models outputs usually results in errors (Lopez-Uribeabarranechea *et al.*, 2012). The major advantage when using an empirical approach includes the simplicity of the model and accuracy due to developments for specific reaction conditions. The limitation of the developed empirical correlations will therefore be for: 1) slow pyrolysis (8 °C/min), 2) final pyrolysis temperatures of 520 °C, 720 °C and 920 °C, and 3) coals of rank ranging between lignite and bituminous C.

A linear regression analysis is a statistical technique which is used in order to determine variable dependencies and the relationship between various variables, and has been used in previous pyrolysis applications (Ateş & Erginel, 2012; Lopez-Uribeabarranechea *et al.*, 2012). In this study, R^2 values were calculated for each input and output variable in relation to all other variables using statistical software SPSS and using the Spearman's rho method. Variables with a two-tailed sigma value of smaller than 0.05 were considered to be statistically significant and the R^2 values were then reported. The input and output variables used to

implement statistical regression can be seen in Table 4-9. Results will be discussed in Section 5.4.

Table 4-9: Inputs and outputs of statistical regression

Inputs		Outputs	
Temperature		Yields	Char as % Tar as % Water as % Gas as % (by difference)
Proximate analysis	wt% Inherent moisture content wt% Ash content wt% Volatile Matter wt% Fixed carbon (by difference)		
Ultimate analysis	C H N S O (by difference)	Char proximate analysis	wt% Ash content wt% Volatile Matter wt% Fixed carbon (by difference)
		Char ultimate analysis	C H N S O (by difference)
XRF	Na ₂ O MgO Al ₂ O ₃ SiO ₂ SO ₃ CaO TiO ₂ Fe ₂ O ₃	Tar elemental analysis	C H N S O (by difference)
		Gas composition	H ₂ CH ₄ CO CO ₂
XRD	Quartz Kaolinite Amorphous		
BET	BET Surface Area Langmuir Surface Area Dubinin-Radushkevich Surface Area	BET	BET Surface Area Langmuir Surface Area Dubinin-Radushkevich Surface Area
		Simdis	Heavy Naphtha Kerosene Diesel Gas Oil Residue

Chapter 5 - Results and discussion

5.1 Introduction

This chapter deals with the experimental results obtained and a critical discussion thereof, as well as the application of models in support of the experimental results found. In Section 5.2 the experimental results will be critically discussed, firstly based on the pyrolysis product yields in Section 5.2.2, followed by a discussion of the composition of the pyrolysis products. A closed mass balance based on elemental carbon, hydrogen, oxygen, nitrogen and sulphur is discussed in Section 5.2.3. The application of statistical regression and the FLASHCHAIN[®] model is lastly discussed in Section 5.3.

5.2 Experimental results and discussion

5.2.1 Thermogravimetric analysis

Thermogravimetric analysis was performed on all five raw coals in order to determine the three pyrolysis temperatures to be used in the Fischer Assay devolatilisation investigation. Information regarding the weight loss of the samples versus temperature was obtained and is shown in Figure 5-1. Duplicate experiments were performed on each sample to ensure repeatability and can be seen in Appendix B-5. A maximum absolute difference of 5.6% was determined which ensured a reasonable repeatability between results.

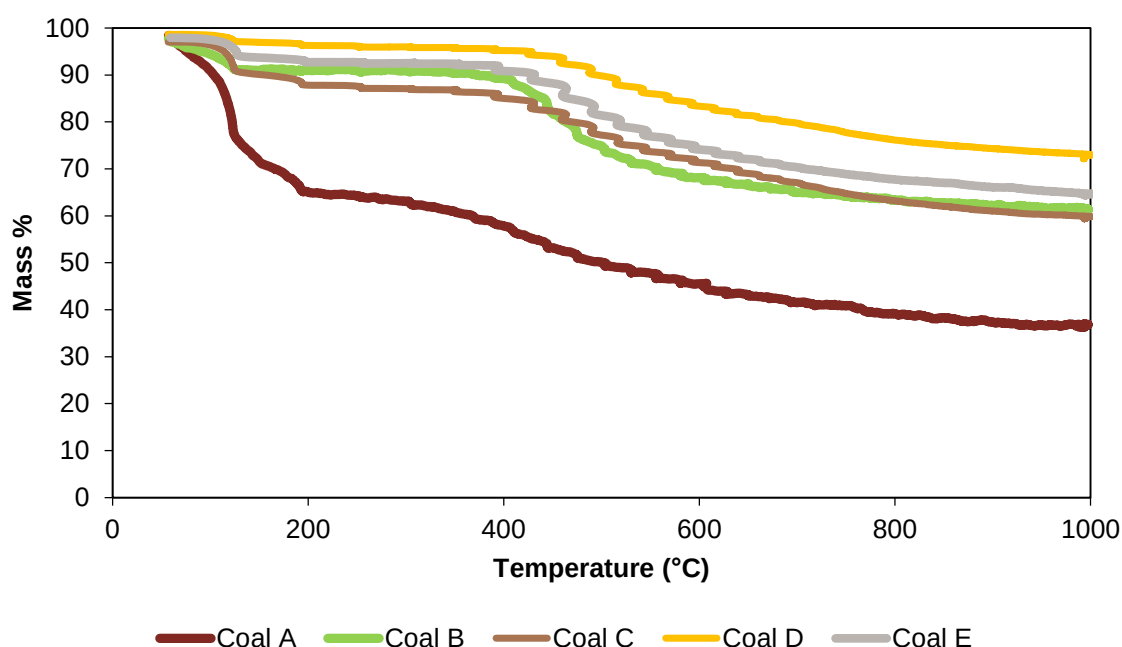


Figure 5-1: Weight loss curves as determined by thermogravimetric analysis for all five raw coals

It can be seen that a significant difference between the mass loss curves exist, with coal A showing the biggest loss in mass. It is further observed for coal A that devolatilisation starts to

occur at lower temperatures than for the other coals. The inherent moisture content of coal A is 30.1% (air dried) and a 30.1% weight loss on this curve corresponds to around 180 °C, where after a further mass loss is observed. On the other hand, a rather flat line can be seen for the other coals where the moisture content has been released, which is followed by a rapid increase in mass loss at temperatures around 450 °C. It can finally be seen that devolatilisation is almost completed at high temperatures approaching 1000 °C.

The selection of three temperatures to perform the pyrolysis experiments at was needed. A temperature of 520 °C was chosen as the first temperature in accordance to the ISO 647 standard as well as a high pyrolysis temperature of 920 °C and a mid-point temperature of 720 °C, in order to better understand the pyrolysis product yields and compositions as a function of temperature.

5.2.2 Pyrolysis product yields

Five coals, ranging from lignite to bituminous were selected as described in Chapter 3, where after pyrolysis experiments were conducted using a modified Fischer Assay procedure as described in Chapter 4. Prepared samples of $50 \pm 0.05\text{g}$ were subjected to these pyrolysis experiments and the product yields obtained are shown in Figure 5-2 and Table 5-1.

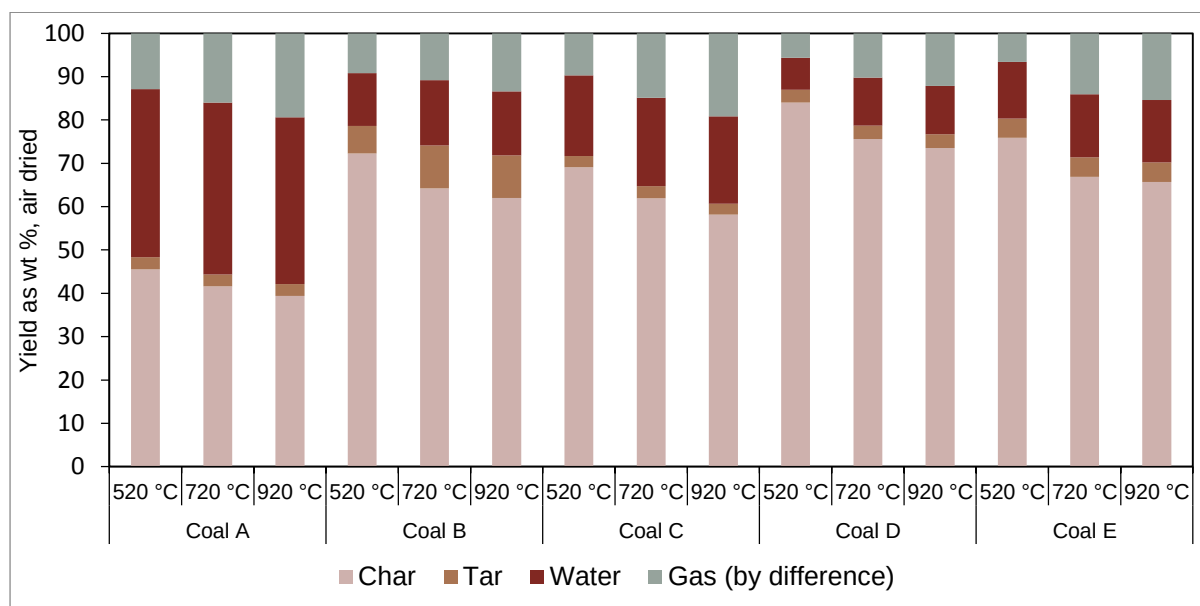


Figure 5-2: Experimental Fischer-Assay yields of five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

Table 5-1: Pyrolysis product yields of five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C. Yields in wt% of coal (ad)

	520 °C				720 °C				920 °C			
	Char	Tar	Water	Gas (by difference)	Char	Tar	Water	Gas (by difference)	Char	Tar	Water	Gas (by difference)
Coal A	45.5	2.8	38.8	12.9	41.6	2.7	39.7	16.0	39.4	2.7	38.5	19.4
Coal B	72.3	6.3	12.2	9.2	64.2	9.9	15.1	10.9	62.0	9.8	14.8	13.4
Coal C	69.1	2.6	18.6	9.7	61.9	2.9	20.4	14.9	58.2	2.5	20.1	19.2
Coal D	84.0	3.0	7.4	5.6	75.6	3.1	11.0	10.2	73.5	3.1	11.2	12.1
Coal E	75.9	4.4	13.1	6.6	66.9	4.5	14.5	14.1	65.7	4.5	14.2	15.8

From Figure 5-2 and Table 5-1 it is evident that the char, tar, water and gas yields as function of temperature are heavily dependent on temperature and the coal sample type. It is observed that the char yields obtained from the thermogravimetric analysis (Figure 5-1 and Table 5-1) compare well with the results obtained from the Fischer Assay experiments (Figure 5-2). The modified Fischer Assay setup showed slightly lower errors between repeats runs and is in accordance with previous modified Fischer Assay work as reported by Kühn (2015). It is also observed that the coals of lower rank (coal A, B and C) have lower char yields (air dried basis) than that of the coals of higher rank (coal D and E). The effect of coal rank on char, tar, water and gas yields will be discussed in subsequent sections. Volatiles evolved during the experiments, which is a mixture of low molecular weight (gas) and high molecular weight hydrocarbons (tar) are also observed to be temperature and rank dependent. An increase in final pyrolysis temperature results in an increase in the mass of volatiles evolved and is in accordance with what several authors have found (Kristiansen, 1996; Ladner, 1988, Xu and Tomita, 1987a). The total volatiles (dry, ash free basis) evolved for lower rank coals, coal A, B and C at 920 °C are 48.2%, 45.0% and 37.9% respectively, which is higher than the total volatiles evolved for the higher rank coals, coal D and E (31.8% and 34.8% respectively). These results are also in agreement with other studies, where it was reported that coals of lower rank experience higher degrees of evolved volatiles than for higher rank coals (Xu and Tomita, 1987b).

The following discussion will compare the yields of the different pyrolysis products (char, tar, gas and water). Experimental errors were calculated at a 90% confidence interval and can be seen in Appendix A-1. The repeatability between experiments were conducted on coal D at 520 °C, 720 °C and 920 °C by doing 10 repeat runs at each temperature. Repeatability errors on char were calculated to be less than 1% for a 90% confidence interval at all temperatures, and on tar the error was less than 12% at all temperatures. Larger errors on water yields were

determined, and the larger errors on gas yield can be explained by the fact that gas yield was determined by difference. This large water error is in accordance with concerns raised by previous authors using the modified Fischer Assay method, and results are usually reported on a dry basis (Kühn, 2015; Roets *et al.*, 2014). This could be further investigated in future studies.

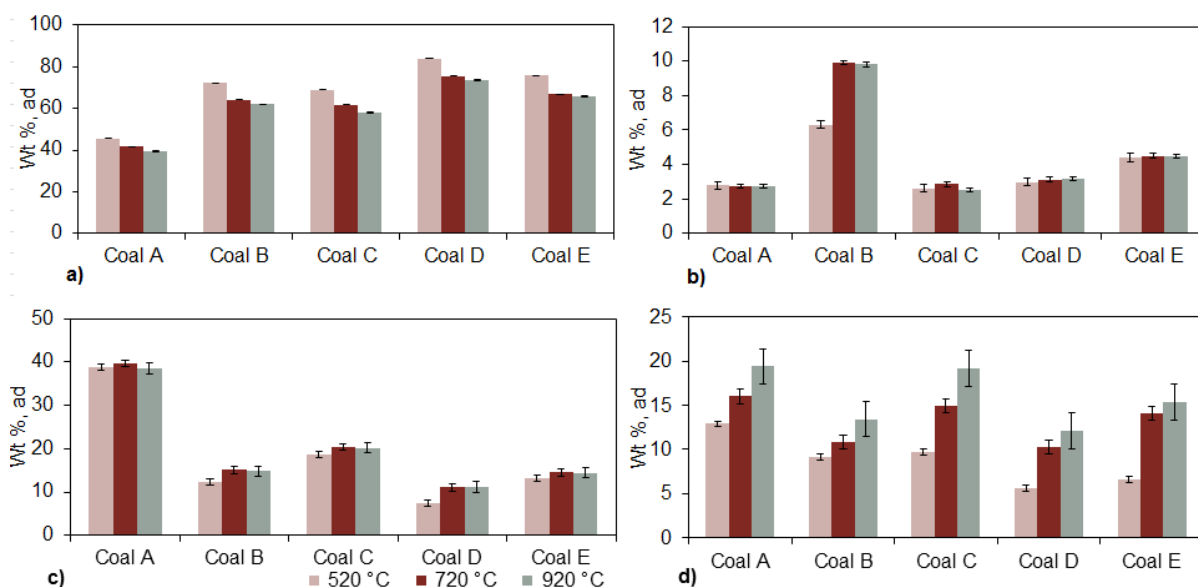


Figure 5-3: a) Char yields, b) Tar yields, c) Water yields and d) Gas yields for five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

Char yield

From Figure 5-3a above, a general trend can be seen for all five coals, i.e. a decrease in char yield is observed as the temperature increases, which is consistent with literature (Kandiyoti *et al.*, 2006; Ladner, 1988). At 520 °C the char yield (air dried basis by weight) for coals A, B, C, D and E are 45.5%, 72.3%, 69.1%, 84.0% and 75.9% respectively. This is followed by a further decrease in char yield from 520 °C to 720 °C for the respective coals to 41.6%, 64.2%, 61.9%, 75.6% and 66.9%, and falls within a range of 3.9 - 9.0%. An even smaller decrease in char yield is finally observed between 720 °C and 920 °C, where the respective char yields for coals A, B, C, D and E are 39.4%, 62.0%, 58.2%, 73.5% and 65.7%. This smaller decrease falls within a range of 1.2 - 3.7%. This could be attributed to the fact that most of the volatile matter (by weight) has been driven off at 720 °C, and only light gases are evolved at the highest temperature of 920 °C (Kim *et al.*, 1988). Further insight into this will be elaborated on when discussing the composition of char, tar and gas formed at each temperature (Sections 5.2.3, 5.2.4 and 5.2.5).

It is also evident from Figure 5-3a that the char yield obtained is also rank dependent. Coal A, which is the coal of the lowest rank, has the lowest char yield (45.5%, 41.6% and 39.4%

produced at temperatures of 520 °C, 720 °C and 920 °C respectively), whereas coal D, the coal of the highest rank, has the highest char yield at all operating temperatures (84.0%, 75.6% and 73.55% at temperatures of 520°C, 720°C and 920°C respectively). Due to the loss in volatile matter and inherent moisture during pyrolysis, the char yield is heavily dependent on the remaining fixed carbon and ash content in the coal, and it was therefore expected that coals with the highest value of fixed carbon and ash content will have the highest char yield. The results obtained here are in accordance with the trend given by the proximate analysis, i.e. where coal A has the lowest fixed carbon and ash content value and coal D the highest. It is known from coal ASTM D388 that lower rank coals (lignites) have higher values of inherent moisture and volatile matter than that of higher rank (bituminous coals). The char yield is therefore dependent on the coal rank and corresponds to the decrease in total volatiles evolved, as found by (Xu & Tomita, 1987b).

Tar yield

Tar is the condensable and higher molecular weight fraction of the total evolved volatiles. It was stated in earlier in Section 5.5.2 that the total evolved volatiles generally increase with an increase in temperature, and decrease with an increase in coal rank in agreement with Xu & Tomita (1987b). Such a premise can, however, not be made for the condensable fraction of the evolved volatiles. The general trend seen in the pyrolysis experiments (Figure 5-3b) is that a maximum tar yield value is observed at 720 °C, which either stays the same at 920 °C, or decreases to a lower tar yield, i.e. maximum tar yield for coal A, B, C, D and E are seen to be 2.8%, 8.8%, 2.9%, 3.2% and 4.9% respectively. This same phenomenon has been observed by authors who conducted experiments aimed at minimising this effect to obtain as much of the medium hydrocarbon liquids as possible (Xiong, 2010; Cui *et al.*, 2006; Wang *et al.*, 2005). With slow pyrolysis, as in this case, the evaporation and transport of tar molecules towards the exterior of the coal particle is also slow. When this occurs at slow rates, the role of secondary reactions of the tar compounds becomes critical, which is minimised with faster heating rates (Kristiansen, 1996). As stated, many authors have also found that the tar yield increases to a maximum, where after it starts to decrease as the temperature is increased (Park *et al.*, 1989; Xu & Tomita, 1987b; Scott *et al.*, 1986). These authors stated that peak temperatures for maximum tar formation were found to be in the range of 550 °C and 650 °C. Observing the results of this study, there is no evidence of changes in the tar yields for all coals at temperatures higher than 720 °C. This is therefore an indication that secondary pyrolysis and tar cracking has started to take place. The temperature where maximum tar yield is observed is however dependent on the stability of the tar and the coal rank (Park *et al.*, 1989).

From Figure 5-3b, it can further be seen that no rank dependence was observed in terms of tar yield. Coal A and B are both of similar rank, yet maximum tar yield (air dried basis) was found to be 2.8% and 8.8% respectively, which is the lowest and highest tar yields observed for the range of coals tested in this study. An early study conducted by Xu & Tomita (1987a) showed that a scatter of tar yields existed for coals with a carbon content (dry, ash free) of 75-85wt%, and was explained by the variation in tar aromaticity. Coals higher in aromaticity are reported to form more stable tars (Kristiansen, 1996). As discussed in Section 5.2.2, the total evolved volatiles decrease with an increase in coal rank.

Figure 5-4 shows the distribution of evolved volatiles into two groups: (1) condensable gases (tar), and (2) non-condensable gases at 520 °C, 720 °C and 920 °C. It is clear that coal B, the coal with the highest tar yield, produces results which are significantly different in terms of evolved volatile distribution when compared to the other coals. At 920 °C, the evolved volatiles that condensed were greater than 40wt% for coal B, whereas for the other coals, not more than 25wt% of the total evolved volatiles partitioned into the tar fraction. It is also noted for all coals that the gas weight percentages increase with an increase in temperature. This could possibly be attributed to temperatures exceeding that of maximum tar yield formation, as well as secondary pyrolysis and tar cracking phenomena. Further insight will be provided in the discussion of the tar and gas compositions in Section 5.2.4 and 5.2.5.

Water yield

Figure 5-3c shows a graph of the water produced from the various coals at 520 °C, 720 °C and 920 °C. It can be observed that the water produced (air dried basis by weight) for coals A, B, C, D and E varies respectively between 35.0 - 39.7%, 9.7% – 14.8%, 14.9% – 20.1%, 7.4% - 11.2 %, and 13.1% – 14.5%.

It can be seen that an increase in temperature results in higher water yield. This finding is analogous to similar work done using a modified Fischer Assay setup for temperatures ranging between 450 °C and 750 °C (Kühn, 2015). From this study it is clear that there is no significant difference between the water yields obtained at 720 ° and 920 °C. Kaolinite, which forms a significant part of the mineral matter, undergoes transformation where water and meta-kaolinite is formed. This occurs at temperatures ranging between 450 – 800 °C, which is at temperatures lower than the highest final pyrolysis temperature investigated in this study. As expected the Fischer Assay water yields exceed that of the inherent moisture content of the coals by values ranging between 2 – 10wt%, and more specifically between 6 – 8% at 920 °C.

No definitive conclusion can be made regarding correlations between coal rank and water yield from this study.

Gas yield

Gas is the non-condensable and lower molecular weight fraction of the total evolved volatiles. It was stated earlier that the total evolved volatiles generally increase with an increase in temperature and decrease with an increase in coal rank (Xu & Tomita, 1987b). The same trend can be seen in the gas yield results obtained in this study, i.e. it is evident from Figure 5-4 that the majority of the total evolved volatiles remains in the gas phase and do not condense into liquid products. It is thus noted that an increase in final pyrolysis temperature will yield higher gas yield; in agreement with literature (Yang *et al.*, (2013), Hatting (2012), Xiong *et al.*, (2010), Bisset, (1988) and Xu & Tomita, (1987a).

From Figure 5-3d it is also evident that the coal rank has an effect on gas yield at 520 °C. Coals of lower rank, coals A, B and C, produced gas yields (air dried basis by weight) of 12.9%, 15.1% and 9.7% respectively, which are higher than the gas yields determined for the coals of higher rank, i.e. coal D and E, with gas yields of 5.6% and 6.6% respectively. At temperatures of 720 °C and 920 °C a linear dependency of gas yield on coal rank can however not be observed. Coal B which is low rank coal produced gas yields of 12.1%, 14.4% at 720 °C and 920 °C respectively, which is lower or at least similar in gas generation propensity when compared to that of higher rank coals D and E with respective gas yields of 10.2% and 12.0% and 13.7% and 15.4% for experiments conducted at 720 °C and 920 °C respectively. As with the tar yield obtained, part of this phenomenon can be attributed to the total evolved volatiles partitioning into tar and gas fractions, where it can be seen in Figure 5-4 that at higher temperatures (920 °C) that the evolved volatiles that condense are greater than 40wt% for coal B, whereas for the other coals, not more than 25wt% of the total evolved volatiles partition into the tar fraction. The highest gas yields at 920 °C is observed for coals A and C, i.e. 23.2% and 19.2% respectively and can possibly be attributed to the oxygen content present in the raw coal - coals with oxygen contents of 26.7% and 20.8% respectively reported on a dry, ash-free basis. Oxygen mitigates into CO and CO₂, which are major components of the total gas phase formed, and it has previously been found that at 1037 °C, that 60-80% of original oxygen atoms in coal is found in the gas phase, irrespective of coal rank (Kristiansen, 1996). This will be further elaborated on in Section 5.2.4, where the composition of the pyrolysis gas will be discussed.

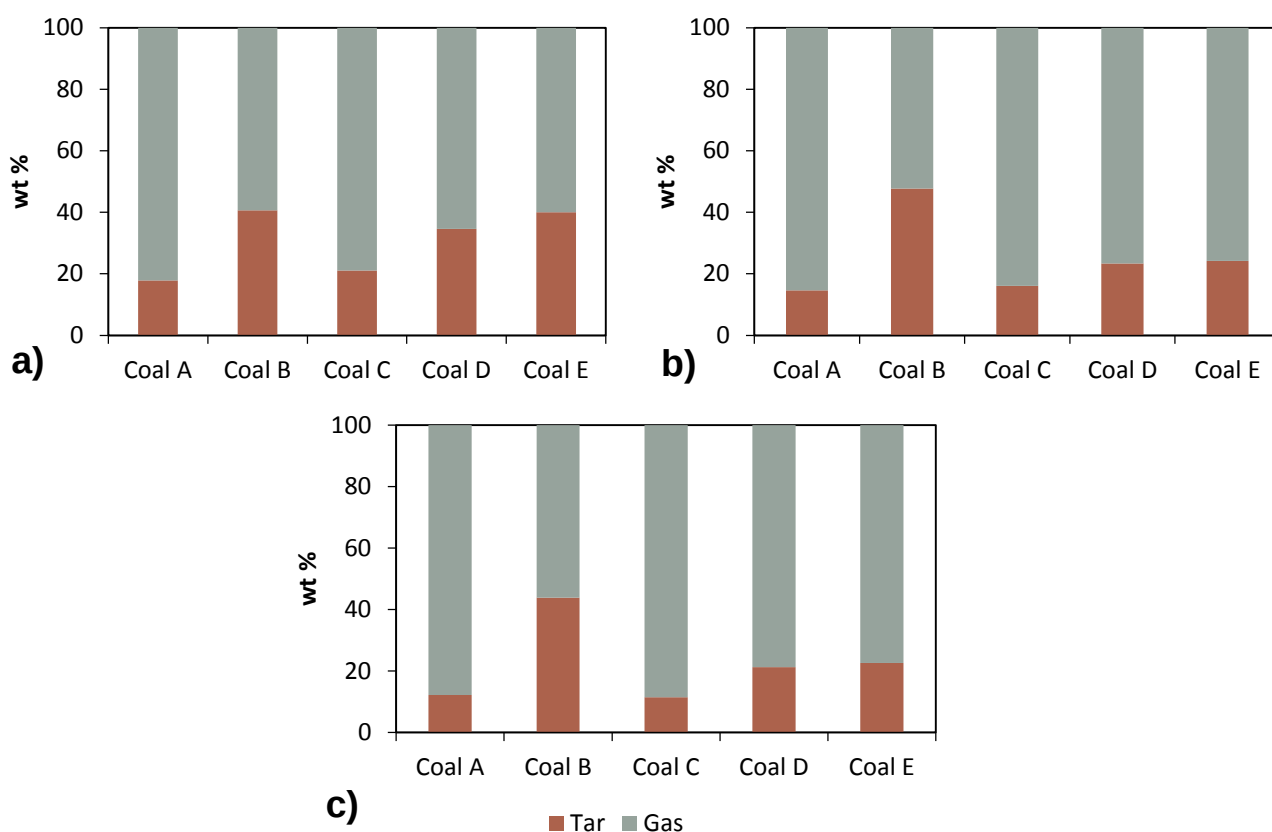


Figure 5-4: Volatile matter release distribution into tar and gas at final pyrolysis temperatures of a) 520 °C, b) 720 °C and c) 920 °C

5.2.3 Char composition

The proximate-and ultimate analysis of the chars derived at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C can be seen in Table 5-2. The volatile matter content of all coals decreased to values below 6wt% (dry, ash free), while the fixed carbon content increased to values above 94wt% (dry, ash free) as the final pyrolysis temperature was increased to 920 °C. For slow heating rates, there is residual volatile matter left in the char when heated to a final pyrolysis temperature of 920 °C, irrespective of coal rank. These residual volatile matter values are however slightly higher when compared to the results of the thermogravimetric analysis (Figure 5-1), and might be attributed to sample mass differences used in the different experimental setups (50 g and 1 g for the Fischer Assay and thermogravimetric analysis respectively). Figure 5-5 shows the percentage of original volatile matter (Table 3-3) present in the raw coal that has been released as a function of temperature. The same trend can be seen for all five coals. An initial increase of between 30 – 37 wt% is observed between 520 °C and 720 °C, whereas the increase between 720 °C and 920 °C (the same temperature increment increase of 200 °C) shows a smaller increase ranging between 10 – 16wt%. It is

clear that between 74 – 85wt% of the volatile matter present in the raw coals are released at 720 °C, with no real rank dependencies observed.

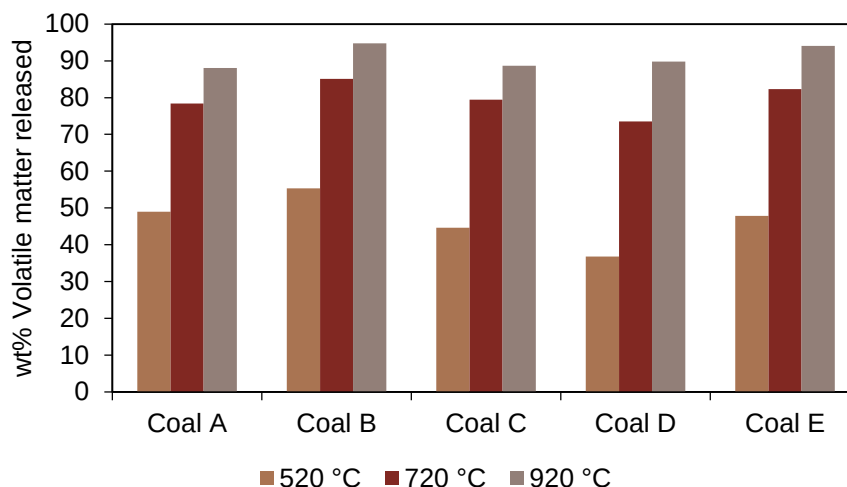


Figure 5-5: Percentage of volatile matter as determined by proximate analysis released at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

Elemental composition, reactivity and the internal surface are largely affected by pyrolysis conditions (Kristiansen, 1996). The effect of temperature on the char elemental composition can be observed in Table 5-2. It can firstly be seen that the carbon contents (dry, ash free) are increased to values greater than 95wt% at 920 °C, which corresponds well with the observed fixed carbon content as determined by the proximate analysis. An initial increase in carbon content of between 7.5 – 10.7wt% is observed between 520 °C and 720 °C, whereas the increase between 720 °C and 920 °C (the same temperature increment increase of 200 °C) shows smaller increases in carbon content ranging between 3.0 – 4.3wt%. This is consistent with the dominant release of volatile matter released at temperatures below 920 °C at slow heating rates, and in agreement with the observations made by various authors (Roets *et al.*, 2014; Bai *et al.*, 2010; Chen *et al.*, 1999). It can further be seen in Table 5-2 that the oxygen and hydrogen values of the chars decreased with an increase in temperature. The decrease in oxygen and hydrogen content is mainly attributed to oxygen containing gases (CO and CO₂) and C₁-C₃ hydrocarbon gases respectively (Kristiansen, 1996). A further discussion on oxygen containing gases and hydrocarbon gases will be given in Section 5.2.4.

A reduction in char-N can only be seen for coal B and D, where nitrogen values (dry, ash free) decreased from 1.8 to 1.0wt% and 2.0 to 2.1wt% (not significant) respectively. The reduction in char-N in coal D can possibly be attributed to the calcite and dolomite content in the raw coal (see Table 3-5 in Section 3.3.1). Calcite and dolomite decomposes into CaO, which in turn reacts with heterocyclic forms of nitrogen in the char to form CaC_xN_y and CaO_xC_yN_z, and

undergoes further reactions to form N_2 (Tsubouchi & Ohstuka, 2002a; Tsubouchi & Ohtsuka, 2002b). The reduction in nitrogen content of the chars observed for coal B was however not expected due to non-detectable calcite, dolomite or alkali metals, i.e. Sr and Ba that could possibly affect N_2 production at temperatures below 920 °C (Tsubouchi *et al.*, 2004). More discussion regarding the elemental partitioning will be given in Section 5.2.6.

Table 5-3 shows the CO_2 adsorption results for chars formed at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C, and addresses the effects of final pyrolysis temperature on internal surface area. The repeatability was calculated at a 95% confidence interval and was calculated to be 2.5%, 2.8% and 7.8% for the BET surface area, Langmuir surface area, and Dubinin-Radushkevich surface area respectively for raw coals. For chars at high temperatures these respective errors have been calculated as 0.6%, 0.7% and 4.3% (refer to Appendix A-1 for error calculations and to Appendix B-6 for details of the duplicate CO_2 adsorption results). It can be seen from Table 5-3 that there is an initial increase in the micropore surface area development from the raw coal values to 520 °C. The same trend can be seen for all coals between 520 °C and 720 °C, but is not observed for a change in micropore surface area between 720 °C and 920 °C. Between 720 °C and 920 °C the surface area either increased by a marginal amount, or it decreased slightly. The large initial increase in surface area, and smaller increases thereafter are directly linked to the volatile matter release during heating, and are attributed to inaccessible pores' volatile matter release (Kristiansen, 1996). It was seen from the results of volatile matter release that the majority of volatile matter release occurred up to a final pyrolysis temperature of 720 °C.

Table 5-2: Proximate- and ultimate analysis of five partially devolatilised coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

Coal A				Coal B			Coal C			Coal D			Coal E		
520 °C	720 °C	920 °C		520 °C	720 °C	920 °C	520 °C	720 °C	920 °C	520 °C	720 °C	920 °C	520 °C	720 °C	920 °C
Proximate analysis (dry basis), wt%															
Ash	12.0	15.7	16.5	35.0	38.6	40.3	14.0	16.0	17.2	35.4	39.4	41.3	20.0	22.3	22.7
Volatile matter	20.8	8.4	4.6	13.3	4.1	1.4	17.7	6.5	3.5	14.9	5.9	2.2	14.8	4.9	1.6
Fixed carbon	67.2	75.9	78.9	51.7	57.3	58.3	68.3	77.5	79.3	49.7	54.7	56.5	65.2	72.8	75.7
Proximate analysis (dry, ash free basis), wt%															
Volatile matter	23.6	10.0	5.5	20.5	6.7	2.3	20.6	7.7	4.2	23.1	9.7	3.7	18.5	6.3	2.1
Fixed carbon	76.4	90.0	94.5	79.5	93.3	97.7	79.4	92.3	95.8	76.9	90.3	96.3	81.5	93.7	97.9
Ultimate analysis (dry, ash free basis), wt%															
Carbon	83.4	93.0	96.7	83.1	92.2	95.4	85.1	92.6	97.0	82.1	92.8	97.1	83.6	92.3	95.3
Hydrogen	3.2	1.7	0.4	3.6	1.8	0.2	3.1	1.7	0.2	3.1	1.4	0.2	3.3	1.6	0.3
Nitrogen	1.3	1.2	1.1	2.3	1.7	1.0	1.0	1.1	0.9	2.3	2.0	1.2	1.5	1.4	1.2
Sulphur	1.0	1.6	1.7	0.9	0.9	0.9	0.4	0.5	1.3	1.4	1.6	2.2	0.9	0.9	0.8
Oxygen (by difference)	11.1	2.6	0.1	10.1	3.4	2.5	10.4	4.0	0.6	11.0	2.2	-0.8	10.7	3.9	2.5

Table 5-3: CO₂ adsorption results for chars formed at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

BET Surface Area (m²/g)			
Sample	Char at 520 °C	Char at 720 °C	Char at 920 °C
Coal A	179	235	256
Coal B	105	142	261
Coal C	148	212	239
Coal D	99	141	147
Coal E	115	183	186
Langmuir Surface Area (m²/g)			
Sample	Char at 520 °C	Char at 720 °C	Char at 920 °C
Coal A	188	246	270
Coal B	111	150	276
Coal C	156	221	252
Coal D	105	149	155
Coal E	122	192	196
Dubinín-Radushkevich Surface Area (m²/g)			
Sample	Char at 520 °C	Char at 720 °C	Char at 920 °C
Coal A	249	285	222
Coal B	165	226	418
Coal C	222	299	374
Coal D	155	223	230
Coal E	181	303	298

5.2.4 Gas composition

The gas composition was determined using a quantitative gas chromatograph (GC) as explained in Section 4.4.3. Molar compositions, as determined by the GC analysis, were used to calculate the gas yields of the major gas species (CO, CO₂, CH₄ and H₂) from the gas yields reported in Section 5.2.2. The gas yields are reported in Figure 5-6 as Nm³/kg coal (dry, ash free) on a N₂, Ar and O₂ free basis (individual gas species yields can be seen in Appendix B-7). In order to make an accurate comparison, the gas yield was determined as volume formed per kilogram of dry, ash free coal. As explained earlier in Section 5.2.2 the gas yields at 520 °C were higher for the low rank coals when compared to the higher ranked coals. No other total gas formation dependencies on coal rank were observed. It is however clear from Figure 5-6 that the composition of the major gas species evolved from the five coals differ significantly.

Similar temperature profiles can be seen for the evolution of the CO, CO₂, CH₄ and H₂ gas species, irrespective of coal rank. This is consistent with a study done by Xu & Tomita, (1987b) where lignites, high and low volatile bituminous coals were studied.

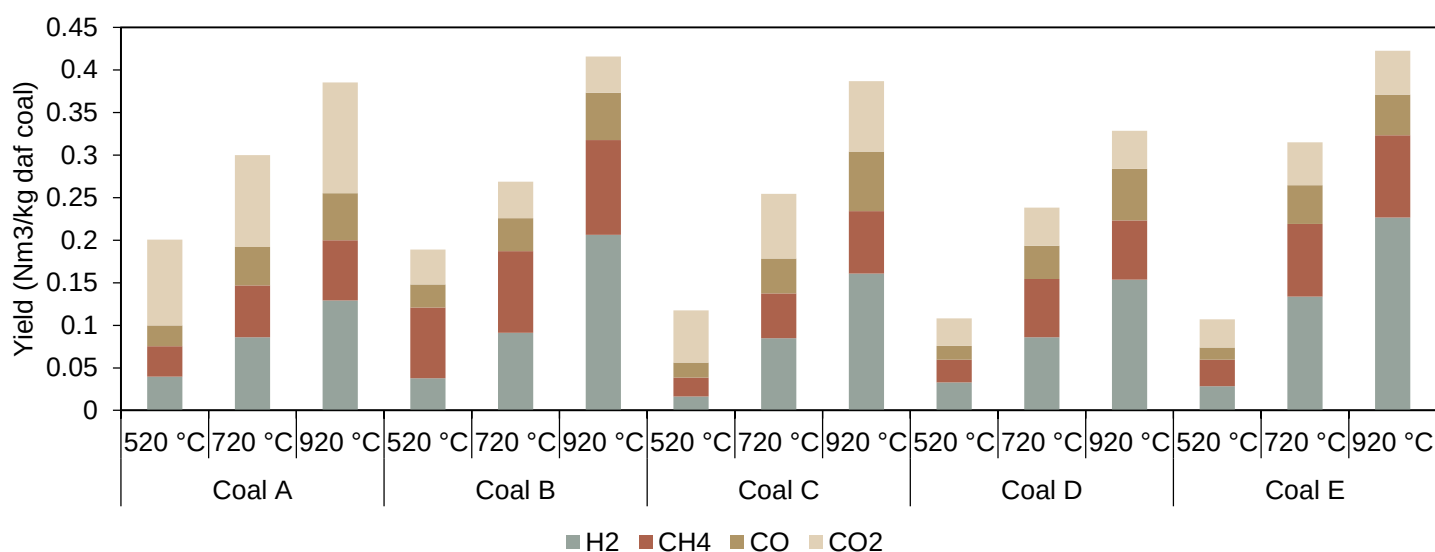


Figure 5-6: Gas yields of H₂, CH₄, CO and CO₂ of five coals at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

In this study it is observed that the H₂ yield increases by 80 - 100% between 520 °C and 720 °C, where after another increase of around 80 - 100% is observed between 720 °C and 920 °C for all coals, irrespective of coal rank. It is known that high temperatures are needed for the dehydration reaction of the aromatic cluster (Kristiansen, 1996), which explains why such a large increase in the H₂ content in the gas phase was seen at the high temperatures. It is also reported that for a large variety of temperatures that the H₂ formation is attributed to hydrogen sources and C-H breaking (Wiktororsson & Wanzl, 2000). In this study, no rank dependence was observed with respect to hydrogen evolution; i.e. coal B, (lignite) and coal E, (subbituminous coal) showed the highest H₂ yields respectively at 920 °C of 2.1×10^{-3} Nm³/kg daf coal and 2.3×10^{-3} Nm³/kg daf coal respectively. The rank independence of H₂ yield is confirmed by an earlier study conducted to study the effect of coal rank on pyrolysis products (Xu & Tomita, 1987b).

For the formation of CH₄ it is observed that an initial increase in CH₄ yield occurs up to 720 °C, where after the yield increases by only a much smaller amount for all coals tested. This could be attributed to the knowledge of CH₄ formation during pyrolysis which occurs in two stages. At lower temperatures methane forms due to the decomposition of methyl groups, and at higher temperatures CH₄ forms due to the decomposition of methylene bridges (Xu & Tomita, 1987b). It is therefore evident that the decomposition of methyl groups contributes to

the majority of CH₄ formation. Coals B, C, D and E are coals with similar carbon and hydrogen contents (elements that make up CH₄), but large differences in the CH₄ was seen between these coals, with coal B showing the highest CH₄ yield of $1.1 \times 10^{-2} \text{ Nm}^3/\text{kg daf coal}$ at 920 °C. No real dependencies on coal rank or carbon content in coal could be made from the CH₄ yields, as was also the case reported by Xu & Tomita, (1987a). A possible effect on the CH₄ yield could be the minerals present in the original coal as confirmed by Roets, (2014), who conducted a study to determine the effects of minerals (calcite, dolomite, pyrite, kaolinite and quartz) on pyrolysis product yield, where it was found that at 920 °C that all of the mentioned minerals had a decreasing effect on the CH₄ yield.

From Figure 5-6 it can be seen that the oxygen containing gases (CO and CO₂) correlate well with the original oxygen content in the coal – coals with higher oxygen content showed the highest combined CO and CO₂ yield. This finding is in agreement with literature which states that lignites produce more oxygen containing compounds, whereas higher rank coals produce more hydrocarbon compounds (Xiong *et al.*, 2010; Kristiansen, 1996). The CO yields follow similar temperature trends as observed for H₂ and CH₄, where the yields increase with an increase in temperature and is attributed to the structure of coal (Kristiansen, 1996). It can however be seen that the yields of CO₂ did not increase as significantly as seen for CO; CO formation occurs at higher temperatures than that of CO₂. CO formation was prominent in all coals throughout the entire temperature profile and can be explained by the various routes to CO formation. CO formation occurs by the decomposition of phenolic hydroxyl groups at temperatures lower than 700 °C, the break of oxygen heterocycles at temperatures higher than 500 °C and lastly by the reaction between CO₂ and C at temperatures higher than 650 °C (Wang *et al.*, 2005; Zhu *et al.*, 1998). CO₂ formation occurs by the decomposition of carboxyl groups at lower temperatures (Kristiansen, 1996). It was thus expected that CO₂ yields at 920 °C do not exceed the values obtained at 720 °C by much, irrespective of coal rank.

5.2.5 Tar composition

Elemental analysis

Tars obtained at 920°C were characterised in order to determine the elemental composition as stipulated in Section 4.4.2, and the results are presented in Table 5-4. It can firstly be seen that the carbon content of coal tar A (69.1 wt%) differs significantly from that of coal tars B, C, D and E, which ranges between 76.0 – 78.5wt%. This correlates to the original carbon content in the respective coals; i.e. the carbon content in coal tar increased with an increase in the carbon content of the original coal from which the respective tar is derived from. Carbon

contents in the original coals are ranked as follows :coal A < coal C < coal B < coal D < coal E, whereas the carbon content in derived tars formed at a pyrolysis temperature of 920 °C are ranked as follows : coal A < coal B < coal C < coal D < coal E. The ranking order is very similar, except for a difference in order of coal B and coal C, but this is likely only due to carbon content values being very close to one other. An identical trend can be seen for the oxygen content in the derived tars at 920 °C. Oxygen contents in the original coal are ranked as follows: coal A < coal C < coal B < coal D < coal E, whereas the oxygen content in tars formed at a pyrolysis temperature of 920 °C are ranked as follows: coal A < coal C < coal B < coal D < coal E. Coals of lower rank therefore form tars that are more oxygen rich than coals of higher rank, as seen by the gas yield results, where lower rank coals formed more oxygen gas species than higher ranked coals. It is further observed that the H/C ratio correlates with the vitrinite content in the original coal. Coals with high vitrinite/huminite contents (75.2 vol% and 69.6 vol% for coal A and coal B respectively) showed the highest H/C values in the derived tar (0.85 and 0.96 for coal A and coal B respectively). Coals with lower vitrinite contents (49.2 vol%, 53.2 vol% and 40.0 vol% for coals C, D and E respectively) showed lower H/C values in the derived tar (0.72, 0.76 and 0.78 for coal C, D and E respectively). This trend was also observed by a study done by Xie *et al.*, (2015), where they investigated the effect of maceral contents on physical and chemical changes as coal is heated. The H/C ratio is also an indication of tar aromaticity, where higher H/C ratio's indicate lower aromaticity (Marcano *et al.*, 2011; Ancheyta *et al.*, 2002). Tars derived from coal C, D and E are thus more aromatic than the tars derived from coal A and B.

Table 5-4: Elemental analysis of tar formed at 920 °C as the final pyrolysis temperature

	Coal A	Coal B	Coal C	Coal D	Coal E
Carbon*	69.1	76.0	76.7	77.3	78.5
Hydrogen*	4.9	6.1	4.6	4.9	5.1
Nitrogen *	1.0	1.8	0.8	2.0	1.3
Sulphur *	0.8	0.8	0.3	1.4	0.9
Oxygen *	24.1	15.3	17.6	14.4	14.3
Atomic H/C ratio	0.85	0.96	0.72	0.76	0.78

*Values are presented as weight percentage on a dry, ash free basis

Size exclusion chromatography

The SEC-UV curves of the tars formed at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C can be seen in Figure 5-7. The peak observed at low elution times (11 – 15 min) is called the excluded peak and is indicative of heavy components (large molecular weight) excluded from the column porosity. After the first peak a valley can be observed and is consistent with previous work (Trejo *et al.*, 2007). This valley is an indication of the formation

of a 3-dimensional structure due to a change in molecular structure. Significantly different material is therefore represented by the retained bimodal peak (15 – 25 min) following the valley (Trejo *et al.*, 2007). From Figure 5-7 definitive conclusions or trends on the heaviness of coal tars cannot easily be determined, although some small differences in maximum elution times are seen. Weight averaged molecular weights were therefore calculated using these chromatograms and the results are presented in Table 5-5. It should be noted that these values are not absolute due to the link made with a calibration curve created using polystyrene standards as explained in Section 4.4.2. It was found that the molecular weight distribution of the derived tars ranges between 200 – 4000 Da for all coals at all temperatures, which is consistent with similar work done by (Suuberg *et al.*, 1985). Weight averaged molecular weights were calculated using the elution time, where a maximum relative intensity was observed due to the normal distribution nature of the curves. The results (212- 415 Da) compared well with a previous study where similar heating rates and temperatures were used to generate coal derived tars (Roets, 2014).

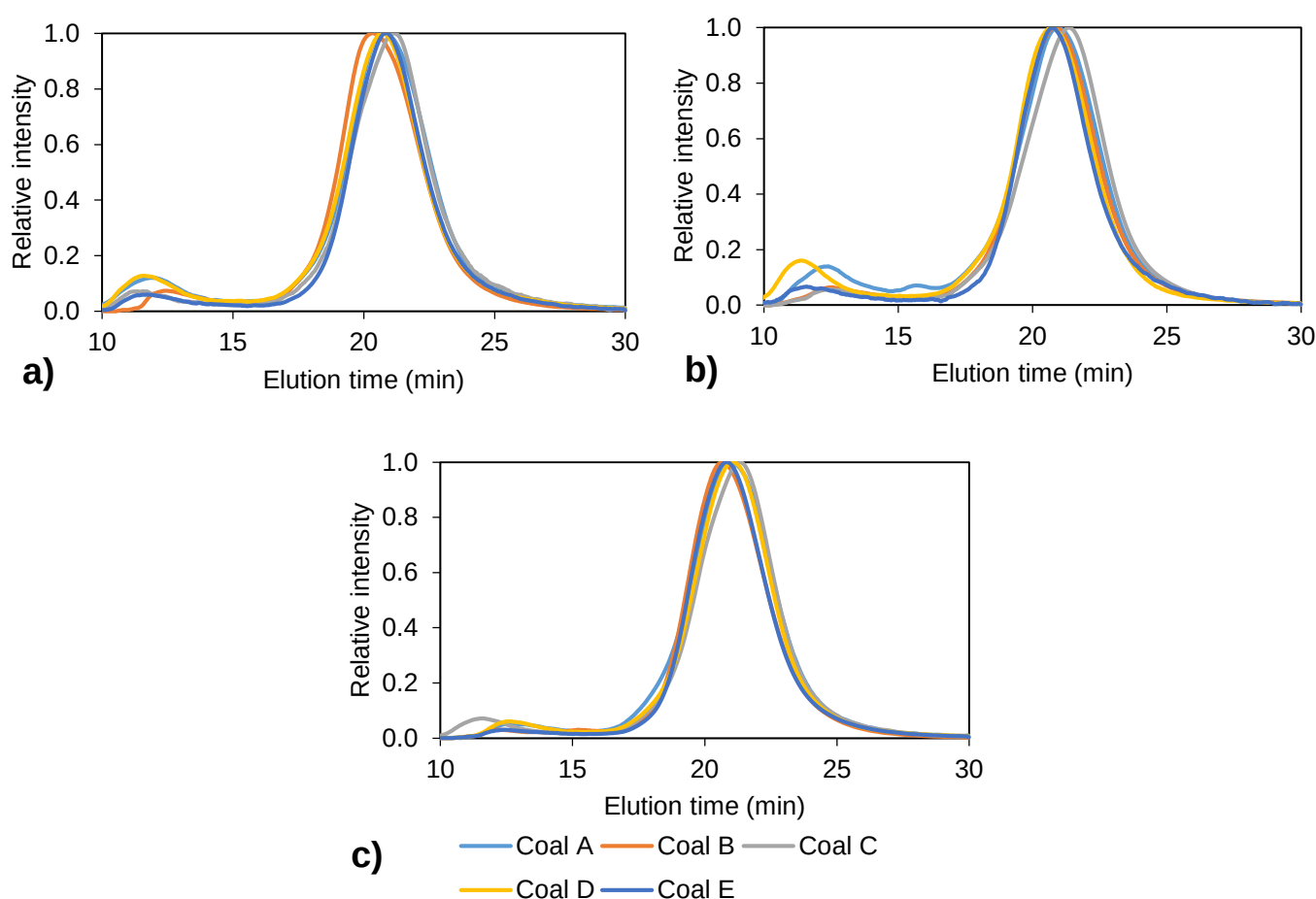


Figure 5-7: Size exclusion chromatography of tars formed at a) 520 °C, b) 720 °C and c) 920 °C

From Table 5-5 it can be seen for coal tars A, C and D that the molecular weight decreases from 520 °C to 720 °C, and stays relatively constant between 720 °C and 920 °C. This can possibly be attributed to tar cracking and secondary pyrolysis reactions occurring whereby aliphatic attachments are decreased, and is analogous to results obtained in a previous study conducted by (Roets, 2014). The low molecular weight of derived tar at 520 °C for coal B (212 Da) could be explained by high cross-linking which needs higher temperatures to break the bonds to form large tar fragments (Suuberg & Unger, 1987). This possibly explains why a large increase in molecular weight for coal tar B was observed at the higher pyrolysis temperatures. Cross-linking is known to affect the average molecular weight of coal derived tars, which in turn is affected by an array of parameters: low or high volatile coal, aliphatic attachments, number of oxygen containing functional groups and even catalytic effects of minerals such as calcium (Zeng *et al.*, 2011; Smith *et al.*, 1994; Suuberg *et al.*, 1985). Roets, (2014) also confirmed that calcite and dolomite in the parent coal affected the average molecular weights of tars. No conclusion on the rank dependence on the molecular weight of the derived tars can therefore be made from this study, yet it is not surprising that contradictions in literature are found: i.e. FTIR (Fourier transform infrared) studies found that low rank coals produce tar with higher molecular weights than higher ranked coals (Freihaut & Proscia, 1989), and MS (mass spectrometry) studies found the opposite (Solomon *et al.*, 1990b).

Table 5-5: Molecular weight estimates from SEC data for tars created at final pyrolysis temperatures of 520 °C, 720 °C and 920 °C

	Coal A	Coal B	Coal C	Coal D	Coal E
Average molecular weight, Da, 520 °C	391	212	318	415	362
Average molecular weight, Da, 720 °C	355	364	289	399	373
Average molecular weight, Da, 920 °C	355	399	292	376	373

Gas chromatography – mass spectrometry (GC-MS)

The complex composition of coal tar can be determined most effectively by GC-MS (Jiang *et al.*, 2007) and several authors have identified as many as 129 – 160 different compounds in the volatile tar region (Zhu *et al.*, 2015; Nguyen *et al.*, 2015; Jiang *et al.*, 2007). A limitation of the GC-MS analysis is that it cannot detect the high boiling point components which are hard to volatilise, thus it is limited to compounds with a boiling point lower than 300 °C (Wang *et al.*, 2013).

Pyrolysis tar can consist of over a hundred compounds, and can therefore be extremely difficult to quantify (Nguyen *et al.*, 2015). The results shown in Table 5-6 are therefore qualitative in nature and are discussed here in order to compare the coal derived tars produced

from coals of different rank in terms of general product classifications. Original gas chromatograms of all the coal tars produced at 520 °C, 720 °C and 920 °C can be seen in Appendix B-8. Small variances are observed for tars formed at the different temperatures, and these small changes are attributed to secondary reactions as found by various authors (Roets, 2014; Wang *et al.*, 2013; Casal *et al.*, 2008), and higher naphthalene contents of up to 10% have been observed for tars derived at elevated temperatures (Jiang *et al.*, 2007).

Table 5-6: Summary of GC-MS results of five coals

Product classification	Coal A	Coal B	Coal C	Coal D	Coal E
Alkyl benzenes	++	++	++	+	++
Phenol	+	+	++	++	++
Cresol and paracresol	+++	+	+++	++	+++
Furans (benzofuran, hudrobenzofuran, methyl benzofuran and dibenzofuran)	+	+	++	++	++
Alkanes (C ₁₆ -C ₃₅)	+	+++	+++	++	+
PAH (polyaromatic hydrocarbons)	+	++	+++	+++	+++
Long chain alcohols	+	+	++	-	+

+ - content of family classification taken as reference,
 ++ - more content of family classification compared to +,
 +++ - more content of family classification compared to ++

It is observed from Table 5-6 that coal tar D, derived from the coal of highest rank, produced the least amount of alkyl benzenes, although all tars contained a small amount of alkyl benzenes. The largest chemical families were found to be phenols, cresols and paracresols as well as PAH (polycyclic aromatic hydrocarbon) components for all coal derived tars. This is consistent with reported literature where it was found that for a Chinese bituminous coal that 55 – 70% of the tar components formed at a final pyrolysis temperature of 750 °C are made up of phenols and alkyl substituted homologs from C₁ to C₃ (Luo *et al.*, 2016). A large amount of phenols were also observed for lower rank coals, which correlates with similar results found for brown coals (Nguyen *et al.*, 2015). Large amounts of cresol and paracresol as well as PAH compounds were observed in all coal tars from this study and are consistent with results found by Jiang *et al.*, (2007), where the GC-MS analysis was critically evaluated for tars produced from coal pyrolysis. Of the PAH components, naphthalene and methyl naphthalene were

detected for all coal tars, azulene was detected for tar A and E, phenanthrene and methyl pyrene was also detected for tar C.

From Table 5-6, it appears as if tars derived from higher rank coals form more phenolic compounds and a similar trend is seen for furans, but no rank dependence is apparent for cresol and paracresol and long chain alcohols. Differences may be due to catalytic effects of minerals as found by (Roets, 2014) and the complexity of the tar forming reactions (Nguyen *et al.*, 2015).

Simulated distillation (Simdis)

Species found in the coal derived tars were placed into boiling point (bp) range categories as explained in Section 4.2.2, and results can be seen in Table 5-7. The following boiling point fractions were used: heavy naphthas (bp < 205 °C), kerosene (205 °C < bp < 260 °C), diesel (260 °C < bp < 340 °C), gas oil (340 °C – 425 °C) and residue fraction (425 °C < bp < 450 °C). It can be observed from Table 5-7 that the analysed tar fraction, i.e. fraction with boiling point < 450 °C increases with an increase in pyrolysis temperature and supports the results of the SEC-UV, which also showed that an increase in temperature yielded lower tar average molecular weights. Analysed tar fractions in this study ranged between 39 – 72wt% and diesel, gas oil and residue fractions contribute to the majority of the analysed fraction, meaning that the majority of the tar has a boiling point higher than 260 °C. Similar trends were also observed in a study done for coal derived tar formed at elevated pressures (30 bar), although even higher values were found for the fraction with a boiling point higher than 260 °C (Fidalgo *et al.*, 2014). For similar pyrolysis experiments with slow heating rates, more comparable values are found, where naphthas were also found to be in the range of 8 – 15wt% (Roets *et al.*, 2014). From the results given in Table 5-7 it can be seen that kerosene and gas oil fractions are relatively similar in all coal tars. Larger differences are seen in the lower boiling point fractions i.e. heavy naphthalene and in the highest boiling point products (gas oil and residue fractions). Tars derived from coals B and E showed the lowest values of heavy naphthalene (10 – 14 wt%), whereas tars derived from coals A and C showed the lowest values of tar residue fraction (10 – 16wt%). A rank dependence was therefore not found for the tar fractions in this study. In a study by Li *et al* (2016) it was reported that an increase in heavy component fraction was observed with an increase in temperature, as also seen in this study, i.e. residue fraction. Another reason for not seeing a rank dependence could be attributed to catalytic effects of minerals as found by Roets *et al.*, (2014).

Table 5-7: Simdis results of tars formed at final pyrolysis product temperatures of 520 °C, 720 °C and 920 °C

Temperature (°C)	Coal A			Coal B			Coal C			Coal D			Coal E		
	520	720	920	520	720	920	520	720	920	520	720	920	520	720	920
Heavy Naphtha	22	39	26	17	15	14	30	19	21	26	14	38	18	14	19
Kerosene	18	14	18	13	14	15	16	16	17	16	14	11	14	12	15
Diesel	24	20	23	26	24	27	24	25	25	24	24	16	24	24	25
Gas Oil	20	16	19	28	28	27	20	26	25	22	29	19	25	28	25
Residue	16	11	13	17	20	18	10	14	12	12	19	16	18	21	17

5.2.6 Elemental partitioning

This section of the dissertation deals with the elemental partitioning of elemental carbon, hydrogen, oxygen, nitrogen and sulphur, and the use of a closed mass balance on all the pyrolysis products (char, tar, gas and water). The pyrolysis product yields were used together with the elemental composition of the char and tar as well as the gas composition in order to close the balance. A comparison of the original contents of the different elements in the raw coal was then done and is presented in Table 5-8 and Figure 5-8. A basis of 100 g raw coal (dry basis) was used. Absolute errors (mass of element in products compared to mass of element in raw coal) can also be seen in this Table, and it was found that the absolute errors were smaller than 10% for carbon, oxygen and hydrogen. No errors were calculated for nitrogen and sulphur, because the mass of the respective elements partitioned into gas was calculated by difference. The reason for this is that no detection of nitrogen and sulphur containing gases were done when the pyrolysis gas was analysed using the gas chromatograph.

From Table 5-8 it can be observed that the amount of carbon in the char correlates well with the carbon content of the original coal. Coals with more carbon in the original coal also contain more carbon in the char, which was also found to be rank dependent; i.e. chars derived from higher rank coals (coal C, D and E) contain more carbon than for chars derived from lower rank coals (coals A and B). From Figure 5-8a it can also be seen that the partitioning of elemental carbon into char is rank dependent and coal structure related. The lower rank coals (coal A and B) showed the lowest values of carbon partitioning into char (71% and 73% respectively) compared to that of coal C, D and E (80%, 80% and 79%) respectively. Observing the tar and gas, it is observed that coal B is the only coal which partitions more carbon into the tar fraction (8.31 g) than into the gas phase (5.82 g). It is observed that for all the other coals that the gas contains more carbon than the tar fraction (more than 100 wt% than observed in the tar). This correlates well with what was observed with the tar yield as

discussed in Section 5.2.2, where it was shown that coal B yields the highest tar fraction (8.8 wt% at 920 °C) of all coals evaluated in this study, i.e. 2.4, 2.5, 3.2 and 4.5 wt% tar yield for coals A, C, D and E respectively.

When observing the elemental hydrogen balance it can be seen from Table 5-8 and Figure 5-8b that the majority of the hydrogen present in the original coal was released into the tar, gas and water fractions, and hydrogen partitioning into the char was found to be less than 4wt%. Hydrogen present in tar and gas follow the same trend as observed for elemental carbon, i.e significantly larger amounts of hydrogen partitioned into the tar fraction (27.4%) for coal B, whereas it was seen for coals A, C, D and E that hydrogen values of 7.3, 7.5, 9.5 and 10.8% respectively partitioned into the tar. This also correlates well with the high tar yield observed for coal B. Similar observations were made for elemental oxygen where it can be seen from Table 5-8 and Figure 5-8c that, for coal B, oxygen partitioned into the tar (3.4%) is higher than that of coals A, C, D and E (1.1, 7.5, 1.7 and 1.9% respectively). Elemental oxygen contained in the char was calculated as less than 6% of the oxygen contained in the original coal, which means that the majority of oxygen went into the tar, gas and water fractions during pyrolysis. Finally, it is known that coals of lower rank will produce more oxygen containing gaseous products than those for coals of higher rank, and that coals of higher rank will produce more hydrocarbon gases than lower rank coals (Kristiansen, 1996). Results discussed in Section 5.2.4 supports this literature, but from the results given in Figure 5-8, it can be seen that this fact does not relate to the elemental partitioning of hydrogen and oxygen into gas, due to no rank dependencies observed in this study.

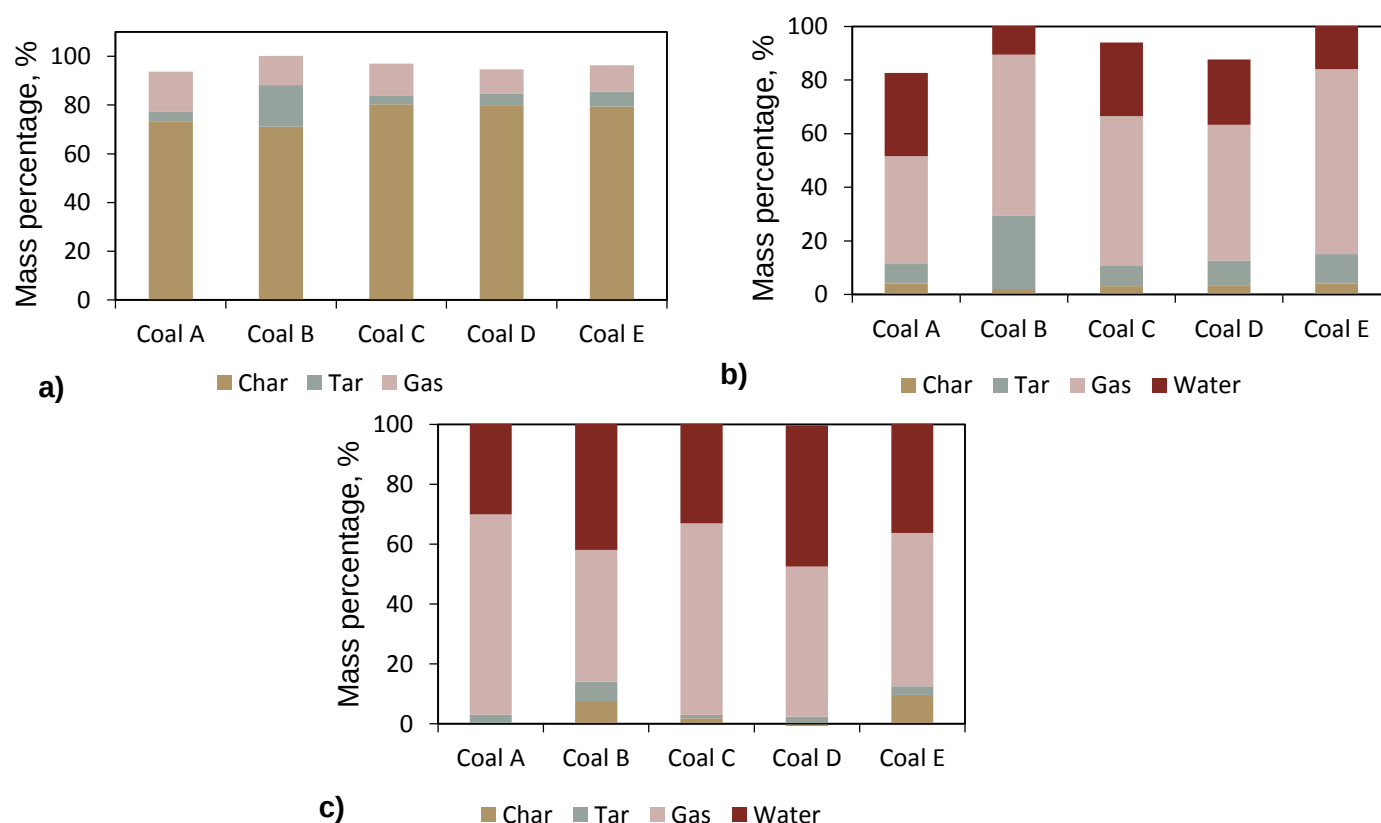


Figure 5-8: Elemental partitioning into char, tar, water and gas (dry basis) of a) carbon, b) hydrogen and c) oxygen

Table 5-8: Mass balance on elemental carbon, hydrogen, oxygen, nitrogen and sulphur. Done on pyrolysis products at 920 °C

		% in dry coal (db)	% in pyrolysis products				Error %
			Char	Tar	Gas	Water product	
Carbon	Coal A	42.13	30.89	1.70	6.88	-	6.3
	Coal B	48.59	34.53	8.31	5.82	-	0.1
	Coal C	56.66	45.53	2.05	7.34	-	3.1
	Coal D	50.45	40.19	2.61	4.96	-	5.3
	Coal E	59.60	47.30	3.69	6.45	-	3.6
Hydrogen	Coal A	3.03	0.12	0.22	1.22	4.32	8.2
	Coal B	3.34	0.07	0.92	2.00	1.66	8.2
	Coal C	3.00	0.09	0.23	1.68	2.26	4.0
	Coal D	2.76	0.09	0.26	1.40	1.26	10.2
	Coal E	3.36	0.14	0.37	2.32	1.62	6.3
Oxygen	Coal A	16.90	0.05	0.47	11.30	34.18	5.5
	Coal B	11.80	0.91	0.75	5.20	13.12	3.3
	Coal C	15.90	0.30	0.19	10.17	17.88	4.7
	Coal D	11.30	-0.34	0.28	5.67	9.94	2.3
	Coal E	12.90	1.24	0.37	6.61	12.80	8.5
Nitrogen	Coal A	0.65	0.34	0.17	0.14*	-	-
	Coal B	1.17	0.37	0.11	0.69*	-	-
	Coal C	0.63	0.41	0.02	0.20*	-	-
	Coal D	1.29	0.51	0.05	0.73*	-	-
	Coal E	0.99	0.58	0.04	0.38*	-	-
Sulphur	Coal A	0.58	0.53	0.14	-0.09*	-	-
	Coal B	0.61	0.34	0.11	0.16*	-	-
	Coal C	0.33	0.59	0.02	-0.27*	-	-
	Coal D	1.09	0.93	0.04	0.12*	-	-
	Coal E	0.75	0.37	0.04	0.34*	-	-

* determined by difference

5.3 Application of FLASHCHAIN®

FLASHCHAIN® pyrolysis modelling was conducted using the software package PC Coal Lab® provided by Niksa Energy Associates LLC (NEA, 2014). FLASHCHAIN® predictions were done in order to acquire an understanding of the pyrolysis products based on the proximate and ultimate analysis, in order to assess which coals are suitable in fixed bed gasification and chemicals production. The proximate- and ultimate analysis together with process conditions used during Fischer Assay experimentation were used as input to the model in order to predict the pyrolysis product yields and compositions as explained in Section 4.6.1, and will be discussed in the following sections.

5.3.1 Pyrolysis product yields

The pyrolysis product yields of all five coals undergoing pyrolysis to final temperatures of 520 °C, 720 °C and 920 °C was predicted using FLASHCHAIN®. Predicted versus experimental product yields of all five coals at the three temperatures studied can be seen in Figure 5-9. It is clear that a very good correlation was found for the char yield (Figure 5-9a) with a correlation coefficient (R^2) of 0.94 and an average error of 5%. Relatively good predictions are also observed (Figure 5-9 b and c) for the tar and water yield (R^2 values of 0.76 and 0.83) respectively, but the y-intercepts for both the tar and water yields were observed to be 4.3 wt% and 5.1 wt% respectively. This means that predicted values were higher than experimentally determined values. Average errors for tar and water were calculated as 64% and 4% respectively. This means that the water, together with the char was well predicted. Finally, it can be seen from Figure 5-9d that no correlation exists between the predicted and experimental results of the gas yields. It was also found that the average error of the predicted gas yields is 20%. FLASHCHAIN® therefore proves to be a relatively good early indicator of the pyrolysis product char yield and to some extent the yield of water when coal undergoes slow pyrolysis (8 °C/min). Further FLASHCHAIN® predictions for the char, tar and gas compositions will be discussed in Sections 5.3.2, 5.3.3 and 5.3.4.

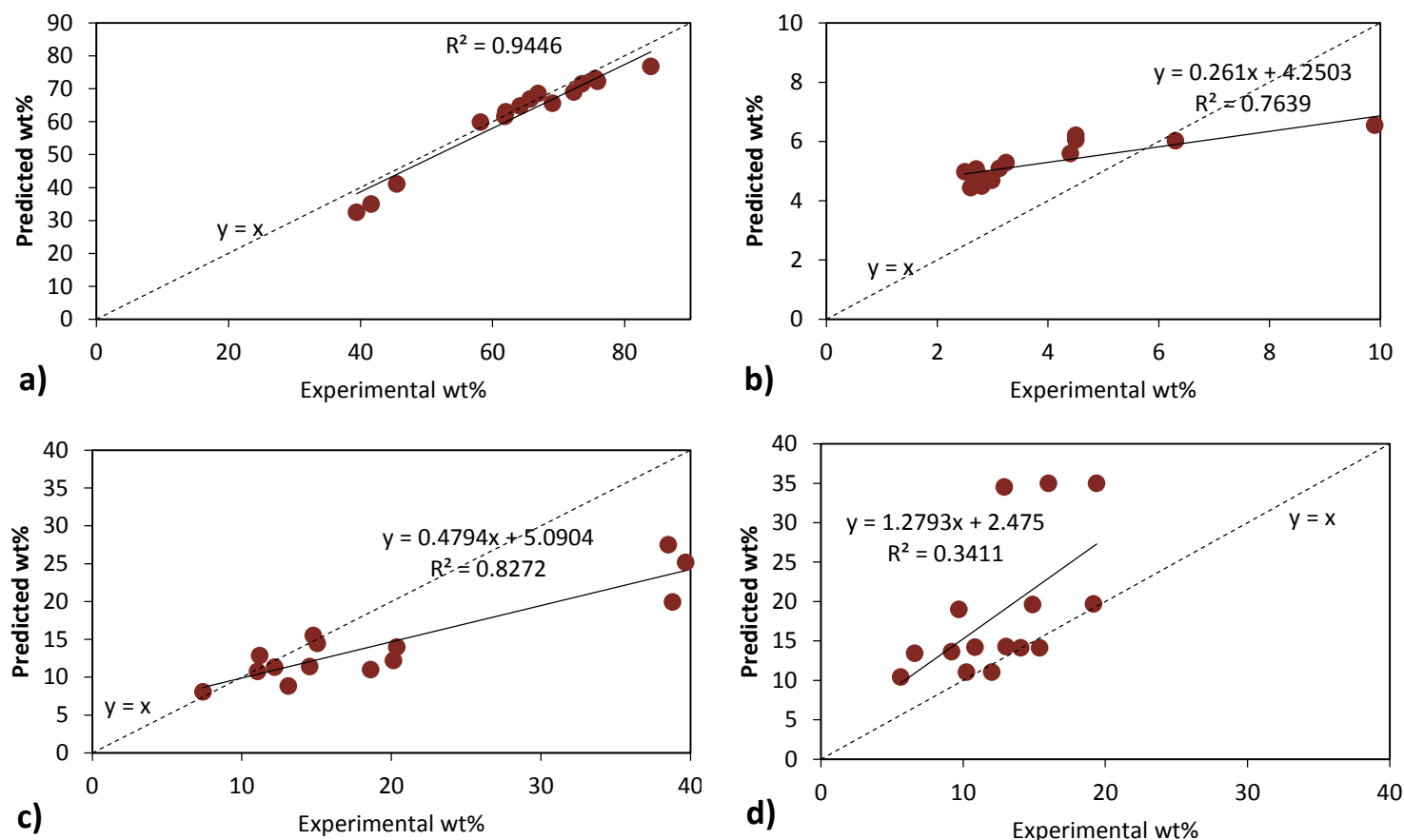


Figure 5-9: FLASHCHAIN® vs. experimental yields of a) char, b) tar, c) water and d) gas

5.3.2 Prediction of char composition

A comparison between the FLASHCHAIN® predicted and Fischer Assay experimental results obtained for elemental carbon, hydrogen, oxygen, nitrogen and sulphur can be seen in Figure 5-10. From Figure 5-10a it can be seen that the elemental carbon trends are well predicted by FLASHCHAIN® for chars formed at the higher temperatures (average predicted errors determined as 2% and 1% for 720 °C and 920 °C respectively), and that for all coal chars (except coal char A) where an under prediction is observed for chars formed at 520 °C (average predicted error of 6%). Nitrogen, on the other hand, was observed to be predicted better at 520 °C (average error of 6%) than at 720 °C and 920 °C (average predicted errors of 17% and 40% respectively), as seen in Figure 5-10d. From Figure 5-10b, c and e it can be seen that FLASHCHAIN® predicted values for elemental hydrogen, oxygen and sulphur in the char did not correlate well with experimental values. This finding shows further limitations of the FLASHCHAIN® predictions, which was also observed for the gas yields as explained in Section 5.3.1.

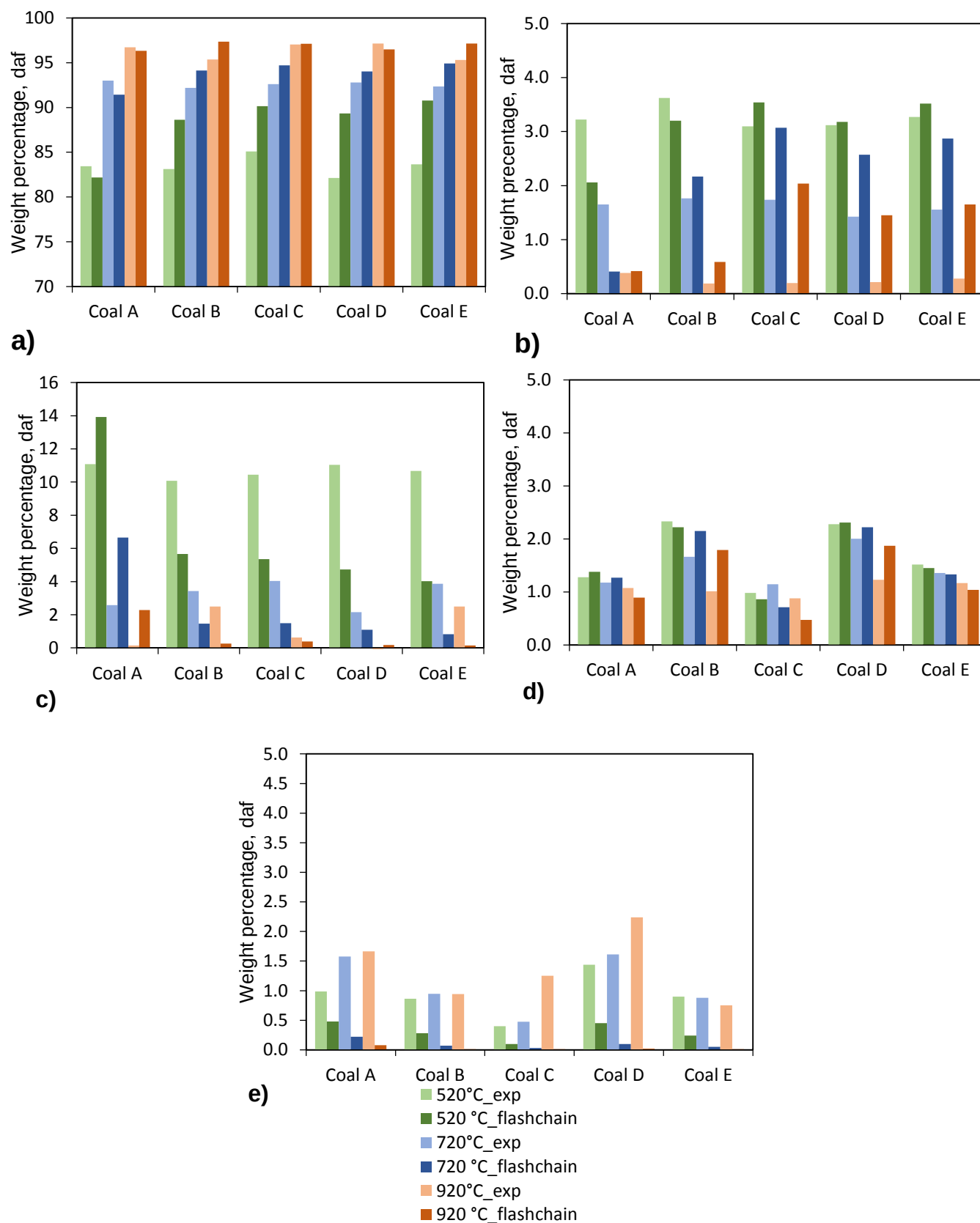


Figure 5-10: FLASHCHAIN® predicted and experimental values for elemental a) carbon, b) hydrogen, c) oxygen d) nitrogen and e) sulphur in char

5.3.3 Prediction of tar composition

FLASHCHAIN® predictions for the elemental composition (C, H, O, N and S) of tar formed at 920 °C can be seen in Figure 5-11. As discussed in Section 5.2.5 the elemental tar composition of tar was only determined for tar formed at a final pyrolysis temperature of 920 °C. It can be seen that elemental carbon predictions using FLASHCHAIN® correlated reasonably well with the experimental results (Figure 5-11a). From the experimental results and discussion in Section 5.3, it was reported that coal A and its pyrolysis products differ significantly from the other four coals.

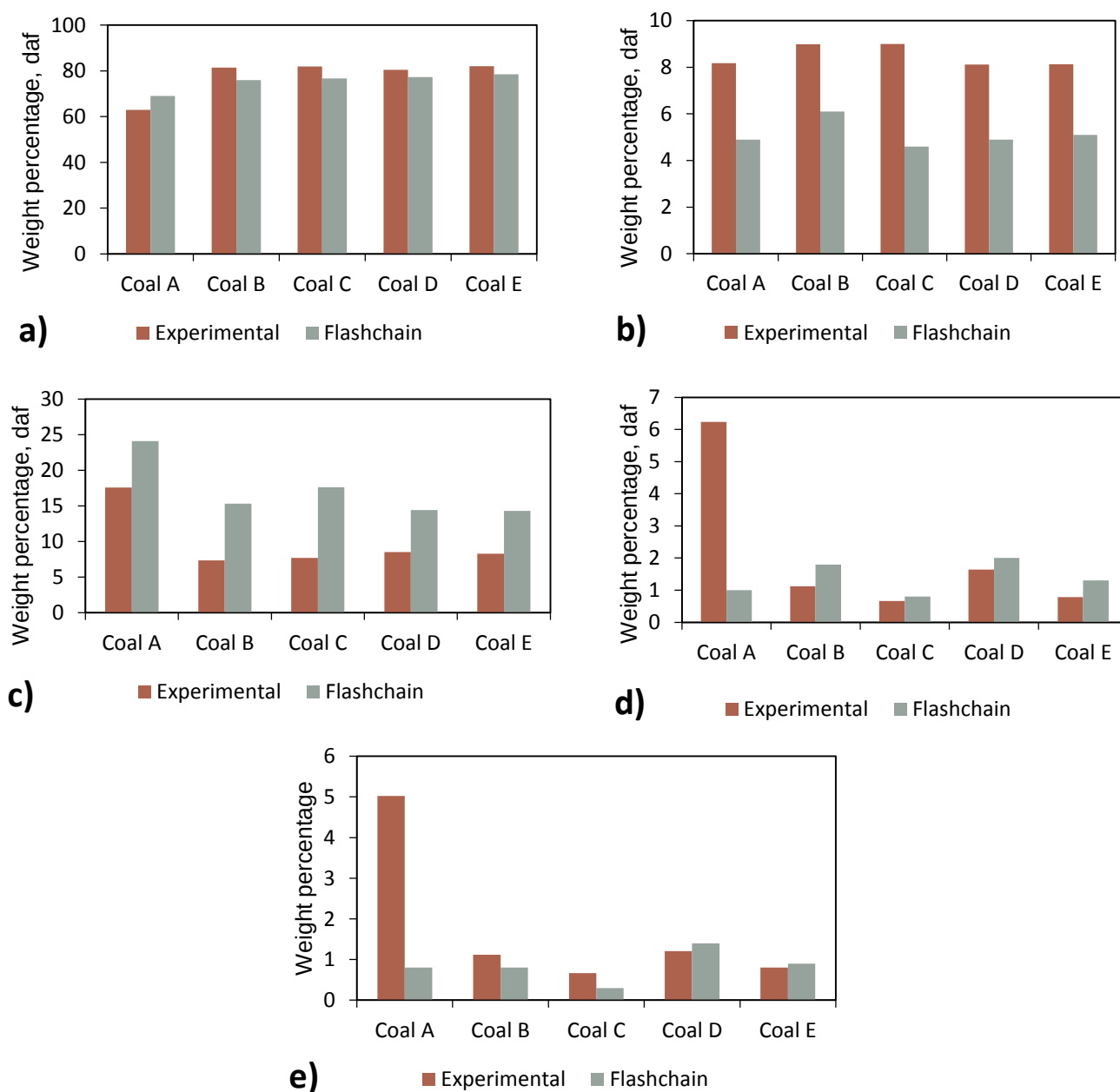


Figure 5-11: Comparison between FLASHCHAIN® predicted and experimental results of elemental a) carbon, b) hydrogen, c) oxygen, d) nitrogen and e) sulphur in tar derived at 920 °C

It is evident from Figure 5-11a that FLASHCHAIN[®] was satisfactory in predicting tar derived from coals of different rank in terms of its elemental carbon content. The predictions for elemental hydrogen, oxygen, nitrogen and sulphur as seen in Figure 5-11b, c, d and e, however did not correlate well with the experimental values. In Figure 5-11b it can be seen that FLASHCHAIN[®] over predicted the elemental hydrogen, and in Figure 5-11c an under prediction of elemental oxygen is observed. Module 7 of FLASHCHAIN[®] includes the homogeneous tar decomposition in the calculations, but heterogeneous tar composition is omitted. This limitation could be a reason for the over and under predictions of elemental hydrogen and oxygen due to the fact that both homogeneous and heterogeneous/catalytic tar decomposition is relevant for slow pyrolysis (Roets *et al.*, 2016; Shen & Yoshikawa, 2013). Catalytic tar decomposition is omitted from the FLASHCHAIN[®] model. Another reason for unsatisfactory predictions could be that the slow pyrolysis is outside of the validation domain of FLASHCHAIN[®].

5.3.4 Prediction of H₂, CH₄, CO and CO₂ yields

FLASHCHAIN[®] predictions of the H₂, CH₄, CO and CO₂ yields were also conducted. These results did however not show satisfactory results, and could be partly attributed to the unpredictability of the gas yields using FLASHCHAIN[®] as shown in Section 5.3.1. Graphs comparing the FLASHCHAIN[®] predicted values for these gas components with the experimentally determined values can be found in Appendix C.

As a summary, FLASHCHAIN[®] was able to provide accurate predictions of char yields, and accurate trends of tar and water yields, although average errors were found as large. Elemental carbon in the char was accurately predicted at 720 °C and 920 °C whereas elemental nitrogen in the char was accurately predicted at 520 °C and 720 °C. Lastly, elemental carbon in tar formed at 920 °C was also accurately predicted.

5.4 Statistical regression

The purpose of the application of statistical regression was to determine relationships between variables by (1) determining whether a statistically significant relationship exists, and (2) if a relationship exists, to determine the correlation coefficient of the relationship. The input variables and method used for the statistical regression are discussed in Section 4.6.2. Correlation coefficients (R^2) were determined between each input and output variable and values that showed statistical significance (2-tailed sigma value less than 0.05) are reported. In the following sections the regression of the pyrolysis product yields, tar composition and gas composition will be discussed. It is important to note that the regression correlation

coefficients are reported, but the equations predicting the various yields and compositions could not be statistically validated to be accurate due to insufficient data points.

5.4.1 Pyrolysis product yields

The correlation coefficients of the pyrolysis product yields can be seen in Table 5-9. It can be seen that a significant number of correlation coefficients were statistically significant for the char, tar and water yields, and lesser so for the gas yields (regression values larger than 0.7 are highlighted in red).

Inherent moisture (-0.87), ash content (0.80), elemental carbon (0.76) and elemental oxygen in the original coal have a good relationship with the char yield and supports finding that coals of higher rank (low moisture and oxygen content) yield higher char yields than coals of lower rank. A negative relationship with inherent moisture content and elemental sulphur, and a positive relationship with ash content, elemental carbon, elemental oxygen and elemental sulphur was found.

On the other hand, tar yields seem to be less dependable on the proximate-and ultimate analysis (which is related to rank) of the coal, and is more dependent on the ash and mineral content of the original coal. It can be seen that Na_2O , MgO , CaO , TiO_2 , Fe_2O_3 , kaolinite content and amorphous content have large correlation coefficients with tar yield. This also supports the experimental findings in this study which showed no rank dependence for the tar yield of these coals undergoing pyrolysis. It also supports a study by Roets, (2014) who reported that mineral matter can have large effects on tar yields.

For the correlation coefficient of the water yield, it is observed that the inherent moisture content (0.95), ash content (-0.92), elemental carbon (-0.82), and elemental oxygen (-0.85) contents (as seen with the char yield, but with opposite effects on the trends e.g. increasing ash content will result in increased char yield and decreased water yield) correlate well. Finally, inherent moisture content, ash content, elemental nitrogen, kaolinite and amorphous content were all found to be statistically significant variables and have a relationship with the gas yield, although not very strong; i.e. R^2 values were found to be below 0.62.

Table 5-9: Statistical correlation coefficients (R^2) for pyrolysis product yields

Input variable		Char	Tar	Water	Gas
Proximate analysis	wt% Inherent moisture content, ad	-0.873	-0.524	0.949	0.556
	wt% Ash content, ad	0.796	0.622	-0.917	-0.622
	wt% Volatile Matter, ad	-0.622		0.589	
Ultimate analysis	wt% C, daf	0.775	0.622	-0.818	
	wt% H, daf		0.590		
	wt% N, daf	0.655	0.655	-0.818	-0.546
	wt% O, daf	0.731	0.557	-0.851	
	wt% S, daf	-0.775	-0.622	0.818	
Ash XRF	wt % Na ₂ O	-0.524	-0.917	0.622	
	wt % MgO	-0.600	-0.819	0.655	
	wt % Al ₂ O ₃	0.775	0.622	-0.818	
	wt % SiO ₂		0.557	-0.589	
	wt % CaO		-0.950	0.524	
	wt % TiO ₂	0.524	0.917	-0.622	
	wt % Fe ₂ O ₃	-0.600	-0.819	0.655	
Mineral XRD	wt % Kaolinite	0.622	0.819	-0.753	-0.567
	wt % Amorphous	-0.622	-0.819	0.753	0.567

Omitted fields are due to no statistically significance between variables

5.4.2 Tar and gas composition

The correlation coefficients of the tar composition based on simdis results can be seen in Table 5-10. It can be seen that only heavy naphtha, gas oil and the residue fraction are reported. No statistically significant dependent variables were found for the other simdis fractions, i.e. kerosene and diesel. From Section 5.2.5 it was reported that heavy naphtha includes the lowest boiling point fraction, whereas gas oil and the residue fraction include the highest boiling point fractions. It is thus noted that both the low boiling point fraction and the high boiling point fractions correlate better with original coal variables than the intermediate

boiling point fractions of the tar. This is analogous to a finding by (Li *et al.*, 2016) who reported that the highest boiling point fraction of the simdis correlates best with coal rank, whereas for other boiling point fractions, no correlation was found.

It can be seen from Table 5-10 that 11 variables have statistical significance with the residue fraction of the tar, of which the ash XRF values (Na₂O, MgO, CaO, TiO₂ and Fe₂O₃) were found to be the highest (R² values above 0.65).

For the gas oil, Na₂O and TiO₂ were seen to have statistical significance and have values of -0.622 and 0.622 respectively. From these two values it can be inferred that higher Na₂O contents will result in smaller gas oil fractions, whereas higher TiO₂ contents will yield higher gas oil fractions.

Table 5-10: Statistical regression parameters (R²) for tar composition

	Input variable	Heavy Naphtha	Gas Oil	Residue
Proximate analysis	wt% Inherent moisture content, ad			-0.524
Ultimate analysis	wt% C			0.611
	wt% O			-0.611
Ash XRF	wt% Na ₂ O	0.546	-0.622	-0.676
	wt% MgO		-0.524	-0.687
	wt% Al ₂ O ₃			0.611
	wt% SiO ₂		0.567	
	wt% CaO	0.556		-0.622
	wt% TiO ₂	-0.546	0.622	0.676
	wt% Fe ₂ O ₃		-0.524	-0.687
Mineral XRD	Kaolinite		0.578	0.589
	Amorphous		-0.578	-0.589
Tar elemental analysis	wt% H			-0.900
	wt% O	0.900	-0.900	

Omitted fields are due to no statistically significance between variables (2-tailed sigma value less than 0.05)

Heavy naphtha was seen to correlate with Na_2O , CaO and Fe_2O_3 , although all values were found to be smaller than 0.6. Finally, it is noted that a strong correlation (R^2 value of 0.9) exists between the elemental hydrogen and elemental oxygen contents in the tar fraction together with some tar boiling point fractions. There is a strong negative relationship between elemental hydrogen in tar and the residue fraction (-0.9), and between the elemental oxygen in tar and the gas oil fraction (-0.9). A strong positive relationship (0.9) between the elemental oxygen and the heavy naphtha fraction is also evident. Knowledge of the elemental analysis of the tar can therefore also be an indication of the heavy and light boiling point simdis tar fractions.

The correlation coefficients of the gas composition based on simdis results can be seen in Table 5-11. No statistically significant variables were found to have a strong relationship with hydrogen gas (H_2) yield, hence the exclusion of H_2 in Table 5-11. The CO yield also showed to have a statistically significant relationship, but a poor correlation exists and an inference can therefore not be made. A number of variables from the proximate analysis, ultimate analysis, ash XRD and ash XRD analysis showed statistical significance for the CH_4 yield. Na_2O , CaO and TiO_2 were found to have the strongest relationship with the CH_4 yield with R^2 values larger than 0.7. Na_2O and CaO showed strong negative relationships (R^2 values of -0.709 and -0.775 respectively), whereas TiO_2 showed a strong positive relationship (R^2 value of 0.709) with the CH_4 yield. Finally, variables that showed the strongest relationship with the CO_2 yield include Na_2O and TiO_2 content (R^2 values of 0.687 and -0.687 respectively). This is in accordance with data from Gulaev *et al.*, (2009) who confirmed that pyrolysis product reactions are affected by mineral components such as Na_2O and TiO_2 .

Conclusively, it was found that, as with the pyrolysis product yields, that ash XRF values carry large statistical significance and supports findings by Roets, (2014) that mineral matter can have large effects on the volatile matter released during slow pyrolysis of coal.

Table 5-9: Statistical regression parameters (R^2) for gas composition

Input variable		CH ₄	CO	CO ₂
Proximate analysis	wt% Inherent moisture content, ad	-0.535		
	wt% Ash content, ad	0.578		
Ultimate analysis	wt% C	0.578		
	wt% N	0.644		
	wt% S	0.600	0.546	
	wt% O	-0.578		
Ash XRF	wt% Na ₂ O	-0.709		0.687
	wt% MgO	-0.666		0.611
	wt% Al ₂ O ₃	0.578		
	wt% SiO ₂			-0.589
	wt% CaO	-0.775		
	wt% TiO ₂	0.709		-0.687
	wt% Fe ₂ O ₃	-0.666		0.611
Mineral XRD	Kaolinite	0.666		-0.622
	Amorphous	-0.666		0.622

Omitted fields are due to no statistical significance between variables (2-tailed sigma value less than 0.05)

Chapter 6 - Conclusions and recommendations

6.1 Introduction

In this study, pyrolysis product yields and compositions of pyrolysis products produced from coals of different rank, ranging from lignite to bituminous, undergoing slow pyrolysis was evaluated. FLASHCHAIN® predictions and statistical regression was done in order predict product yields and compositions and to determine relationships between the products and raw coal data. This chapter provides conclusions formulated from this study in Section 6.2 where after recommendations for future work is provided in Section 6.3.

6.2 Conclusions

Conclusions based on objectives stated in Section 1.2 will be discussed in this section.

Characterisation of five coals of different rank using conventional and advanced methods.

The five coals were characterised in order to determine the coal properties and the coal rank. A large difference in the proximate analysis was firstly found where the inherent moisture content (dry basis) ranged from 5.1 wt% - 30.1 wt%, the ash content (dry basis) ranged from 6.6 wt% - 27.9 wt%, the volatile matter content (dry, ash free) ranged from 35.4 wt% - 46.4 wt% and lastly, the fixed carbon content (dry, ash free) ranged from 53.6 wt% - 64.6wt%. Coal A showed the lowest carbon content (66.6 wt%) compared to coals B, C, D and E which ranged between 74.3 wt% - 76.8 wt%. Coal A also showed the highest oxygen content (26.7 wt%) compared to coals B, C, D and E, which ranged between 16.6 wt% – 20.8 wt%. Based on the proximate and ultimate analysis alone, these coals were observed to differ significantly. Further analyses to determine the ash composition (XRF), the mineral matter content (XRD) and the ash fusion temperatures confirmed large differences in the coals. A petrographic analysis was done in order to classify the five coals into ranks. The coals were found to range between lignite B and bituminous. Coal A, B and C were classified as lignite B coals, coal D as bituminous C, and coal E as subbituminous. Relationships between the coal rank and some of the coal properties were found. The low rank coals had more volatile matter content than the high rank coals, and lower fixed carbon contents. The carbon content was also found to increase with coal rank.

Based on abovementioned characterisation and the results thereof the chosen coals differ in rank, maceral composition and ash composition. The effect of coals of different rank from different origins of the world could on pyrolysis products could therefore be determined.

The use of a modified Fisher Assay setup to investigate the effect of coal rank (ranging from lignite A to bituminous C) temperature on gas, tar, char and water yields.

The effect of coal rank on char yields was evident. Coal A, which is the coal of the lowest rank, has the lowest char yield (45.5%, 41.6% and 39.4% produced at temperatures of 520 °C, 720 °C and 920 °C respectively), whereas coal D, the coal of the highest rank, has the highest char yield at all operating temperatures (84.0%, 75.6% and 73.55% at temperatures of 520°C, 720°C and 920°C respectively). This was explained by the proximate analysis of the coals. Coals of higher rank contained less volatile matter, which will yield higher char yields. It was seen from the proximate analysis of the derived chars that the majority of the original volatile matter present, 75 wt% - 85 wt%, in the coals have been released at 720 °C and that 88 wt% - 95 wt% of original volatile matter was released at 920 °C. Char yield is therefore closely related to the volatile matter content of the coal. Gas yields at 520 °C was observed to be affected by coal rank, whereas no effect of coal rank was observed at 720 °C and 920 °C. Coal B had the highest maximum tar yield (8.8 wt%) compared to that of coals A, C, D and E (2.8 wt%, 2.9 wt%, 3.2 wt% and 4.9 wt% respectively). It was lastly found that the water yield correlates with the inherent moisture content of the raw coal; coals with higher inherent moisture contents yielded higher water yields.

An increased final pyrolysis temperature therefore results in increased water and gas yields and decreased char yields. This is attributed to an increase in total volatiles evolved from volatile matter in the original coal. Maximum tar yields were observed at 720 °C where after the yields decreased or stayed the same, which is attributed to tar cracking and secondary pyrolysis reactions. Although a decrease in volatile matter was observed with an increase in coal rank, the same was not observed for the gas yields. Part of this phenomenon can be attributed to the total evolved volatiles partitioning into tar and gas fractions, where it was found that at higher temperatures (920 °C) the evolved condensed volatiles (tar) were greater than 40 wt% for coal B, whereas for the other coals, not more than 25 wt% of the total evolved volatiles partitioned into the tar fraction. The same was observed for the tar yields and partly explains why no rank dependence was observed for the tar yield.

Analyses and evaluation of the tar liquid and gas (H₂, CO, CO₂ and CH₄) products.

The elemental carbon and oxygen contents of the tars formed at a final pyrolysis temperature of 920 °C have been found to correlate well with the elemental analysis of the raw coals. Carbon contents in the original coals are ranked as follows: coal A < coal C < coal B < coal D < coal E, whereas the carbon content in derived tars formed at a pyrolysis temperature of 920 °C are ranked as follows: coal A < coal B < coal C < coal D < coal E. Identical trends were

found for oxygen. Coals of lower rank therefore form tars that are more oxygen rich than coals of higher rank, as seen by the gas yield results, where lower rank coals formed more oxygen containing gas species than higher ranked coals.

Simdis, GC-MS and SEC-UV analyses on tars formed at 520 °C, 720 °C and 920 °C showed that final pyrolysis temperature did not have a significant effect on the results thereof. The average molecular weight results (212- 415 Da) compared well with a previous study where similar heating rates and temperatures were used to generate coal derived tars (Roets, 2014). The lower boiling point fraction (<300 °C) was analysed using GC-MS where tars derived from different coals were compared based on the following product classification: alkyl benzenes, phenol, cresol and paracresol, furans, alkanes, PAHs and long chain alcohols. It was found that, for all derived tars that the largest components in the tar consisted of phenols, cresols and paracresols. It appears as if tars derived from higher rank coals form more phenolic compounds and a similar trend is seen for furans, but no rank dependence is apparent for cresol and paracresol and long chain alcohols. Differences could be ascribed to catalytic effects of minerals and the complexity of tar forming reactions. No rank dependence was found for the boiling point range groups as determined by Simdis where higher boiling point fractions of the tar were analysed: heavy naphthas (bp < 205 °C), kerosene (205 °C < bp < 260 °C), diesel (260 °C < bp < 340 °C), gas oil (340 °C – 425 °C) and residue fraction (425 °C < bp < 450 °C). The only temperature dependence found here was that the residue fraction at 920 °C was higher than observed at 520 °C, which indicated that lighter tars cracked while heated to 920 °C. No rank dependence was found with the Simdis results.

It was also seen that the CO and CO₂ yields were rank dependent and closely related to the oxygen content in the original coal. Lower rank coals had higher oxygen contents and produced more oxygen containing gases (CO and CO₂). On the other hand, no rank dependence was found for the H₂ yields.

It is therefore concluded that for the rank dependence of the composition of the evolved volatiles (tar and gas), only a few results have been found to be linearly rank related and includes results that relate back to the elemental analysis of the coal. These compositions include the elemental oxygen and carbon of the derived tar as well as the oxygen containing gases (CO and CO₂). Lastly, an investigation into the effect of coal rank on the average tar molecular weight by the use of coals of different origin proved to be inconclusive. This is due to many factors (low or high volatile coal, aliphatic attachments number of oxygen containing functional groups and catalytic effects of minerals such as calcium) playing a role in cross-linking. These coals differ in rank, maceral composition and ash composition, therefore no definite rank dependence of the tar compositions was found.

Perform a total elemental balance of the overall process on a CHSNO basis.

A total elemental balance was performed for the elemental C, H, S, N and O in the pyrolysis products at 920 °C in order to better understand the partitioning into char, tar, water and gas during pyrolysis.

The lower rank coals (coal A and B) showed the lowest values of original carbon partitioned into char (71% and 73% respectively) compared to that of coal C, D and E (80%, 80% and 79%) respectively. It was observed for coal B, relative to the other coals that more carbon and hydrogen partitioned into the gas phase than into tar. From the Fischer Assay results it was shown that coal B is the coal that yielded significantly higher tar yields than for the other coals. This partitioning therefore seems to correlate well with the tar yield observed.

From this balance, the most valuable conclusion regarding the tar yield and formation can be made by observing the partitioning of hydrogen and carbon. For coals resulting in higher tar yields during slow pyrolysis, a larger percentage of hydrogen and carbon evolved from the coal into volatiles (gas and tar) seem to partition into the tar compared to coals with lower tar yields.

Explore existing analytical model, FLASHCHAIN®, to predict liquid product yields and quality, as well as develop own statistical model.

FLASHCHAIN® predictions were done in order to have knowledge about the pyrolysis products based on the proximate and ultimate analysis in order to assess which coals are suitable in fixed bed gasification and chemicals production. FLASHCHAIN® was able to provide accurate predictions of char yields, and accurate trends of tar and gas yields, although average errors were found as large. Elemental carbon in the char was accurately predicted at 720 °C and 920 °C, whereas elemental nitrogen in the char was accurately predicted at 520 °C and 720 °C. Lastly, elemental carbon in tar formed at 920 °C was also accurately predicted. Poor predictions were found for the gas yields and subsequently the gas compositions. This package was developed in order to include tar composition chemistry due to the knowledge of tar cracking at moderate temperatures. A limitation of this package is the omission of non-condensable volatiles chemistry, which means that the conversion of volatiles cannot be quantitatively simulated. This limitation, together with the slow heating rate that was out of the validation domain could explain why certain values were not predicted accurately. Statistical regression was applied in order to determine the relationship between raw coal properties and pyrolysis products and its composition. A number of coal properties have been found to have good correlations with the char and water yield, with proximate analysis properties (moisture content, ash content), ultimate analysis properties (oxygen and sulphur) and Al₂O₃ content.

Only weak relationships between the proximate-and ultimate analysis values and tar yield were found, but the strongest relationships were found to be with ash XRF values (Na_2O , MgO , CaO , TiO_2 and Fe_2O_3). Catalytic effects therefore seemed to play a large role in the formation of tar. No good relationships with coal properties were found for the simdis tar composition. It is concluded that knowledge of the elemental hydrogen and oxygen content present in tar can be used to predict heavy naphtha, gas oil and the residue fraction based on strong correlation coefficients found (0.9 between O and heavy naphtha, -0.9 between O and gas oil, and lastly -0.9 between H and the residue fraction). CH_4 and CO_2 were found to be the only gases with statistical significance relating to some extent with some coal properties.

6.3 Recommendations for future work

Recommendations for future work based on findings and limitations realised during this study is made:

- Better characterisation of the gas fraction with a more advanced GC system which will identify more gas species such as H_2S , COS , SO_2 , NH_3 and NO_2 amongst others. This will assist in better describing distributions between the various pyrolysis products.
- The lower boiling point fraction of the tar was investigated, but more advanced methods can be used to characterise the tar which includes: GC-MS fitted with a FFAP column to separate the fraction of the mixed aliphatic and aromatic components detected together in the GC-MS used in this study, FTIR to investigate structural families.
- In order to better understand the pyrolysis step during gasification in fixed bed gasifiers, experiments could be conducted under pressure. This will better represent the conditions of the industry.
- Better sample selection in order to remove extraneous variables (such as ash content) in order to better determine the effect of coal rank.
- Due to a variety of factors including the proximate and ultimate analysis of the coal, the maceral composition and catalytic effect of minerals (especially dolomite and calcite) affecting pyrolysis product yields and specifically the gas and tar composition, FLASHCHAIN® was found to be unsuitable for satisfactory predictions in its entirety due to heating rate limitations outside of the validation domain, since the validation of FLASHCHAIN® was done with numerous data points collected from flash pyrolysis. In this study, insufficient data points were used to create validated statistical models and regression equations. Data generated from future slow pyrolysis studies should be generated in order to set up validated statistical models.

- Other modelling software such as the chemical percolation model (CPD) and the functional group depolymerisation, vaporisation and crosslinking models should be assessed for pyrolysis predictions.
- Mineral additions to demineralised coals can be used to increase the count of data points used and to study the effects of mineral additions on different coal ranks as determined in this study.

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Appendix A – Calculations and calibrations

A-1 Repeatability calculations

Due to small samples sizes, the critical t-value was used to determine errors based on confidence intervals. The critical t-value was determined from the degrees of freedom (experimental points (n) – 1) for confidence intervals of 80%, 90% or 95%. The lower and upper limits of the interval limit were then calculated as:

$$\text{Lower limit} = \bar{x} - t_{crit} \times \frac{\sigma}{\sqrt{n}} \quad (\text{Eq. A-1})$$

$$\text{Upper limit} = \bar{x} + t_{crit} \times \frac{\sigma}{\sqrt{n}} \quad (\text{Eq. A-2})$$

With $\bar{x}$ the mean, t_{crit} as discussed above, σ the standard deviation and n the number of data point. The error percentage was the calculated as:

$$\text{Error \%} = (\bar{x} - \text{lower limit}) \times 100 \quad (\text{Eq. A-3})$$

A-2 TGA flow calibration

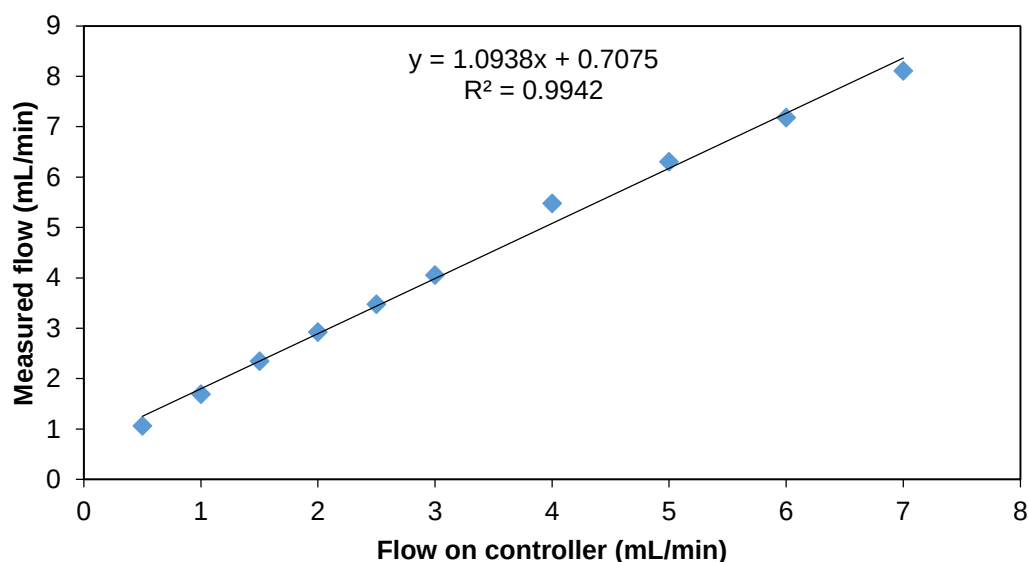


Figure 0-1:TGA flow calibration curve

A-3 SEC-UV calibration curve

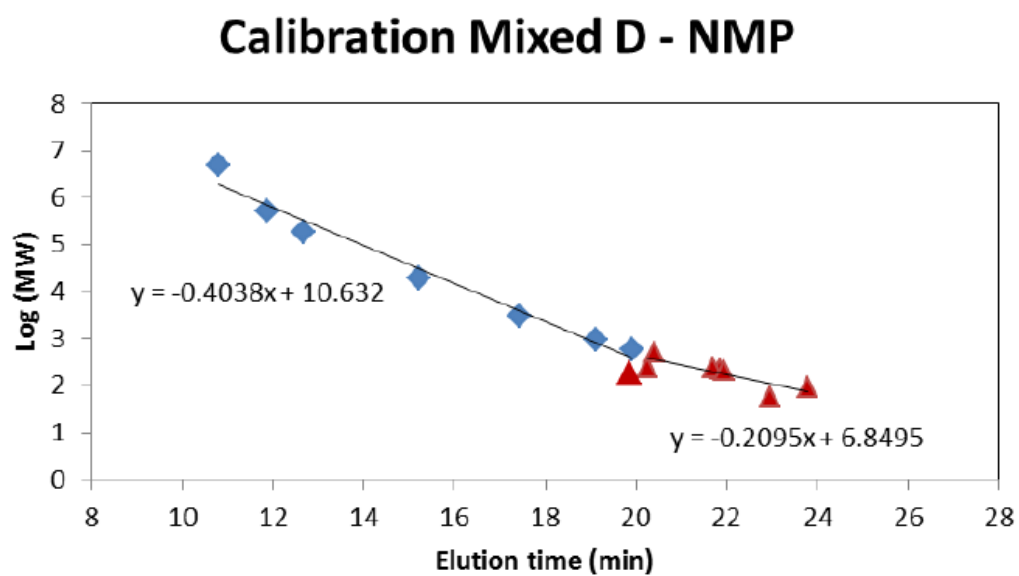


Figure 0-2: SEC-UV calibration curve

Appendix B – Experimental results and repeatability data

B-1 Full XRF analysis

Table 0-1: Full XRF analysis

Compound Name	Coal A	Coal B	Coal C	Coal D	Coal E
Na ₂ O	5.5	0.1	0.7	0.5	0.1
MgO	3.3	0.5	3.3	1.7	0.2
Al ₂ O ₃	8.4	25.3	12.7	26.5	28.0
SiO ₂	12.6	50.9	26.3	40.1	26.2
P ₂ O ₅	0.1	1.3	0.4	1.0	0.5
SO ₃	19.5	8.3	4.9	9.8	11.1
Cl	0.2	0.1	0.1	0.1	0.4
Br	0.0	0.0	-	-	16.3
K ₂ O	0.5	1.3	1.1	1.2	0.2
CaO	24.0	2.4	32.0	8.3	4.1
TiO ₂	0.7	2.8	1.4	2.3	2.4
Fe ₂ O ₃	22.2	6.2	13.9	6.7	2.2
SrO	1.9	0.1	1.9	1.1	1.5

B-2 Repeatability on pyrolysis product yields

Table 0-2: Error calculations of repeatability done on coal D

		Gas	Tar	Water	Char
920 °C	Av	6.08	1.62	4.03	36.77
	SD	1.52	0.13	0.77	0.22
	SE	0.62	0.05	0.31	0.09
	CI (-)	4.87	1.52	3.42	36.59
	CI (+)	7.28	1.73	4.64	36.94
	Error	2.41	0.21	1.22	0.35
	Error				
	%	39.71	12.96	30.26	0.94
720 °C	Av	5.13	1.56	5.52	37.87
	SD	0.67	0.14	0.67	0.16
	SE	0.21	0.04	0.21	0.05
	CI (-)	4.75	1.48	5.14	37.78
	CI (+)	5.52	1.64	5.91	37.96
	Error	0.77	0.16	0.77	0.18
	Error				
	%	14.96	10.02	13.88	0.48
520 °C	Av	0.83	1.51	3.59	42.04
	SD	0.17	0.14	0.33	0.12

SE	0.07	0.06	0.14	0.05
CI (-)	0.70	1.40	3.34	41.95
CI (+)	0.96	1.62	3.84	42.13
Error	0.26	0.22	0.50	0.18
Error				
%	30.96	14.43	13.99	0.42

B-3 Repeatability on gas compositions

Table 0-3: Errors calculated (%) for gas compositions

Component	520 °C	720 °C	920 °C
H ₂	40	17	31
CH ₄	31	13	38
CO	31	17	31
CO ₂	41	14	15

B-4 Statistical report on CHSNO determination of tar

Table 0-4: Statistical report on repeatability done on determinations of elemental CHSNO of tar

No. Name	C [%]	H [%]	N [%]	S/TCD [%]
7 A	54.39	7.390	6.231	4.721
8 A	56.52	7.422	5.745	4.413
9 A	54.45	7.188	6.246	5.042
10 A	61.77	7.560	4.644	4.160
11 A	58.53	7.513	5.398	4.443
Mean value	57.13	7.414	5.653	4.556
Deviation (abs.)	3.10	0.144	0.666	0.336
12 B	81.40	8.991	1.031	1.141
13 B	81.49	8.990	1.034	1.120
14 B	81.51	8.994	1.415	1.113
15 B	80.77	8.907	0.992	1.087
Mean value	81.30	8.970	1.118	1.115
Deviation (abs.)	0.35	0.042	0.199	0.022
16 C	82.00	8.999	0.829	0.553
17 C	82.22	9.014	0.599	0.555
18 C	82.03	9.011	0.614	0.557
19 C	81.97	9.012	0.613	0.550
Mean value	82.05	9.009	0.664	0.554
Deviation (abs.)	0.12	0.007	0.111	0.003

20 D	80.17	8.072	1.596	1.186
21 D	79.98	8.087	1.952	1.218
22 D	80.13	8.067	1.472	1.191
23 D	80.16	8.077	1.521	1.204
Mean value	80.11	8.076	1.635	1.200
Deviation (abs.)	0.09	0.009	0.217	0.014
24 E	81.85	8.104	0.784	0.808
25 E	81.82	8.106	0.768	0.791
26 E	81.85	8.109	0.767	0.796
27 E	81.92	8.104	0.794	0.807
Mean value	81.86	8.106	0.778	0.801
Deviation (abs.)	0.04	0.002	0.013	0.008

No. Name	O [%]
7 A	16.883
8 A	15.870
9 A	15.938
10 A	15.015
Mean value	15.927
Deviation, abs.	0.764
11 B	7.357
12 B	7.306
13 B	7.346
14 B	7.293
Mean value	7.325
Deviation, abs.	0.031
15 C	7.709
16 C	7.698
17 C	7.660
18 C	7.704
Mean value	7.693
Deviation, abs.	0.022

19 D	8.604
20 D	8.422
21 D	8.518
22 D	8.373
Mean value	8.479
Deviation, abs.	0.103
23 E	8.077
24 E	8.263
25 E	8.295
26 E	8.307
Mean value	8.236
Deviation, abs.	0.107

B-5 Thermogravimetric analysis repeats

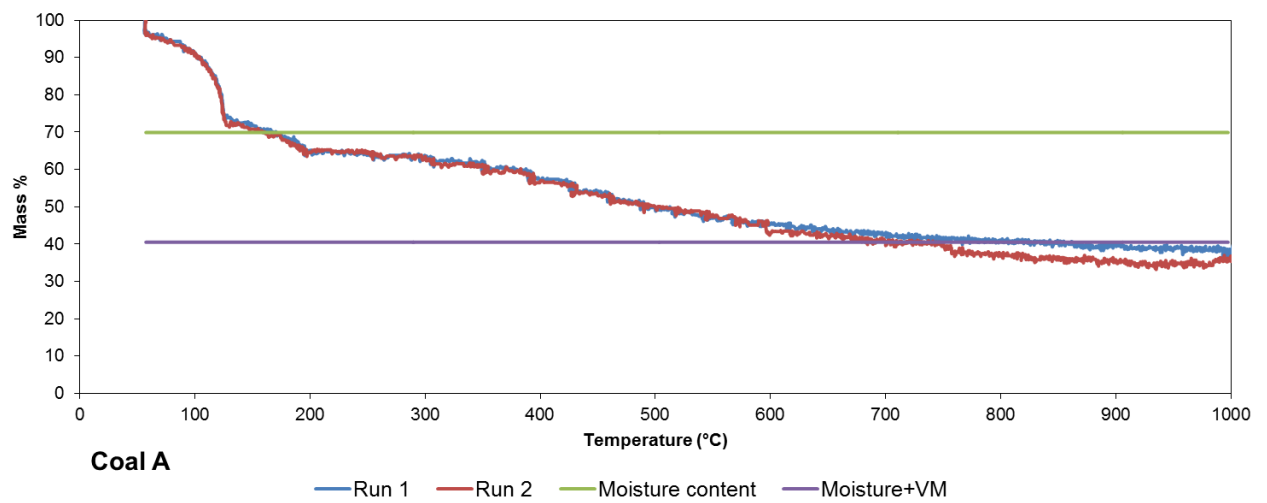


Figure 0-3: Mass los curve of coal A

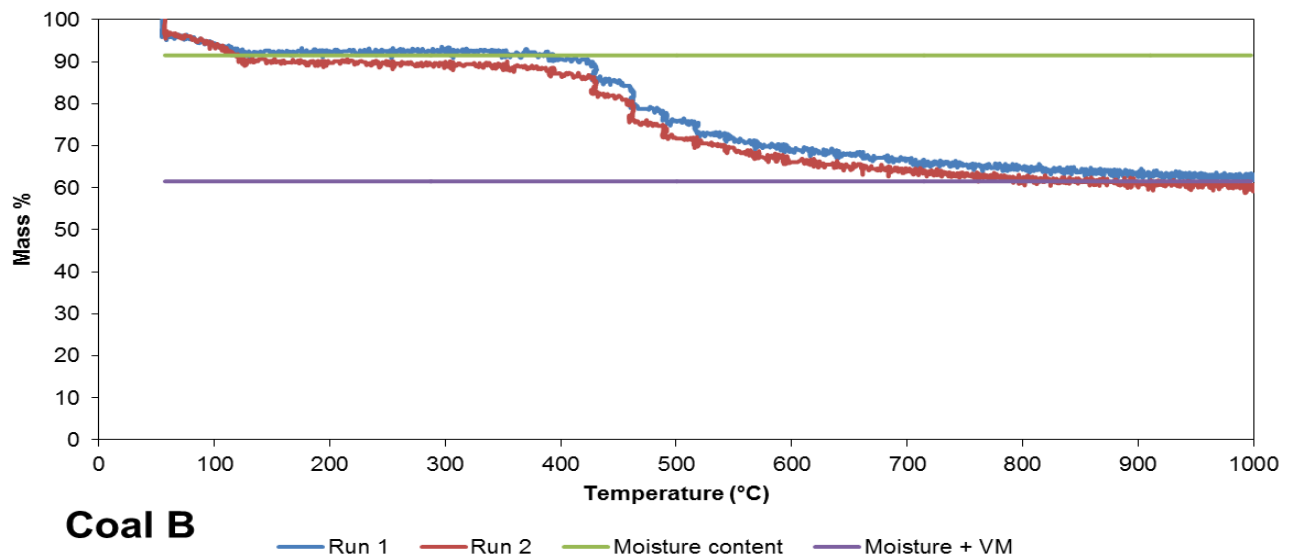


Figure 0-4: Mass loss curve of coal B

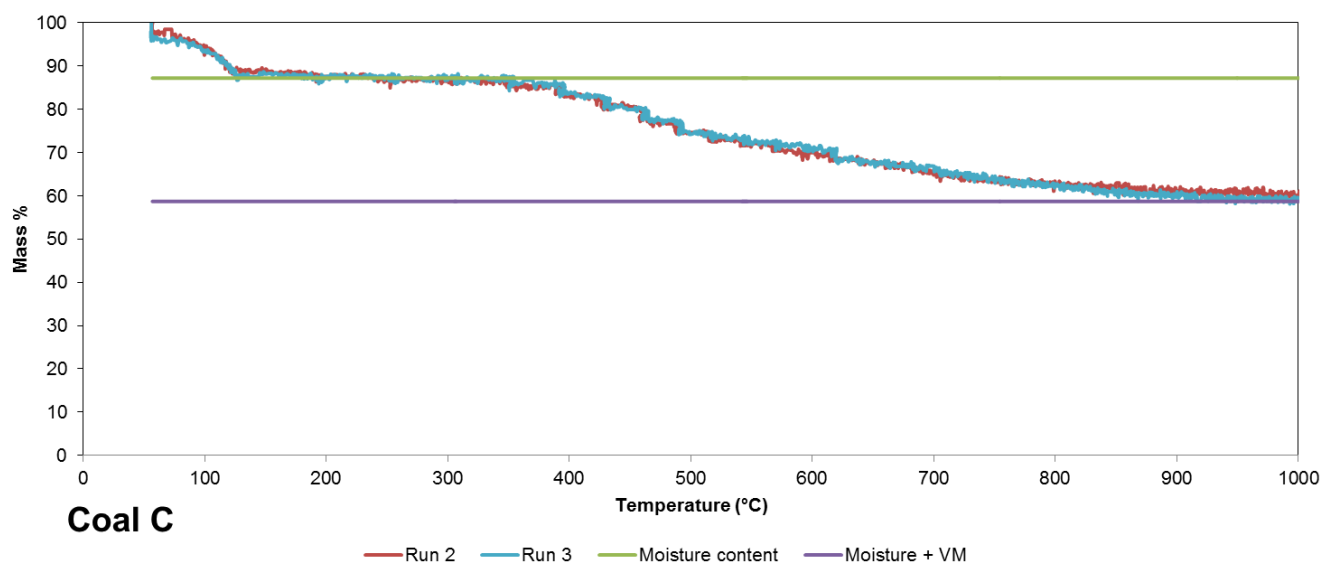


Figure 0-5: Mass loss curve of coal C

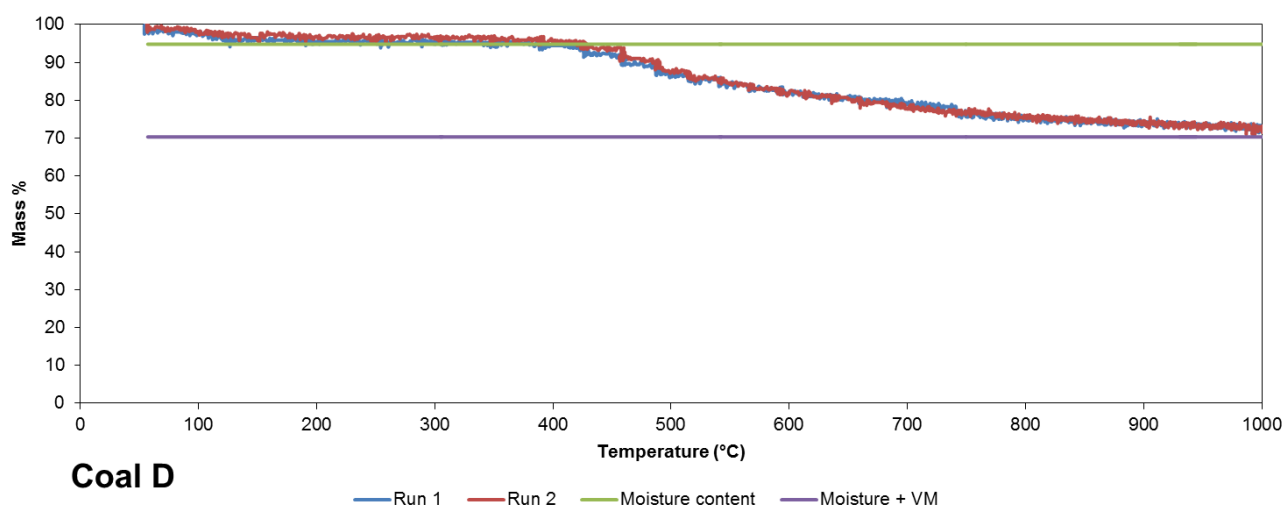


Figure 0-6: Mass loss curve of coal D

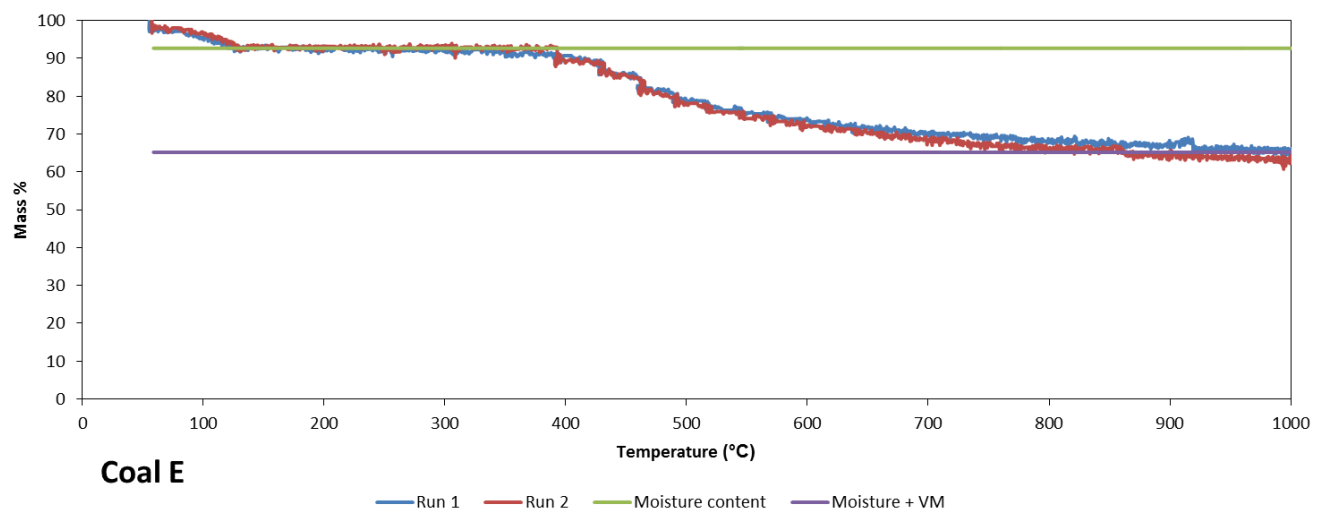


Figure 0-7: Mass loss curve of coal E

B-6 Repeatability runs for CO₂ adsorption parameters

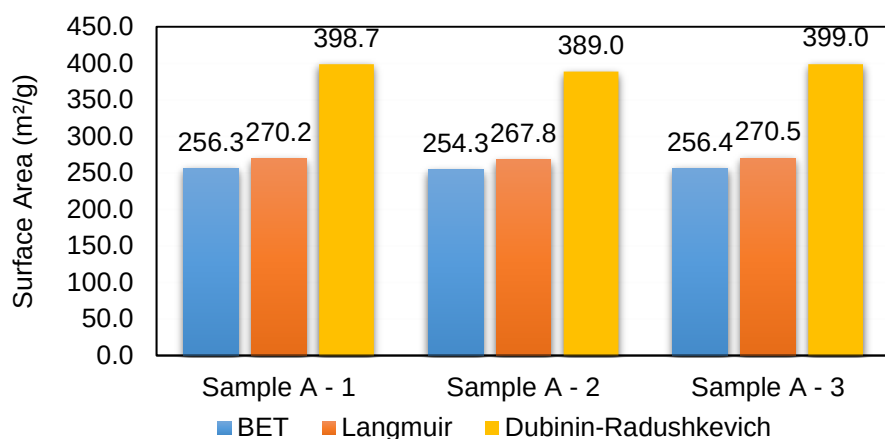


Figure 0-8: Sample A - Char at 920 °C

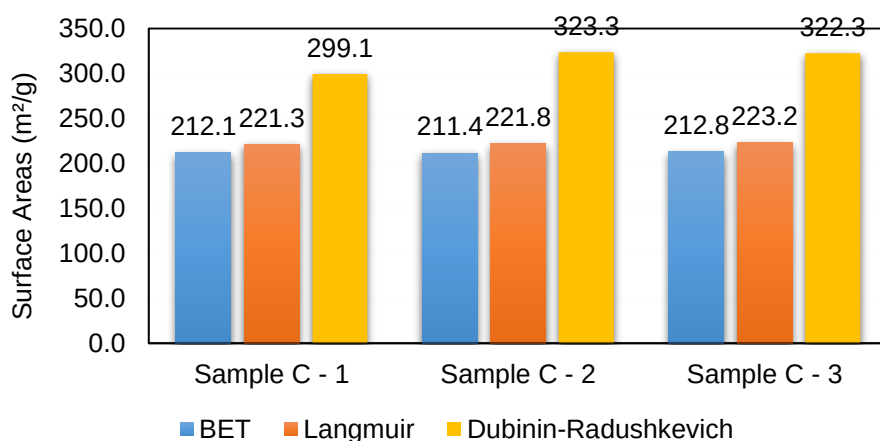


Figure 0-9: Sample C - Char at 720 °C

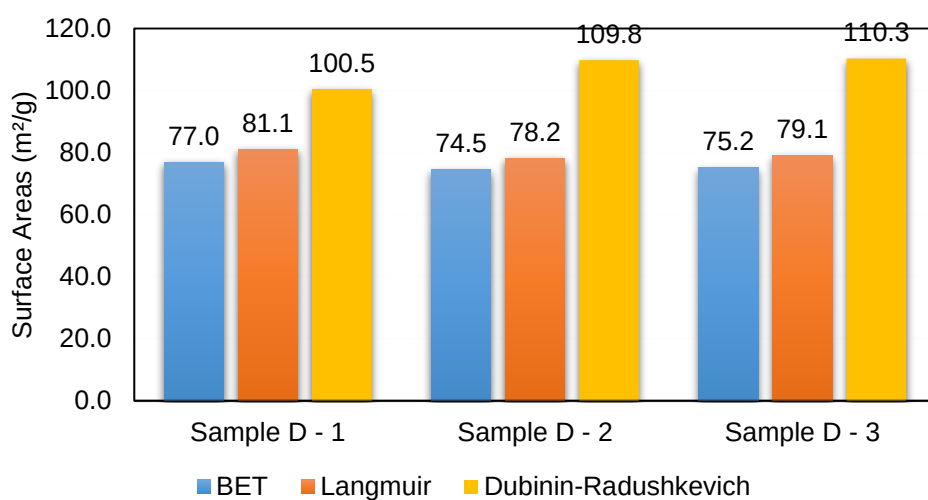


Figure 0-10: Coal D raw coal

B-7 Gas yields of H₂, CH₄, CO and CO₂

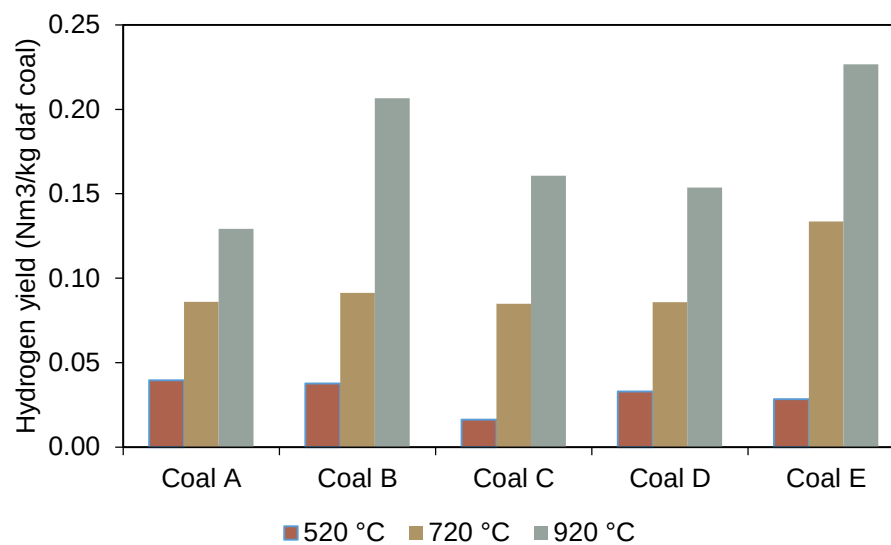


Figure 0-11: Hydrogen gas yields

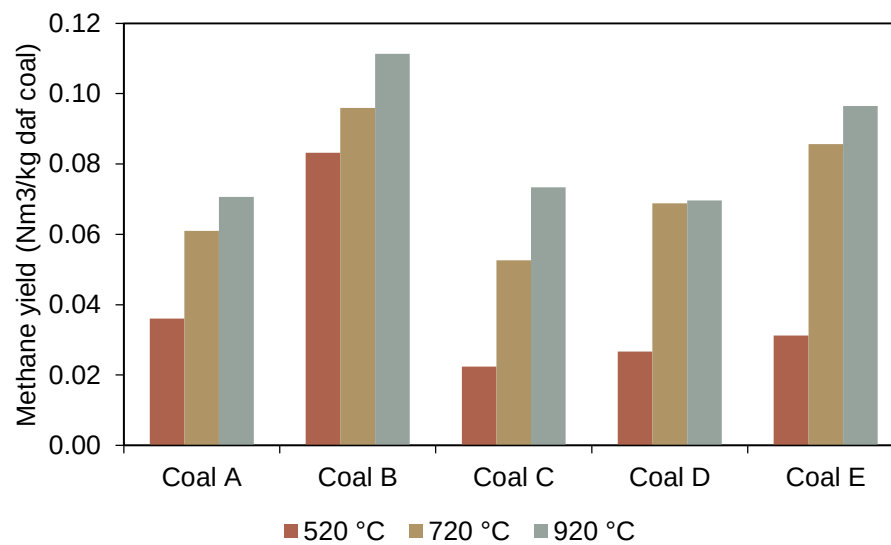


Figure 0-12: Methane gas yields

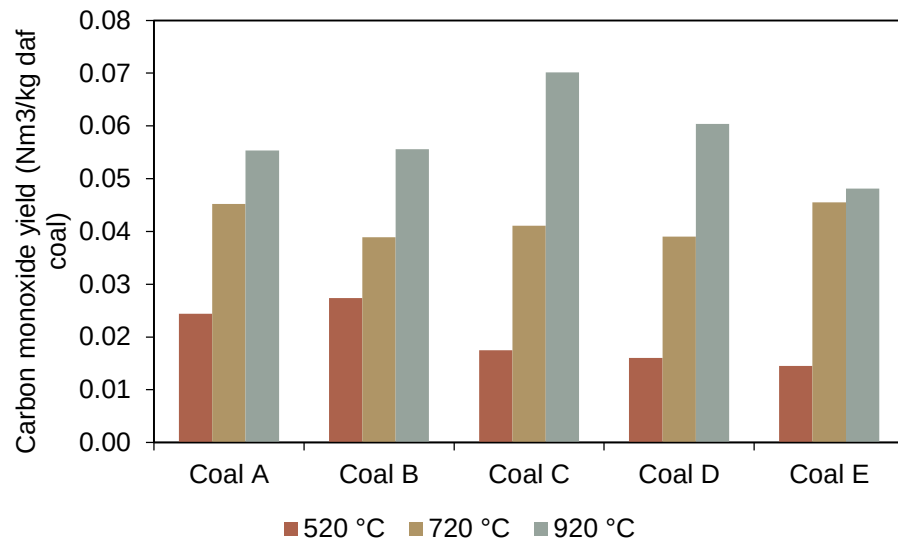


Figure 0-13: Carbon monoxide gas yields

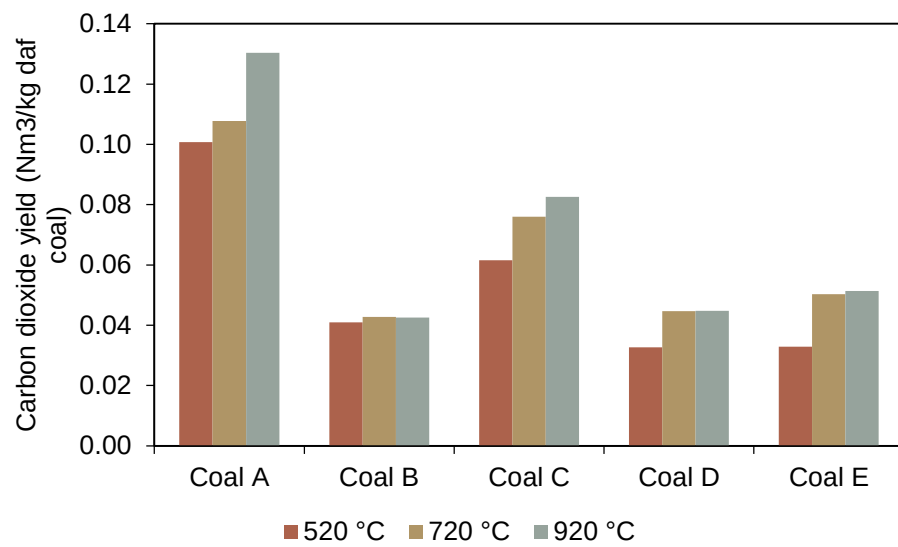
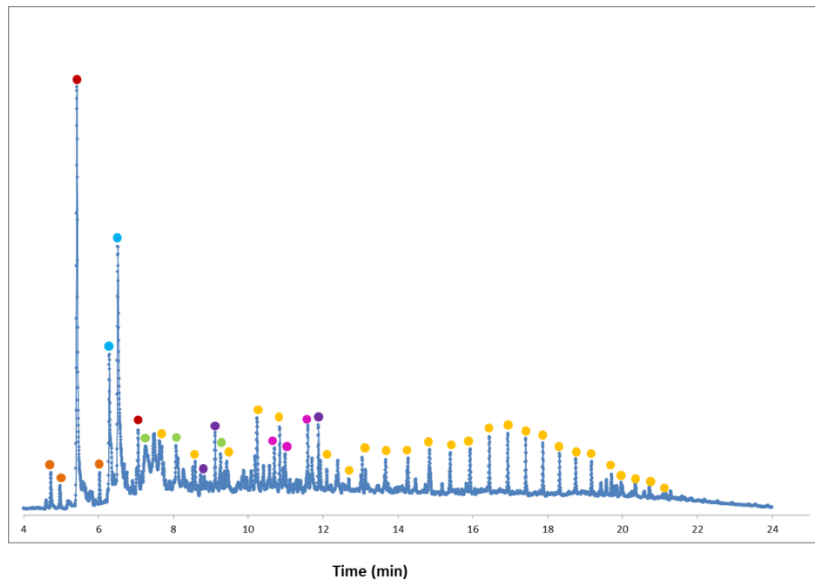


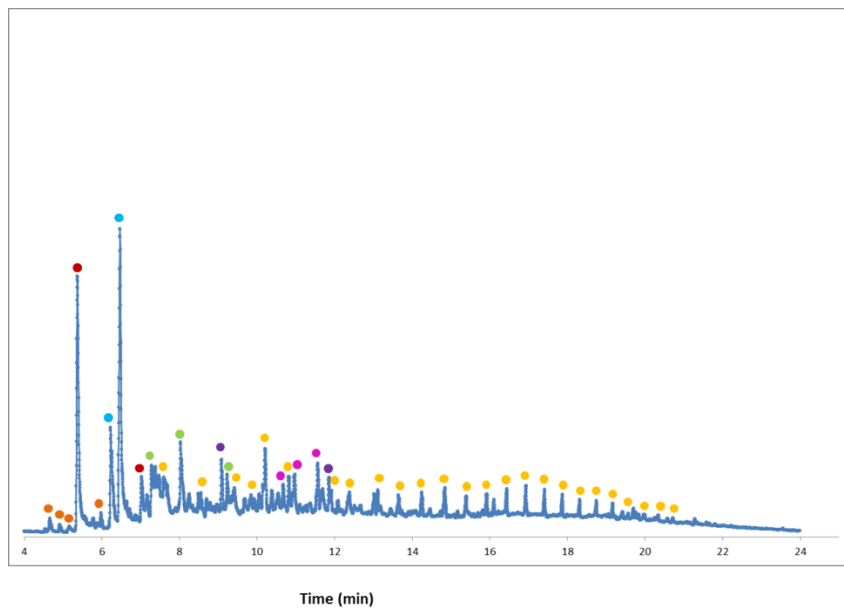
Figure 0-14: Carbon dioxide gas yields

B-8 Gas chromatograms for coal tars



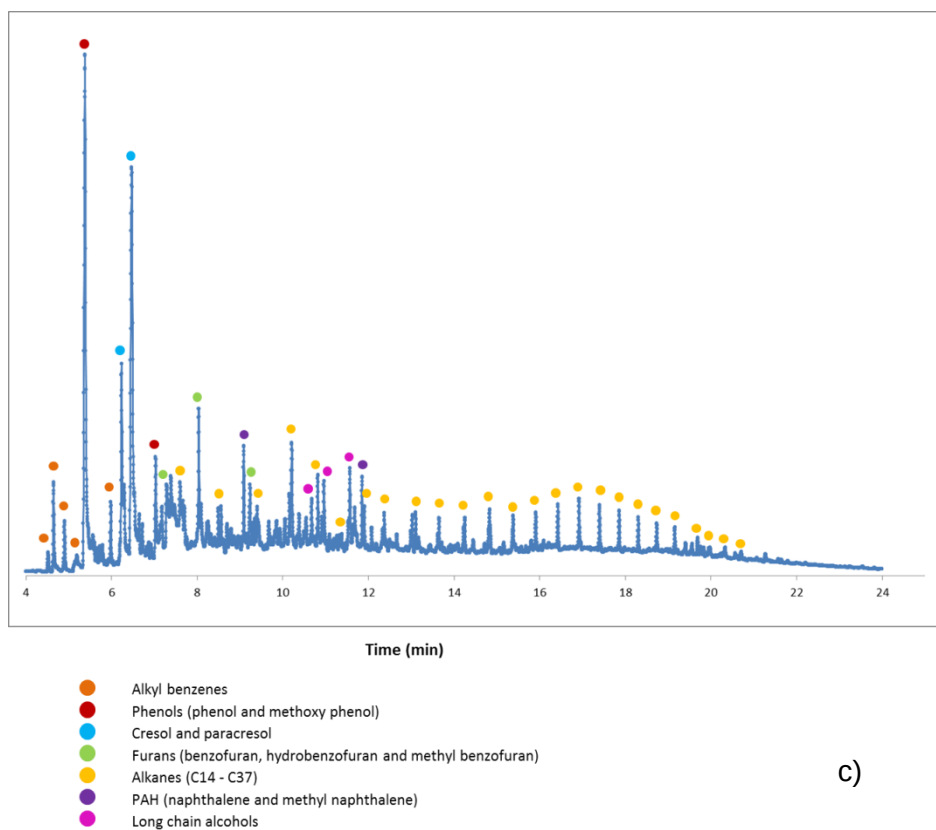
- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran, hydrobenzofuran and methyl benzofuran)
- Alkanes (C14 - C37)
- PAH (azulene, naphthalene and methyl naphthalene)
- Long chain alcohols

a)



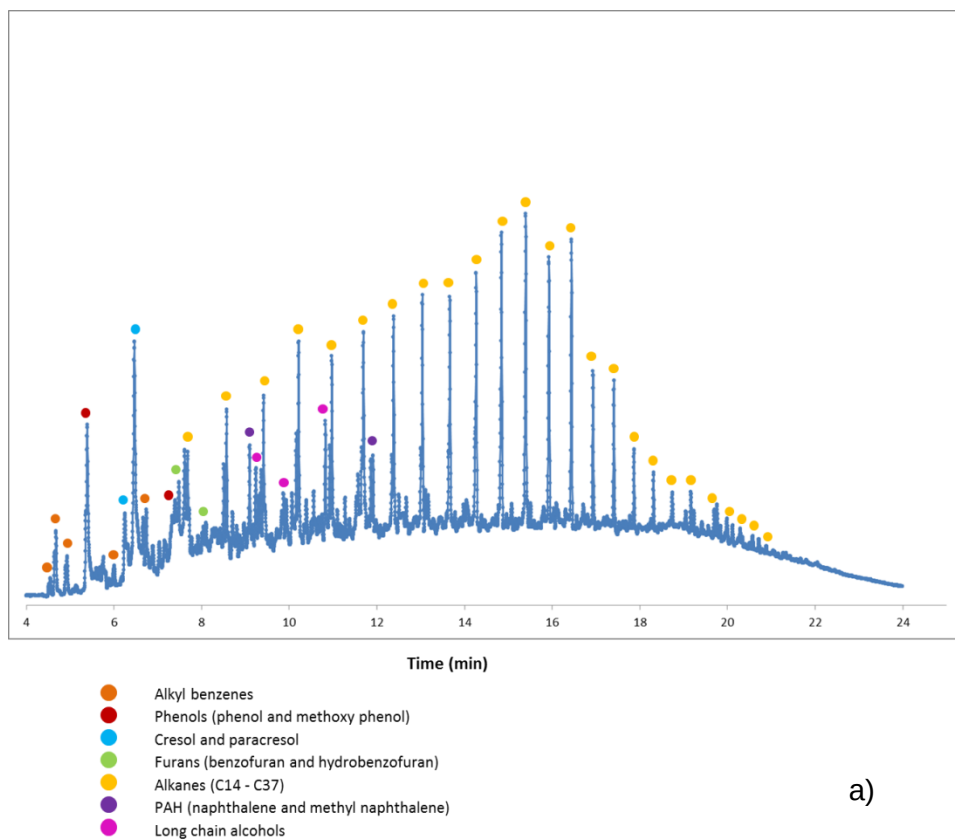
- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran, hydrobenzofuran and methyl benzofuran)
- Alkanes (C14 - C37)
- PAH (naphthalene and methyl naphthalene)
- Long chain alcohols

b)

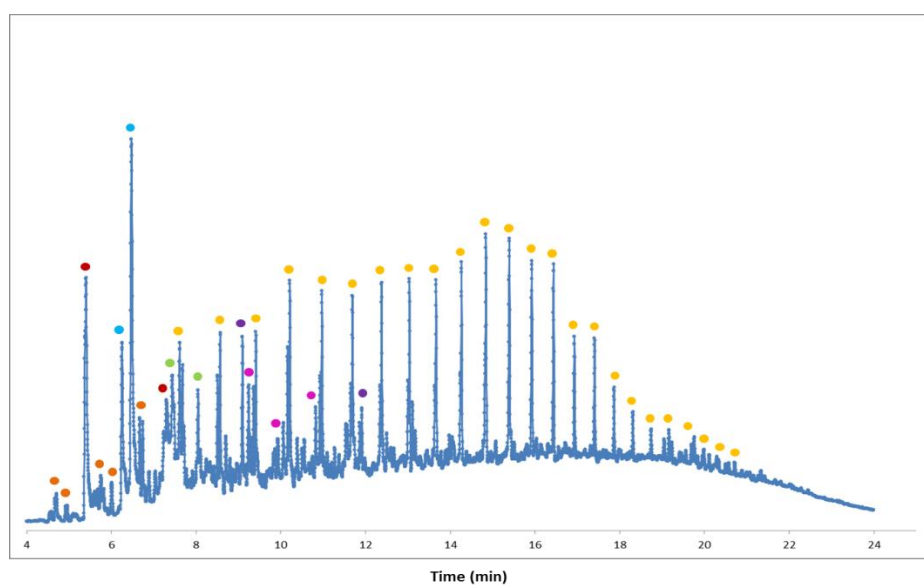


c)

Figure 0-15: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal A

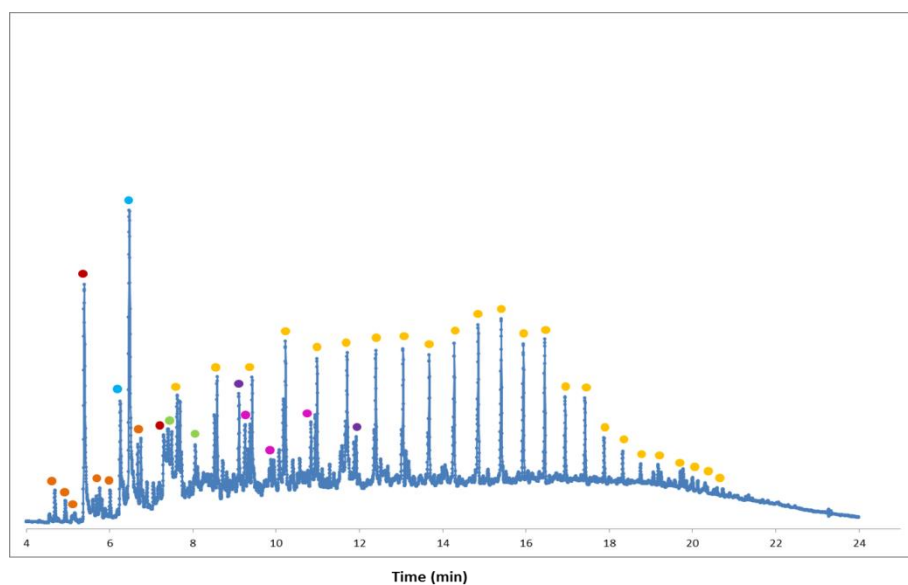


a)



- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran and hydrobenzofuran)
- Alkanes (C14 - C37)
- PAH (naphthalene and methyl naphthalene)
- Long chain alcohols

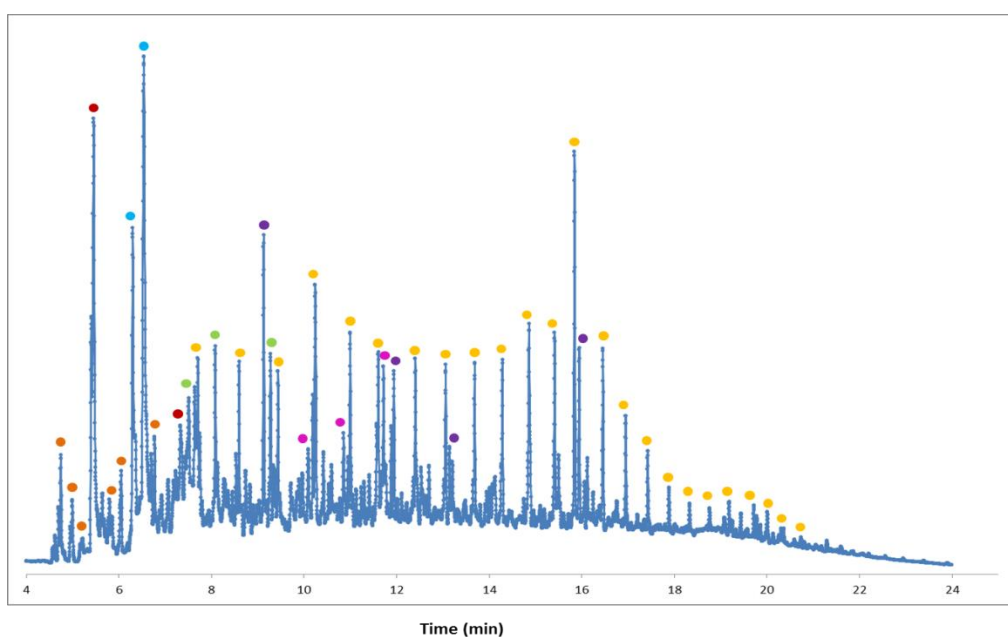
b)



- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran and hydrobenzofuran)
- Alkanes (C14 - C37)
- PAH (naphthalene and methyl naphthalene)
- Long chain alcohols

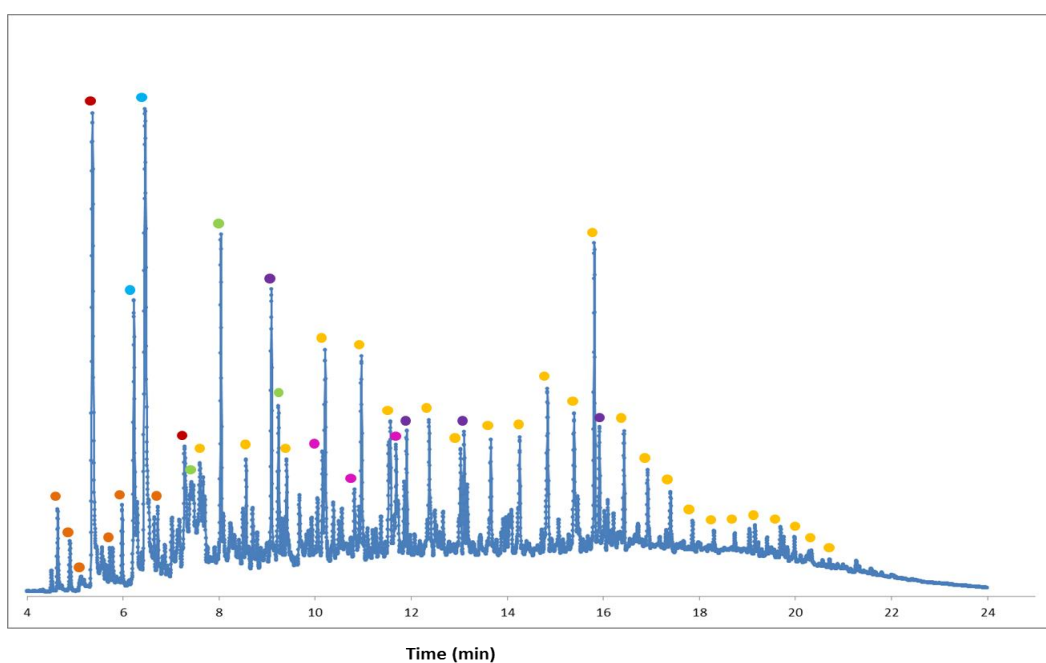
c)

Figure 0-16: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal B



- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran, hydrobenzofuran and methyl benzofuran)
- Alkanes (C14 - C37)
- PAH (naphthalene, methyl naphthalene, phenanthrene and methyl pyrene)
- Long chain alcohols

a)



- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran, hydrobenzofuran and methyl benzofuran)
- Alkanes (C14 - C37)
- PAH (naphthalene, methyl naphthalene, phenanthrene and methyl pyrene)
- Long chain alcohols

b)

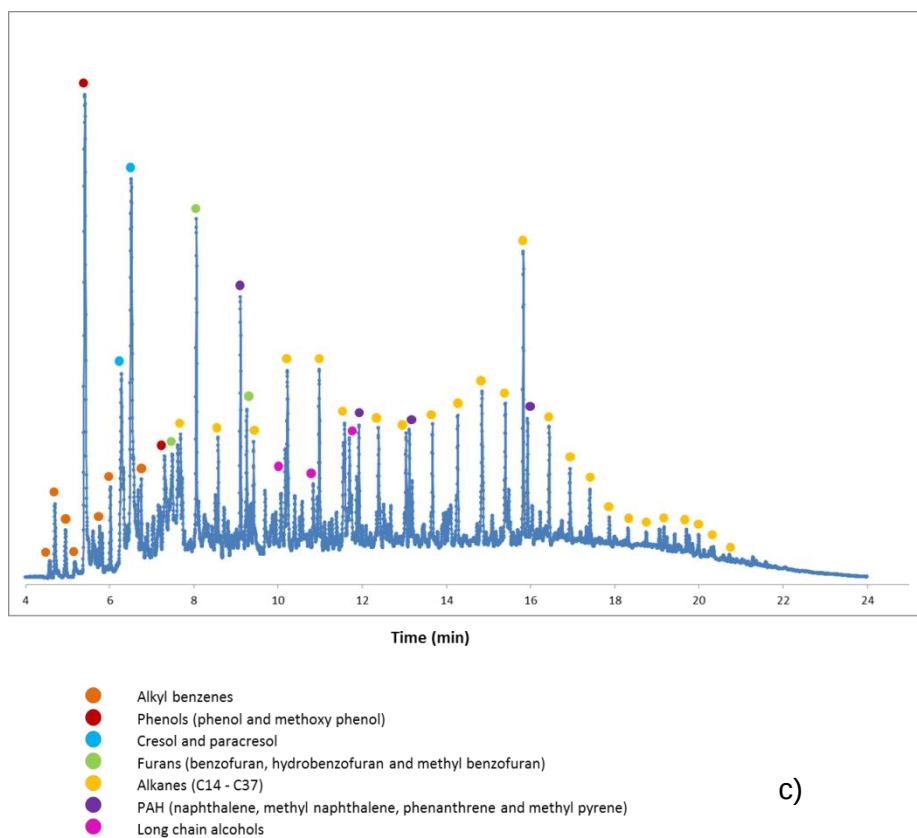
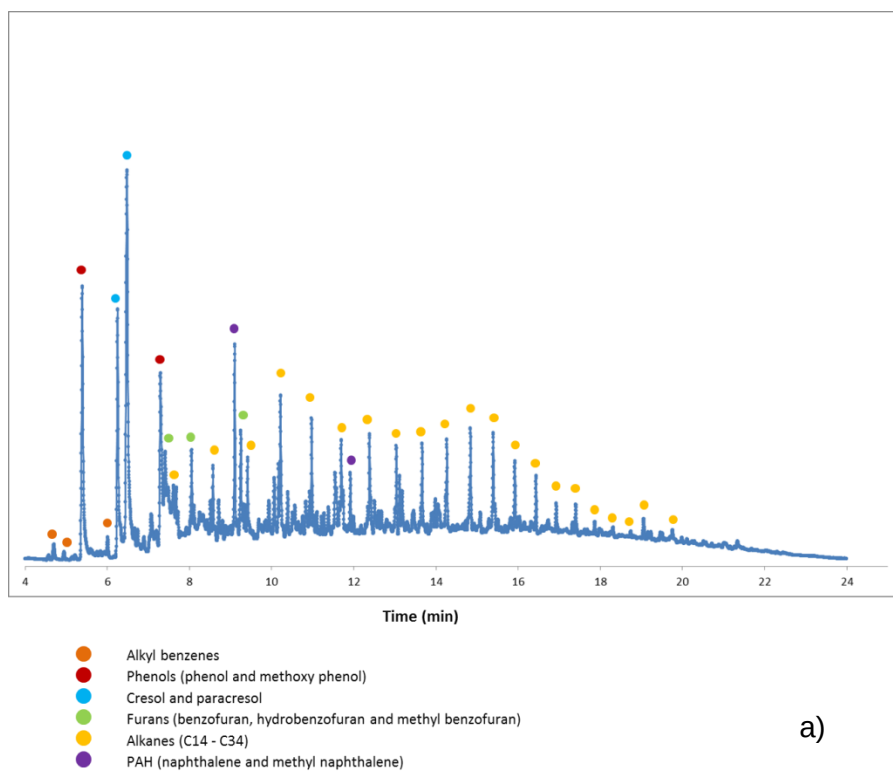


Figure 0-17: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal C



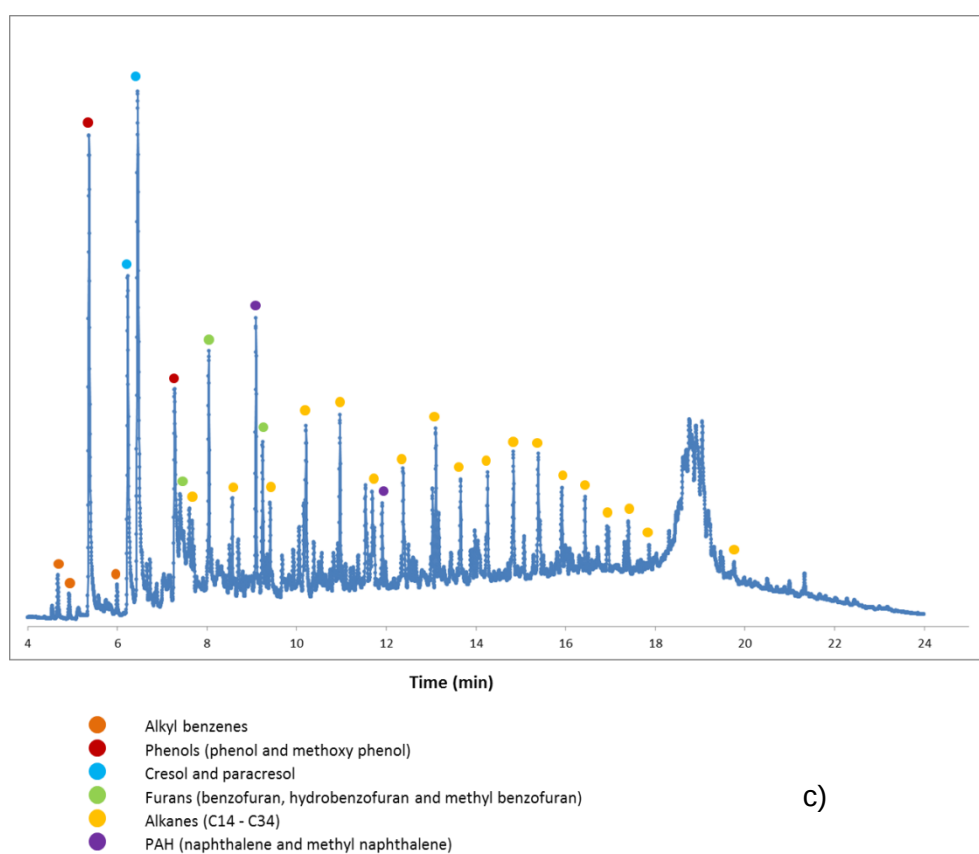
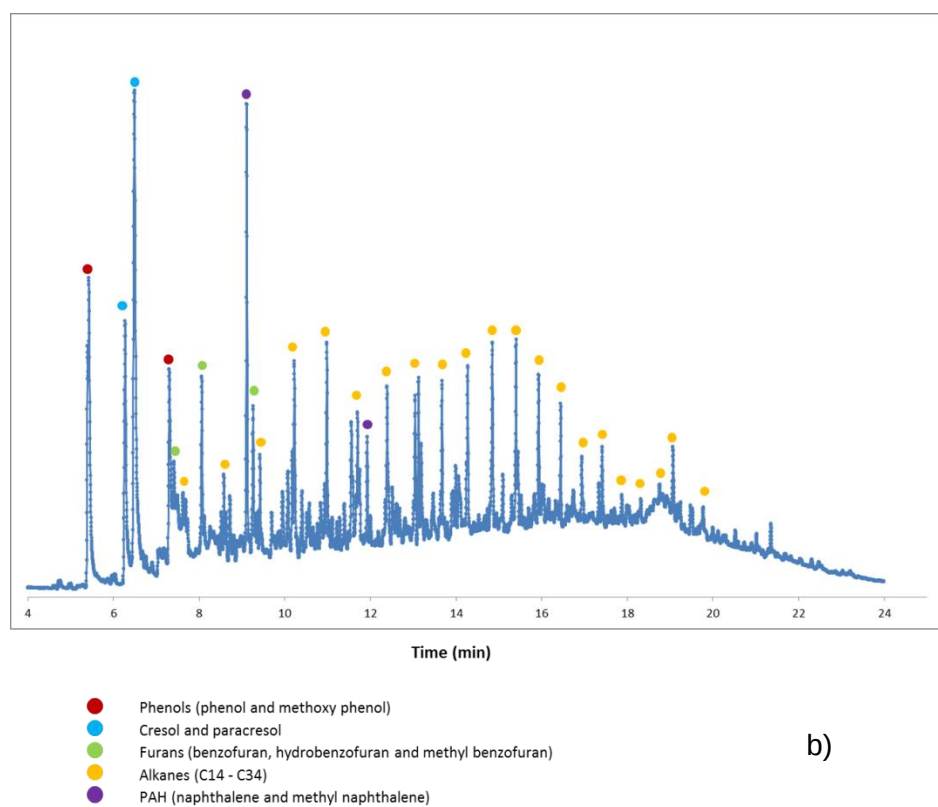
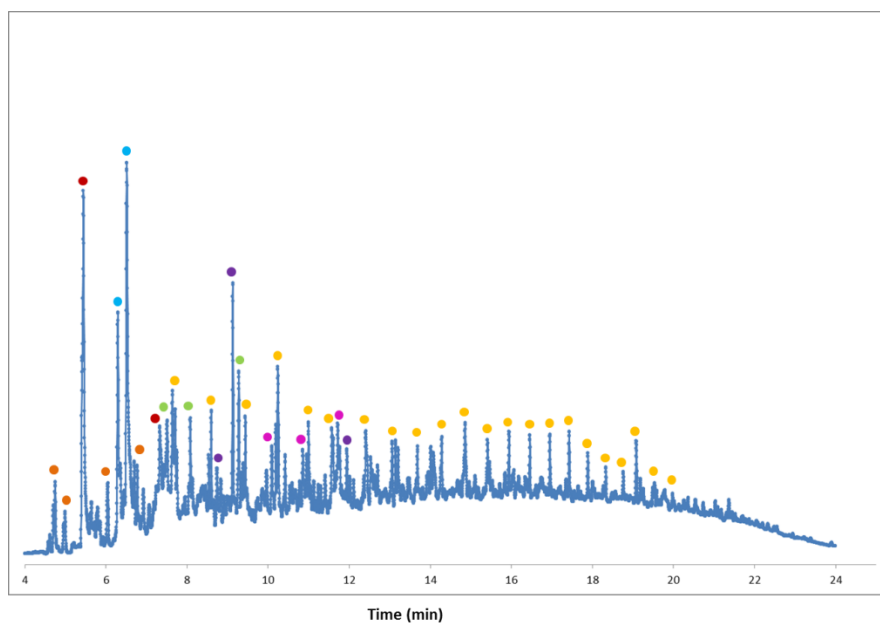
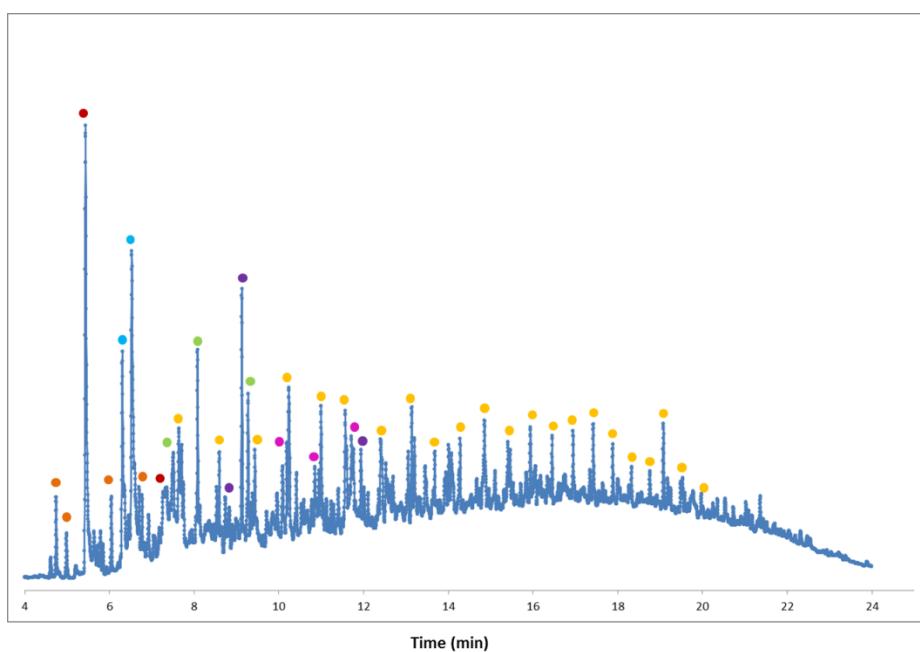


Figure 0-18: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal D



- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran, hydrobenzofuran and methyl benzofuran)
- Alkanes (C14 - C35)
- PAH (azulene, naphthalene and methyl naphthalene)
- Long chain alcohols

a)



- Alkyl benzenes
- Phenols (phenol and methoxy phenol)
- Cresol and paracresol
- Furans (benzofuran, hydrobenzofuran and methyl benzofuran)
- Alkanes (C14 - C35)
- PAH (azulene, naphthalene and methyl naphthalene)
- Long chain alcohols

b)

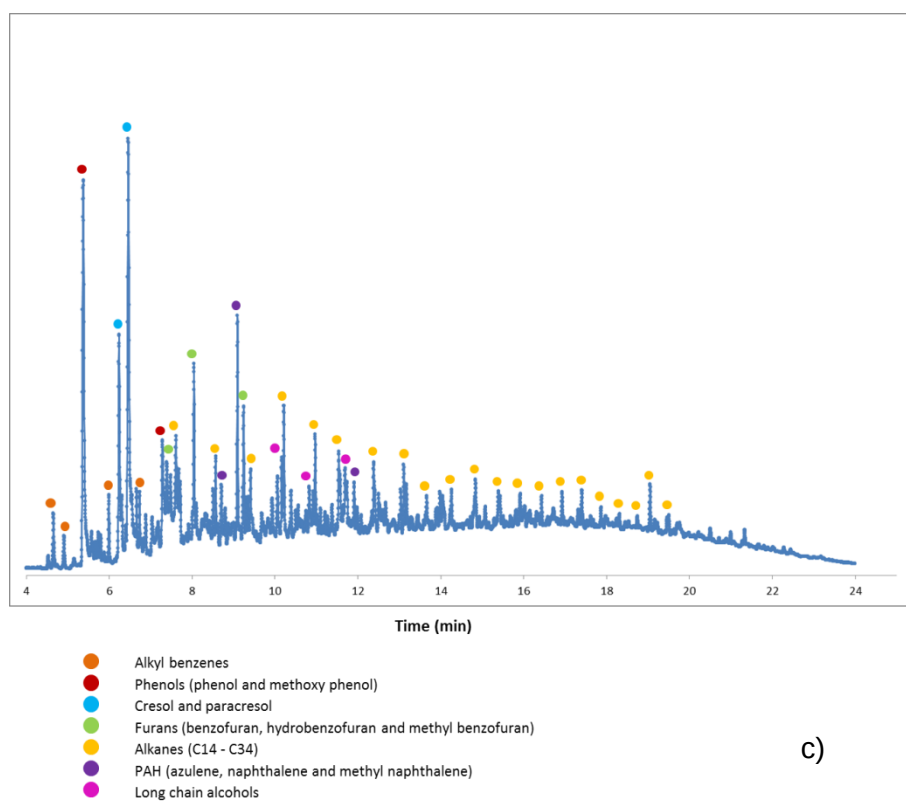
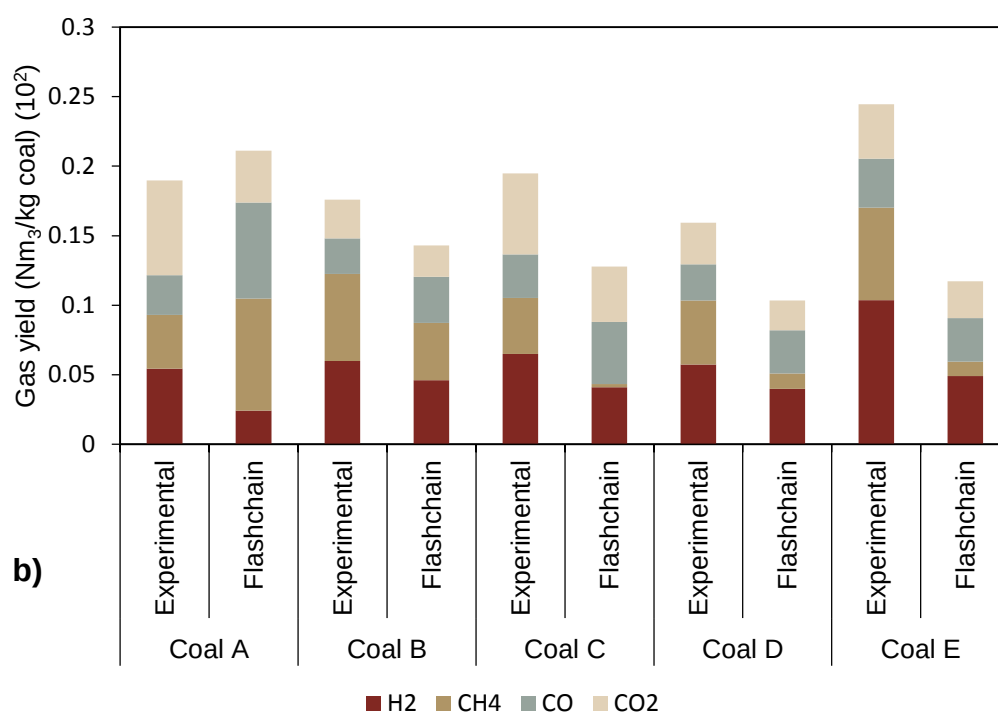
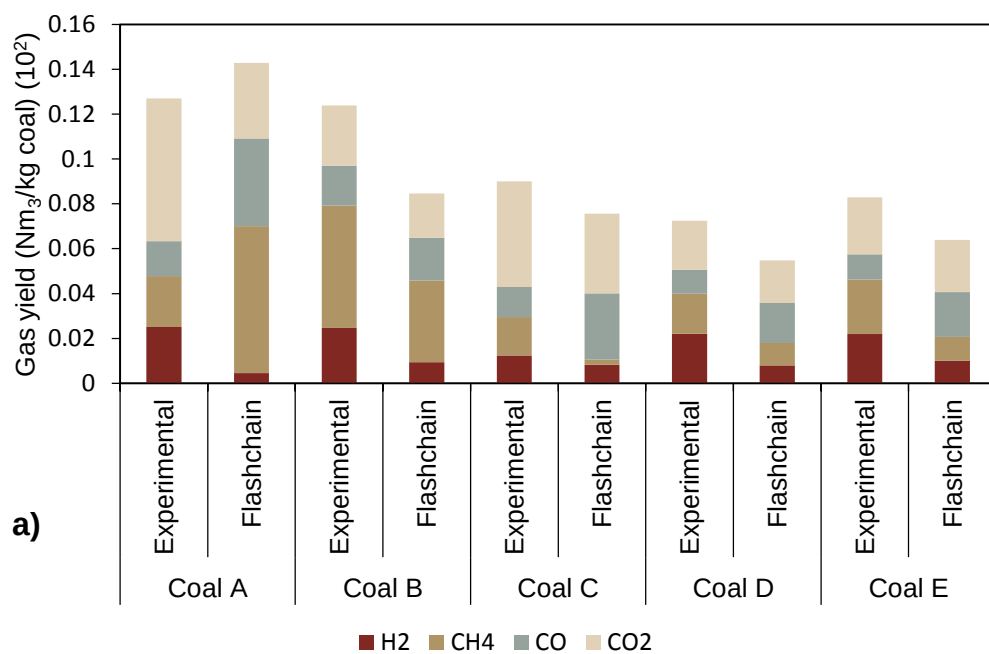


Figure 0-19: Gas chromatograms of tar formed at a) 520 °C, b) 720 °C and c) 920 °C evolved from coal E

Appendix C – Statistical and FLASHCHAIN® modelling



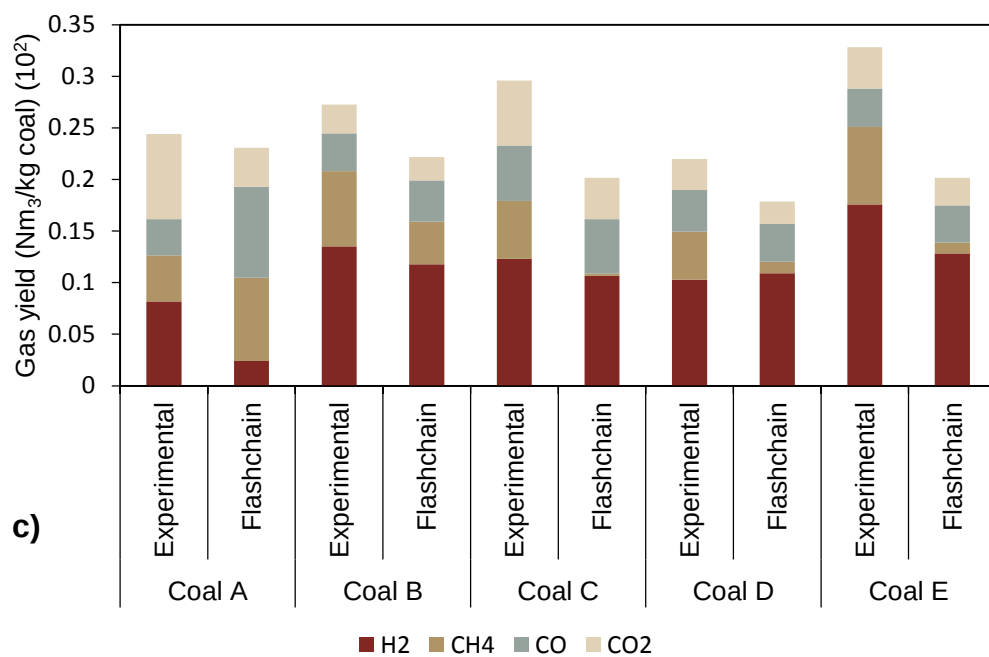


Figure 0-20: FLASHCHAIN® predicted gas yields compared with experimentally determined gas yields for final pyrolysis temperatures of a) 520 °C, b) 720 °C and c) 920 °C