NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT

# Solvent extraction of South African coal using a low volatile, coal-derived solvent

Eulouka Janse van Rensburg (B.Eng, Chemical)

Dissertation submitted in fulfilment of the requirements for the degree *Master of Engineering* in the School of Chemical and Minerals Engineering at the Potchefstroom campus of the North-West University.

Supervisor: Prof. O.S.L Bruinsma

November 2007
POTCHEFSTROOM

# DECLARATION

I, Eulouka Janse van Rensburg, hereby declare to be the sole author of the report entitled:

SOLVENT EXTRACTION OF SOUTH AFRICAN COAL USING A LOW VOLATILE, COAL-DERIVED SOLVENT

for completion of the degree, M.Eng Chemical Engineering at the North-West University.

---------------------------------------

Eulouka Janse van Rensburg
Potchefstroom
23 November 2007

# ACKNOWLEDGEMENTS

A lot of persons are usually involved during a project like this. I would like to use this opportunity to thank them. First of all I would like to give thanks to God for giving me the talent and opportunity to do this project. I would also like to thank my family and friends for their support during my studies.

A big thanks to my supervisor, Prof. Bruinsma, for his guidance and inspiration throughout the course of my studies. I would also like to thank Dr. Tjaart van der Walt and Gerda de Jager of Sasol Research and Development, Syngas and coal technology, for all their help and assistance. A special thanks to Prof. Harold Schobert of PennState University, U.S.A for his contributions and input.

Furthermore, I would like to thank the students Marnus Beukman and Burgert Hattingh for performing the continuous extraction experiments. As well as Mac Pedlow, exchange student of PennState University, U.S.A for assisting them with the experiments.

I would like to thank the following people for their assistance with either training me or performing analyses:

- Mr. Ashton of Sasol as well as Mr. Van Dyk of SABS for performing the proximate and ultimate analyses.
- Prof. Campbell of North-West University for training me to do calorific value and particle size distribution analyses.
- Mr. Bisset of North-West University for training in porosity measurements.
- Dr. Tiedt of North-West University for performing SEM analysis.
- Me. Du Sautoy of Sasol for the pyrolysis-GC/MS analysis.
- Dr. Jordaan of North-West University for performing GC/MS analysis.

Lastly I would also like to thank Mr. Kroeze and Mr. Brock of the Chemical Engineering technical workshop for their assistance with the experimental setups.

A special thanks to Sasol for funding this project.

# ABSTRACT

Coal is an important fuel for countries with large coal reserves such as South Africa since it is expected that oil and natural gas prices will continue to rise. The Waterberg coalfield contains 40% of South Africa's remaining coal reserves, but due to the lack of a good infrastructure (water and railway) there are currently only a few operations in the Waterberg. The utilization of remote coal reserves, such as the Waterberg coalfield, is difficult and requires an investigation of possible coal conversion processes. The extraction of high-ash bituminous coal, using an organic solvent, had been studied by coal researchers before as a possible method to convert coal into valuable products. The purpose of the solvent is to extract organic material from the coal while the inorganic mineral matter (ash) is left behind. Advantages of the solvent extraction process include mild operating conditions compared to an indirect liquefaction process, low $CO_2$ release and coal as major utility since the solvent can be recycled. Therefore, the aim of this study was to investigate the solvent extraction of South African coal using a coal-derived solvent.

Batch extraction experiments were carried out for two South African coals – one a vitrinite-rich coal (Waterberg) and the other an inertinite-rich coal (Brandspruit). A vitrinite-rich American coal (Illinois#6) was used as benchmark. Residue oil was the selected coal-derived industrial solvent used for the extractions.

High extraction yields (d.a.f) were obtained for Waterberg (29-63%) and Illinois#6 coal (55-74%), while only limited success was achieved with Brandspruit coal (maximum 17%). This shows that solvent extraction, using residue oil as solvent, is a possible coal conversion process to convert vitrinite-rich South African coal into valuable products. For the operating conditions investigated in this study it was found that 370°C is the optimum extraction temperature and 5:1 the optimum solvent to coal ratio, while the particle size did not have a significant influence on the extraction yield.

Continuous extraction experiments were carried out for the same two South African coals used in the batch extraction experiments and also with residue oil as solvent. Extraction temperatures and residence times were limited by the experimental setup. Negative extraction yields were obtained that could be explained by the effect of coal particles adsorbing compounds in the residue oil during the filtration step, which was performed at room temperature. To compensate for the adsorption process, the extraction yields were calculated with the extraction data at the lowest temperature as basis instead of the feed coal data. Extraction yields (d.a.f) of 20-52% were then obtained for the Waterberg coal and 3-12% for Brandspruit coal, with the highest extraction yield observed at 340℃ and residence time of 12 min. In general, an increase in extraction yield with increase in temperature as well as with increase in residence time was observed.

The shrinking-core model was used to describe the solvent extraction process and provided a good fit for the experimental data. Activation energies of 324 kJ/mol for Waterberg coal and 134 kJ/mol for Brandspruit coal were determined. Finally, it was found that most of the results of the continuous extraction experiments were in line with the results of the batch extraction experiments.

In conclusion, the objectives of this investigation were met and form a good basis for further extraction research. In general it can be recommended to expand the conditions of this investigation to check the accuracy of the conclusions made. The most important areas for future research in developing a commercial-scale process include separation of residue coal from the extract, recycling of the solvent, and hydrogenation studies on the liquid extract product.

# OPSOMMING

Steenkool is 'n belangrike brandstof vir lande met groot steenkool reserwes soos Suid-Afrika, veral aangesien dit verwag word dat die prys van ru-olie en natuurlike gas sal aanhou styg. Die Waterberg steenkoolveld bevat 40% van Suid-Afrika se oorblywende steenkool reserwes, maar as gevolg van 'n gebrek aan 'n goeie infrastruktuur (water en spoorweg) is daar op die oomblik nie baie ontginning in die Waterberg nie. Die ontginning van afgeleë steenkoolvelde, soos die Waterberg steenkoolveld, is moeilik en daarom is dit nodig om verskillende steenkool omsettingsprosessse te ondersoek. Die ekstraksie van hoë-as bitumineuse steenkool met 'n organiese oplosmiddel is al in die verlede deur steenkool navorsers ondersoek as 'n moontlike proses om steenkool om te skakel na waardevolle produkte. Die doel van die oplosmiddel is om organiese material vanuit die steenkool te ekstraheer terwyl die anorganiese material (as) agtergelaat word. Voordele van die ekstraksie proses is matige bedryfstoestande in vergelyking met 'n indirekte vervloeiingsproses, lae vrystelling van $CO_2$ en steenkool as belangrikste utiliteit aangesien dit moontlik is om die oplosmiddel te hersirkuleer. Die doel van hierdie projek was dus om die ekstraksie van Suid-Afrikaanse steenkool te ondersoek deur gebruik te maak van 'n oplosmiddel wat vanaf steenkool verkry word.

Enkellading ekstraksie eksperimente is uitgevoer met twee tipes Suid-Afrikaanse steenkool – een vitriniet-ryk (Waterberg) en die ander een inertiniet-ryk (Brandspruit). 'n Vitriniet-ryke Amerikaanse steenkool (Illinois#6) is ook gebruik vir vergelykings doeleindes. Residu-olie is gebruik as die steenkool-afgeleide oplosmiddel.

Hoë ekstraksie opbrengste (d.a.f) is verkry vir Waterberg (29-63%) en Illinois#6 steenkool (55-74%), terwyl 'n maksimum ekstraksie opbrengs van slegs 17% verkry is met Brandspruit steenkool. Dit dui daarop dat ekstraksie, met residu-olie as oplosmiddel, 'n moontlike proses is om vitriniet-ryke Suid-Afrikaanse steenkool om te skakel in waardevolle produkte. Vir die bedryfstoestande wat ondersoek is in hierdie studie is dit gevind dat 370°C die optimum ekstraksie temperatuur is en 5:1 die optimum oplosmiddel tot steenkool verhouding, terwyl die partikelgrootte van die steenkool nie 'n groot invloed gehad het op die ekstraksie opbrengs nie.

OPSOMMING

Kontinue ekstraksie eksperimente is ook gedoen met dieselfde twee tipes Suid-Afrikaanse steenkool as in die enkellading ekstraksies en ook met residu-olie as oplosmiddel. Ekstraksie temperature en verblyfstye was beperk deur die eksperimentele opstelling. Negatiewe ekstraksie opbrengste was verkry. Dit kan verduidelik word deur die moontlike effek van steenkool partikels wat komponenete in die residu-olie adsorbeer tydens die filtrasie proses wat by kamertemperatuur uitgevoer is. Om vir die adsorpsie proses te kompenseer is die ekstraksie opbrengste bereken met die ekstraksie data by die laagste temperatuur as basis in plaas van die voer steenkool data. Ekstraksie opbrengste (d.a.f) van 20-52% is gevolglik verkry vir die Waterberg steenkool en 3-12% vir Brandspruit steenkool. Die hoogste ekstraksie opbrengs is verkry by 340°C en verblyfstyd van 12 min. In die algemeen is 'n verhoging in ekstraksie opbrengs met verhoging in temperatuur asook met 'n verlenging in verblyfstyd waargeneem.

Die krimpende-kern model is gebruik om die ekstraksie proses te beskryf en het 'n goeie passing gelewer vir die eksperimentele data. Die aktiveringsenergie vir Waterberg steenkool is bereken as 324 kJ/mol en vir Brandspruit steenkool as 134 kJ/mol. Die meeste van die resultate vir kontinue ekstraksie stem ooreen met die resultate vir enkellading ekstraksie.

Die doelwitte van hierdie projek is bereik en vorm 'n goeie basis vir verdere ekstraksie navorsing. In die algemeen kan dit aanbeveel word dat die bedryfstoestande van hierdie ondersoek uitgebrei moet word om die akkuraatheid van die gevolgtrekkings te verifieër. Die belangrikste areas vir toekomstige navorsing om 'n industriële proses te ontwikkel behels die skeiding van die residu steenkool van die ekstrak, hersirkulering van die oplosmiddel en hidrogeneringstoetse op die vloeistof ekstrak.

# TABLE OF CONTENTS

## 1. INTRODUCTION

## 2. COAL AND COAL CONVERSION PROCESSES: A LITERATURE REVIEW

## 3. EXPERIMENTAL METHODOLOGY AND ANALYTICAL METHODS

## 4. EQUILIBRIUM BATCH EXTRACTION

## 5. CONTINUOUS EXTRACTION AND KINETIC MODEL: A FIRST APPROACH

## 6. CONCLUSIONS

## 7. RECOMMENDATIONS AND OUTLOOK

## B. YIELD CALCULATIONS AND REPRODUCIBILITY

## C. PROXIMATE AND ULTIMATE ANALYSES: BATCH EXTRACTION

## D. CALORIFIC VALUE

## E. POROSITY

## H. PROXIMATE AND ULTIMATE ANALYSES: CONTINUOUS EXTRACTION

# LIST OF FIGURES

# LIST OF TABLES

# LIST OF SYMBOLS

| Symbol | Description | Unit |
|---|---|---|
| A | Arhenius constant | - |
| B | Brandspruit coal | - |
| $B$ | Arhenius constant for shrinking-core model | - |
| $d_i$ | Pore diameter | nm |
| $d_p$ | Particle diameter | µm |
| $E_a$ | Activation energy | kJ/mol |
| C | Feed coal | - |
| I | Illinois#6 coal | - |
| k | Rate constant | $min^{-1}$ |
| P | Pressure | bar |
| $r_p$ | Pore radius | nm |
| R | Gas constant | J/mol.K |
| RC | Residue coal | - |
| RO | Residue oil | - |
| $t$ | Time | min |
| T | Temperature | ℃ or K |
| W | Waterberg coal | - |
| $x$ | Proximate/ultimate constituent | - |
| $x_E$ | Amount of $x$ in the extract | g |
| $x_C$ | Amount of $x$ in the feed coal | g |
| $x_{RC}$ | Amount of $x$ in the residue coal | g |
| X | Conversion. Extraction yield at specific operating conditions and time divided by the maximum or final extraction yield at these conditions. | - |
| $y$ | Extraction yield | - |
| $y_f$ | Maximum or final extraction yield. | - |
| $y_i$ | Differential intrusion | mL/g/nm |

LIST OF SYMBOLS

| Symbol | Description | Unit |
|---|---|---|
| $\alpha$ | Conversion. Extraction yield at a given time divided by the extraction yield at infinite time. | - |
| $\gamma$ | Surface tension. | N/m |
| $\tau$ | Residence time in a plug flow reactor. | min |
| $\tau_f$ | Residence time required for complete extraction. | min |
| $\theta$ | Contact angle | ° |

# CD-ROM CONTENTS

- SEM-movie of heated feed coal particles.
- SEM images.
- Particle size distribution graphs.
- Pyrolysis-GC/MS data.
- GC/MS data.

# CHAPTER 1

# INTRODUCTION

In this chapter, a broad overview of the contents presented in the undertaken study will be given. Firstly, the background and motivation for the research will be discussed. Then the aim and objectives will be formulated, whereafter the scope of the investigation will be laid out.

## 1.1 Background and motivation

Coal is one of the most important fossil fuels and with oil and natural gas prices expected to continue rising, coal is an important fuel for countries with large coal reserves. South Africa's recoverable coal reserves are estimated at 54 billion short tons and provide for 75% of South Africa's total energy needs as shown in Figure 1.1 (Energy information administration, 2007). In 2005, South Africa's total primary energy consumption was 5.041 quadrillion ($10^{15}$) BTU which is equal to 5.3 x $10^{12}$ MJ (Energy information administration, 2007). This indicates the importance of the effective utilization of coal in South Africa.

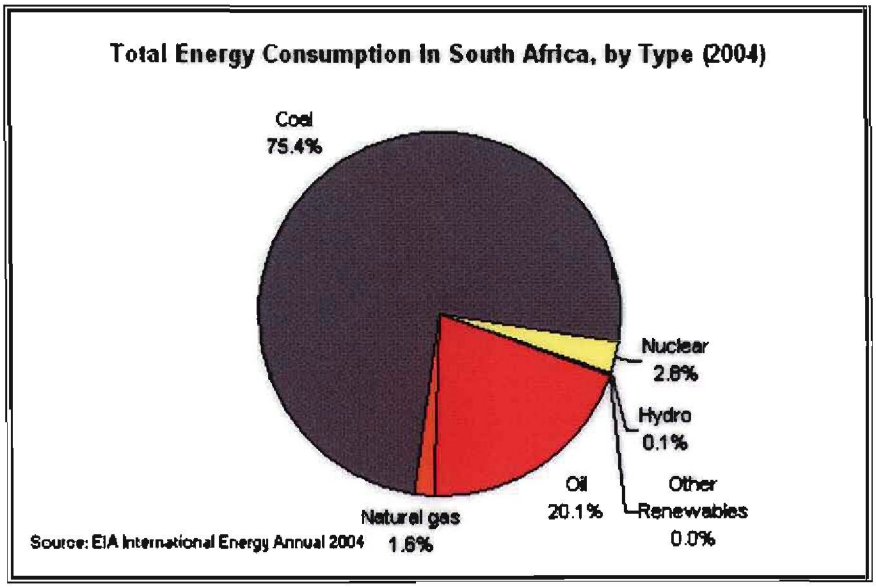


Figure 1.1: Total energy consumption in South Africa (Energy information administration, 2007).

# 1. INTRODUCTION

There are several coalfields in South Africa of which the Witbank and Mpumalanga coalfields are currently the most important in terms of coal production. These coalfields however are slowly but surely being used up. The Waterberg coalfield, situated in the Limpopo province of South Africa, contains 40% of South Africa's remaining coal reserves. Currently, Exxaro's Grootegeluk coal mine and Matimba power station are the only operations in the Waterberg, mainly due to the lack of a good infrastructure (water and railway) (Venter, 2003). Therefore, research on the effective utilization of Waterberg coal for the future is necessary.

The economic driving force for the conversion of coal into more valuable products is illustrated in Figure 1.2. In this figure, the relationship between the value (R/ton) of a CH-product and the molar H/C ratio of the product is given (Energy information administration, 2007; World refining and fuels today, 2007). This again illustrates the importance of effective conversion processes to convert coal to more valuable products, in particular liquid fuels. The hydrogen required for production of the high value liquid fuels might be obtained from the production of coke, which has a much lower economic value compared to the liquid fuels as can be seen from Figure 1.2.

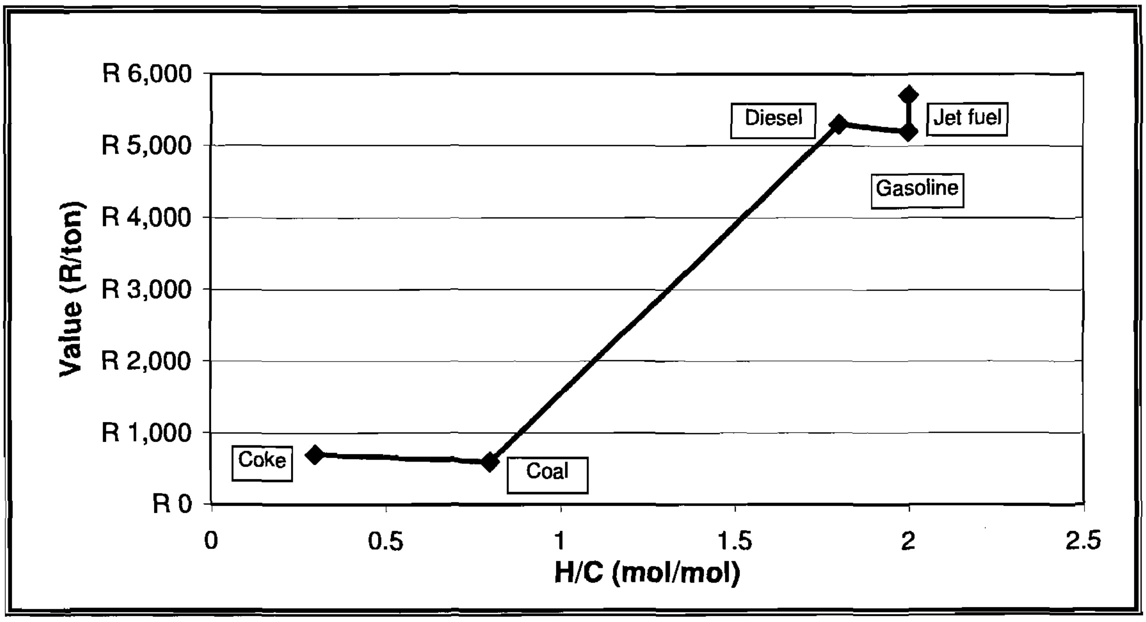


Figure 1.2: Economic diagram.

# 1. INTRODUCTION

SASOL uses an indirect liquefaction process to produce liquid fuels and chemicals from coal. This process is carried out under severe operating conditions and is accompanied by the release of $CO_2$. SASOL mines about 45 million tons per annum of coal (Sasol facts, 2007). In Secunda, one third of the coal is send to the boilers for producing high-pressure (HP) steam, while the remaining two thirds is send to the Sasol-Lurgi gasifiers (Van der Walt, 2007). The reaction in the boilers is given by equation (1.1), while the overall reaction in the gasifiers is given by equation (1.2).

$$Coal + O_2(in\ air) \rightarrow CO_2 + N_2 + HP\ steam \tag{1.1}$$

$$\begin{aligned} Coal + O_2 + Steam \rightarrow\ & CO_2(30vol\%) + CO(20vol\%) + H_2(40vol\%) + CH_4(10vol\%) \\ & + Unconverted\ steam + Tar + Phenols,\ NH_3, \ldots \end{aligned} \tag{1.2}$$

Therefore, during SASOL's indirect liquefaction process approximately 25 million tons per year $CO_2$ from the gasifiers and another 28 million tons per year $CO_2$ from the boilers are produced. In addition to these disadvantages, utilities, such as water, and a good infrastructure are also required for this process, which makes the utilization of more remote coal reserves, such as the Waterberg coalfield, difficult (Van der Walt, 2007). All these factors work together to make an investigation into alternative coal conversion processes necessary.

The extraction of high-ash bituminous coal, using an organic solvent, had been studied by coal researchers before as a possible method to convert coal into valuable products. The purpose of the organic solvent is to extract organic material from the coal while the inorganic mineral matter (ash) is left behind. However, most of this research was conducted on a small scale using organic solvents such as tetralin (Miura *et al.*, 2001) or N-methylpyrrolidone (NMP) (Renganathan *et al.*, 1988).

If a coal has a high vitrinite content, it may be possible to convert this coal into valuable products by solvent extraction. The operating conditions of the proposed solvent extraction process are mild compared to those of the indirect liquefaction process. Other advantages of the solvent extraction process is that the $CO_2$ release is low and that coal is the major utility since the solvent can be recycled.

Solvent dissolution (extraction) as a coal conversion process can be explained by the following reaction:

Coal + Solvent → Residue coal + Coal extract

During the dissolution process, coal is digested in the solvent. The digest, after a liquid/solid separation step, yields a high-ash solid residue coal and a low-ash liquid or pitch-like product, called extract. The residue coal contains the inorganic mineral matter as well as the insoluble coal. The coal extract consists of the solvent and soluble organic part of the coal. From here on different paths can be taken to obtain different products, either a liquid, a pitch, or a solid, each with different applications.

Figure 1.3 illustrates what a conceptual solvent extraction process could look like. For the scope of this investigation, we only concentrated on studying the solvent extraction step. A lot of future work can be done on optimizing the solid/liquid separation step, while the process for recovering the recycle solvent from the extract to obtain a low-ash product also presents its own challenges. In addition to this, the processing of the low-ash product to a commercial fuel is also a major field of research.

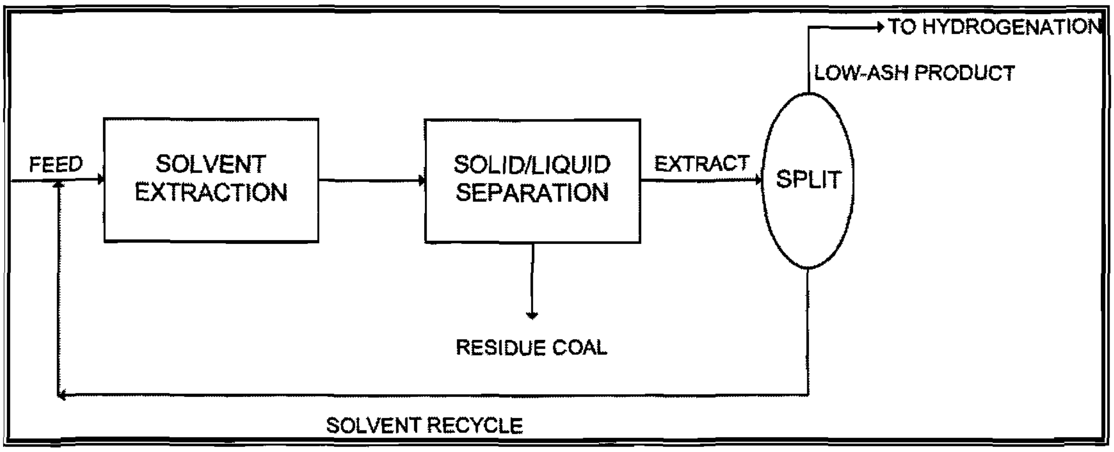


Figure 1.3: Conceptual solvent extraction process.

High-vitrinite coal is often found to better suit direct coal conversion routes (e.g. via solvent extraction or direct liquefaction) than coal with a high inertinite content. Coals with a high inertinite content are often more suitable for indirect coal conversion routes (e.g. via coal gasification followed by Fischer-Tropsch synthesis) (Smook, 2007).

For this reason it was decided to investigate the solvent extraction of two South African coals – one a vitrinite-rich coal and the other an inertinite-rich coal. The vitrinite-rich coal that was used in this study is Waterberg coal due to its importance as described above, while the inertinite-rich coal used is Brandspruit coal. In addition, it was decided to use Illinois#6 coal as a benchmark to compare the extraction results of this study with the results of previous research reported in literature.

## 1.2 Aim and objectives

As in any research project it is important to clearly define the aim of the project. The aim of this study is to investigate the solvent extraction of South African coal using a coal-derived solvent.

In addition to the general aim of the project it is also important to state the more detailed objectives in order to guide the investigation. The research objectives of this study are given below.

- In the past a lot of research was conducted on the topic of solvent extraction, mostly in the U.S.A (Griffith *et al.*, 2004) and Japan (Okuyama *et al.*, 2004). Very little research had been done on the solvent extraction of South African coal. Therefore, the first objective of this investigation is to determine if it is possible to use solvent extraction to convert *South African coal* to valuable products.

- In most of the previous research, expensive organic solvents such as tetralin or N-methylpyrrolidone (NMP) were used. A drawback encountered with this type of solvents is the high vapour pressure of the solvents. Pressures at which solvent extraction have been carried out in previous research range from 10 to 100 bar. Therefore, in an attempt to lower the operating pressure of the process to about 5 bar and to find a more suitable commercial-scale solvent, the second objective of this investigation is to determine if high extraction yields could be obtained using a *coal-derived industrial solvent*.

- Another objective is to investigate different process conditions, which include the temperature of the extraction, the particle size of the feed coal and the solvent/coal ratio, in order to determine the *optimum process conditions* for the extraction process.

- Most previous research had been done using batch extraction. Therefore, in addition to the investigation of a batch extraction process, the objective is also to develop an experimental setup to investigate a *continuous extraction process*.

- Little research had been done regarding the kinetics of the extraction process. Therefore, the last objective of this project is to obtain more accurate *reaction kinetics data* by investigating a continuous extraction process. These reaction kinetics data would then be used to develop a model for the solvent extraction process.

## 1.3 Scope of investigation

The scope of this investigation, in order to meet the objectives of this study as described in the previous section, will be outlined in this section.

Firstly, an intensive literature study was done in order to better understand coal in general, as well as to know about different coal conversion processes and solvents used. It was also important to make a study of previous work done on this subject in order to compare the results of this study with previous results. The information obtained from the literature study is given in Chapter 2.

After studying the available literature, the experimental work was planned. Firstly, the experimental setup and equipment used for the batch and continuous extraction experiments were designed. Furthermore, the experimental program and the experimental procedures were laid out. In addition, the analyses that would be carried out were also decided on. All the work regarding the experimental work of this investigation is reported in Chapter 3.

Batch extraction data at different operating conditions and with different coals using a selected coal-derived industrial solvent were obtained. The batch extraction data were then processed to obtain extraction yields and graphs illustrating the effects of the different operating conditions. Chapter 4 gives a discussion of the results of the batch extraction investigation, together with the results of the analyses that were carried out.

In addition to the batch extraction data, continuous extraction data were also obtained. Chapter 5 gives a discussion of the results of the continuous extraction investigation, together with the results of the analyses that were carried out. The data collected during the continuous extraction experiments were processed to determine the reaction kinetics of the solvent extraction process. In Chapter 5, the chosen kinetic model and determination of the kinetic parameters are also presented.

Finally, all the conclusions made during this investigation were summarized and some recommendations for future work on this subject were made. This is done in Chapters 6 and 7.

# CHAPTER 2

# COAL AND COAL CONVERSION PROCESSES:

# A LITERATURE REVIEW

In this chapter, the background of coal will be discussed briefly in order to better understand the complex nature of coal. The importance of coal to South Africa will be highlighted and different conversion processes will be discussed. Some of the previous work done by other researchers on the extraction of coal using a solvent will also be discussed in this chapter, as well as the classification of solvents.

## 2.1 Coal

Coal is well known for its use as fuel, as feedstock in the generation of electricity and in the manufacturing of steel, but what exactly is coal? Falcon and Snyman (1986) defined coal as "fundamentally composed of the fossilized remains of plant debris which have undergone progressive physical and chemical alteration through geological time". Vorres (2002) defined coal as "the result of combined biological, chemical and physical degradation of accumulated plant matter over geological ages".

### 2.1.1 Formation of coal

Coal was formed over millions of years from plant debris by the process of coalification. Coalification is the process where coal is formed through the progression of peat to lignite to bituminous coal and to anthracite (Stach *et al.*, 1982). Coalification takes place over time and conditions of high temperature and pressure are needed for the process. The formation of coal in terms of rank is shown in Figure 2.1, with the rank progressing from swamp to anthracite being the highest rank coal. In this context, rank is an indication of the level of maturity of the coal (Falcon & Snyman, 1986).

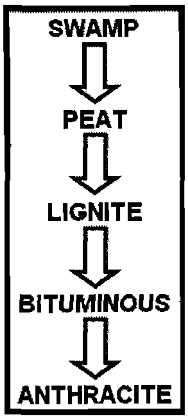


Figure 2.1: Formation of coal in terms of rank (Falcon & Snyman, 1986).

The formation of coal can be divided into two stages, biochemical and geochemical, where chemical and physical changes take place (Vorres, 2002). When plants growing in swamps die and decay, they form peat. During the first stage of coal formation the peat subsides and becomes covered with water. Layers of clay and sand then form above the peat as the water drains away. With increasing time, more layers of sediment are formed and under conditions of increasing temperature and pressure the formation of coal progresses (England *et al.*, 1975). During the geochemical stage, the oxygen and hydrogen content of the coal decreases while the carbon content increases. The volatile matter also decreases while moisture is lost (Vorres, 2002).

### 2.1.2 Structure of coal

Carbon, hydrogen and oxygen are the main elemental components present in coal while nitrogen and sulphur are also present in smaller amounts (Vorres, 2002).

It is very important to understand the structure of coal in order to utilize it effectively in different coal conversion processes. Coal is an organic rock that is composed of organic materials and also contains inorganic constituents. The organic materials are called macerals and are formed through the chemical and physical changes of plant remains (Meyers, 1982). Macerals have characteristic chemical and physical properties and are divided into three main groups, namely (Stach *et al.*, 1982):

1) Vitrinite
2) Liptinite (Exinite)
3) Inertinite

Knowing the origin of the different macerals will give us a better understanding of their characteristics. Vitrinite has its origin from woody tissues and is derived from stems, roots and leaves, whereas liptinite has formed from waxy parts of plants such as spore, cuticles and resins. It is believed that inertinite has primarily developed from partial carbonization of plant tissue in the peat swamp (Meyers, 1982).

The inorganic material in coal is called mineral matter and consists of clay, quartz, carbonates, sulphides, sulphates, etc. (Meyers, 1982). The main elemental components present in the mineral matter are aluminium, calcium, iron, magnesium, silicon, sodium and sulphur (Vorres, 2002). A part of the mineral matter remains behind as ash when coal is burnt, while the other part decomposes and releases gasses.

Coal has a very complex structure and after many years of research no one can still explain the exact nature of coal. It is generally believed that coal has a macromolecular network structure. According to Larsen *et al.* (1985), coal consists of clusters which are held together by hydrogen bonds, forming a network that is covalently bonded. Van Heek (2000) explained the macromolecular network structure of coal as three to five ring aromatic and hydroaromatic components held together by short aliphatic and ether bridges. The macromolecules in the coal structure are formed by aromatic clusters held together by hydrogen bonds, bonds through oxygen, methylene or longer aliphatic groups, and disulfide bridges (Vorres, 2002).

It is believed that the vitrinite structure of bituminous coals and anthracites contains molecules composed of aromatic clusters, each containing one to four benzene rings and held together by hydroaromatic ring structures. Another characteristic of the vitrinite structure is that methyl, and occasionally larger aliphatic groups, replaced large amounts of hydrogen on the aromatic and hydroaromatic rings. The hydrogen on the aromatic rings is also replaced with oxygen present in phenolic hydroxyl groups and ethers. A small amount of oxygen is present as quinone on aromatic rings or ketones on hydroaromatic rings. The structure of bituminous coal is represented in Figure 2.2 (Shinn, 1984).

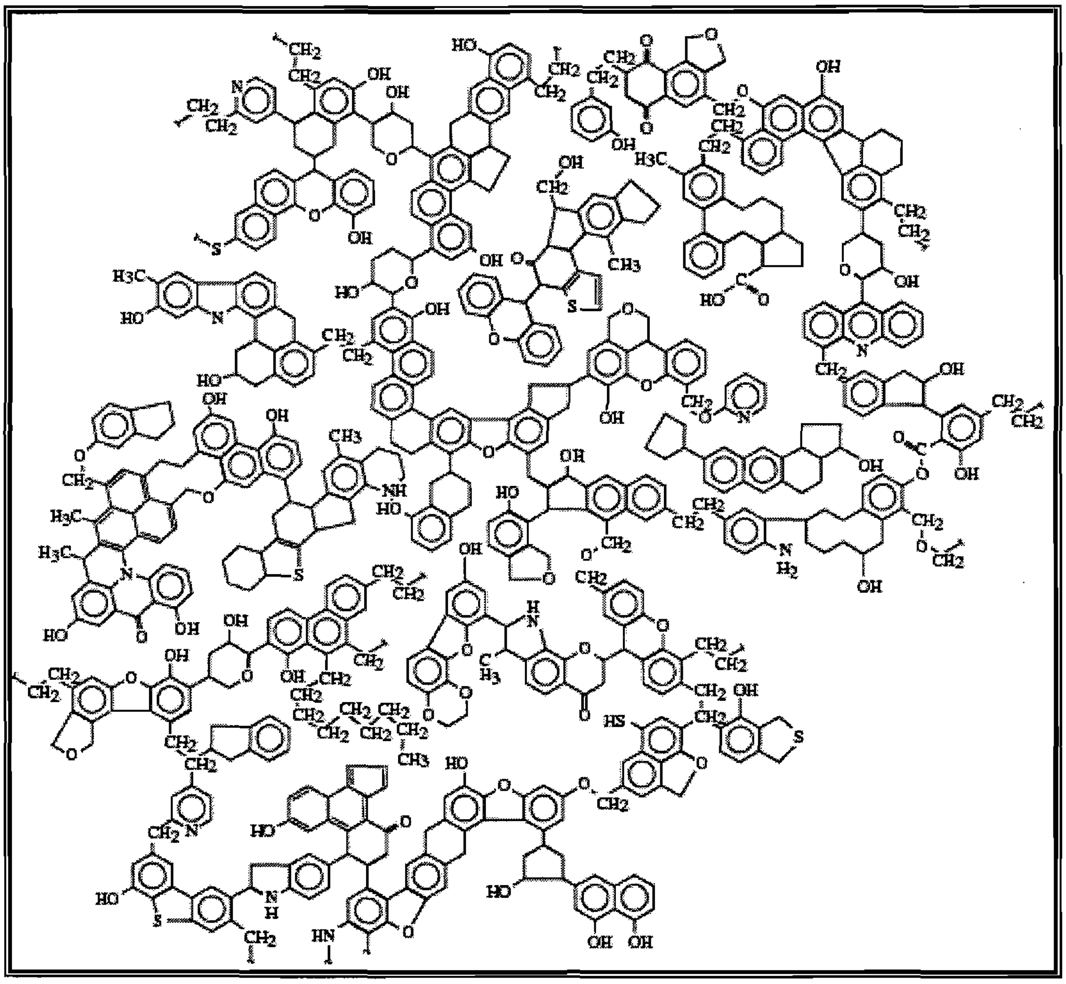


Figure 2.2: Representation of the structure of bituminous coal (Shinn, 1984).

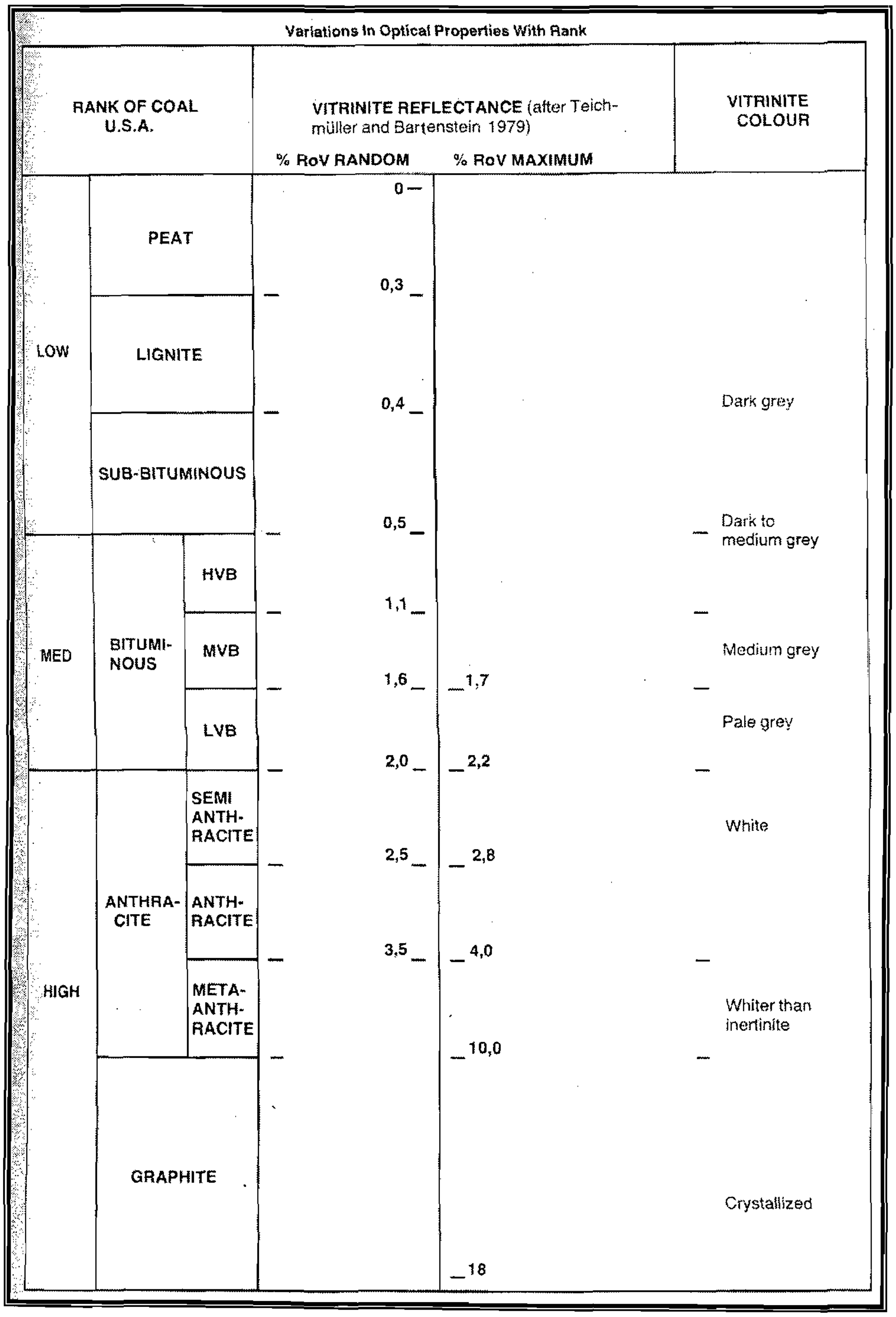
### 2.1.3 Classification of coal

Coal is a complex material that varies widely in rank and grade as well as chemical and physical properties. This makes the classification of coal difficult and therefore a good classification system is needed.

Until 1800 coal was simply classified as bright coal, black coal and brown coal. In the years that followed, various systems were developed for the classification of coal. These classification systems were based on oxygen content, carbon content, fuel ratio, calorific value, *etc.* (Van Krevelen, 1981).

One of the most commonly used classification systems today is a system where the rank of coal is determined by measuring the reflectance of vitrinite. According to Falcon and

Snyman (1986) this method can be used since the amount of light that is reflected off the surface of vitrinite particles, is directly related to changes in the volatile matter and carbon content of coal with rank. Figure 2.3 shows this classification of coal based on vitrinite reflectance (Falcon & Snyman, 1986). In Figure 2.3, %RoV Random is the random percentage reflectance of vitrinite particles while %RoV Maximum is the maximum percentage reflectance of vitrinite particles. According to Figure 2.3 peat, lignite and sub-bituminous coals are classified as low rank coals. Medium rank coals are bituminous coals that are subdivided into high, medium and low volatile coals. High rank coals consist of different classes of anthracite. As the rank of coal increases from peat to anthracite, the carbon content of the coal increases while the oxygen content decreases (Vorres, 2002).



Variations In Optical Properties With Rank

| RANK OF COAL U.S.A. | | | VITRINITE REFLECTANCE (after Teichmüller and Bartenstein 1979) | | VITRINITE COLOUR |
|---|---|---|---|---|---|
| | | | % RoV RANDOM | % RoV MAXIMUM | |
| LOW | PEAT | | 0 | | |
| | | | 0,3 | | |
| | LIGNITE | | | | |
| | | | 0,4 | | Dark grey |
| | SUB-BITUMINOUS | | | | |
| | | | 0,5 | | Dark to medium grey |
| MED | BITUMINOUS | HVB | | | |
| | | | 1,1 | | |
| | | MVB | | | Medium grey |
| | | | 1,6 | 1,7 | |
| | | LVB | | | Pale grey |
| | | | 2,0 | 2,2 | |
| HIGH | ANTHRACITE | SEMI ANTHRACITE | | | White |
| | | | 2,5 | 2,8 | |
| | | ANTHRACITE | | | |
| | | | 3,5 | 4,0 | |
| | | META-ANTHRACITE | | | Whiter than inertinite |
| | | | | 10,0 | |
| | GRAPHITE | | | | Crystallized |
| | | | | 18 | |

Figure 2.3: Classification of coal based on vitrinite reflectance (Vorres, 2002).

### 2.1.4 South African coal

In South Africa, a lot of research and development has been done regarding coal since it is the primary fuel produced and consumed. South Africa, having large coal reserves but no significant oil and gas reserves, realised the potential of coal and started developing processes for the production of liquid fuels from coal since the 1950's, when other countries still heavily depended on the availability of crude oil (Department of Minerals and Energy, 2005).

The coal seams found in South Africa are believed to be about 200 million years old. Approximately 5% of the world's total coal reserves are situated in South Africa. South Africa's recoverable coal reserves are estimated at 54 billion short tons[1], placing South Africa among the top 8 coal reserves holders in the world as shown in Figure 2.4. South Africa is the world's sixth largest producer of coal with a production of 245 million short tons in 2002, while 74 million short tons of coal was exported in 2002 making South Africa the third largest exporter of coal in the world (Energy information administration, 2005). In 2005, 36% of South Africa's liquid fuel needs were met by synthetic fuels produced from coal and natural gas, while the remaining 64% was imported crude oil (Department of Minerals and Energy, 2005). From these figures it is clear that coal is very important to the economy of South Africa. Therefore a lot of time, effort and money are spent to research and further develop the effective utilization of coal.

---

[1] 1 short ton = 0.91 metric ton

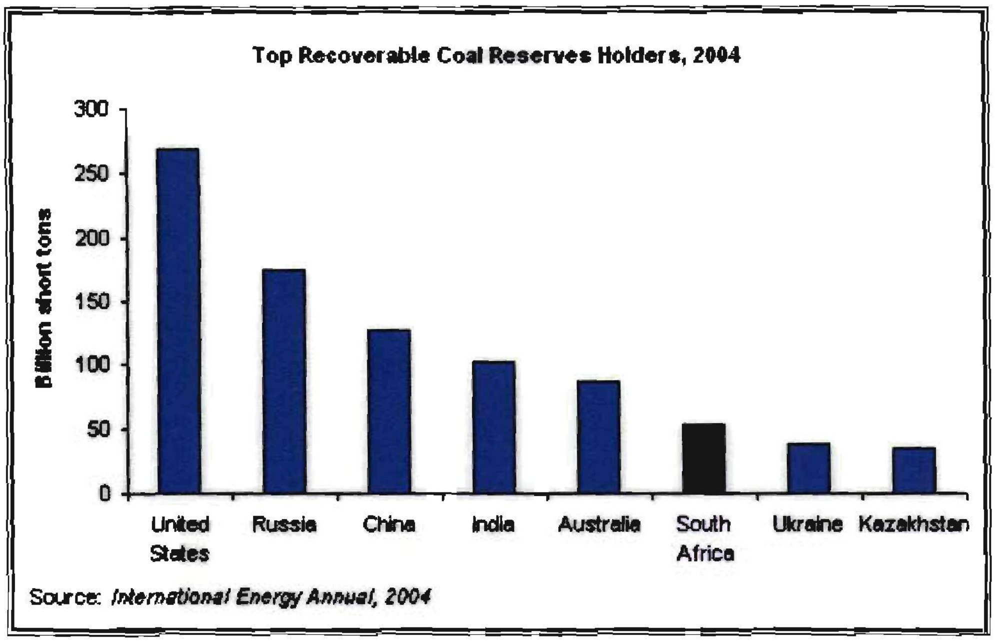


Figure 2.4: Top recoverable coal reserves holders (Energy information administration, 2005).

## 2.2 Coal conversion processes

There are different coal conversion processes that operate at different conditions and convert coal into different products for different applications. In general, to produce liquid fuels or gas from coal, the H/C ratio needs to be increased, either by adding hydrogen or by removing carbon (Dadyburjor & Liu, 2002). When hydrogen is added to coal the process is known as liquefaction while the process for removing carbon is known as pyrolysis (Department of Trade and Industry, 1999). These coal conversion processes will be discussed briefly in the next section.

### 2.2.1 Pyrolysis

Pyrolysis is the process where coal is heated in an inert atmosphere. Coal-derived tars and distillates are then recovered from the off-gas stream (Vorres, 2002).

Pyrolysis can be divided into mild and rapid processes. In mild pyrolysis coal is heated to a temperature of about 450-650°C to drive off original volatile matter, while thermal decomposition causes new volatile organic compounds to be formed. This produces a char with a lower hydrogen and heteroatom content. Rapid pyrolysis on the other hand operates at higher temperatures of up to 1200°C with a residence time of a few seconds.

However, this process is rather used to produce chemical products than liquid fuels. The liquid products obtained from pyrolysis processes are of low quality and require upgrading for further use (Department of Trade and Industry, 1999). Another pyrolysis process uses high temperatures and long processing times to convert coking coal to metallurgical coke in coke ovens. The products of this process also include fuel gas, crude tar, light oils and ammonia gas. Metallurgical coke is used in the iron and steel industry (Vorres, 2002).

A disadvantage of pyrolysis processes is the poor liquid yield, while the liquid products are not very pure. The liquid products contain large amounts of heteroatoms as well as organic and inorganic matter. Therefore, pyrolysis processes are not used to produce transportation fuels (Vorres, 2002).

## 2.2.2 Liquefaction

The liquefaction of coal, where coal is converted to liquid or gaseous fuels and chemicals, can also be divided into two processes, a direct and indirect process, which will be discussed in more detail below.

### 2.2.2.1 Direct Liquefaction

Direct liquefaction is believed to be the most efficient way for the production of liquid fuels from coal. However, these processes have only been developed to pilot plant scale and have not been implemented on commercial scale yet. KOBE Steel Ltd. (Japan) is reported to have a facility under construction (Okuyama *et al.*, 2004). Direct liquefaction can be carried out either in a single stage or in two separate stages. Generally, the first stage then consists of the dissolution of coal in a solvent at high temperatures and pressures while the second stage then generally consists of the hydrocracking of the dissolved coal using hydrogen gas with or without a catalyst (Dadyburjor & Liu, 2002). Compared to the liquid products of pyrolysis processes, the liquid products of direct liquefaction processes are of much higher quality but still require further upgrading before it can be used as a fuel (Vorres, 2002).

The first direct liquefaction process, developed by Bergius in 1913, consisted of the dissolution of coal at a high temperature and pressure using a solvent, without using hydrogen or catalysts, to produce high boiling point liquids (Department of Trade and

Industry, 1999). This is similar to the solvent extraction process studied in this investigation. I.G Farben further developed the Bergius process to a two-stage direct-hydrogenation liquefaction process. In the first stage coal is dissolved followed by the second stage where the product is upgraded to liquid transportation fuels using hydrotreating/hydrocracking catalysts. This process was used during World War II to produce gasoline of commercial quality (Dadyburjor & Liu, 2002).

Another early industrial solvent extraction process was the Pott-Broche process. In this process coal was extracted using a coal-derived solvent at 400°C and a hydrogen pressure of 100-150 bar for 1-1.5 hours. An extract yield of 80% and product containing <0.05% mineral matter was obtained with a plant capacity of 5 ton/hour (Vorres, 2002).

In the mid-1960's and 1970's two solvent-refined coal (SRC) processes were developed by the Spencer Chemical Co. and the Gulf Chemical Corp. A low-ash, solid boiler fuel called solvent-refined coal (SRC) was produced with the SRC-I process and liquid fuels with the SRC-II process. A schematic flow diagram of the SRC-I process is shown in Figure 2.5 (Dadyburjor & Liu, 2002).

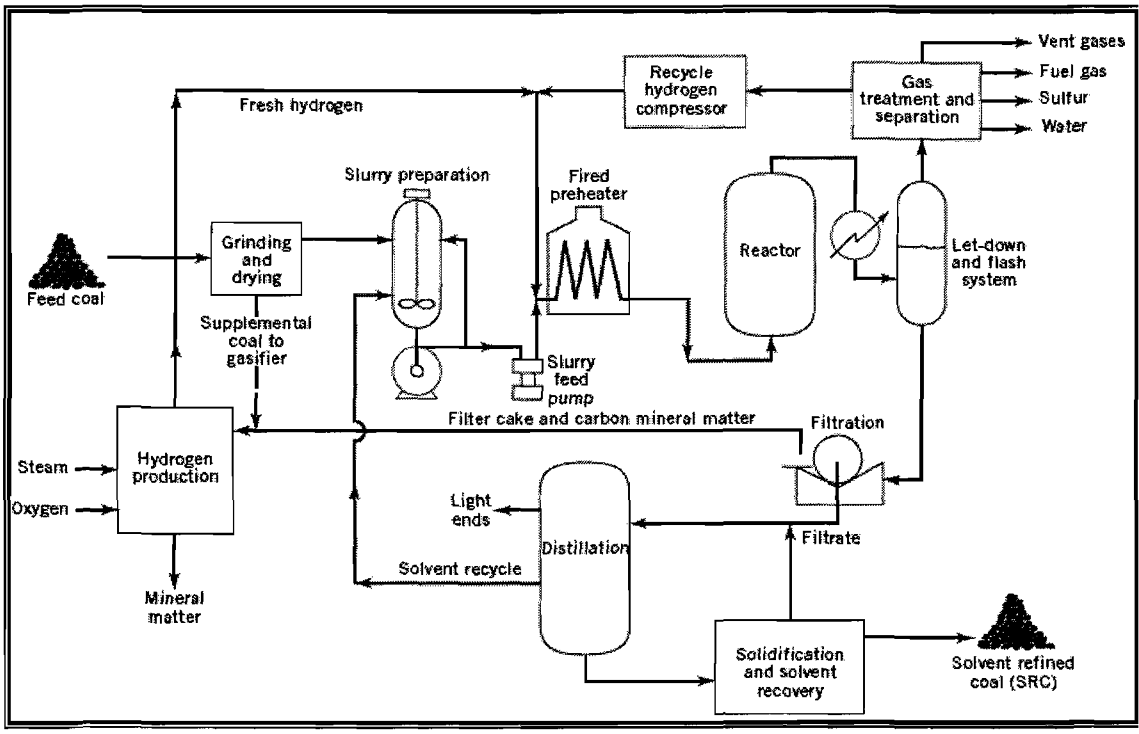


Figure 2.5: Schematic flow diagram of SRC-I process (Dadyburjor & Liu, 2002).

In the SRC-I process coal was mixed with a recycle solvent and preheated before entering the reactor. Extraction in the reactor was carried out at a temperature of 450℃ and hydrogen pressure of 69 bar with a residence time of about 30 min. After separating the volatile products from the extracted liquid product, the extracted liquid product was separated into a residue and filtrate using rotary pressure precoat filters or hydrocyclones. The residue, together with steam and oxygen, was used to generate hydrogen for the process while the filtrate was separated into a recycle solvent and a solid low-ash boiler fuel called solvent-refined coal (SRC). Extraction yields of ±60% were achieved with the SRC-I process while the solid low-ash boiler fuel (SRC) showed significant reduction in ash and sulphur contents. In 1974 a 50 ton/day SRC-I plant was commissioned but were later closed due to severe problems regarding the solvent balance and solids-separation part of the plant (Dadyburjor & Liu, 2002).

The SRC-II process was just a modification of the process configuration of the SRC-I process in order to produce more liquid fuels (distillate products) rather than solids. With the SRC-II process the dissolved coal was hydrocracked to liquid and gases by recycling the product slurry to increase the residence time in the reactor. The product slurry, which is recycled to be mixed with the feed coal, consists of a distillate liquid similar to the coal-derived solvent used originally with a boiling range of 200-480℃, the dissolved coal with a boiling range above 480℃ and a residue consisting of the mineral matter and insoluble coal (Schmid & Jackson, 1981). With these modifications it was possible to produce about 50% more oil than in the SRC-I process (Dadyburjor & Liu, 2002). The SRC-I pilot plant was converted to a SRC-II pilot plant with a capacity of 25 ton/day (Department of Trade and Industry, 1999). A schematic flow diagram of the SRC-II process is shown in Figure 2.6 (Dadyburjor & Liu, 2002).

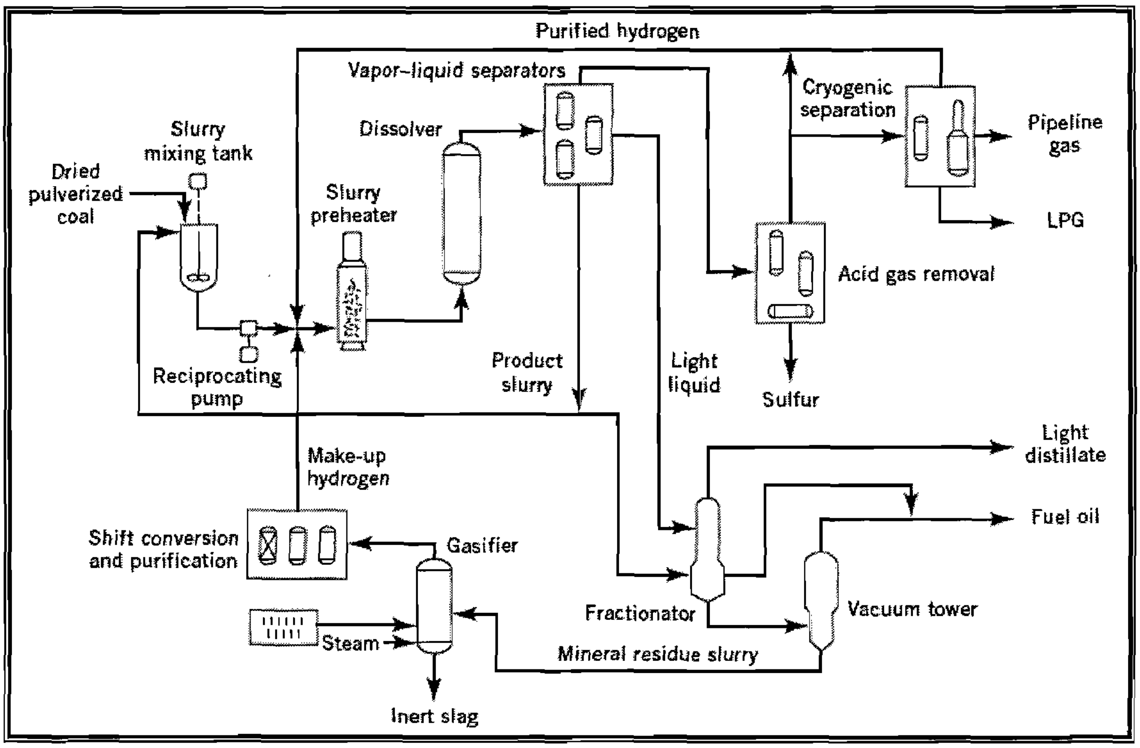


Figure 2.6: Schematic flow diagram of SRC-II process (Dadyburjor & Liu, 2002).

With the SRC-II process, feed coal is pulverized and dried whereafter it is mixed with hot recycle product slurry. The coal-recycle slurry mixture is then pumped through a pre-heater together with hydrogen. In the pre-heater the coal is almost completely dissolved in the solvent part of the recycle slurry. The coal-recycle slurry mixture then goes to the reactor (dissolver) where the hydrocracking takes place. The reactor is operated at 14 bar and the heat generated by the hydrocracking reactions cause the temperature of the mixture to rise to about 438-466°C at the reactor outlet. The reactor product is then sent through a series of vapour-liquid separators where it is separated into process gas, light hydrocarbon liquid and product slurry. The gas, which consists mainly of hydrogen and gaseous hydrocarbons, is sent through an acid gas removal step to remove $H_2S$ and $CO_2$. The treated gas is then sent to a cryogenic separation step to remove the hydrocarbons, while the purified hydrogen is recycled. The $C_1$ fraction of the hydrocarbons is sent to a methanator to convert remaining CO to methane which is then sold as pipeline gas. Ethane, propane and butane are produced from the fractionation of the other light hydrocarbon gases. The light hydrocarbon liquid is sent to a fractionator where it is separated into a light (naphtha) and medium distillate. The naphtha can be used to produce high-octane gasoline after hydrotreatment to remove nitrogen. The product slurry is split into a stream that is recycled to be mixed with the feed coal while the other stream is sent to a vacuum tower. The heavy distillate, removed overhead, together with the medium distillate from the fractionation step is then the fuel oil product of the SRC-II process. The middle distillate has a boiling range of 180-290°C while the heavy distillate has a boiling range of 290-480°C. A high pressure gasifier is used to produce synthesis gas from the residue obtained from the vacuum tower. A part of the synthesis gas is used to produce pure hydrogen for the process by shift conversion and acid gas removal steps. The excess synthesis gas, after going through a separate acid gas removal step to remove $H_2S$ and $CO_2$, is burnt as plant fuel (Schmid & Jackson, 1981).

Several direct liquefaction processes have been developed over the years and many have been tested on pilot plant scale but have not been commercialized. This is due to the fact that direct liquefaction processes are unable to compete economically with available petroleum products. Solvent extraction is a type of direct liquefaction process. The difference between the solvent extraction process investigated in this study and typical direct liquefaction processes is that no catalyst or hydrogen-donor solvent, usually required for direct liquefaction processes, is needed for this process.

#### 2.2.2.2 Indirect Liquefaction

The first step in the indirect liquefaction process is the gasification of coal using steam and $O_2$ in order to break down the coal structure completely. The result is a synthesis gas consisting of hydrogen and carbon monoxide (CO), which is then reacted over a suitable catalyst to produce different liquid products (Dadyburjor & Liu, 2002). Currently, SASOL, South Africa operates the only indirect liquefaction process at commercial scale. In this process coal is converted to synthesis gas via the SASOL-Lurgi fixed bed dry bottom gasification process whereafter the synthesis gas is converted to gasoline, diesel fuel and a variety of chemicals and waxes via the Fischer-Tropsch process (Department of Trade and Industry, 1999).

Figure 2.7 is a representation of the SASOL process. In the first step of this process (gasification), water and air under high pressure and temperature conditions are used to convert coal to synthesis gas. Co-products of this process include tar, oils, ammonia, sulphur, cresols and phenols. At the SASOL plants in Secunda the synthesis gas is sent to Sasol Advanced Synthol (SAS) reactors for high-temperature Fischer-Tropsch conversion. During this step, a variety of hydrocarbons ($C_1$-$C_{15}$) is formed through the reaction of hydrogen and carbon monoxide (CO) in the presence of an iron-based catalyst. Liquid fuels are the main products of this process, while valuable chemicals such as alpha olefins are also produced (Van Dyk *et al.*, 2004).

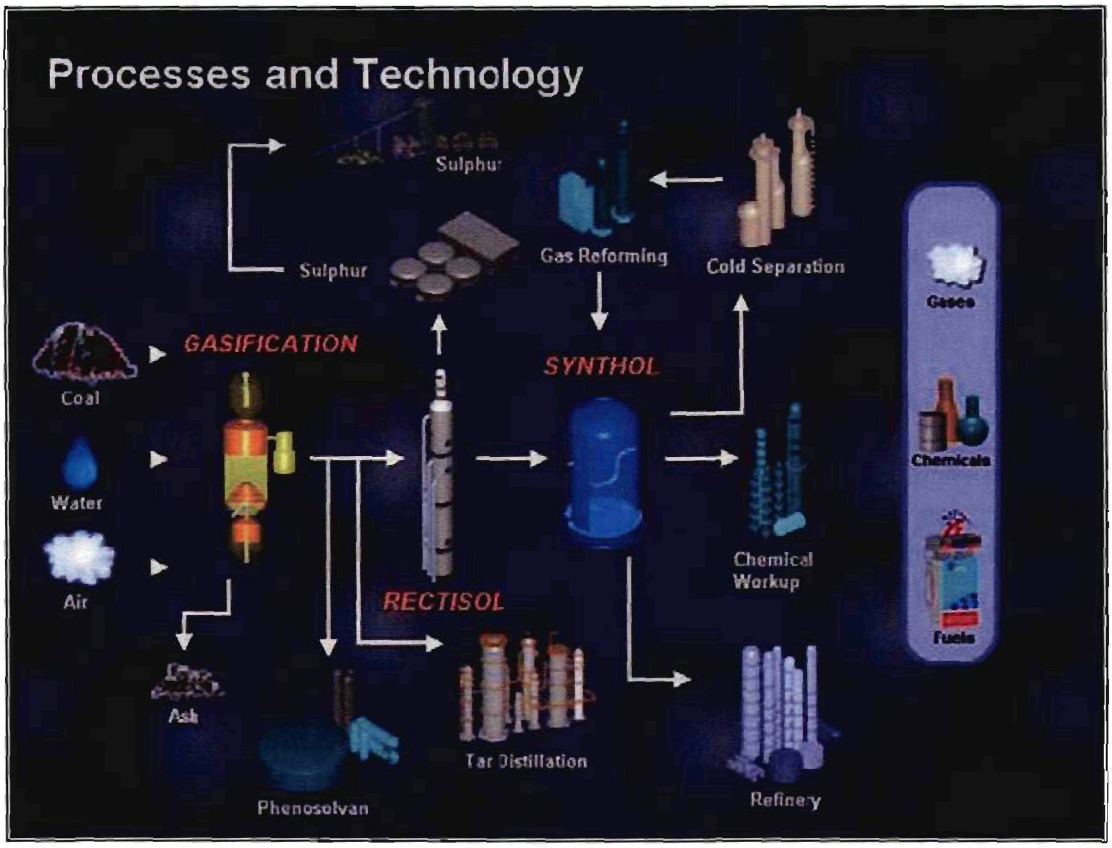


Figure 2.7: SASOL indirect liquefaction process (Van Dyk *et al.*, 2004).

## 2.3 Solvent extraction

The extraction of coal using a solvent has more than one purpose. Firstly, solvent extraction is a commonly used technique to study the composition and structure of coal and dates back to 1860. For this purpose, solvent extraction using different organic solvents is applied to separate the coal into different compounds. These compounds are then characterized and their contribution to the coal properties studied (Van Krevelen, 1981). For the above purpose, most of the research done on extraction of coal has been conducted at room temperature to prevent the coal from decomposing (Miura *et al.*, 2001). In addition to helping us understand the structure of coal, solvent extraction also leads to the partial separation of the mineral matter from the organic part of coal. Therefore, solvent extraction can also be used as a conversion process to convert coal into valuable products. In this investigation, the focus will be on solvent extraction as coal conversion process to produce valuable products as described in Chapter 1.

The interactions between coal and solvents are very complex and not fully understood, but are heavily dependent on the nature of the coal, the nature of the solvent and the extraction conditions. In the following section, the solvent extraction process conditions investigated and extraction yields obtained by different researchers will be reported. Some applications of solvent extraction products and reaction kinetics of the extraction process will also be discussed briefly.

### 2.3.1 Solvent extraction conditions and yields

*Harrison (1975)*

Harrison (1975) reported that the National Coal Board (NCB) of the United Kingdom investigated a coal liquefaction process using a liquid solvent to produce high-grade products for the manufacturing of electrodes or carbon fibre. In their process, the coal/solvent slurry was preheated whereafter it was dissolved at 400°C for 1 hour, followed by filtration at about 200°C. A solvent to coal ratio of 2-4:1 was used. Coal dissolution of 90% was reported, while a filtrate containing less than 0.1% ash was obtained (Harrison, 1975).

*Renganathan et al. (1988)*

Renganathan *et al.* (1988) investigated the extraction of three bituminous coals with N-methylpyrrolidone (NMP), a dipolar aprotic solvent. The extractions were carried out at atmospheric pressure in an Erlenmeyer flask with NMP at its boiling point (202°C) for 1 hour. The lowest extract yield obtained was 38% (d.a.f) and the highest 74% (d.a.f) while a significant reduction of ash content was observed for the extract compared to the feed coal. They found that the product obtained after solvent recovery is a low-ash solid with a high heating value that can be used as a fuel or as a feedstock for several coal conversion processes.

*Miura et al. (2001)*

Miura *et al.* (2001) pointed out that for extraction processes carried out in a batch autoclave and at high temperatures, the extraction yield cannot be determined very accurately. The reason for this is that it is impossible to separate the insoluble fraction (residue) from the fraction that is soluble at high temperatures but precipitates at room temperature. They called the solid mixture of the residue and the precipitated fraction, obtained at room temperature after extraction experiments, the deposit.

Research was done on the extraction of coals in a flow-type reactor at temperatures of 200-400°C. Both tetralin and 1-methylnaphthalene (1-MN) were used as solvents, continuously fed at a flow rate of 0.2-5 ml/min, while the reactor was kept at a pressure of 100 or 200 bar. After their investigations, Miura *et al.* (2001) found that the extraction yield is not affected by either pressure, or the hydrogen-donor ability of solvents below 350°C.

Extraction of bituminous coals with tetralin at 350°C for 1 hour resulted in extract yields of 63-80% (d.a.f), with an extract yield of 63% (d.a.f) for Illinois#6 coal. When comparing the extraction of Pittsburgh#8 coal in the flow reactor and in a batch reactor with tetralin at 350°C for 1 hour, it was found that the solvent flow-system is more efficient. An extract yield of 67% (d.a.f) was obtained in the flow reactor with an extract yield of only 27% (d.a.f) in the batch reactor. Miura *et al.* (2001) explained this result in terms of the contact efficiency between the coal and solvent. They believed that the macromolecular structure of coal becomes relaxed at high temperatures, resulting in covalent bonds between coal molecules to be broken. Therefore, when using a flow reactor, the solvent can wash out large amounts of smaller molecules from the relaxed coal structure, while in a batch reactor it would not be possible to wash out all the smaller molecules. Another explanation for this result may be that coal-coal interactions, causing the insoluble aggregates to form, are more likely in a batch reactor than in a flow reactor because of the longer residence time in the batch reactor.

When conducting matrix-assisted laser desorption ionization – time-of-flight - mass spectrometry (MALDI-TOF-MS) analysis on raw bituminous coal (Pittsburgh#8), the soluble, deposit and residue, Miura *et al.* (2001) found that the raw coal as well as the deposit and residue showed bimodal molecular weight distributions in the ranges of 130-

600 amu and 1300-3500 amu. The soluble however, consisted only of components with a molecular weight smaller than 600 amu.

Yoshida *et al.* (2002)

The solvent extraction of coal with the purpose of producing ash-less coal, called Hyper-coal, that can be used directly in gas turbines has been studied for many years by Yoshida *et al.* (2002) as well as Okuyama *et al.* (2004). It is specified that the Hyper-coal should be produced at low pressures and a temperature below 400°C with an extract yield greater than 60%. The product should be a coal-like powder with ash content less than 0.02%. Yoshida *et al.* (2002) pointed out that in order to develop a commercial-scale extraction plant that will be economical, solvents that are more suitable in terms of recycling and cost are required.

Tetralin, 1-methylnaphthalene (1-MN), dimethylnaphthalene (DMN) and light cycle oil (LCO) were used as solvents for the extraction of several coals. LCO is a by-product in the production of gasoline from the cracking of vacuum gas oil. A batch reactor was used for the extraction experiments at temperatures of 300-380°C and nitrogen pressure of 4 bar, followed by filtration at room temperature. When investigating the effect of extraction time on the extract yield at 360°C, Yoshida *et al.* (2002) observed an increase in extract yield up to 60 minutes whereafter the yield remained constant.

Yoshida *et al.* (2002) concluded that the hydrogen-donor ability of tetralin does not have a significant effect on the extract yield, since almost the same extract yield (24-25%) (d.a.f) was obtained for Nantun coal (China) using tetralin, 1-methylnaphthalene (1-MN) and dimethylnaphthalene (DMN) at 360°C. This corresponds to the results obtained by Miura *et al.* (2001) when they compared tetralin and 1-MN as described above. They also found that LCO has potential as a cost-effective, commercial-scale solvent since an extract yield of 22% (d.a.f) was obtained at 360°C. A study of the relationship between the softening temperatures of several feed coals and their corresponding extract yields, showed that higher extract yields were obtained by the coals with the lower softening temperatures (Yoshida *et al.*, 2002).

During their investigations, Yoshida *et al.* (2002) were able to produce a product with an ash content less than 0.1% for seven of the nine coals they investigated, but were unable to meet the extract yield specification of Hyper-coal.

*Yoshida et al. (2004)*

In further studies, Yoshida *et al.* (2004) used 1-methylnaphthalene (1-MN), dimethylnaphthalene (DMN), light cycle oil (LCO) and crude methylnaphthalene oil (CMNO) to extract three bituminous coals. The CMNO used is a product of coal tar distillation. The extractions were carried out at 360℃ and 10 bar for 1 hour using a flow reactor, while filtration was carried out at 360℃. Of the four solvents, CMNO gave the highest extract yields (75-81%) (d.a.f), showing that coal derived oils can be used as industrial solvents for extraction processes.

*Okuyama et al. (2004)*

In previous studies conducted by Okuyama *et al.* (2004), they found that although N-methylpyrrolidone (NMP) is a very effective solvent that gives high extraction yields, it is not very effective as a recycle solvent. The reason for this is that NMP forms strong bonds with the coal molecules that cause a significant amount of solvent to be lost. A disadvantage of using a hydrogen-donor solvent such as tetralin as recycling solvent is the need for an additional solvent hydrogenation system. Therefore Okuyama *et al.* (2004) decided to use a coal-derived solvent that contains two-ring aromatics such as methylnaphthalenes, since this type of solvent is stable under thermal conditions and shows a good affinity to coal.

When investigating the extraction step of the Hyper-coal process, Okuyama *et al.* (2004) used a high temperature extraction and filtration setup with nitrogen pressure of 1 bar. From their studies of the effect of extraction temperature on the extraction yield with 1-methylnaphthalene (1-MN) for 1 hour, they observed an increase in yield with increase in temperature, with a maximum yield at temperatures of 360-380℃. Extraction of 20 different coals with 1-MN at 360℃ gave yields of 30-70% (d.a.f) with an extraction yield of 60% (d.a.f) for Illinois#6. Like Yoshida *et al.* (2002), Okuyama *et al.* (2004) also found that the closer the softening temperature of the coal is to the extraction temperature, the higher the extraction yield that is obtained.

*Griffith et al. (2004)*

The Penn State University conducted research showing that the effect of pressure and reaction time on the extraction process is not significant. In investigations using light cycle oil (LCO) as solvent and Pittsburgh coal, they found that the highest extraction yield of 39% (d.a.f) is obtained at 350°C, a nitrogen pressure of 7 bar, reaction time of 1 hour and a solvent/coal ratio of 10:1 (Griffith *et al.*, 2004).

*Griffith et al. (2006)*

Griffith *et al.* (2006) continued their previous research and conducted extraction experiments for several bituminous coals with LCO at the above-mentioned extraction conditions. These experiments were conducted for solvent/coal ratios of 10:1, 5:1 and 3:1. The results showed that the highest extract yields were obtained with a solvent/coal ratio of 10:1.

*Burgess Clifford et al. (2007)*

Burgess Clifford *et al.* (2007) extracted several coals with light cycle oil (LCO) at 360°C for 1 hour with a solvent/coal ratio of 10:1. Extract yields of 39-51% (d.a.f) were obtained for extractions followed by filtration at room temperature, with Illinois#6 showing a yield of 51% (d.a.f). Repeating these experiments with filtration at a high temperature resulted in higher extract yields ranging from 36% to 59% (d.a.f), with 55% (d.a.f) extract yield for Illinois#6. The reason for the increase in extract yield with hot filtration is that at low temperatures some material that is soluble at high temperatures precipitates.

*Conclusion*

From the investigations discussed above, no strong pressure effect on the extraction yield is expected. At 360°C, the extract yield shows an increase with extraction time up to 60 minutes whereafter it remains constant. In addition, the extract yield increases with an increase in extraction temperature with a maximum extract yield obtained at 360-380°C. It should be noted that no catalyst was used in the reported solvent extraction research compared to traditional direct liquefaction processes.

Research reported by Van Krevelen (1981) showed that the size of the coal particles has no influence on the extraction yield and that chemical changes occur in the coal at extraction temperatures higher than 250 °C. Like Okuyama *et al.* (2004), he also reported that the extraction yield increases with an increase in the extraction temperature.

*This investigation*

Literature showed that at temperatures below 350 °C the extraction of coal is not complete while at temperatures above 450 °C coking takes place (Ellington, 1977). Therefore, the extraction temperatures for this study were chosen as 350 °C, 360 °C and 370 °C. Based on literature, the particle size of the feed coal was chosen as 120 µm and 200 µm while solvent/coal ratios of 3:1, 5:1 and 10:1 were investigated. From literature it is known that the pressure as such does not really influence the extraction process, it is merely the result of the vapour pressure of the solvent/extract at the reaction temperature. However, from an industrial and operational point of view high pressures can be disadvantageous, especially in scaling-up bulk processes such as this. Therefore, it was decided to investigate the possibility to use a medium pressure of 5 bar.

### 2.3.2 Solvent extraction products

*Wise (1971)*

Several tests have been undertaken to investigate the use of solvent extraction products. Some of the applications suggested are that the low-ash coal product can be used in the manufacturing of graphite or as binder pitch for electrodes. Another suggestion was the production of jet fuels by hydrogenation of the low-ash coal product (Wise, 1971).

*Howard-Smith and Werner (1976)*

In 1976, the Coal Research Establishment (United Kingdom) operated a pilot plant where coal was continuously dissolved in a hydrogen-donor solvent such as anthracene oil at a rate of 15 kg/hour. Their research showed that it is possible to produce calcined coke from the coal extract for the manufacturing of electrodes, as well as carbon fiber from solid solvent refined coal (SRC). Another application they found to be possible, is the production of a range of liquid hydrocarbon fuels obtained by the catalytic hydrogenation of the coal extract (Howard-Smith & Werner, 1976).

Zondlo *et al.* (2003)

Zondlo *et al.* (2003) investigated the use of solvent extraction to obtain a coal product suitable for use in a direct carbon fuel cell. Raw coal is unsuitable for this application since it contains ash that contaminates the electrolyte as well as sulphur that causes the electrodes to degrade. In order to reduce the mineral matter in the raw coal they extracted several coals with N-methylpyrrolidone (NMP) at 202°C for 1 hour. A significant ash reduction was observed with extracts containing 0.1-0.3% ash. As a result of the ash reduction, the extract showed a higher heating value than the raw coal. Another advantage of solvent extraction was that all inorganic sulphur was removed and some organic sulphur. Zondlo *et al.* (2003) concluded that by reducing the volatile matter of the extract through coking and calcining, as well as altering the microstructure through heat treatment of the coke, solvent extraction could be used to produce a coal product suitable for use in a direct carbon fuel cell. Further, they suggested that the residue could be used as a boiler fuel when it is blended with low-ash coal, as a gasification feedstock for hydrogen production, as starting material for production of activated carbon or as a catalyst/catalyst support.

As mentioned before and discussed above, there are several possibilities for the application of the product obtained with solvent extraction.

### 2.3.3 Solvent extraction kinetics

Some research has been done on aspects regarding the reaction kinetics of the solvent extraction process. Through research done by Neavel (1976) it was found that mass-transfer is not a limitation of the extraction rate, due to the insignificant effect of the particle size (below 2-3 mm) on the extraction yield. He also observed that about two-thirds of the total extraction of high volatile C bituminous coal and lower rank coals occur within the first 20 minutes of extraction, while higher rank coals are extracted at a slower rate.

Giri and Sharma (2000) also conducted studies to determine the kinetics of solvent extraction of coal. They used N-methylpyrrolidone (NMP) at 150°C and 202°C, anthracene oil at 150°C and 270°C and cetene at 250°C and 274°C as solvents for the extraction of Samla coal and assumed an extraction process of:

$$\text{Coal} + \text{Solvent} \rightarrow \text{Residue coal} + \text{Coal extract.}$$

After their investigations, they concluded that the solvent extraction of Samla coal has a first order rate law and that the shrinking-core model can be used to describe the extraction process. They used equation (2.1) for the shrinking-core model.

$$-\ln(1-\alpha)^{1/3} = \frac{k}{3}t \tag{2.1}$$

In equation (2.1), t is the time, k the rate constant and α the conversion defined as the extraction yield at a given time divided by the extraction yield at infinite time. They obtained the rate constant at two different temperatures for each solvent by plotting $-\ln(1-\alpha)^{1/3}$ against t. Furthermore, they derived equation (2.2) from the Arrhenius equation to calculate the activation energy for the extraction of Samla coal.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E_a(T_2 - T_1)}{R(T_1 T_2)} \tag{2.2}$$

In equation (2.2), $k_1$ and $k_2$ are the rate constants at temperatures $T_1$ and $T_2$, $E_a$ is the activation energy and R is the universal gas constant. They calculated the activation energy, using the shrinking-core model parameters, as 59 kJ/mol with NMP, 90 kJ/mol with athracene oil and 106 kJ/mol with cetene. From these activation energies Giri and Sharma (2000) concluded that solvent extraction using NMP as solvent was diffusion controlled, while solvent extraction using anthracene oil and cetene was diffusion as well as kinetically controlled.

In further studies, Giri and Sharma (2000) observed a correlation between the vitrinite content of the feed coal and the activation energy for solvent swelling when investigating the swelling of coals in N-methylpyrrolidone (NMP). The correlation showed that the activation energy necessary for solvent swelling decreases as the vitrinite content of the coal increases, making it easier for solvents to diffuse into coals with a high vitrinite content.

The model used in this investigation to describe the reaction kinetics of the continuous solvent extraction process, will be discussed in Chapter 5.

### 2.3.4 Solvent classification

The study of solvents goes a long way back. As early as 1951, a classification system for solvents was developed based on their effect on coal. Solvents were classified as follows (Wise, 1971):

1) Non-specific solvents
2) Specific solvents
3) Degrading solvents
4) Reactive solvents
5) Highly-reactive solvents

These solvents will be discussed in more detail below (Wise, 1971).

1) Non-specific solvents extract a small amount of material that is not a major part of the coal structure at low temperatures to about 100°C. An example of a non-specific solvent is ethyl alcohol.

2) Specific solvents, for example pyridine, are able to dissolve a significant amount of the coal at temperatures below 230°C by physical solution. However, specific solvents are rather applied in coal chemistry than being used in an extraction process. The reason for this being that low extract yields are obtained and that most specific solvents are too expensive for use of large quantities on commercial scale.

3) Degrading solvents break the coal into smaller and more soluble fragments by thermal degradation at high temperatures up to 430°C. These solvents, for example anthracene oil (tar-oil fraction), can be recovered from the solution almost unchanged.

   Tar-oil solvents do not exactly answer to the definition of degrading solvents since it is not always true that they are unchanged when recovered from the solution. This is shown by the effect where the power of tar-oil solvents decreases when it is recovered by distillation after dissolving a coal and then reused in further extraction cycles. This may be explained by reactive solvent species present in the original oil, which are used in the first few cycles of extraction.

4) Reactive solvents react chemically with the coal in order to dissolve the coal. An example of a reactive solvent is tetralin. Unlike degrading solvents, reactive solvents show chemical changes after being recovered from the solution.

5) Highly-reactive solvents are more associated with industrial organic chemistry than being used in coal technology.

# CHAPTER 3

# EXPERIMENTAL METHODOLOGY AND ANALYTICAL METHODS

The materials and equipment used in this project, as well as the experimental design for both the batch and continuous extraction experiments, will be discussed in this chapter. The experimental procedures to carry out the solvent extraction experiments will also be explained, as well as the analytical methods used to characterize the extraction products.

## 3.1 Materials used

### 3.1.1 Coal

As discussed in Chapter 1, a vitrinite-rich South African coal (Waterberg) and an inertinite-rich South African coal (Brandspruit) were investigated, while Illinois#6 coal (vitrinite-rich American coal) was investigated as a benchmark.

Waterberg coal is obtained from the Waterberg coalfield in the Limpopo province of South Africa while Brandspruit coal is obtained from the Highveld coalfield located in the Mpumalanga province of South Africa. Waterberg coal has a vitrinite content of 90% and Brandspruit coal has an inertinite content of 71% as shown in Table 3.1. Illinois#6 coal is obtained from the Herrin seam in Macoupin County, Illinois, USA and has a vitrinite content of 92%. Table 3.1 shows the complete maceral analysis of the three coals using the ISO 7404/3 method.

Table 3.1: Maceral analysis of coals used.

| COAL | MACERAL ANALYSIS (Volume %, mineral free) | | |
|---|---|---|---|
| | VITRINITE | LIPTINITE | INERTINITE |
| Waterberg | 89.6 | 3.2 | 6.8 |
| Brandspruit | 15 | 5 | 71 |
| Illinois#6 | 92 | 2 | 2.2 |

The proximate and ultimate analyses of the coals, as reported in Tables 3.2 and 3.3, were determined according to standard ISO and ASTM methods as described in sections 3.3.1 and 3.3.2. In Table 3.2, VM is the volatile matter and FC the fixed carbon content of the coal. The volatile matter, fixed carbon and ash content are reported on a dry basis, while the values of Table 3.3 are reported on a dry ash-free basis. In Table 3.2 the value for fixed carbon is by difference, as well as the value for oxygen in Table 3.3.

Table 3.2: Proximate analysis of coals used.

| COAL | PROXIMATE ANALYSIS (wt%) | | | |
|---|---|---|---|---|
| | MOISTURE | VM (d.b) | FC (d.b.) | ASH (d.b.) |
| Waterberg | 2.9 | 35.6 | 54.7 | 9.8 |
| Brandspruit | 4.3 | 21.6 | 52.1 | 26.3 |
| Illinois#6 | 5.5 | 37.4 | 48.7 | 13.9 |

Table 3.3: Ultimate analysis of coals used.

| COAL | ULTIMATE ANALYSIS (wt%) (d.a.f) | | | | |
|---|---|---|---|---|---|
| | C | H | N | O | S |
| Waterberg | 81.6 | 5.8 | 1.7 | 9.7 | 1.2 |
| Brandspruit | 79.5 | 3.9 | 2.0 | 13.3 | 1.3 |
| Illinois#6 | 75.8 | 5.8 | 1.4 | 9.4 | 7.6 |

From Table 3.2 it can be seen that Brandspruit coal has a much higher ash content than Waterberg and Illinois#6 coal, while Table 3.3 shows that Illinois#6 coal has a much higher sulphur content than the other two coals.

The coal samples used are classified using a system where the rank of the coal is determined according to vitrinite reflectance as shown in Figure 2.3 in Chapter 2. The vitrinite reflectance is determined with the ISO 7404-5 method, while the rank is reported as RoVmr% (mean random reflectance) according to the ISO 11760:2005 method. The random reflectance of Waterberg coal is determined as 0.6% and for Brandspruit as well as Illinois#6 coal as 0.57%, placing these three coals in the range of 0.5-1.1%. Therefore, all three feed coals can be classified as medium rank, high volatile bituminous coals.

The coal samples as received were put through a jaw crusher to obtain particles in the order of 1-2 mm, whereafter a rotary splitter was used to fill bags with 1 kg coal samples. These bags were then sealed and stored in a dry, dark place. Prior to each extraction experiment, the desired amount of coal is pulverized to the desired particle size.

### 3.1.2 Solvent

As mentioned in Chapter 1, one of the aims of this study was to investigate if high extraction yields can be obtained by using an industrial solvent rather than a pure chemical solvent such as tetralin or N-methylpyrrolidone (NMP). With future investigations of solvent recycling in mind, it was decided to use a coal-derived solvent. Therefore, residue oil was chosen as solvent in this study. Residue oil is a distillation cut of tar distillation in the coal gasification process and is obtained from Sasol, Secunda. A distillation curve for the residue oil, together with other industrial oils, is shown in Figure 3.1 (De Jager, 2006). The residue oil, received in 10 L containers, was thoroughly mixed whereafter it was transferred to 500 ml containers and stored in a dry, dark place.

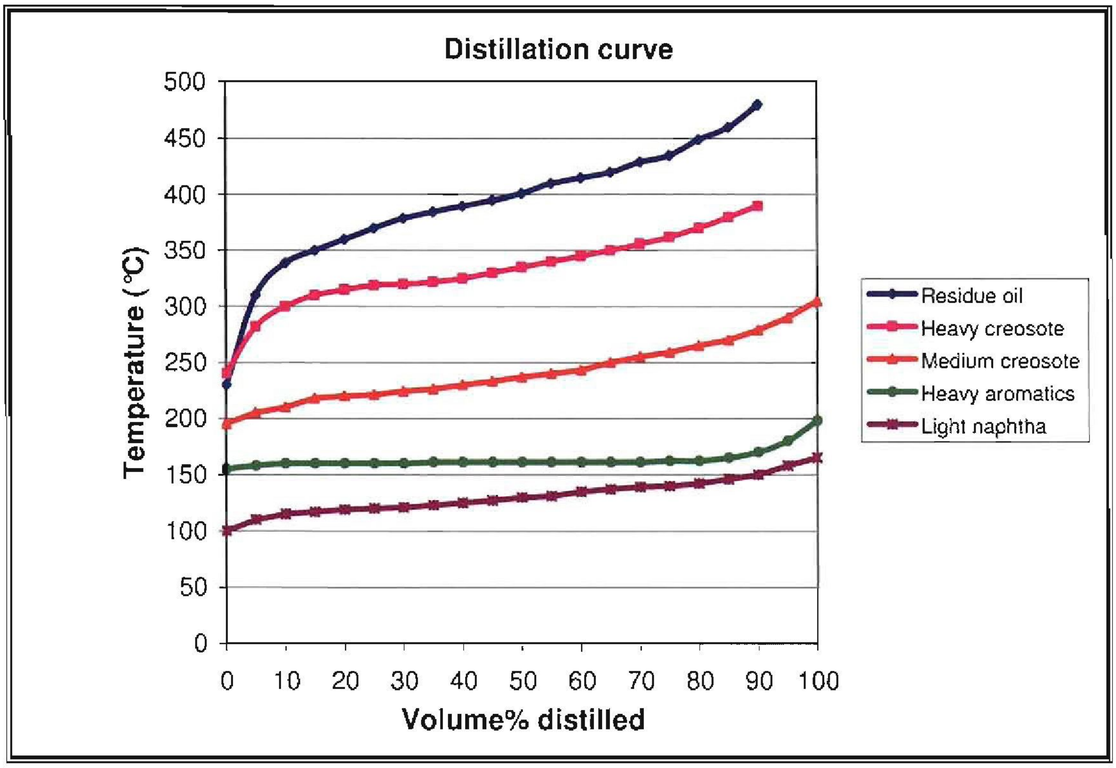


Figure 3.1: Distillation curves for different industrial oils.

## 3.2 Experimental methodology

### 3.2.1 Equipment design

Two types of extraction experiments were conducted – one with a batch system and the other with a continuous system. The purpose of the batch system was to investigate the solvent extraction of the different coals at equilibrium in order to determine the ultimate extraction yields, as well as to investigate the effect of different operating conditions on the extraction process in order to determine the optimum operating conditions. The purpose of the continuous system was to investigate the possibility of performing solvent extraction continuously, as well as to obtain reaction kinetics data that could be used to describe the extraction process. The continuous extraction results will also provide better data for the design and assessment of an industrial plant. In the next section the equipment used in the batch and continuous systems will be discussed.

#### 3.2.1.1 Batch extraction

The batch system consisted of a stainless steel PARR 4843 autoclave with a volume of 1 litre as shown in Figure 3.2. The autoclave consisted of a reactor head and a separate reactor vessel that could be moved up and down. The inside of the reactor was equipped with a cooling coil, a stirrer blade (used to mix the coal/solvent slurry), as well as a stainless steel sheath that holds the thermocouple for measuring the temperature of the coal/solvent slurry. This thermocouple was connected to a temperature controller.

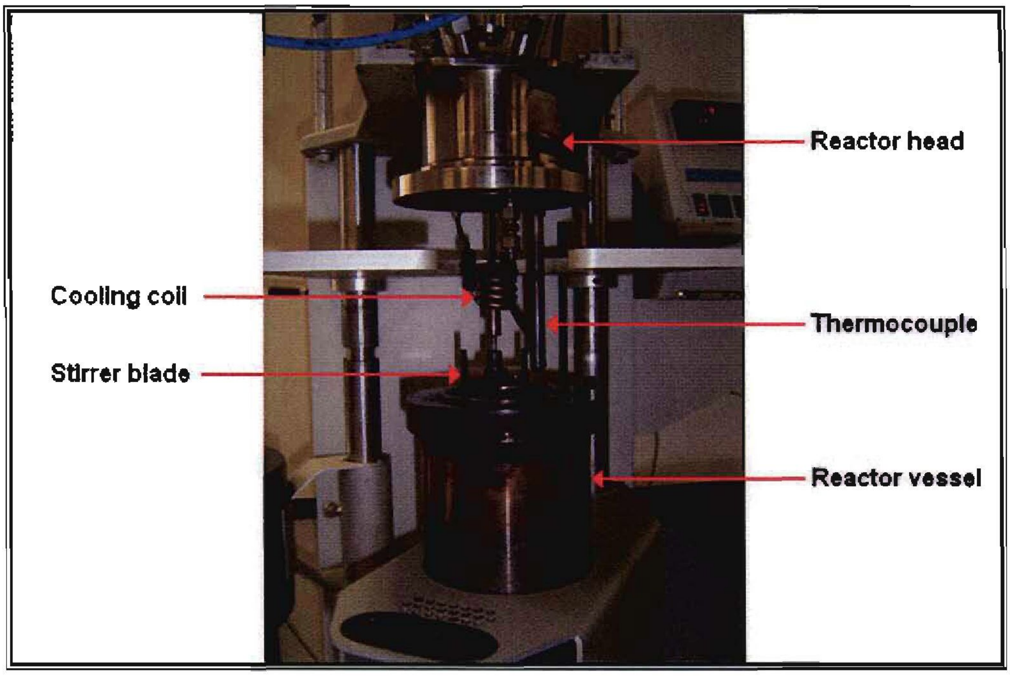


Figure 3.2: Reactor head and vessel

The top of the reactor head was equipped with several valves that could be used as inlets and outlets, as well as the magnetic stirrer. Figure 3.3 shows this in more detail. For this project, one of the valves was connected to a nitrogen supply line that was used to flush the reactor free of air at the start of each experiment and to supply the initial operating pressure for the extraction experiments. A gas release valve was also present to reduce the pressure during the extraction experiments in order to maintain the desired pressure. The released gas was cooled down and collected as a liquid, called the volatile extract.

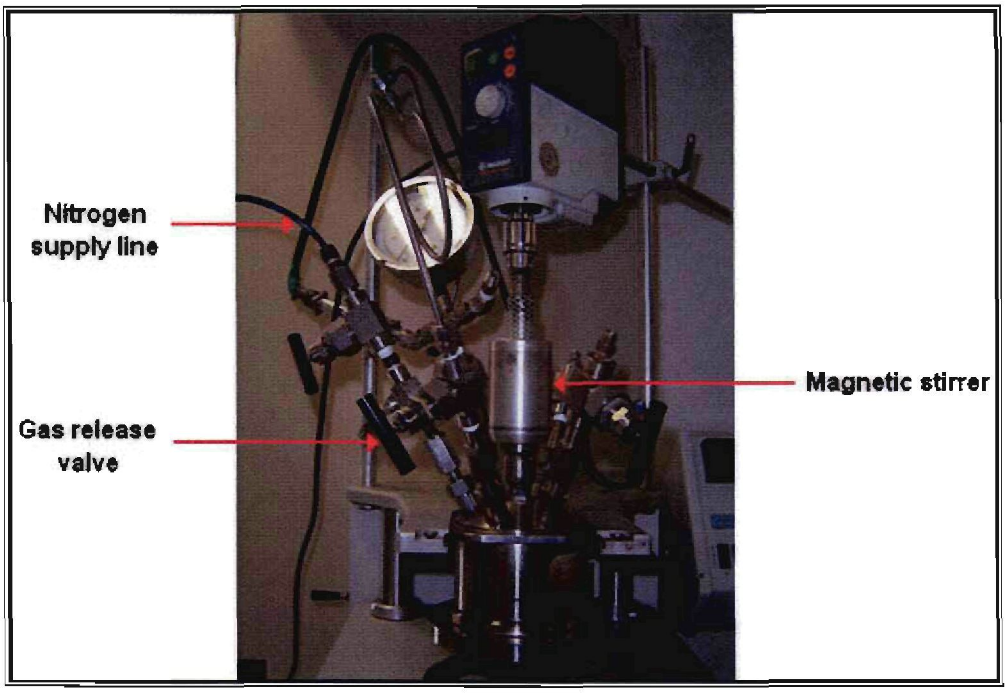


Figure 3.3: Top of reactor head.

Figure 3.4 shows how the reactor head and vessel are kept together by a clamp that contains cap screws that need to be tightened.

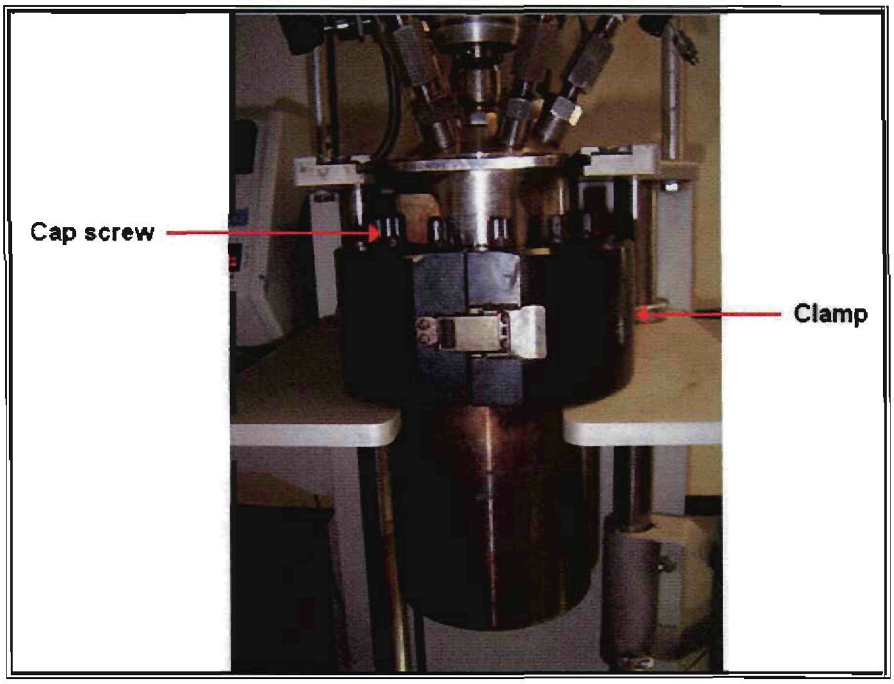


Figure 3.4: Clamp.

After the reactor head and vessel were closed, the heater that fits around the reactor vessel was lifted. This heater was supplied with a thermocouple connected to a temperature indicator, while a pressure indicator, showing the pressure inside the reactor, was also present as shown in Figure 3.5.

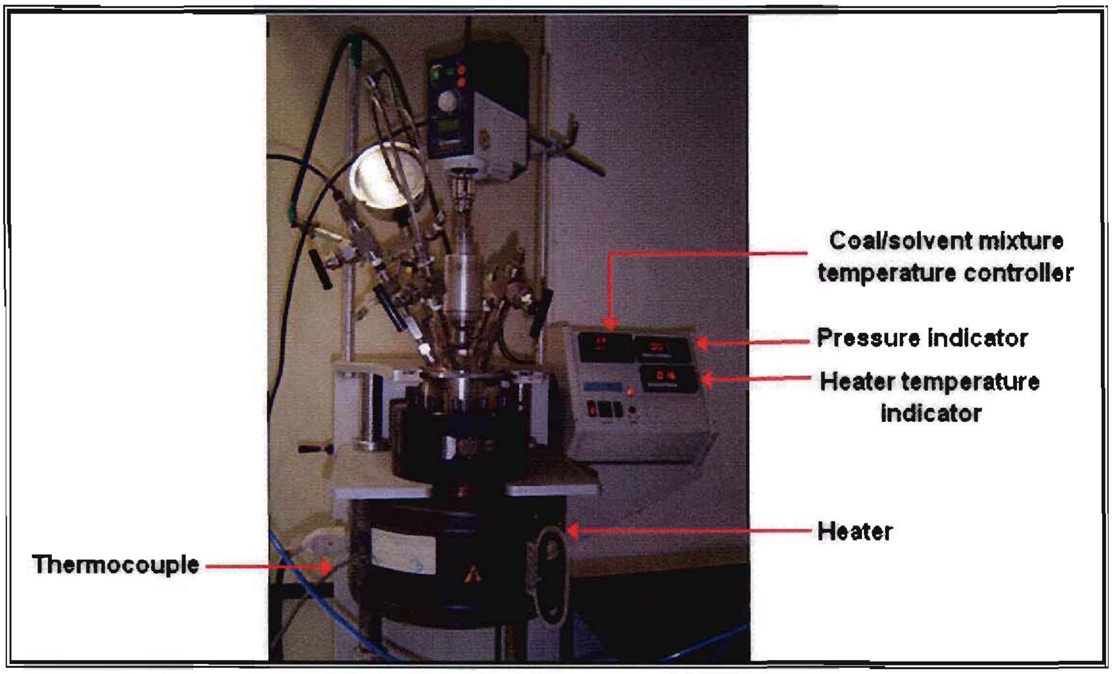


Figure 3.5: Autoclave with heater.

### 3.2.1.2 Continuous extraction

The continuous extraction system consisted of a flow reactor with a heating mantle, a storage vessel with a magnetic stirrer, a pump and a condenser. The experimental setup of the continuous system is shown in Figure 3.6. The coal/solvent slurry was held in a glass storage vessel in order to easily monitor the amount of slurry. The slurry in the storage vessel was continuously stirred to keep the coal particles from settling, while heating tape around the storage vessel was used to pre-heat the slurry to about 40°C. This was done to reduce the viscosity of the slurry so that it could easily be pumped through the system. A MasterFlex peristaltic pump obtained from Cole-Parmer Instrument Company was used to pump the pre-heated slurry through the flow reactor from the bottom. The pump had no flow indicators and therefore needed to be calibrated before every experimental run. Because of the sensitivity of the pump's flow settings, only flow rates of 5, 10, 20, 30, 40 and 50 ml/min could be achieved. Thus, with the available pump residence times for the coal/solvent slurry in the range of 2.4-24 min could be achieved. The heating mantle around the flow reactor was used to heat and maintain the slurry at the desired reaction temperature. The heating mantle was connected to a temperature controller, while the reading of a thermocouple inside the flow reactor showed the temperature of the slurry. A condenser, using water as cooling medium, was used to cool down the volatile extract. The volatile extract was then collected as a liquid for further analyses. The flow reactor used is shown in Figure 3.7.

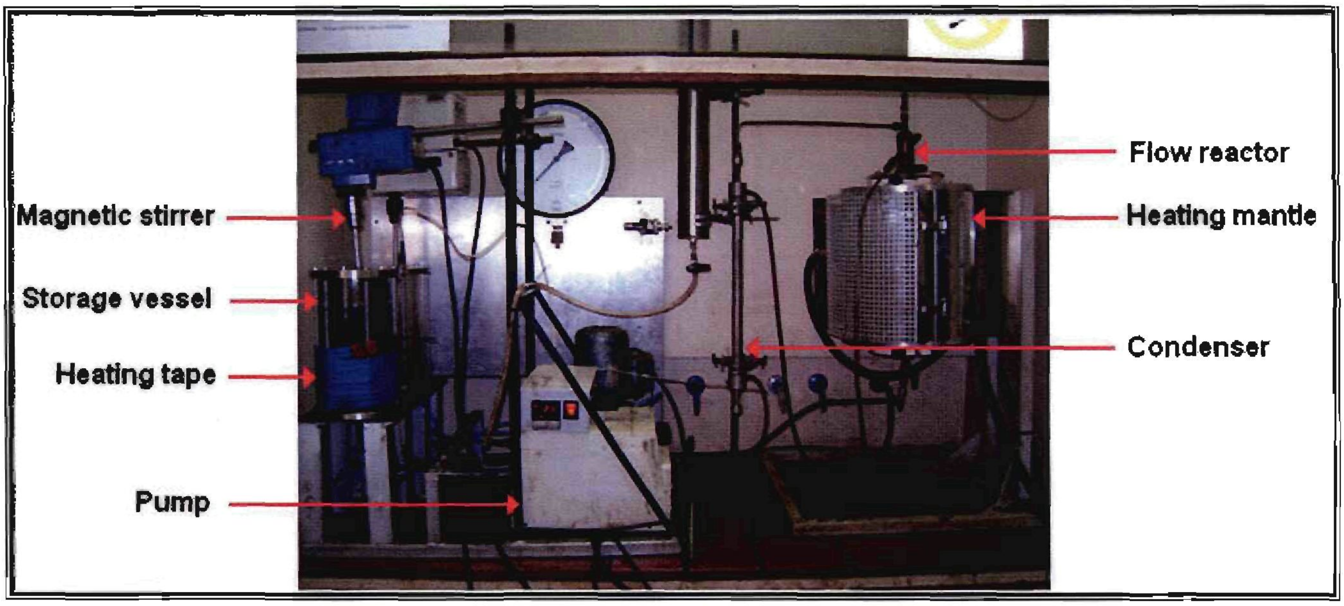


Figure 3.6: Continuous experimental setup.

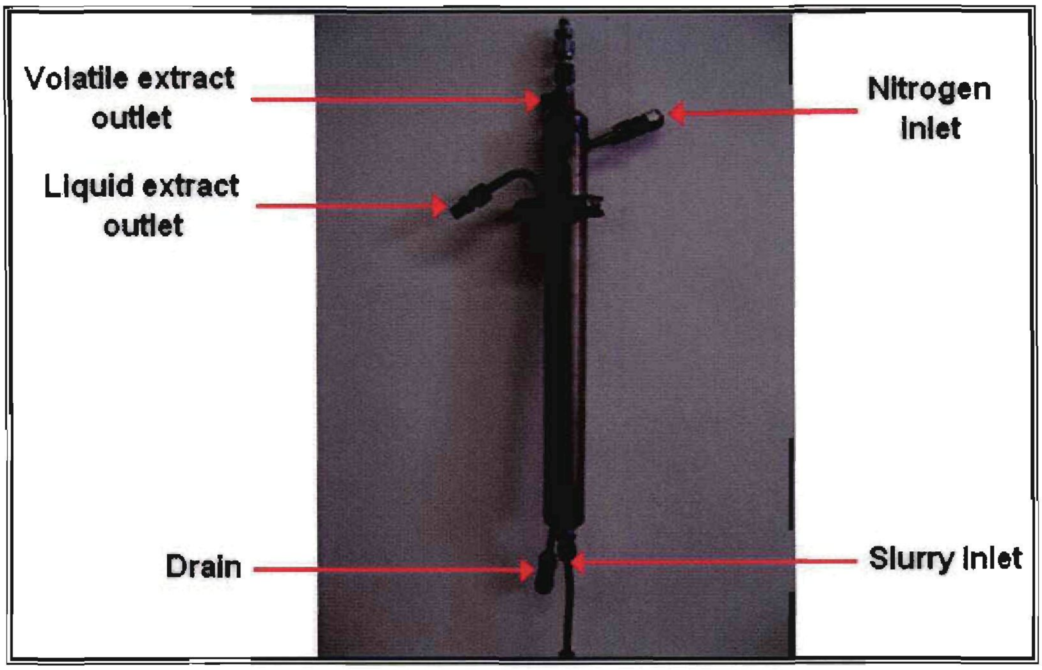


Figure 3.7: Flow reactor.

The flow reactor in Figure 3.7 can be divided into two sections, a reaction section and a separation section. The reaction section of the reactor has a length of 26 cm, an internal diameter of 2.4 cm and therefore a volume of 120 mL and is the part from the bottom until just below the liquid extract outlet. The section from the liquid extract outlet upwards can be treated as a separation section. As can be seen from Figure 3.7, the plug flow reactor used for the continuous extraction experiments consisted of two inlets and three outlets. The inlet at the bottom of the reactor was used to pump the coal/solvent slurry into the reactor. The nitrogen inlet was used to purge the reactor before an experiment. The volatiles produced during the continuous extraction process were removed through the volatile extract outlet whereafter it was liquefied by using a condenser. The liquid extract outlet was used to remove the liquid extract (coal dissolved in solvent) together with the residue coal. The outlet at the bottom of the reactor is used to drain the reactor after an experiment. This configuration of the continuous flow reactor with two product outlets was selected in order to investigate the possibility to obtain a solids free liquid which could be used as a washing liquid in the residue coal separation step instead of tetrahydrofuran.

## 3.2.2 Experimental design

### 3.2.2.1 Batch extraction

The first variable of the batch extraction experiments is the coal type. Three coals were chosen for these experiments, namely Waterberg, Brandspruit and Illinois#6 coal. As mentioned in Chapter 1, one of the aims of this study was to determine the optimum operating conditions for the solvent extraction process. This was achieved by using the batch extraction system to investigate the effect of different operating conditions on the extraction yield. The operating conditions that were chosen as variables for this investigation are the coal, the extraction temperature, the particle size of the feed coal and the solvent to coal ratio. As discussed in Chapter 2, the extraction temperatures were chosen as 350°C, 360°C and 370°C, the particle size of the feed coal was chosen as 120 μm and 200 μm while solvent/coal ratios of 3:1, 5:1 and 10:1 were investigated. The batch reactor for this investigation was operated at a constant pressure of 5 bar by means of a gas release valve, as described in sections 3.2.1.1 and 3.2.3.1. Based on literature, the residence time for the batch extraction experiments was taken as 1 hour. Table 3.4 shows the experimental design for the batch extraction experiments.

Table 3.4: Experimental design - batch extraction.

| WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|
| **Temperature** | | | **Temperature** | | | **Temperature** | | |
| ***350°C*** | ***360°C*** | ***370°C*** | ***350°C*** | ***360°C*** | ***370°C*** | ***350°C*** | ***360°C*** | ***370°C*** |
| 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm |
| 10:1 | 10:1 | 10:1 | 10:1 | 10:1 | 10:1 | 10:1 | 10:1 | 10:1 |
| **Particle size** | | | **Particle size** | | | **Particle size** | | |
| 360°C | 360°C | | 360°C | 360°C | | 360°C | 360°C | |
| ***120 μm*** | ***200 μm*** | | ***120 μm*** | ***200 μm*** | | ***120 μm*** | ***200 μm*** | |
| 10:1 | 10:1 | | 10:1 | 10:1 | | 10:1 | 10:1 | |
| **Solvent/Coal ratio** | | | **Solvent/Coal ratio** | | | **Solvent/Coal ratio** | | |
| 360°C | 360°C | 360°C | 360°C | 360°C | 360°C | 360°C | 360°C | 360°C |
| 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm | 120 μm |
| ***3:1*** | ***5:1*** | ***10:1*** | ***3:1*** | ***5:1*** | ***10:1*** | ***3:1*** | ***5:1*** | ***10:1*** |

A temperature of 360°C, particle size of 120 μm and solvent/coal ratio of 10:1 were chosen as the basis for the batch extraction experiments. The extraction experiment at these basic operating conditions is repeated three times for each coal to check the repeatability of the experimental procedure. In Table 3.4 these repeated experiments at the basic operating conditions are indicated by the grey areas. For the other batch extraction experiments, two of the operating conditions were kept constant at the basic values mentioned above, while the third operating condition was varied.

### 3.2.2.2 Continuous extraction

As with the batch extraction experiments, the coal type was also a variable during the continuous extraction experiments. Waterberg and Brandspruit coal was used in the continuous extraction experiments. The first objective of the continuous extraction process was to develop a continuous experimental setup. Therefore, a lot of time was spent on troubleshooting and on finding the best possible way to conduct the continuous experiments with the available equipment (Hattingh, 2007; Beukman, 2007). The second objective of the continuous extraction process was to obtain kinetic data. In order to do this, the reaction temperature and residence time were chosen as variables. The residence time was varied by adjusting the flow rate of the pump.

Even though the ideal would have been to carry out the continuous extraction experiments at the same conditions as the batch experiments, this was not possible. Because of the open storage vessel and peristaltic pump the continuous system could not be operated under pressure, whereas the batch system was operated at a pressure of 5 bar. For al the continuous extraction experiments a 10:1 solvent to coal ratio was used with a feed coal particle size of 120 μm. After several trial runs it was found that certain temperatures could not be reached with the heating system and that certain flow rates caused the reactor to block. The conditions at which the experiments were carried out are therefore the conditions that could be achieved with the experimental setup. The experimental design for the continuous extraction experiments is shown in Table 3.5.

Table 3.5: Experimental design - continuous extraction.

| **Temperature** | **Flow rate (ml/min)** | | | |
|---|---|---|---|---|
| | **5** | **10** | **20** | **30** |
| **320°C** | X | X | X | X |
| **330°C** | X | X | X | |
| **340°C** | | X | X | |

In Table 3.5 the experiments that were carried out are marked with an X. Experiments at a flow rate of 5 ml/min and temperature of 340°C caused the reactor to block at the slurry inlet due to the settling of particles. Some problems were also encountered at a 30 ml/min flow rate. For reaction temperatures above 320°C the heating mantle was unable to heat the slurry to the desired reaction temperature due to the high flow rate. During the trial runs it was attempted to run the continuous system at 360°C. However, this caused the reactor to be blocked with a hard, solid coal/solvent formation. A possible cause for this problem may be an insufficient heating system. A difference of about 200°C was observed between the temperature of the heating mantle and the reaction temperature inside the reactor. When the coal/solvent slurry starts boiling it increases the heat transfer coefficient sharply, causing the temperature to rise rapidly. Another explanation may be a coking reaction that takes place due to exothermic reactions at this high temperature.

## 3.2.3 Experimental procedure

### 3.2.3.1 Batch extraction

The experimental procedure that was followed for the batch extraction experiments is illustrated in Figure 3.8.

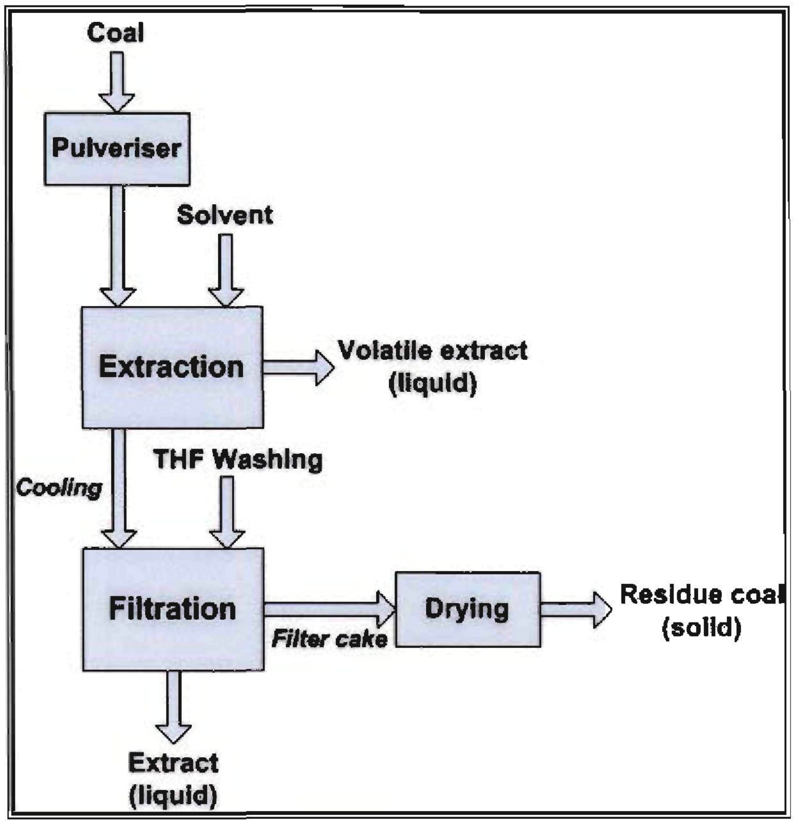


Figure 3.8: Experimental procedure - batch extraction.

A Fritsch Pulverisette 14 is used to pulverise the feed coal to the desired particle size and is shown in Figure 3.9.

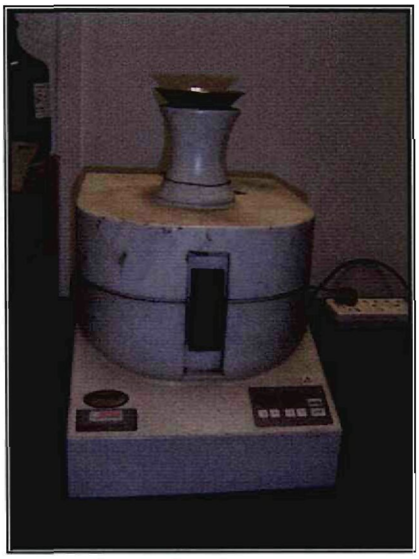


Figure 3.9: Pulveriser.

For the different solvent/coal ratios, the amount of solvent is kept constant while the amount of coal is varied to obtain the different solvent/coal ratios. The autoclave is filled with ±500 g solvent whereafter the desired amount of coal is added. After the reactor is closed by the clamp, the heater and stirrer are switched on. The stirrer is operated at a rate of ±400 rpm. The valve connected to the nitrogen supply line is opened to supply a pressure of 5 bar whereafter it is closed again. The solvent/coal slurry is heated to the desired temperature whereafter it is kept at this temperature for 1 hour. The pressure in the reactor is manually regulated at 5 bar by using the gas release valve. The volatile extract is collected as a liquid in a sampling bottle for further analysis. After an hour the stirrer and heater are switched off. A fan is used to cool down the reactor. When the content of the reactor reaches room temperature, the reactor is opened and its content transferred to a filter containing a pre-weighed Whatman No. 54 filter paper with a particle retention of 20-25 µm. The filter used in this study is shown in Figure 3.10.

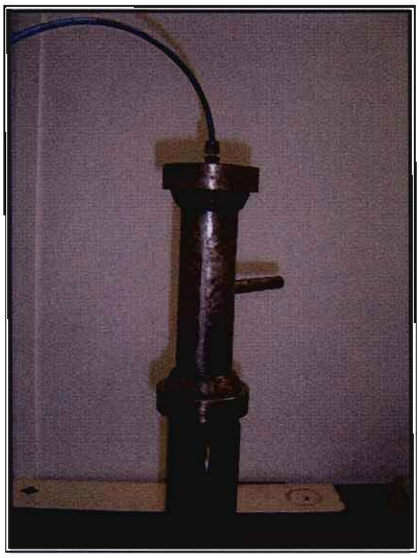


Figure 3.10: Filter.

Tetrahydrofuran with a purity of 99.5%, obtained from Merck, is used as washing solvent to ensure that all of the content of the reactor is transferred to the filter. The reactor is then cleaned and prepared for the next experiment. The filter is closed and connected to a nitrogen supply line. The nitrogen is used to pressurize the filter to ±3 bar, resulting in a filtrate called the extract and a filter cake called the residue coal. The liquid extract is collected in a sampling bottle for further analysis. Tetrahydrofuran is used to wash the residue coal until the filtrate becomes almost colourless. The volume of tetrahydrofuran used to wash the residue coal is almost in the same order as the volume of residue oil used. After the filtration is completed, the nitrogen supply line is disconnected and the filter opened. The filter cake together with the pre-weighed filter paper is transferred to a pre-weighed watch glass and introduced in an oven to be dried overnight at 100°C. The filter is cleaned and prepared for the next filtration. The next day the watch glass with the dry filter paper and residue coal is weighed. The amount of residue coal obtained in the experiment is calculated by using equation (3.1).

$$\begin{aligned} Residue\ coal(g) &= (Watch\ glass + dry\ filter\ paper + residue\ coal) \\ &\quad -(Watch\ glass + dry\ filter\ paper) \end{aligned} \tag{3.1}$$

### 3.2.3.2 Continuous extraction

The experimental procedure that was followed for the continuous extraction experiments is shown in Figure 3.11.

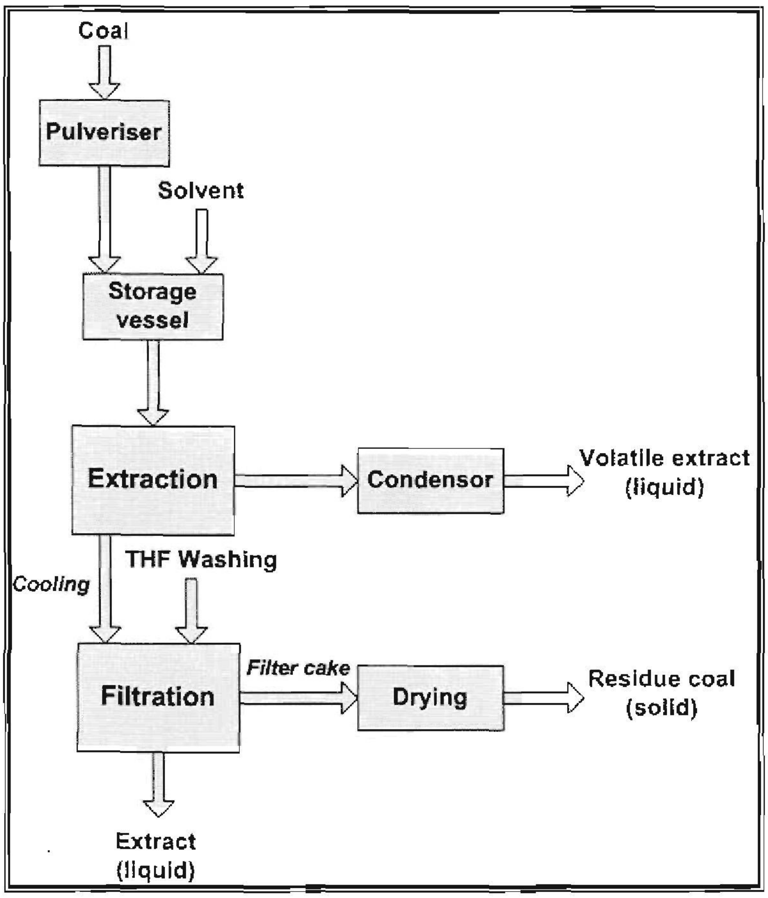


Figure 3.11: Experimental procedure - continuous extraction.

A Fritsch Pulverisette 14 was also used to pulverise the feed coal to 120 µm for the continuous experiments. A feed coal/residue oil slurry is then prepared in the storage vessel in a 10:1 solvent to coal ratio. The stirrer is switched on, while the slurry is pre-heated to 40°C. The reactor is purged with nitrogen, whereafter the heating mantle is switched on. Before every experimental run the pump was calibrated to the desired flow rate. When the temperature in the reactor reached steady state, the cooling water to the condenser was opened and the pump switched on. The temperature controller is then adjusted to reach the desired reaction temperature in the reactor. When the temperature of the coal/solvent slurry in the reactor is more or less stable and approximately two residence times have passed, the flow rates of the volatile extract and liquid extract streams are measured and samples are taken. Two to three samples are taken during every experiment, one residence time apart from each other. When the experiment is finished, the pump and heating mantle is switched off while the cooling water is closed. The reactor is then drained while still hot since the coal/solvent slurry becomes very viscous when cooled down. Tetrahydrofuran is then used to wash all the piping as well as the reactor when it has cooled down. When the liquid extract product is cooled down it is filtered in the exact same way as described in the batch extraction procedure. Washing of the filter cake with tetrahydrofuran and drying of the residue coal is also done in the same manner as described in section 3.2.3.1.

## 3.3 Calculation of extraction yield

The extraction yield can be calculated in a number of ways. In the following section the method used to calculate the extraction yield in this investigation will be discussed. For this method the proximate analyses of the feed and residue coals were used. The yield was calculated on a dry, ash-free (d.a.f) basis since the moisture and ash content of the coals are not of primary interest but rather the organic content. The extraction yield is defined as the mass extracted per mass of coal. With this method an ash balance was used to calculate the extraction yield and is explained below.

The reaction equation describing the extraction process was taken as:

$$Coal = Extract + Residue\ coal$$

Then 1 kg of coal on a dry, ash-free (d.a.f) basis will result in $y$ kg extract (d.a.f) and $(1-y)$ kg residue coal (d.a.f). The ash fraction in the coal ($Ash_C$) and ash fraction in the residue coal ($Ash_{RC}$) are then defined as shown in equations (3.2) and (3.3).

$$Ash_C = \frac{kg\ ash}{kg\ coal\,(d.a.f)} \tag{3.2}$$

$$Ash_{RC} = \frac{kg\ ash}{kg\ \ residue\,coal\,(d.a.f)} \tag{3.3}$$

Assuming that all the ash remains in the residue coal, in other words no ash reports to the extract, the ash balance is:

$$Ash_C = (1-y)\ Ash_{RC} \tag{3.4}$$

The extraction yield (d.a.f) is then calculated using equation (3.5).

$$y = 1 - \frac{Ash_C}{Ash_{RC}} \tag{3.5}$$

Equation (3.5) was used to calculate the extraction yields for all the batch as well as the continuous extraction experiments and a sample calculation can be seen in Appendix B.

## 3.4 Analytical methods

Different analytical methods were used to characterize the products obtained during the solvent extraction experiments. These methods will be discussed briefly in the next section.

### 3.4.1 Proximate analysis

Proximate analyses of the feed coals as well as the residue coals were performed by the South African Bureau of Standards (SABS). This was done for the batch extraction as well as the continuous extraction coals. Proximate analysis is the determination of the moisture, ash, volatile matter and fixed carbon content of coal. The pores in the coal contain moisture, which is the inherent moisture, that is measured in the proximate analysis and the material that remains after combustion of the mineral matter in coal is called ash. When heating coal to a high temperature, a certain part of the coal can be driven off as gases and condensable liquids while a part remains behind as solid carbon. The part that is driven off is called the volatile matter while the part that remains behind is the fixed carbon (England *et al.*, 1975). The total inherent moisture of the coal is determined with the SABS 925 method, while the ash content is determined with the ISO 1171 (1981) method. The ISO 562 (1998) method is used to determine the volatile matter content of the coal sample. The moisture, ash and volatile matter content can be measured directly while the fixed carbon content is determined by the difference as shown in equation (3.6).

$$Fixed\ carbon\% = 100 - (Moisture + Ash + Volatile\ matter)\% \qquad (3.6)$$

### 3.4.2 Ultimate analysis

The SABS conducted the ultimate analyses for the feed and residue coals of the batch and continuous extraction experiments. Ultimate analysis is the determination of the amount of carbon, hydrogen, nitrogen, sulphur and oxygen present in the organic matter of coal (England *et al.*, 1975). The carbon, hydrogen and nitrogen content of the coal sample are determined with the ASTM D5373 (2002) method, while the ASTM D4239 (2002) method is used to determine the sulphur content. The weight percentage (on a dry, ash-free basis) of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) are determined directly while the percentage oxygen (O) is calculated by difference, shown in equation (3.7).

$$O\% = 100 - (C + H + N + S)\% \qquad (3.7)$$

### 3.4.3 Calorific value

The calorific value of the feed coals as well as the residue coals is determined using a MC-1000 Modular Bomb Calorimeter obtained from Energy Instrumentation and shown in Figure 3.12. The bomb head is shown in Figure 3.13.

Figure 3.12: MC-1000 Modular Bomb Calorimeter.

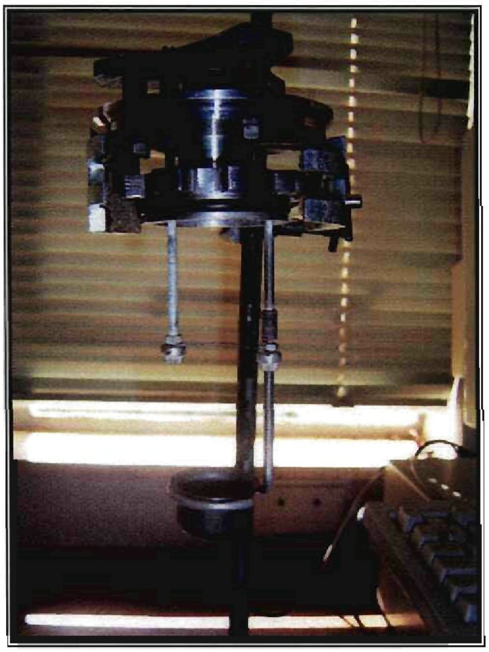


Figure 3.13: Bomb head.

The calorific value of coal can be defined as the amount of heat that is produced when a specific weight of the coal is burnt. About one gram of coal, in a crucible, is placed inside the bomb, which is pressurized with oxygen, and ignited. The bomb inside the calorimeter is surrounded by a water bath (Vorres, 2002). The increase in water temperature is measured and together with the weight of the coal that was put in and the calorimeter's effective heat capacity, it is used to determine the calorific value of the coal sample (England *et al.*, 1975).

The calorific value can be reported as a higher heating value (HHV) or a lower heating value (LHV). Water vapour forms at high temperatures when hydrogen and oxygen combine, causing the bomb calorimeter vessel and its contents to cool down to the starting temperature of about 25℃. The amount of heat released between the same starting and final temperatures are then reported as the HHV. When the bomb calorimeter vessel and its contents are cooled down to 150℃, the heat of formation is not fully recovered. The amount of heat released between the starting temperature and the final temperature of 150℃ are then reported as the LHV (Bossel, 2003). The bomb calorimeter used in this study mesures the HHV.

In addition to the analytical determination of the coal's calorific value using a bomb calorimeter, the calorific values were also calculated theoretically. Neavel *et al.* (1986) suggested that the elemental composition of coal could be used to predict certain properties. Equation (3.8) shows how the elemental composition of coal (dry basis) can be used to estimate the calorific value.

$$Calorific\ value\ (Btu/lb) = 145.9C + 569.6H - 53.89O + 43.08S - 6.3Ash \qquad (3.8)$$

In equation (3.8): $C = carbon,\ wt\%$

$H = hydrogen,\ wt\%$

$O = oxygen,\ wt\%$

$S = sulphur,\ wt\%$

$Ash = ash\ yield,\ wt\%$

Equation (3.9) gives equation (3.8) in terms of MJ/kg, where 1 Btu/lb = 2.33 x $10^{-3}$ MJ/kg.

$$Calorific\ value\ (MJ/kg) = 0.339C + 1.325H - 0.125O + 0.100S - 0.015Ash \qquad (3.9)$$

Neavel *et al.* (1986) found a standard deviation of 86 Btu/lb (20 x $10^{-2}$ MJ/kg) for the correlation in equation (3.8). This equation will be used to evaluate the analytically measured calorific data. The calorific value of the residue coal is particularly of importance as it is foreseen that the residue coal will be used as a fuel utility.

### 3.4.4 Porosity

Coal has a certain porosity that can be defined as the volume percentage of the coal that is occupied by the pores in the coal (Van Krevelen, 1981). According to their size, the pores in coal can be divided into three classes, namely (Vorres, 2002):

1) Micropores with a size of <0.4 – 2.0 nm.
2) Mesopores in the size range of 2.0 – 50 nm.
3) Macropores having sizes larger than 50 nm

For this investigation, the porosity of the feed and residue coals was determined using mercury intrusion porosimetry. With this method, the volume of mercury that is forced into the sample is measured at different pressures. The relationship between the pressure and pore size can then be represented by the Laplace equation given in equation (3.10) where $r_p$ is the pore size (nm), P the pressure (bar), $\gamma$ the surface tension and θ the contact angle.

$$r_p = -\frac{2\gamma \cos\theta}{\Delta P} \tag{3.10}$$

According to equation (3.10) the largest pores will be filled with mercury at the lowest pressures while smaller pores will be filled at higher pressures. The pressure will be increased until a maximum intrusion value is reached. With this method, the pore size distribution can be determined since a specific pore size is assigned to every pressure. A disadvantage of the mercury intrusion method is that the dead-end pores are also measured (Mulder, 1996).

The Micromeritics AutoPore IV 9500 V 1.07 was used in this investigation and is shown in Figure 3.14. A contact angle (θ) of 130° and surface tension ($\gamma$) of 485 x $10^{-3}$ N/m was used for the data handling of the porosity measurements. This mercury porosimeter has a pressure range of 0.52-60000 PSI and is therefore able to measure pore diameters in the size range of 3.0 nm–3.5 x $10^5$ nm. Therefore, mesopores and macropores could be measured with this mercury porosimeter.

Figure 3.14: Micromeritics AutoPore IV 9500 V 1.07 mercury porosimeter.

### 3.4.5 Particle size distribution

Different techniques are available for determining particle size distribution. In this study, the particle size distribution of the original pulverized feed coals as well as the residue coals was determined using a Malvern Mastersizer 2000 shown in Figure 3.15.

Figure 3.15: Malvern Mastersizer 2000.

The Malvern Mastersizer 2000 is designed on the principle of laser diffraction. This principle states that if a particle passes through a laser beam it will scatter the light at an angle that can be directly related to the size of the particle. The Malvern Mastersizer 2000 consists of a laser that provides a light of fixed wavelength and several detectors that measure the light pattern produced by the passing particle. The particle size distribution is then calculated by comparing the scattering light pattern of the sample with an optical model (Kippax, 2007).

### 3.4.6 Density

In order to compare the liquid product obtained during solvent extraction with petrol and diesel, the densities were compared. The densities were obtained by distillation of the liquid extracts at atmospheric pressure. Two distillation cuts were used, a petrol cut at 200℃ and a diesel cut from 200℃ to 350℃. Petrol has a density of about 0.75-0.78 g/cm$^3$ while diesel has a density of about 0.8 g/cm$^3$. The densities of the distillation cuts were calculated using equation (3.11).

$$Density = \frac{Mass(g)}{Volume(cm^3)} \tag{3.11}$$

### 3.4.7 Gas chromatography/mass spectrometry (GC/MS)

GC/MS analyses were conducted to determine the composition of the residue oil and the volatile extracts as well as the liquid extracts obtained during the batch and continuous extraction experiments. A GC/MS consists of two parts, a gas chromatograph and a mass spectrometer. Firstly, the gas chromatograph separates the mixture that is being analyzed into different compounds based on their retention time. The retention time is the time needed for a compound to come out of the gas chromatograph and each compound has a different retention time. In the mass spectrometer, every compound is ionized into its specific fragment spectrum. A computer is then used to compare the obtained spectrum with a spectrum library in order to identify the compound. Quantitative and qualitative data is then provided showing the amount and chemical structure of each compound (McMaster & McMaster, 1998). For the GC/MS analyses conducted in this investigation, a 6890 GC connected to a 5973 Mass Selective Detector obtained from Agilent Technologies was used and is shown in Figure 3.16. A ZB-1 column (model number: Phenomen 010287) with a length of 30 m, internal diameter of 0.32 mm and film thickness of 1 µm was used. Helium was used as carrier gas while a split ratio of 40:1 was used. The temperature program developed for these analyses was as follow:

Oven

Initial temperature: 40℃ Initial time: 10 min
Rate: 6℃/min Final temperature: 150℃ Final time: 5 min
Rate: 4℃/min Final temperature: 290℃ Final time: 12 min

Column

Maximum temperature: 340℃

Figure 3.16: 6890 GC/5973 MS.

### 3.4.8 Pyrolysis- Gas chromatography/mass spectrometry (GC/MS)

The difference between the pyrolysis-GC/MS and the GC/MS analysis is the type of sample that can be analyzed. With the pyrolysis-GC/MS a solid sample can be analyzed directly whereas a solution is needed for normal GC/MS analysis. The pyrolysis-GC/MS consists of three parts, namely the pyrolysis part where the sample is heated to break the molecule down into simpler gaseous compounds that are then introduced to the gas chromatograph and mass spectrometer sections where the compounds are separated and identified as described in the previous section (Bull, 2005). Pyrolysis-GC/MS analyses were carried out for the Waterberg, Brandspruit and Illinois#6 feed coals using a HP 5890 GC connected to a HP 5972 Mass Selective Detector. A Restek Rxi-5 MS column with a length of 30 m, internal diameter of 0.25 mm and film thickness of 0.25 μm was used. The injector used was a CDS 1500 valved interface.

### 3.4.9 Scanning electron microscope (SEM)

In the scanning electron microscope (SEM), a beam of electrons, produced by an electron gun and accelerated using a high voltage, is used to light up the sample. The electron beam is send through a series of electromagnetic lenses in a column that is held under a high vacuum. This is done to ensure that the electrons have an open path to travel through. Deflection coils are used to raster the electron beam across the surface of the sample. This produces signals that are collected by a detector whereafter it is amplified and displayed on a cathode ray tube (CRT). The relationship between the length of the scan line on the sample and the length of the scan line on the CRT is the magnification of the image of the sample. The magnification is changed by changing the degree at which the electron beam is deflected (Chapman, 1986). A FEI Quanta 200 ESEM was used to generate images of the feed and residue coals of the batch and continuous extraction experiments and is shown in Figure 3.17.

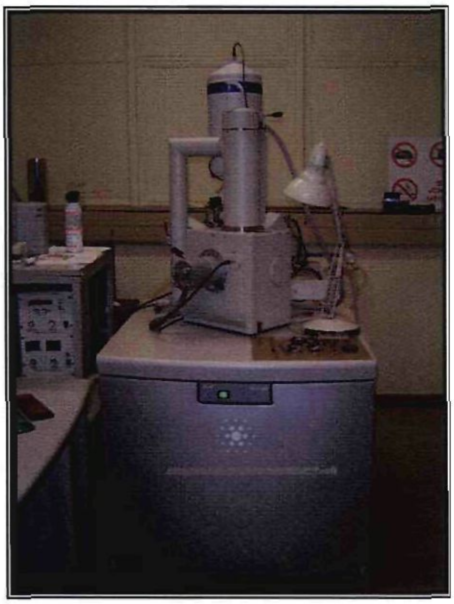


Figure 3.17: FEI Quanta 200 ESEM.

In addition to the images of the feed and residue coals, images were taken of Waterberg coal being heated. These images were used to create a movie which can be seen on the CD-ROM. A few images showing the coal sample at different temperatures are shown in Figure 3.18. It is clear from the first image that no change in the physical appearance of the coal sample can be seen at 360℃. At 450℃ agglomeration of particles occurs and some of the particles start swelling. At 470℃ more particles start swelling and cracks can be seen in some particles. At 508℃ the particles are completely swollen while pores start to open up, releasing gases. From these images it can be concluded that not much swelling occurs at 360℃ for just the coal alone, therefore a solvent is needed for extraction at 360℃.

WATERBERG – 360°C WATERBERG – 450°C

WATERBERG – 470°C WATERBERG – 508°C

Figure 3.18: SEM-images of heated coal particles.

# CHAPTER 4

# EQUILIBRIUM BATCH EXTRACTION

In this chapter, all the results regarding the batch extraction will be presented. These include the extraction yields obtained with the batch extraction experiments as well as the results of the analyses that were performed on the extraction products.

## 4.1 Introduction

As mentioned in the previous chapters, the purpose of the batch extraction experiments was firstly to determine if solvent extraction is a possible coal conversion process for South African coals and if high extraction yields can be obtained using an industrial solvent. Secondly, the batch extraction experiments were used to determine the optimum operating conditions of the solvent extraction process.

The procedure for carrying out the batch extraction experiments was discussed in detail in Chapter 3. In short, the feed coal is pulverized to the desired particle size and mixed with residue oil to obtain the desired solvent/coal ratio. In the autoclave the solvent/coal slurry is heated to the desired extraction temperature and kept there for 1 hour while the pressure is regulated at 5 bar. After the solvent/coal slurry is cooled down to room temperature, it is transferred to a pressure filter to separate the residue coal from the liquid extract.

## 4.2 Extraction yield

As discussed in Chapter 3, the extraction temperature, particle size of the feed coal and the solvent to coal ratio were investigated as operating conditions. The effect of these different operating conditions as well as the effect of the different feed coals used was studied, based on the extraction yields obtained during the batch extraction experiments.

### 4.2.1 Effect of coal type

The experimental data of the batch extraction experiments, in other words the amount of feed coal and residue oil used and residue coal obtained with each experiment can be seen in Appendix A. Since the results of the first set of batch extraction experiments with

Waterberg as feed coal were not very consistent, it was decided to treat them as a test run and to repeat the Waterberg coal experiments. The extraction yields obtained during this first set of Waterberg coal experiments are also given in Appendix A.

The extraction yields obtained with the batch extraction experiments for the Waterberg coal are given in Table 4.1 with the corresponding operating conditions and in the order the experiments were carried out. The same data are given for the Brandspruit coal in Table 4.2 and for the Illinois#6 coal in Table 4.3. In Tables 4.1-4.3 the reproducibility of the experiments is also reported in terms of the absolute standard deviation. More detail on how the standard deviation was calculated is given in Appendix B, together with a sample calculation.

Table 4.1: Extraction yields - Waterberg coal/Residue oil.

| WATERBERG COAL | | | | |
|---|---|---|---|---|
| **Experiment** | **Temperature** | **Particle size** | **Solvent/Coal ratio** | **Extraction yield (d.a.f)** |
| W1 | 360℃ | 120 μm | 10:1 | 50.9%±3.1% |
| W2 | 360℃ | 200 μm | 10:1 | 59.5%±3.1% |
| W3 | 360℃ | 120 μm | 5:1 | 53.3%±3.1% |
| W4 | 360℃ | 120 μm | 10:1 | 57.1%±3.1% |
| W5 | 360℃ | 120 μm | 3:1 | 28.8%±3.1% |
| W6 | 370℃ | 120 μm | 10:1 | 62.9%±3.1% |
| W7 | 360℃ | 120 μm | 10:1 | 57.9%±3.1% |
| W8 | 350℃ | 120 μm | 10:1 | 43.9%±3.1% |

As can be seen from Table 4.1, relative high extraction yields of 29-63% were obtained with the batch extraction experiments using Waterberg coal as feed. These results were expected. As discussed in Chapter 1, it is believed that coals with a high vitrinite content such as Waterberg coal (90%) will be more suitable for conversion via solvent extraction processes. Thus, it can be concluded that it is possible to use solvent extraction as a coal conversion process for Waterberg coal, with residue oil as solvent, based on the extraction yields obtained.

The lowest extraction yield was obtained with a solvent/coal ratio of 3:1 (experiment 5) while the highest extraction yield was obtained at an extraction temperature of 370°C (experiment 6).

As mentioned in Chapter 3, the extraction experiment at operating conditions of 360°C, 120 µm and 10:1 solvent/coal ratio was repeated three times to check the reproducibility of the experimental procedure. It was assumed that the reproducibility obtained for these conditions would apply to all the operating conditions for the Waterberg coal experiments. It should be noted that the standard deviation is only an indication of the experimental error. The standard deviation can be used to calculate the experimental error for different confidence intervals. Table 4.1 shows that the results were very consistent with extraction yields of 51%, 57% and 58% for the experiments at 360°C, 120 µm and 10:1 solvent/coal ratio. The absolute standard deviation for the Waterberg batch extraction experiments was calculated as ±3.1% which is relatively small and therefore it can be said that the experimental procedure was consistent. The consistency of the experimental procedure is also supported by the trends observed with temperature and solvent/coal ratio, as will be discussed in sections 4.2.2 and 4.2.4.

Table 4.2: Extraction yields - Brandspruit coal/Residue oil.

| BRANDSPRUIT COAL | | | | |
|---|---|---|---|---|
| **Experiment** | **Temperature** | **Particle size** | **Solvent/Coal ratio** | **Extraction yield (d.a.f)** |
| B1 | 360°C | 120 µm | 10:1 | 9.7%±3.9% |
| B2 | 360°C | 200 µm | 10:1 | 13.3%±3.9% |
| B3 | 360°C | 120 µm | 5:1 | 10.2%±3.9% |
| B4 | 360°C | 120 µm | 10:1 | 17.4%±3.9% |
| B5 | 360°C | 120 µm | 3:1 | -24.3%±3.9% |
| B6 | 370°C | 120 µm | 10:1 | 8.4%±3.9% |
| B7 | 360°C | 120 µm | 10:1 | 8.8%±3.9% |
| B8 | 350°C | 120 µm | 10:1 | 8.5%±3.9% |

Table 4.2 shows that low extraction yields with a maximum of 17% were obtained with the batch extraction experiments using Brandspruit coal as feed. These results are also what were expected since it is expected that coal with a high inertinite content such as Brandspruit coal (71%) is not suitable for conversion via solvent extraction. It can

therefore be concluded that solvent extraction, using residue oil as solvent, can be used to convert inertinite-rich South African coal into valuable products with limited success, obtaining yields up to 17%.

As with Waterberg coal the lowest extraction yield was obtained with a solvent/coal ratio of 3:1 (experiment 5). The highest extraction yield was obtained at the basic operating conditions of 360℃, 120 µm and 10:1 solvent/coal ratio (experiment 4).

The repeated extraction experiments (B1, B4 and B7) gave yields of 10%, 17% and 9%. The absolute standard deviation for the Brandspruit batch extraction experiments was calculated as ±3.9%. This is a bit higher than the standard deviation of the Waterberg experiments, but is still relatively small which again illustrates the consistency of the experimental procedure.

From Table 4.2 it can be seen that a negative extraction yield was obtained for the experiment with a 3:1 solvent/coal ratio. A possible explanation for this negative extraction yield could be that compounds in the residue oil are adsorbed by the coal particles. This would possibly occur at the filtration step, which is performed at room temperature, assuming that the "solvation power" of tetrahydrofuran for these adsorbed compounds is less than the residue oil. Adsorption effects will be further discussed in the GC/MS analyses (paragraph 4.4.1) and in the continuous extraction chapter (Chapter 5).

Table 4.3: Extraction yields - Illinois#6 coal/Residue oil.

| **ILLINOIS#6 COAL** | | | | |
|---|---|---|---|---|
| **Experiment** | **Temperature** | **Particle size** | **Solvent/Coal ratio** | **Extraction yield (d.a.f)** |
| I1 | 360℃ | 120 µm | 10:1 | 70.2%±1.6% |
| I2 | 360℃ | 200 µm | 10:1 | 71.3%±1.6% |
| I3 | 360℃ | 120 µm | 5:1 | 64.4%±1.6% |
| I4 | 360℃ | 120 µm | 10:1 | 69.8%±1.6% |
| I5 | 360℃ | 120 µm | 3:1 | 55.3%±1.6% |
| I6 | 370℃ | 120 µm | 10:1 | 74.1%±1.6% |
| I7 | 360℃ | 120 µm | 10:1 | 66.6%±1.6% |
| I8 | 350℃ | 120 µm | 10:1 | 68.9%±1.6% |

High extraction yields of 55-74% were obtained for the solvent extraction of Illinois#6 coal, as shown in Table 4.3. Since Illinois#6 coal is a vitrinite-rich coal with even a higher vitrinite content (92%) than Waterberg coal, these results are also not very surprising. This again illustrates that solvent extraction using residue oil as solvent is more suitable as conversion process for vitrinite-rich coals.

The lowest extraction yield was obtained with a solvent/coal ratio of 3:1 (experiment 5) while the highest extraction yield was obtained at an extraction temperature of 370°C (experiment 6). This phenomenon was also observed with the Waterberg coal experiments. For all three feed coals the lowest extraction yield was obtained with a solvent/coal ratio of 3:1 (experiment 5).

Yields of 70%, 70% and 67% were obtained with the repeated extraction experiments for Illinois#6 coal. These yields resulted in an absolute standard deviation of ±1.6%. This standard deviation is very small, therefore it can again be concluded that the experimental procedure for the batch extraction experiments was consistent.

Compared to the results of previous research done on the solvent extraction of Illinois#6 coal reported in literature, the results obtained in this study with residue oil as solvent are very good. Table 4.4 gives a comparison between the results obtained in this study with the results reported by other researchers in literature. Miura *et al.* (2001) obtained an extraction yield of 63% for Illinois#6 coal using tetralin as solvent at 350°C for 1 hour, while an extraction yield of 69% was obtained in this study using residue oil as solvent. Okuyama *et al.* (2004) reported an extraction yield of 60% for Illinois#6 coal at 360°C using 1-methylnaphthalene as solvent, while Burgess Clifford *et al.* (2007) obtained an extraction yield of 51% using light cycle oil as solvent at 360°C for 1 hour. The extraction yield of 69%-71% obtained in this study with residue oil as solvent is in both cases much higher. By comparing the extraction yields of Illinois#6 coal obtained in this study, using residue oil as solvent, with those obtained in previous studies, it can be concluded that an industrial, coal-derived solvent such as residue oil can be successfully used as solvent in a solvent extraction process.

Table 4.4: Batch extraction yields comparison.

| RESULTS COMPARISON | | | | | |
|---|---|---|---|---|---|
| **Condition** | **Miura *et al.* (2001)** | **This study** | **Okuyama *et al.* (2004)** | **Burgess Clifford *et al.* (2007)** | **This study** |
| **Coal** | Illinois#6 | Illinois#6 | Illinois#6 | Illinois#6 | Illinois#6 |
| **Solvent** | Tetralin | Residue oil | 1-Methyl naphthalene | Light cycle oil | Residue oil |
| **Temperature** | 350℃ | 350℃ | 360℃ | 360℃ | 360℃ |
| **Residence time** | 1 hour | 1 hour | 1 hour | 1 hour | 1 hour |
| **Particle size** | | 120 μm | | 250 μm | 120 μm/200 μm |
| **Solvent/Coal ratio** | | 10:1 | | 10:1 | 10:1 |
| **Extraction yield (wt% daf)** | 63% | 69% | 60% | 51% | 69% / 71% |

## 4.2.2 Effect of temperature

In order to study the effect of the extraction temperature on the extraction process, the extraction yields obtained in the batch extraction experiments are plotted against the different extraction temperatures investigated in this study, as shown in Figure 4.1. The Y error bars at each data point represent the absolute standard deviation for the specific coal's experiments.

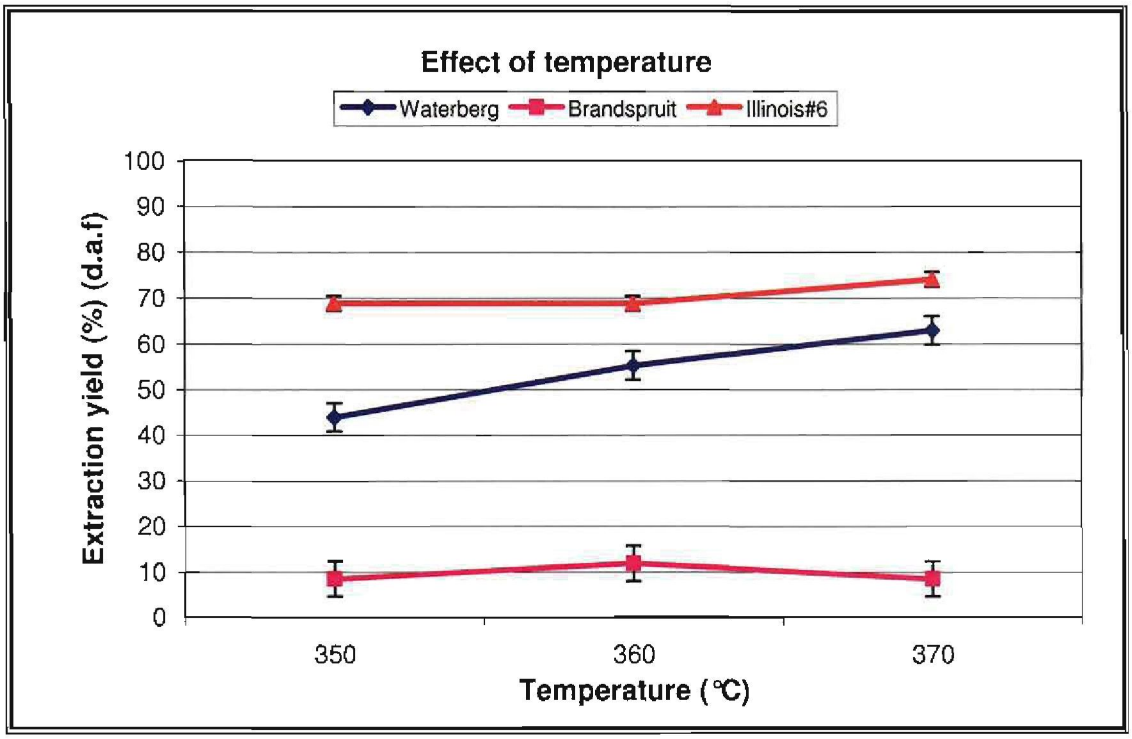


Figure 4.1: Effect of temperature on the solvent extraction process.

When each feed coal's results are studied individually, it can be seen that Waterberg coal showed an absolute increase of 11% in extraction yield from 350°C to 360°C and an 8% increase in extraction yield from 360°C to 370°C. These results clearly show an increase in extraction yield with an increase in temperature for Waterberg as feed coal, with a maximum extraction yield obtained at 370°C. For the Brandspruit coal no trend is observed for the temperature range investigated when the 3.9% standard deviation is taken into account. The results for Illinois#6 coal showed no significant difference between the yields at 350°C and 360°C, but an absolute increase of 5% in extraction yield from 360°C to 370°C. Therefore, the highest extraction yield was obtained for an extraction temperature of 370°C for Waterberg and Illinois#6 coals. Whether an increase in extraction yield with an increase in temperature can be observed when the extraction process is operated in a more kinetically controlled mode, will be discussed in Chapter 5.

From their research, Okuyama *et al.* (2004) concluded that the extraction yield increases with an increase in temperature. In their research, they investigated the extraction of different coals with 1-methylnaphthalene as solvent and a residence time of 1 hour. They studied a temperature range of 300-400°C with increments of ±10°C and observed the highest extraction yield at 360-380°C. In this investigation, the phenomenon of increased extraction yield with increased temperature was also observed for the Waterberg, and in some extent for the Illinois#6 coal experiments within the temperature range of 350-370°C.

### 4.2.3 Effect of particle size

The extraction yields obtained with the different particle sizes for all three coals are shown in Figure 4.2 in order to illustrate the effect of particle size on the extraction process.

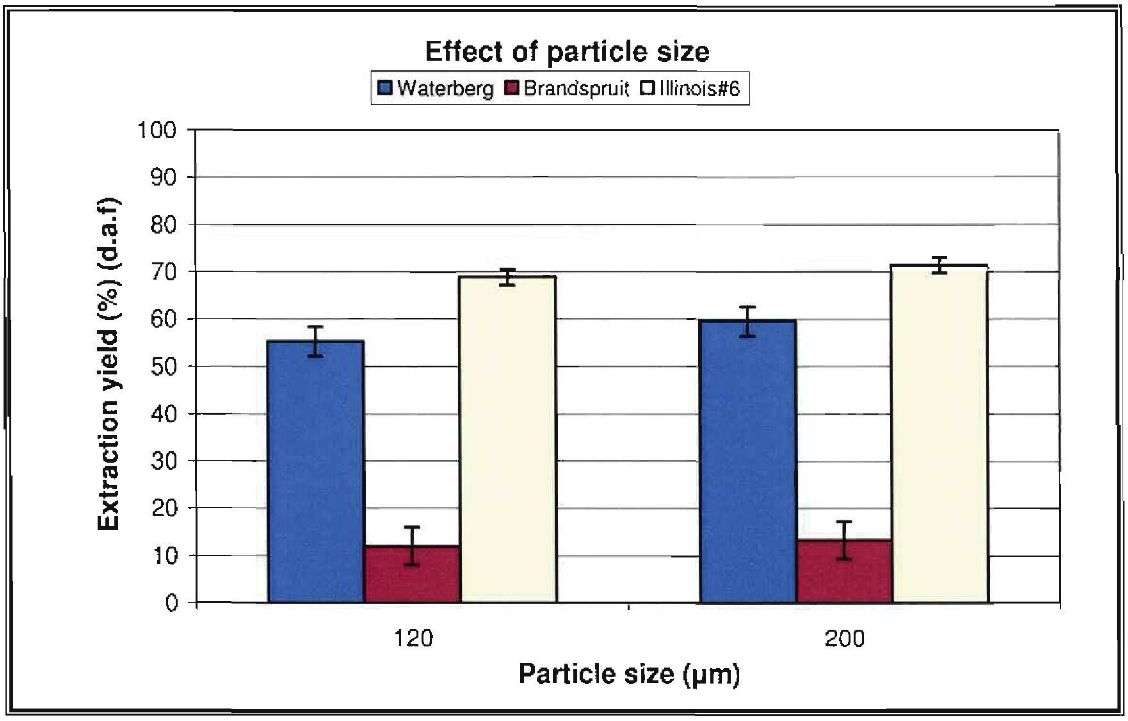


Figure 4.2: Effect of particle size on the solvent extraction process.

Firstly, when just looking at the extraction yield values, a slightly higher extraction yield is observed for a feed particle size of 200 μm than 120 μm. However, when each feed coal's absolute standard deviation is taken into account, it is clear that the particle size of the feed coal, for the particle range studied in this investigation, had no effect on the extraction yield of the solvent extraction process. These results also confirm that 1 hour is enough to obtain equilibrium extraction since the yields obtained with the 120 μm feed particles were the same as the 200 μm feed particles after 1 hour. However, the results obtained from the continuous extraction experiments will indicate more accurately the time necessary to reach complete extraction.

### 4.2.4 Effect of solvent/coal ratio

To illustrate the effect of the solvent to coal ratio on the extraction process, the extraction yields of all three coals obtained for the different solvent to coal ratios are shown in Figure 4.3.

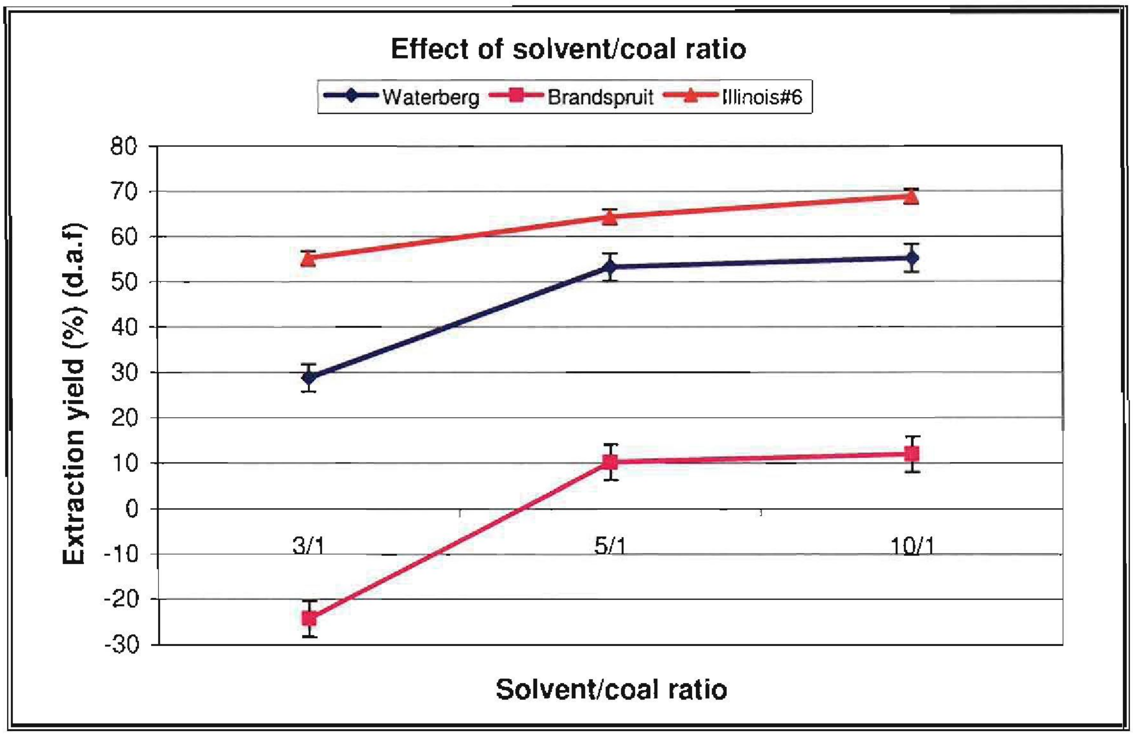


Figure 4.3: Effect of solvent/coal ratio on the solvent extraction process.

If the standard deviations are not considered, it can be seen from Figure 4.3 that the extraction yield for all three feed coals increases with an increase in solvent to coal ratio, with the largest increase in yield from a 3:1 to a 5:1 solvent/coal ratio. If the standard deviations are taken into account however, an increase in solvent/coal ratio from 5:1 to 10:1 does not influence the extraction yield significantly for Waterberg and Brandspruit coal. For Illinois#6 coal it can be concluded that the extraction yield increases with an increase in solvent/coal ratio for the range investigated, with the highest extraction yield obtained at a 10:1 solvent/coal ratio. The much lower extraction yields obtained at a 3:1

solvent/coal ratio for all three feed coals can again be explained by the effect of adsorption as was described in section 4.2.1.

Griffith *et al.* (2006) also investigated the extraction of coal with 3:1, 5:1 and 10:1 solvent to coal ratios. Using light cycle oil as solvent, a particle size of 250 μm, temperature of 350℃ for 1 hour and pressure of 7 bar, they observed that the highest extraction yields were obtained with a solvent to coal ratio of 10:1. In this investigation, the highest extraction yields were also obtained at a 10:1 solvent to coal ratio for all three feed coals using residue oil as solvent, a particle size of 120 μm, temperature of 360℃ for 1 hour and pressure of 5 bar.

## 4.3 Feed and residue coal analyses

In this section, the results of all the analyses that were carried out on the feed coal as well as the residue coal will be given and discussed.

### 4.3.1 Proximate analysis

Proximate analyses were done by SABS on the dry residue coal products to determine the moisture content as well as the volatile matter (VM), fixed carbon (FC) and ash contents. These data are reported in Appendix C. Tables 4.5-4.7 show the results of the proximate analyses for the residue coals obtained during the batch extraction experiments as well as the proximate analyses of the feed coals as reported in Chapter 3. In these tables the volatile matter (VM), fixed carbon (FC) and ash contents are reported on a dry basis (d.b). A sample calculation of how these values were converted to dry basis is also shown in Appendix C.

Table 4.5: Proximate analyses of Waterberg feed and residue coals.

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Waterberg - Proximate analysis (wt %)** | | | |
|---|---|---|---|---|---|
| | | **MOISTURE** | **VM (d.b)** | **FC (d.b)** | **ASH (d.b)** |
| *Feed coal* | | *2.9* | *35.6* | *54.7* | *9.8* |
| W1 | 50.9 | 0.9 | 30.6 | 51.4 | 18.1 |
| W2 | 59.5 | 1.9 | 23.6 | 55.2 | 21.1 |
| W3 | 53.3 | 1.7 | 23.8 | 57.4 | 18.8 |
| W4 | 57.1 | 1.7 | 25.2 | 54.6 | 20.1 |
| W5 | 28.8 | 0.8 | 38.2 | 48.6 | 13.2 |
| W6 | 62.9 | 1.4 | 21.6 | 55.8 | 22.6 |
| W7 | 57.9 | 1.2 | 26.4 | 53.2 | 20.4 |
| W8 | 43.9 | 0.6 | 39.4 | 44.4 | 16.2 |

Table 4.6: Proximate analyses of Brandspruit feed and residue coals.

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Brandspruit – Proximate analysis (wt %)** | | | |
|---|---|---|---|---|---|
| | | **MOISTURE** | **VM (d.b)** | **FC (d.b)** | **ASH (d.b)** |
| *Feed coal* | | *4.3* | *21.6* | *52.1* | *26.3* |
| B1 | 9.7 | 1.4 | 24.2 | 47.5 | 28.3 |
| B2 | 13.3 | 1.3 | 24.6 | 46.1 | 29.3 |
| B3 | 10.2 | 1.5 | 24.3 | 47.5 | 28.2 |
| B4 | 17.4 | 1.2 | 23.4 | 46.7 | 30.0 |
| B5 | -24.3 | 0.6 | 32.5 | 45.2 | 22.3 |
| B6 | 8.4 | 1.1 | 22.5 | 48.9 | 28.5 |
| B7 | 8.8 | 0.9 | 25.2 | 46.8 | 28.0 |
| B8 | 8.5 | 1.4 | 23.3 | 48.9 | 27.8 |

Table 4.7: Proximate analyses of Illinois#6 feed and residue coals.

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Illinois#6 – Proximate analysis (wt %)** | | | |
|---|---|---|---|---|---|
| | | **MOISTURE** | **VM (d.b)** | **FC (d.b)** | **ASH (d.b)** |
| *Feed coal* | | *5.5* | *37.4* | *48.7* | *13.9* |
| I1 | 70.2 | 1.4 | 18.8 | 45.3 | 35.9 |
| I2 | 71.3 | 1.2 | 19.7 | 43.7 | 36.5 |
| I3 | 64.4 | 1.2 | 21.9 | 46.2 | 32.0 |
| I4 | 69.8 | 1.2 | 21.8 | 43.2 | 35.0 |
| I5 | 55.3 | 1.0 | 25.2 | 48.8 | 26.1 |
| I6 | 74.1 | 1.3 | 18.6 | 44.4 | 37.0 |
| I7 | 66.6 | 0.7 | 24.8 | 42.9 | 32.3 |
| I8 | 68.9 | 1.3 | 22.5 | 43.7 | 33.8 |

In solvent extraction it is expected that most of the ash in the feed coal would report to the residue coal, that most of the volatile matter in the feed coal would report to the extract and that it is not clear what would happen with the fixed carbon. This can be investigated by performing mass balances for the proximate constituents. An explanation of how the mass balances were done is given in Appendix C together with the mass distribution of the proximate constituents between the residue coal and extract. Apart from the fact that it is relevant to know where the proximate constituents of the feed coal report to, it is also a method to analyze the consistency of data and to investigate the specific extraction character of the three coals investigated.

Using the results of the mass balances given in Appendix C, it can be concluded that for all three feed coals most of the moisture reports to the extract. The moisture content is not of much importance for the scope of this investigation since numerous factors can have an influence on the moisture content of coal, such as the method of storage, transport and drying. For all three feed coals, most of the ash in the feed coal reports to the residue coal as was expected. Only for experiment 8 of Illinois#6 coal most of the ash reports to the extract. For Waterberg and Illinois#6 coal most of the volatile matter in the feed coal reports to the extract except for experiments 5 and 8 of Waterberg coal. For Brandspruit coal most of the volatile matter in the feed coal remains in the residue coal. Most of the fixed carbon in Waterberg feed coal, except for experiments 3, 5 and 8, reports to the extract while most of the fixed carbon in Illinois#6 feed coal also reports to the extract. Most of the fixed carbon in Brandspruit feed coal reports to the residue coal. From these results it can also be concluded that the extraction of Waterberg and Illinois#6 coal using residue oil as solvent was successful since most of the volatile matter and fixed carbon in the feed coals report to the extract, while most of the ash in the feed coals report to the residue coal. The extraction of Brandspruit coal using residue oil as solvent had limited success since most of the volatile matter, fixed carbon and ash in the feed coal remain in the residue coal.

The data obtained from the mass balances were further used to calculate the percentage of a proximate constituent in the feed coal that was extracted during the solvent extraction process using equation (4.1).

$$\%x\ Extracted = \frac{C(g)\cdot \%x_C - RC(g)\cdot \%x_{RC}}{C(g)\cdot \%x_C} \times 100 \tag{4.1}$$

In equations (4.1), $x$ represents a specific proximate constituent, $\%x_C$ is the percentage of $x$ in the coal, $\%x_{RC}$ is the percentage of $x$ in the residue coal, C is the amount of feed coal and RC the amount of residue coal. A sample calculation can be seen in Appendix C while the results of these calculations are reported in Tables 4.8-4.10.

Table 4.8: Waterberg - Proximate mass balances.

| Exp | Conditions | | | Extraction yield (d.a.f) | %VM Extracted (d.a.f) | %FC Extracted (d.a.f) | %Ash Extracted (d.b) |
|---|---|---|---|---|---|---|---|
| | Temp | Particle size | S/C ratio | | | | |
| W1 | 360℃ | 120 µm | 10:1 | 50.9% | 60.2 | 56.5 | 22.3 |
| W2 | 360℃ | 200 µm | 10:1 | 59.5% | 70.0 | 54.5 | 15.2 |
| W3 | 360℃ | 120 µm | 5:1 | 53.3% | 66.7 | 47.7 | 14.1 |
| W4 | 360℃ | 120 µm | 10:1 | 57.1% | 68.1 | 55.1 | 18.4 |
| W5 | 360℃ | 120 µm | 3:1 | 28.8% | 31.4 | 43.2 | 17.2 |
| W6 | 370℃ | 120 µm | 10:1 | 62.9% | 74.1 | 56.5 | 15.6 |
| W7 | 360℃ | 120 µm | 10:1 | 57.9% | 65.6 | 54.7 | 14.7 |
| W8 | 350℃ | 120 µm | 10:1 | 43.9% | 31.1 | 49.4 | 4.5 |

Table 4.9: Brandspruit - Proximate mass balances.

| Exp | Conditions | | | Extraction yield (d.a.f) | %VM Extracted (d.a.f) | %FC Extracted (d.a.f) | %Ash Extracted (d.b) |
|---|---|---|---|---|---|---|---|
| | Temp | Particle size | S/C ratio | | | | |
| B1 | 360℃ | 120 µm | 10:1 | 9.7% | 0.3 | 20.6 | 8.3 |
| B2 | 360℃ | 200 µm | 10:1 | 13.3% | -2.2 | 22.1 | 5.8 |
| B3 | 360℃ | 120 µm | 5:1 | 10.2% | -2.2 | 19.0 | 5.9 |
| B4 | 360℃ | 120 µm | 10:1 | 17.4% | 1.4 | 19.7 | 1.6 |
| B5 | 360℃ | 120 µm | 3:1 | -24.3% | -41.8 | 17.8 | 15.5 |
| B6 | 370℃ | 120 µm | 10:1 | 8.4% | 9.1 | 16.1 | 8.5 |
| B7 | 360℃ | 120 µm | 10:1 | 8.8% | -2.2 | 20.2 | 7.7 |
| B8 | 350℃ | 120 µm | 10:1 | 8.5% | 6.2 | 16.5 | 7.4 |

Table 4.10: Illinois#6 - Proximate mass balances.

| **Exp** | **Conditions** | | | **Extraction yield (d.a.f)** | **%VM Extracted (d.a.f)** | **%FC Extracted (d.a.f)** | **%Ash Extracted (d.b)** |
|---|---|---|---|---|---|---|---|
| | **Temp** | **Particle size** | **S/C ratio** | | | | |
| I1 | 360°C | 120 µm | 10:1 | 70.2% | 79.3 | 61.0 | 22.2 |
| I2 | 360°C | 200 µm | 10:1 | 71.3% | 77.9 | 62.1 | 20.3 |
| I3 | 360°C | 120 µm | 5:1 | 64.4% | 78.2 | 63.9 | 33.3 |
| I4 | 360°C | 120 µm | 10:1 | 69.8% | 76.0 | 62.8 | 21.5 |
| I5 | 360°C | 120 µm | 3:1 | 55.3% | 79.2 | 69.1 | 49.1 |
| I6 | 370°C | 120 µm | 10:1 | 74.1% | 81.0 | 65.9 | 22.6 |
| I7 | 360°C | 120 µm | 10:1 | 66.6% | 72.2 | 63.8 | 23.7 |
| I8 | 350°C | 120 µm | 10:1 | 68.9% | 86.7 | 80.5 | 58.6 |

The data in Tables 4.8-4.10 were used to construct graphs of *%x Extracted* versus the corresponding extraction yield and are shown in Figures 4.4-4.6. Note that the data of the Brandspruit experiment with the negative yield was not used in constructing these graphs.

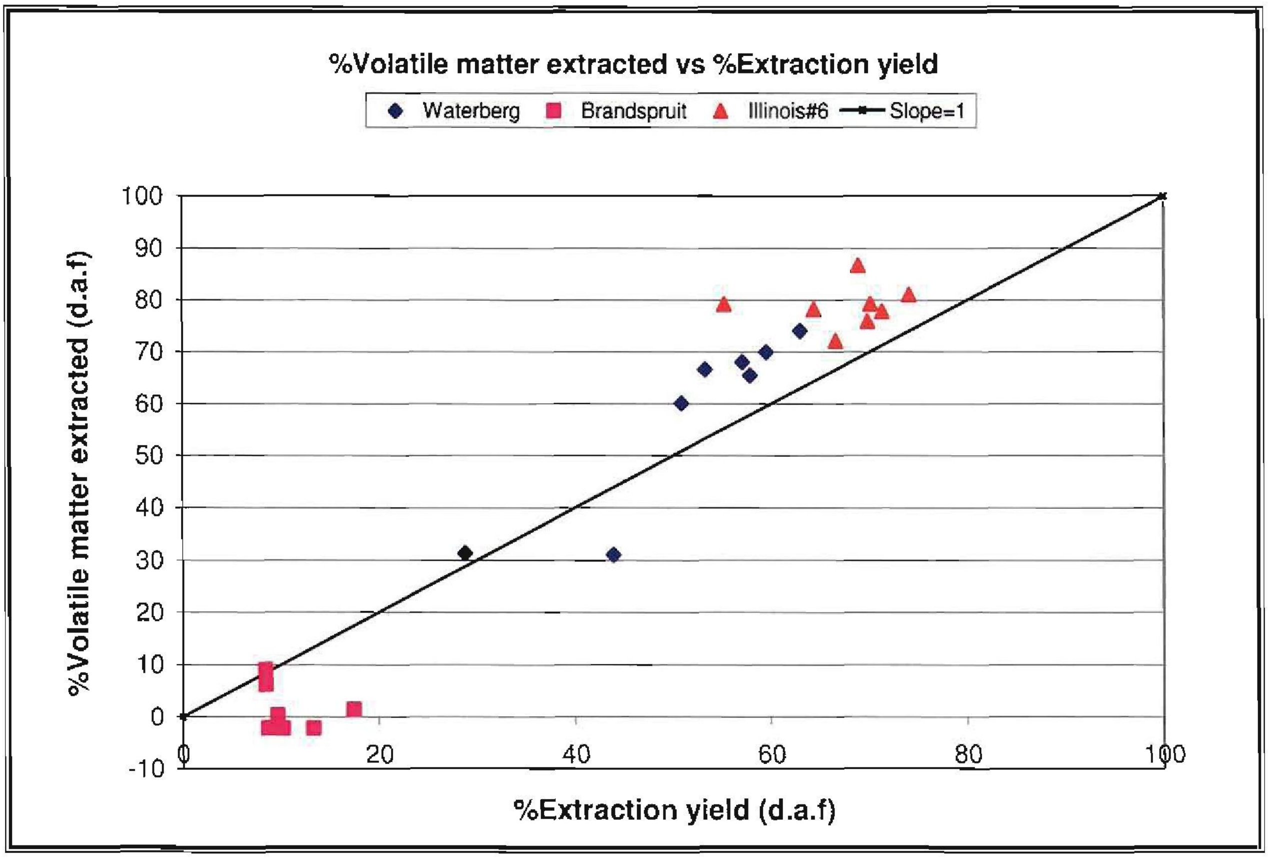


Figure 4.4: %Volatile matter extracted vs. %Extraction yield.

Compared to the line with slope equal to 1, it can be seen from Figure 4.4 that the volatile matter of the Waterberg experiments over-report in the extract except for experiment 8. The volatile matter of the Illinois#6 experiments also over-report in the extract compared to the extraction yield. From Figure 4.4 it is clear that the volatile matter of the Brandspruit experiments under-report in the extract which is in contrast with the results of Waterberg and Illinois#6 coals. The very low and in some cases negative values obtained for the percentage volatile matter in the Brandspruit feed coal extracted, again illustrate the possible effect of adsorption taking place. It may be possible that the coal particles re-adsorbs residue oil and extracted compounds that during the proximate analysis report to the volatile matter.

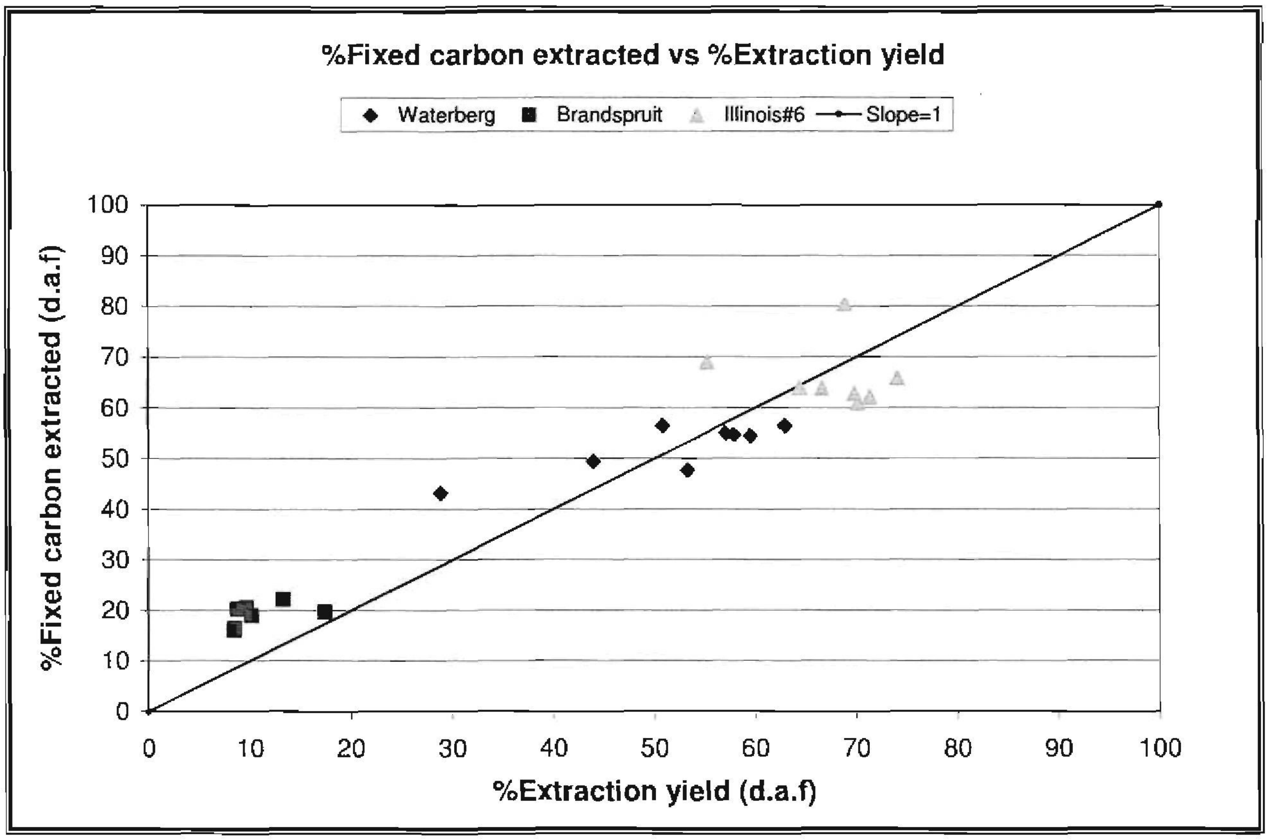


Figure 4.5: %Fixed carbon extracted vs. %Extraction yield.

From Figure 4.5 it can be seen that the fixed carbon of the Waterberg and Illinois#6 experiments, on average, under-report in the extract compared to the extraction yields, while the fixed carbon of the Brandspruit experiments over-report in the extract.

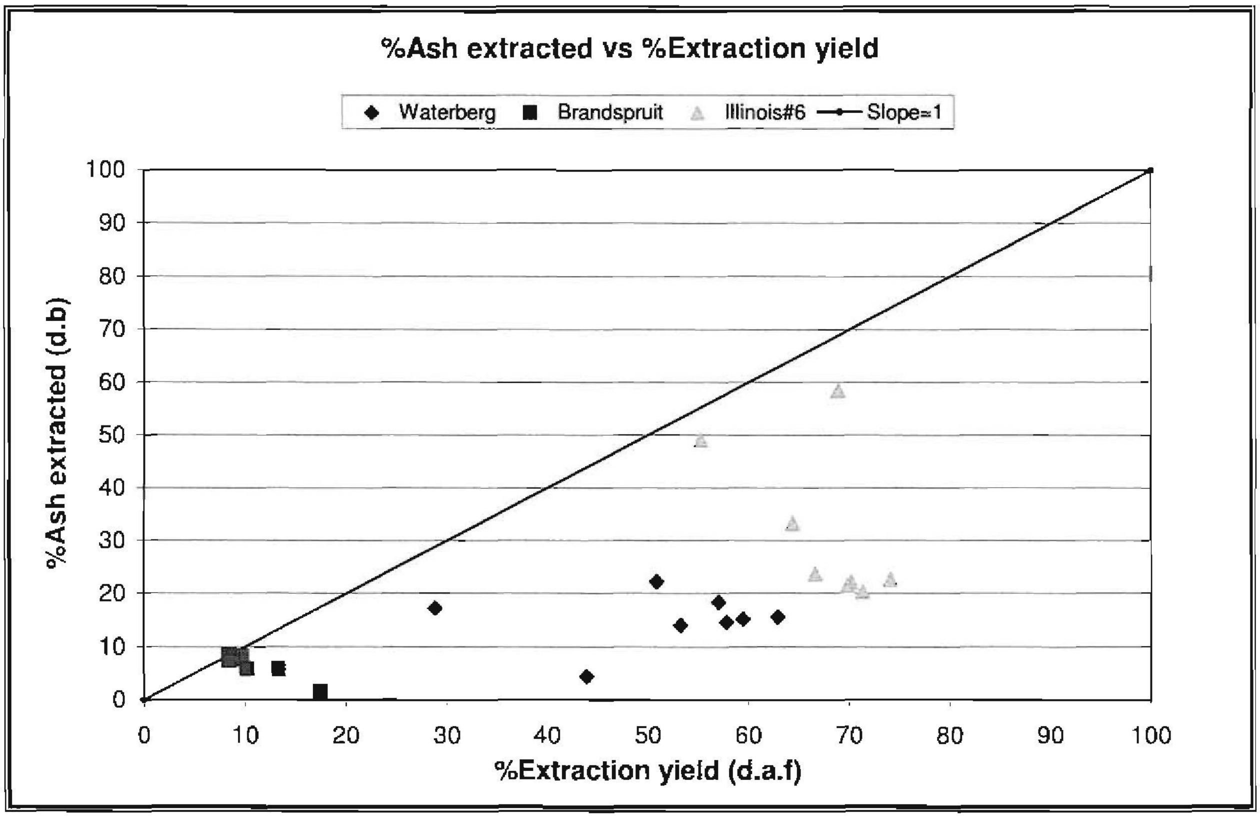


Figure 4.6: %Ash extracted vs. %Extraction yield.

It is expected that all the ash in the feed coal will report in the residue coal with no ash being extracted. From the ash mass balances and Figure 4.6 it can be seen that this was in fact not the case for the experiments conducted during this investigation. Since the ash mass balance calculations were done using the measured quantities of feed and residue coal, the extracted ash may be the result of experimental errors. Looking at Figure 4.6, the slope of the lines is almost zero, also suggesting that the ash reported as being extracted may be a systematic error during the experiments. It may be possible that fine particles of ash or coal containing ash are transported out of the system, for example during filtration. The filterpaper used for filtration might not be sufficient enough to retain all the ash particles, letting some of it through to the extract.

## 4.3.2 Ultimate analysis

Ultimate analyses were also carried out for the dry residue coal products in order to determine the carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulphur (S) contents. These data are also reported in Appendix C. Tables 4.11-4.13 show the results of the ultimate analyses for the residue coals obtained during the batch extraction experiments as well as the ultimate analyses of the feed coals. In these tables the contents are reported on a dry, ash-free basis (d.a.f). A sample calculation of how these values were converted to dry, ash-free basis is shown in Appendix C.

Table 4.11: Ultimate analyses of Waterberg feed and residue coals.

| EXP | Extraction yield (wt%) (d.a.f) | Waterberg - Ultimate analysis (wt %) (d.a.f) | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | O | S (Total) |
| *Feed coal* | | *81.6* | *5.8* | *1.7* | *9.7* | *1.2* |
| W1 | 50.9 | 82.2 | 5.7 | 2.0 | 9.2 | 0.9 |
| W2 | 59.5 | 81.2 | 5.1 | 2.1 | 10.7 | 0.9 |
| W3 | 53.3 | 81.6 | 4.6 | 2.0 | 10.8 | 0.9 |
| W4 | 57.1 | 80.3 | 4.7 | 2.0 | 12.2 | 0.9 |
| W5 | 28.8 | 84.6 | 5.6 | 1.9 | 7.1 | 0.8 |
| W6 | 62.9 | 82.0 | 4.6 | 2.1 | 10.5 | 0.8 |
| W7 | 57.9 | 81.6 | 4.8 | 2.0 | 10.7 | 0.9 |
| W8 | 43.9 | 83.0 | 5.7 | 2.0 | 8.5 | 0.8 |

Table 4.12: Ultimate analyses of Brandspruit feed and residue coals.

| EXP | Extraction yield (wt%) (d.a.f) | Brandspruit - Ultimate analysis (wt %) (d.a.f) | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | O | S (Total) |
| *Feed coal* | | *79.5* | *3.9* | *2.0* | *13.3* | *1.3* |
| B1 | 9.7 | 79.6 | 4.1 | 2.2 | 13.1 | 0.9 |
| B2 | 13.3 | 81.1 | 3.6 | 2.3 | 12.1 | 1.0 |
| B3 | 10.2 | 81.1 | 4.2 | 2.2 | 11.4 | 1.0 |
| B4 | 17.4 | 81.9 | 4.2 | 2.3 | 10.6 | 1.0 |
| B5 | -24.3 | 82.9 | 4.6 | 2.1 | 9.4 | 0.9 |
| B6 | 8.4 | 80.7 | 4.2 | 2.2 | 12.0 | 0.9 |
| B7 | 8.8 | 80.7 | 4.0 | 2.2 | 12.2 | 0.9 |
| B8 | 8.5 | 80.8 | 3.7 | 2.3 | 12.2 | 1.0 |

Table 4.13: Ultimate analyses of Illinois#6 feed and residue coals.

| EXP | Extraction yield (wt%) (d.a.f) | Illinois#6 - Ultimate analysis (wt %) (d.a.f) | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | O | S (Total) |
| *Feed coal* | | *75.8* | *5.8* | *1.4* | *9.4* | *7.6* |
| I1 | 70.2 | 78.8 | 4.1 | 2.0 | 7.0 | 8.0 |
| I2 | 71.3 | 78.2 | 4.2 | 2.0 | 7.4 | 8.2 |
| I3 | 64.4 | 80.6 | 4.4 | 2.0 | 5.5 | 7.5 |
| I4 | 69.8 | 78.9 | 4.2 | 2.1 | 7.4 | 7.4 |
| I5 | 55.3 | 79.9 | 4.5 | 2.0 | 7.4 | 6.2 |
| I6 | 74.1 | 79.8 | 4.0 | 2.0 | 6.1 | 8.0 |
| I7 | 66.6 | 80.9 | 4.6 | 2.1 | 6.0 | 6.5 |
| I8 | 68.9 | 78.0 | 4.2 | 1.9 | 8.4 | 7.5 |

Mass balances for the ultimate constituents were performed in the same way as for the proximate constituents and for the same reasons. The mass distribution of the ultimate constituents between the residue coal and the extract are shown in Appendix C. From those data it can be seen that most of the carbon, hydrogen, oxygen and sulphur in Waterberg feed coal report to the extract while the nitrogen is more or less equally distributed. For the Brandspruit experiments most of the carbon, hydrogen, nitrogen, oxygen and sulphur in the feed coal report to the residue coal which also illustrates the limited success for solvent extraction of Brandspruit coal. As for the Waterberg experiments, the Illinois#6 data show that most of the carbon, hydrogen, oxygen and sulphur in the feed coal report to the extract with the nitrogen more or less equally distributed.

The data obtained from the mass balances were also used to calculate the percentage of an ultimate constituent in the feed coal that was extracted during the solvent extraction process. This was done in the same way as for the proximate constituents and the results are reported in Tables 4.14-4.16. The data in Tables 4.14-4.16 were also used to construct graphs of $\%x$ *Extracted* versus the corresponding extraction yield and are shown in Figures 4.7-4.11.

Table 4.14: Waterberg - Ultimate mass balances.

| Exp | Conditions | | | Extraction yield (d.a.f) | %C Extracted (d.a.f) | %H Extracted (d.a.f) | %N Extracted (d.a.f) | %O Extracted (d.a.f) | %S Extracted (d.a.f) |
|---|---|---|---|---|---|---|---|---|---|
| | Temp | Particle size | S/C ratio | | | | | | |
| W1 | 360°C | 120μm | 10:1 | 50.9% | 57.6 | 58.6 | 50.5 | 60.1 | 68.4 |
| W2 | 360°C | 200μm | 10:1 | 59.5% | 60.8 | 65.4 | 51.3 | 56.5 | 70.5 |
| W3 | 360°C | 120μm | 5:1 | 53.3% | 55.2 | 64.5 | 47.3 | 50.1 | 66.4 |
| W4 | 360°C | 120μm | 10:1 | 57.1% | 60.8 | 67.7 | 53.2 | 49.9 | 70.2 |
| W5 | 360°C | 120μm | 3:1 | 28.8% | 36.3 | 40.7 | 31.3 | 55.0 | 59.0 |
| W6 | 370°C | 120μm | 10:1 | 62.9% | 63.2 | 71.0 | 54.8 | 60.4 | 75.6 |
| W7 | 360°C | 120μm | 10:1 | 57.9% | 59.0 | 66.1 | 51.8 | 54.8 | 69.3 |
| W8 | 350°C | 120μm | 10:1 | 43.9% | 41.2 | 43.2 | 32.0 | 49.4 | 61.5 |

Table 4.15: Brandspruit - Ultimate mass balances.

| Exp | Conditions | | | Extraction yield (d.a.f) | %C Extracted (d.a.f) | %H Extracted (d.a.f) | %N Extracted (d.a.f) | %O Extracted (d.a.f) | %S Extracted (d.a.f) |
|---|---|---|---|---|---|---|---|---|---|
| | Temp | Particle size | S/C ratio | | | | | | |
| B1 | 360°C | 120μm | 10:1 | 9.7% | 14.1 | 20.6 | 6.2 | 16.0 | 45.2 |
| B2 | 360°C | 200μm | 10:1 | 13.3% | 13.0 | 30.5 | 2.4 | 22.2 | 39.4 |
| B3 | 360°C | 120μm | 5:1 | 10.2% | 11.3 | 3.7 | 4.2 | 25.3 | 33.0 |
| B4 | 360°C | 120μm | 10:1 | 17.4% | 11.8 | 5.4 | 1.6 | 32.3 | 34.2 |
| B5 | 360°C | 120μm | 3:1 | -24.3% | -3.6 | -20.7 | 0.3 | 28.5 | 31.0 |
| B6 | 370°C | 120μm | 10:1 | 8.4% | 12.2 | -0.4 | 5.4 | 25.7 | 44.7 |
| B7 | 360°C | 120μm | 10:1 | 8.8% | 13.2 | 9.1 | 5.0 | 16.3 | 40.2 |
| B8 | 350°C | 120μm | 10:1 | 8.5% | 12.2 | 13.4 | 0.4 | 20.6 | 33.4 |

Table 4.16: Illinois#6 - Ultimate mass balances.

| **Exp** | **Conditions** | | | **Extraction yield (d.a.f)** | **%C Extracted (d.a.f)** | **%H Extracted (d.a.f)** | **%N Extracted (d.a.f)** | **%O Extracted (d.a.f)** | **%S Extracted (d.a.f)** |
|---|---|---|---|---|---|---|---|---|---|
| | **Temp** | **Particle size** | **S/C ratio** | | | | | | |
| I1 | 360°C | 120µm | 10:1 | 70.2% | 67.7 | 77.3 | 55.7 | 75.9 | 69.8 |
| I2 | 360°C | 200µm | 10:1 | 71.3% | 68.0 | 77.9 | 55.7 | 75.3 | 67.0 |
| I3 | 360°C | 120µm | 5:1 | 64.4% | 68.4 | 77.4 | 57.4 | 82.2 | 70.6 |
| I4 | 360°C | 120µm | 10:1 | 69.8% | 67.2 | 79.1 | 52.9 | 75.3 | 68.2 |
| I5 | 360°C | 120µm | 3:1 | 55.3% | 72.0 | 79.1 | 62.1 | 80.0 | 78.1 |
| I6 | 370°C | 120µm | 10:1 | 74.1% | 71.0 | 81.0 | 60.6 | 82.3 | 70.2 |
| I7 | 360°C | 120µm | 10:1 | 66.6% | 65.3 | 73.7 | 51.1 | 79.6 | 71.7 |
| I8 | 350°C | 120µm | 10:1 | 68.9% | 82.7 | 87.8 | 77.2 | 85.0 | 83.2 |

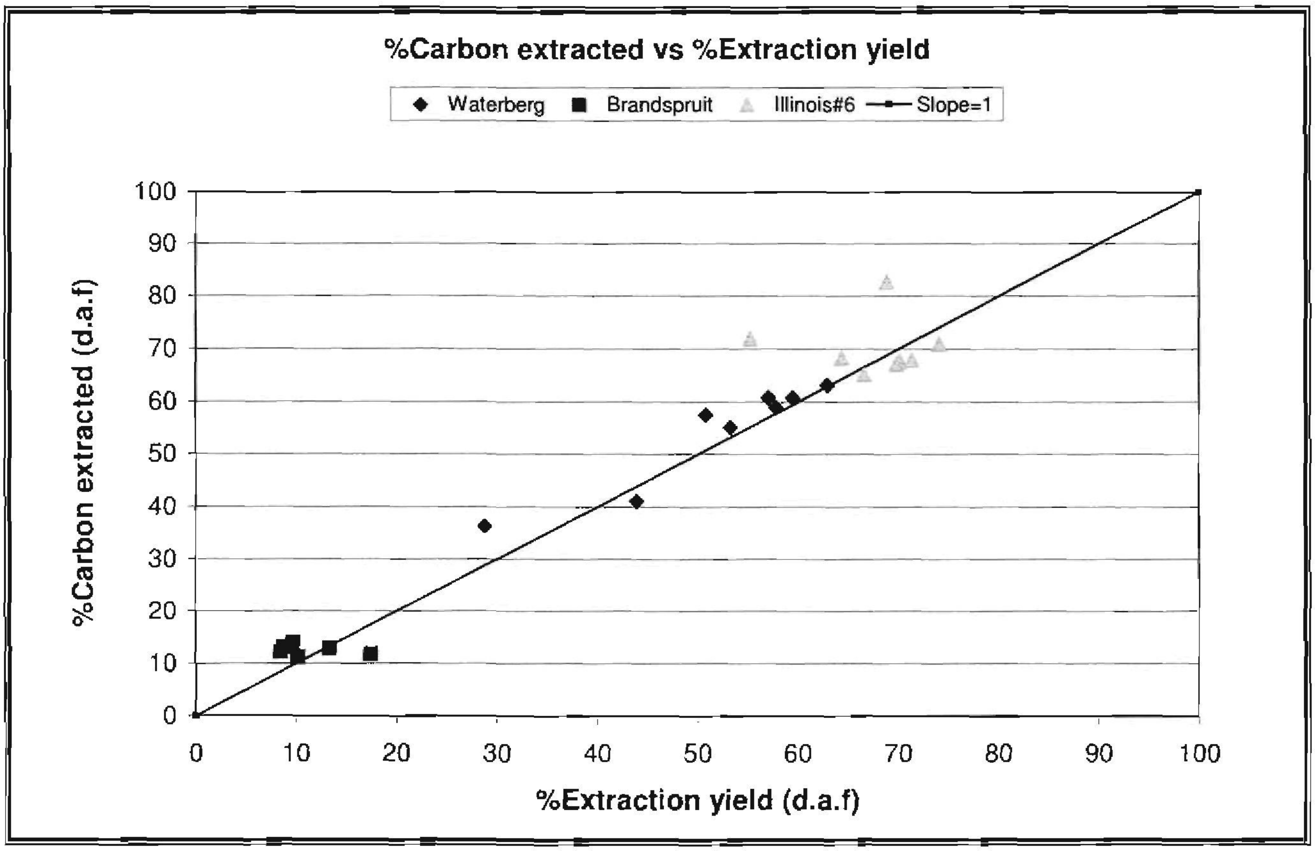


Figure 4.7: %Carbon extracted vs. %Extraction yield.

From Figure 4.7 it can be seen that the carbon content of all three feed coals more or less equally report in the extract compared to the extraction yields. It is interesting to note that if the data for the three coals are treated as a single data set and plotted in the same way as in Figure 4.7, a good linear fit is obtained with a slope almost equal to one. This graph can be seen in Appendix C. This suggests that the extraction of coal may be independent of the type of coal that is used, since the higher the extraction yield, the more carbon is extracted from the feed coal.

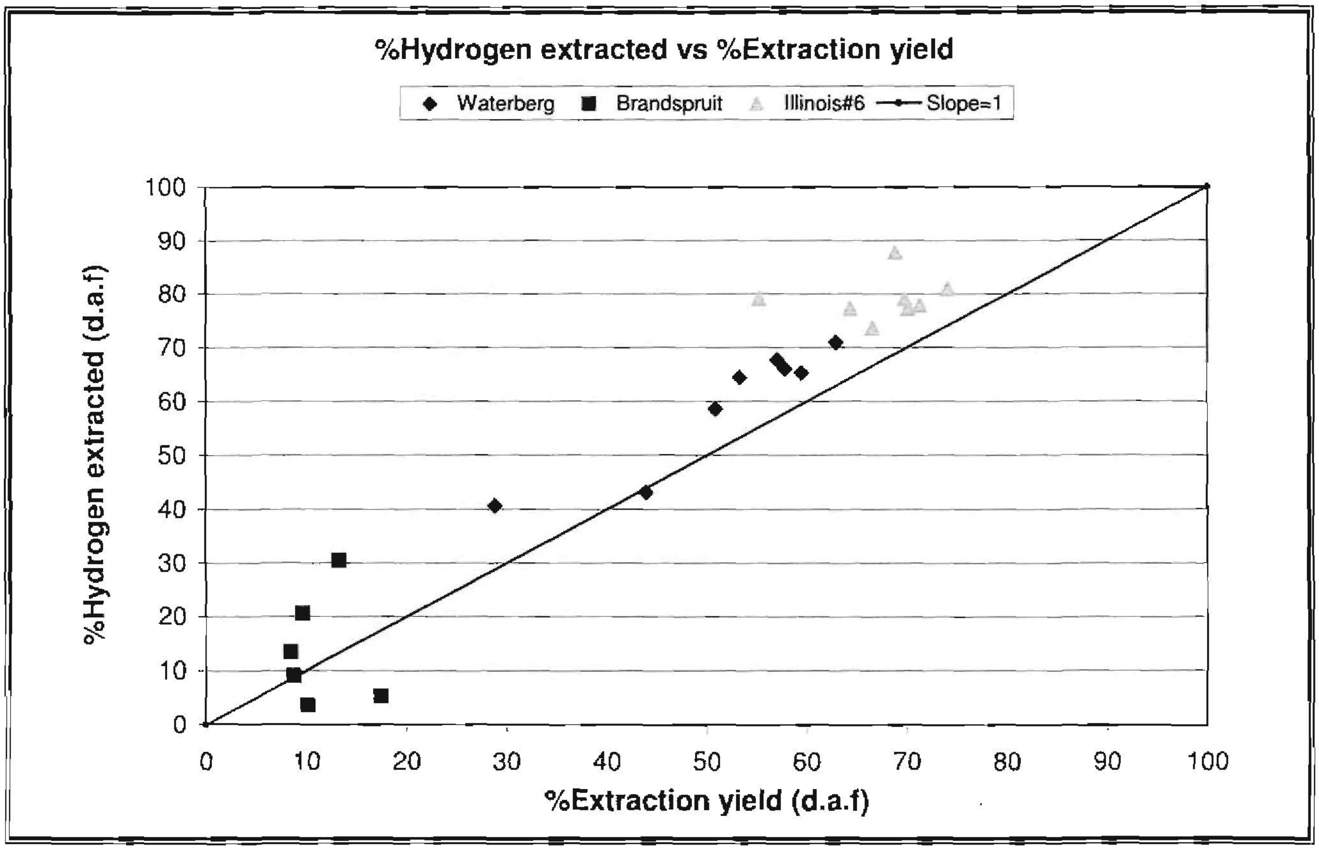


Figure 4.8: %Hydrogen extracted vs. %Extraction yield.

Figure 4.8 show that the hydrogen of all three feed coals over-report in the extract compared to the extraction yields.

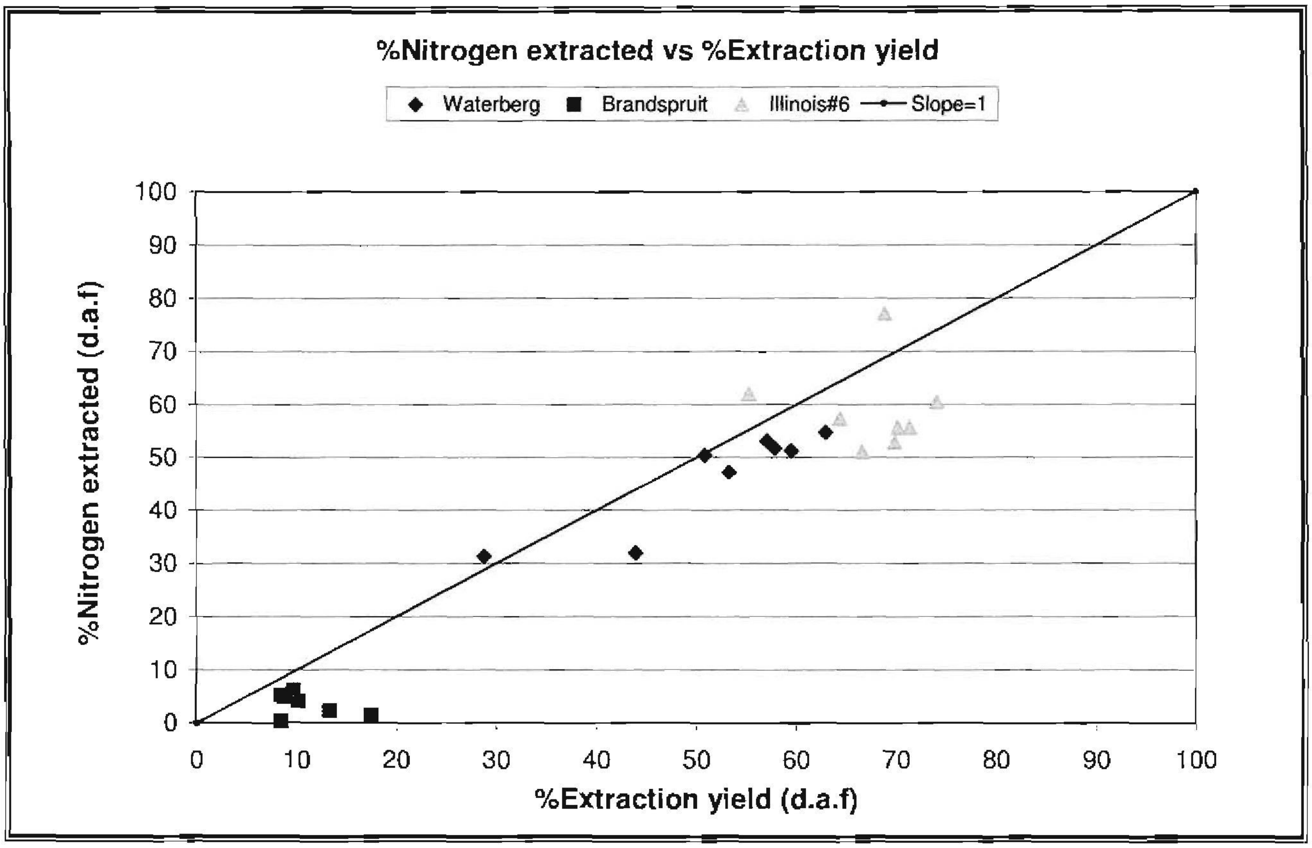


Figure 4.9: %Nitrogen extracted vs. %Extraction yield.

For Waterberg coal, the nitrogen more or less equally report in the extract compared to the extraction yields while the nitrogen under-report in the extract for Brandspruit and Illinois#6 coal.

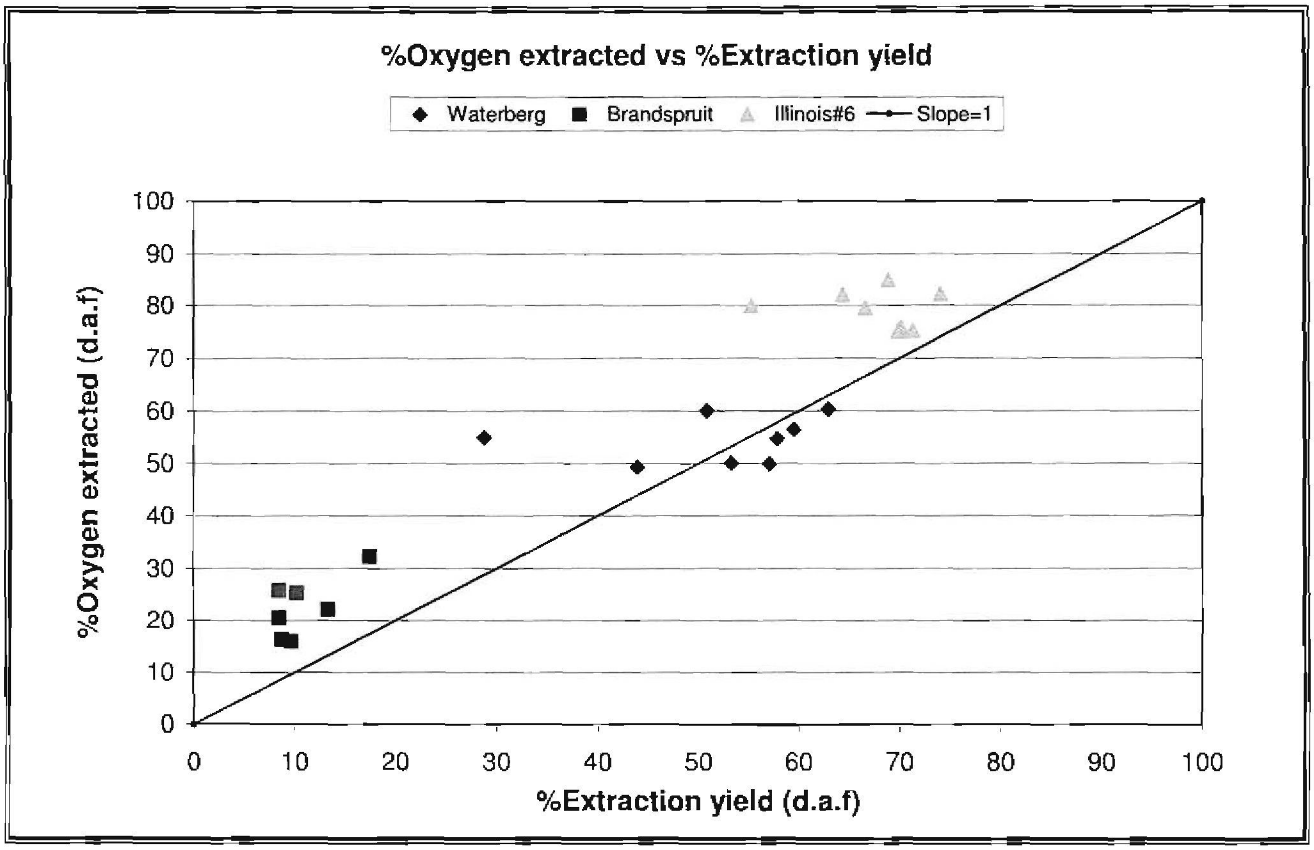


Figure 4.10: %Oxygen extracted vs. %Extraction yield.

Figure 4.10 show that the oxygen over-report in the extract for Brandspruit and Illinois#6 coal while no conclusion can be made about the oxygen for the Waterberg coal.

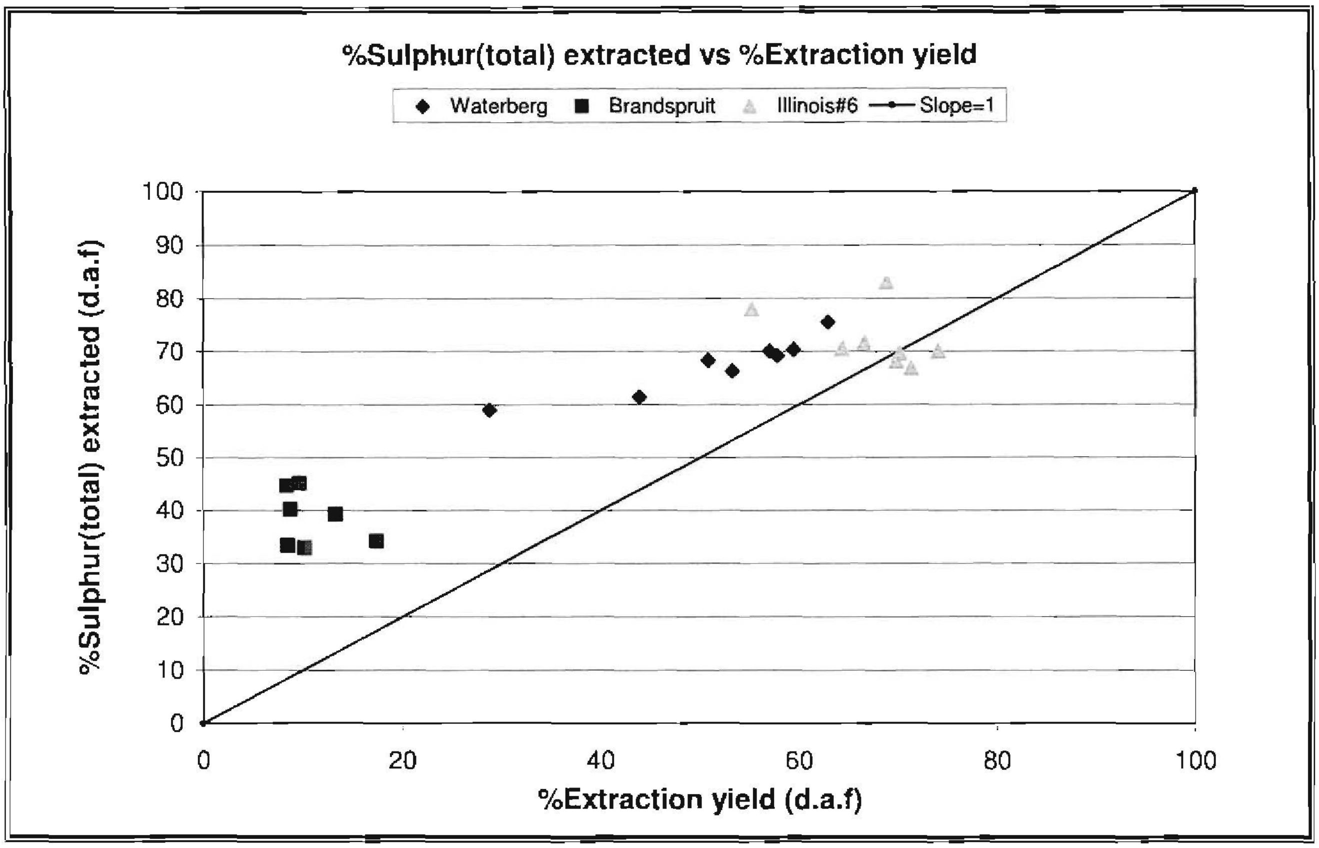


Figure 4.11: %Sulphur extracted vs. %Extraction yield.

The sulphur over-report in the extract for Brandspruit and Waterberg coal while no conclusion can be made about the sulphur for the Illinois#6 coal as can be seen from Figure 4.11.

It is important to know how much of the ultimate constituents end up in the extract since it determines the quality of the liquid fuel. The nitrogen, oxygen and sulphur in the extract will be hydrogenated to $NH_3$, $H_2O$ and $H_2S$ which need to be removed to improve the quality of the fuel.

In addition to the above, the ultimate analyses were also used to calculate the atomic H/C and O/C ratios on dry, ash-free basis for the feed as well as the residue coals and the liquid extracts. These values are reported in Tables 4.17-4.19 while sample calculations are shown in Appendix C. The H/C ratio is an indication of much hydrogen will be needed during catalytic hydrogenation of the extract.

Table 4.17: Waterberg – Atomic H/C and O/C ratios.

| WATERBERG | | | | | |
|---|---|---|---|---|---|
| **Exp** | **Extraction yield (wt%) (d.a.f)** | **Extract** | | **Residue coal** | |
| | | **H/C ratio** | **O/C ratio** | **H/C ratio** | **O/C ratio** |
| *Feed coal* | | *0.85* | *0.09* | *0.85* | *0.09* |
| 1 | 50.9 | 0.86 | 0.09 | 0.83 | 0.08 |
| 2 | 59.5 | 0.91 | 0.08 | 0.76 | 0.10 |
| 3 | 53.3 | 0.99 | 0.08 | 0.68 | 0.10 |
| 4 | 57.1 | 0.94 | 0.07 | 0.69 | 0.11 |
| 5 | 28.8 | 0.95 | 0.14 | 0.79 | 0.06 |
| 6 | 62.9 | 0.95 | 0.09 | 0.67 | 0.10 |
| 7 | 57.9 | 0.95 | 0.08 | 0.70 | 0.10 |
| 8 | 43.9 | 0.89 | 0.11 | 0.82 | 0.08 |

Table 4.18: Brandspruit – Atomic H/C and O/C ratios.

| BRANDSPRUIT | | | | | |
|---|---|---|---|---|---|
| **Exp** | **Extraction yield (wt%) (d.a.f)** | **Extract** | | **Residue coal** | |
| | | **H/C ratio** | **O/C ratio** | **H/C ratio** | **O/C ratio** |
| *Feed coal* | | *0.58* | *0.13* | *0.58* | *0.13* |
| 1 | 9.7 | 0.97 | 0.14 | 0.61 | 0.12 |
| 2 | 13.3 | 1.56 | 0.21 | 0.53 | 0.11 |
| 3 | 10.2 | 0.19 | 0.28 | 0.62 | 0.11 |
| 4 | 17.4 | 0.26 | 0.35 | 0.61 | 0.10 |
| 5 | -24.3 | 3.29 | -0.98 | 0.66 | 0.09 |
| 6 | 8.4 | -0.02 | 0.28 | 0.62 | 0.11 |
| 7 | 8.8 | 0.39 | 0.15 | 0.59 | 0.11 |
| 8 | 8.5 | 0.61 | 0.21 | 0.55 | 0.11 |

Table 4.19: Illinois#6 – Atomic H/C and O/C ratios.

| ILLINOIS#6 | | | | | |
|---|---|---|---|---|---|
| **Exp** | **Extraction yield (wt%) (d.a.f)** | **Extract** | | **Residue coal** | |
| | | **H/C ratio** | **O/C ratio** | **H/C ratio** | **O/C ratio** |
| *Feed coal* | | *0.91* | *0.09* | *0.91* | *0.09* |
| 1 | 70.2 | 1.01 | 0.10 | 0.62 | 0.07 |
| 2 | 71.3 | 1.06 | 0.10 | 0.64 | 0.07 |
| 3 | 64.4 | 1.03 | 0.11 | 0.65 | 0.05 |
| 4 | 69.8 | 1.17 | 0.10 | 0.63 | 0.07 |
| 5 | 55.3 | 0.99 | 0.11 | 0.67 | 0.07 |
| 6 | 74.1 | 1.04 | 0.11 | 0.60 | 0.06 |
| 7 | 66.6 | 1.01 | 0.12 | 0.68 | 0.06 |
| 8 | 68.9 | 0.97 | 0.10 | 0.64 | 0.08 |

From Tables 4.17 and 4.19 it can be seen that the H/C ratios of the Waterberg and Illinois#6 extracts are higher than the H/C ratios of the feed coals. This suggests that lighter compounds, with higher H/C ratios, were extracted first leaving behind heavier compounds with lower H/C ratios. That is why the residue coals of the Waterberg and Illinois#6 experiments have lower H/C ratios compared to their feed coals. Furthermore, it can be noticed that 50% of the Brandspruit extracts have higher H/C ratios while the other 50% have lower H/C ratios than the feed coal. Just to give an indication, benzene has an atomic H/C ratio of 1 while alkanes have an H/C ratio of 2. However, it should be remembered that the H/C ratios reported in Tables 4.17-4.19 are an average of the H/C ratios of all the compounds present in the extract and residue coal.

### 4.3.3 Calorific value

A bomb calorimeter was used to determine the calorific values (Higher heating values) of the feed coals used as well as the residue coals obtained with the solvent extraction experiments. The values as measured with the bomb calorimeter are given in Appendix D, while the calorific values (CV) converted to a dry basis are reported in Table 4.20. The method used to convert the calorific values to dry basis is also shown in Appendix D. In Table 4.20, Exp1 RC means the residue coal obtained with the first experiment etc.

Table 4.20: Analytical calorific values (d.b) (MJ/kg).

| | **WATERBERG** | | **BRANDSPRUIT** | | **ILLINOIS#6** | |
|---|---|---|---|---|---|---|
| | **CV (d.b) (MJ/kg)** | **Yield (wt%) (d.a.f)** | **CV (d.b) (MJ/kg)** | **Yield (wt%) (d.a.f)** | **CV (d.b) (MJ/kg)** | **Yield (wt%) (d.a.f)** |
| *Feed coal* | *30.7* | | *23.7* | | *26.9* | |
| Exp1 RC | 26.4 | 50.9 | 22.7 | 9.7 | 21.1 | 70.2 |
| Exp2 RC | 25.8 | 59.5 | 22.6 | 13.3 | 22.5 | 71.3 |
| Exp3 RC | 26.8 | 53.3 | 22.4 | 10.2 | 23.7 | 64.4 |
| Exp4 RC | 25.1 | 57.1 | 20.6 | 17.4 | 22.1 | 69.8 |
| Exp5 RC | 30.7 | 28.8 | 24.4 | -24.3 | 24.9 | 55.3 |
| Exp6 RC | 25.6 | 62.9 | N/A | 8.4 | 26.0 | 74.1 |
| Exp7 RC | 25.9 | 57.9 | 22.2 | 8.8 | 22.1 | 66.6 |
| Exp8 RC | 28.1 | 43.9 | 25.2 | 8.5 | 25.1 | 68.9 |

Table 4.20 shows that the residue coals have a slightly lower calorific value than the feed coals. However, the calorific values of the residue coals are still relatively high, indicating the possibility to use the residue coal as a boiler fuel for example. The calorific values of the Waterberg experiments show a trend of decreasing calorific value with increasing extraction yield. This suggests that with a higher extraction yield more of the organic material is extracted from the feed coal, leaving behind a residue coal with a lower calorific value. It can also be noticed from Table 4.20 that the calorific values of the Brandspruit residue coals do not differ that much from the calorific values of the feed coal, whereas the calorific values of the Waterberg and Illinois#6 residue coals differ more from the feed coals as more organic material was extracted than with the Brandspruit experiments.

One of the runs was repeated five times to check the accuracy of the measured calorific values. This reproducibility data can be seen in Appendix D. The standard deviation for these five runs was determined as ±1.0 MJ/kg (d.b), showing that the experimental procedure for determining the calorific values using a bomb calorimeter was accurate.

In addition to the analytically determined calorific values, the calorific values were also calculated theoretically using the correlation of Neavel *et al.* (1986) as explained in Chapter3. A sample calculation of the theoretical calorific values can be seen in

Appendix D. Table 4.21 gives a comparison between the analytical and theoretical calorific values.

Table 4.21: Theoretical calorific values (d.b) (MJ/kg).

| | **WATERBERG** | | **BRANDSPRUIT** | | **ILLINOIS#6** | |
|---|---|---|---|---|---|---|
| | **Analytical CV** | **Theoretical CV** | **Analytical CV** | **Theoretical CV** | **Analytical CV** | **Theoretical CV** |
| *Feed coal* | *30.7* | *30.8* | *23.7* | *22.2* | *26.9* | *28.2* |
| Exp1 RC | 26.4 | 27.9 | 22.7 | 21.7 | 21.1 | 20.0 |
| Exp2 RC | 25.8 | 25.8 | 22.6 | 21.4 | 22.5 | 19.7 |
| Exp3 RC | 26.8 | 26.1 | 22.4 | 22.4 | 23.7 | 22.1 |
| Exp4 RC | 25.1 | 25.2 | 20.6 | 22.0 | 22.1 | 20.4 |
| Exp5 RC | 30.7 | 30.4 | 24.4 | 25.4 | 24.9 | 23.8 |
| Exp6 RC | 25.6 | 24.9 | N/A | 22.1 | 26.0 | 19.9 |
| Exp7 RC | 25.9 | 25.8 | 22.2 | 22.0 | 22.1 | 22.1 |
| Exp8 RC | 28.1 | 28.8 | 25.2 | 21.5 | 25.1 | 20.4 |

From Table 4.21 it can be seen that the calculated theoretical calorific values in general are within the accuracy range of ±1.0 MJ/kg from the analytically determined calorific values.

### 4.3.4 Porosity

As mentioned in Chapter 3, mercury intrusion porosimetry was used to determine the porosity of the three feed coals as well as one residue coal of each feed coal. The residue coals used were obtained from experiments with reaction conditions of 360℃, 120 µm particle size and 10:1 solvent to coal ratio. In addition to the porosity, the amount of meso- and macropores present in each sample was also determined and are reported in Table 4.22. The method for determining the amount of different pores is explained in Appendix E, together with pore size distribution graphs. As mentioned in Chapter 3 mesopores are in the size range of 2.0 – 50 nm while macropores are larger than 50 nm.

Table 4.22: Porosity.

| POROSITY | | | |
|---|---|---|---|
| | **Waterberg** | **Brandspruit** | **Illinois#6** |
| ***Feed coal*** | | | |
| Porosity (vol%) | 47.5 | 37.3 | 30.4 |
| Mesopores (vol%) | 0.9 | 0.6 | 0.7 |
| Macropores (vol%) | 46.6 | 36.7 | 29.7 |
| ***Residue coal*** | | | |
| Porosity (vol%) | 46.4 | 48.7 | 34.1 |
| Mesopores (vol%) | 0.7 | 0.7 | 0.7 |
| Macropores (vol%) | 45.7 | 48.0 | 33.4 |
| Yield (wt%) (d.a.f) | 57.9 | 9.7 | 70.2 |

From Table 4.22 it can be seen that there is not a very large difference between the porosity of the Waterberg and Illinois#6 feed and residue coals. However, for the Brandspruit coal there is a significant increase in porosity for the residue coal compared to the feed coal. This suggests that during the extraction process some pores in the Brandspruit coal open up in order to increase the porosity. No micropores were detected using mercury intrusion porosimetry, while the data showed much larger quantities of macropores compared to the mesopores. Table 4.22 shows that there is an increase in macropores from feed to residue coal for Brandspruit and Illinois#6 coal. For Waterberg a slight decrease in mesopores as well as in macropores from feed to residue coal is observed. From Table 4.22 it is clear that there is no relation between the extraction yield and the porosity increase observed for Brandspruit residue coal after extraction.

### 4.3.5 Particle size distribution

The particle size distribution of the feed and residue coals was determined using a Malvern Mastersizer 2000. Analyses for the Waterberg and Brandspruit coals were carried out, but since no significant difference was observed between the particle size distribution of the feed and residue coals, analyses of the Illinois#6 coals were not done. All the particle size distribution graphs for the Waterberg and Brandspruit feed and residue coals can be found on the CD-ROM, while a few are discussed in this section. Figure 4.12 show the particle size distribution of Waterberg feed coal that was pulverized to 120 µm, while Figure 4.13 shows the particle size distribution of Waterberg feed coal that was pulverized to 200 µm. Figure 4.14 shows the particle size distribution of Waterberg residue coal obtained at reaction conditions of 360°C, 120 µm particle size and 10:1 solvent to coal ratio.

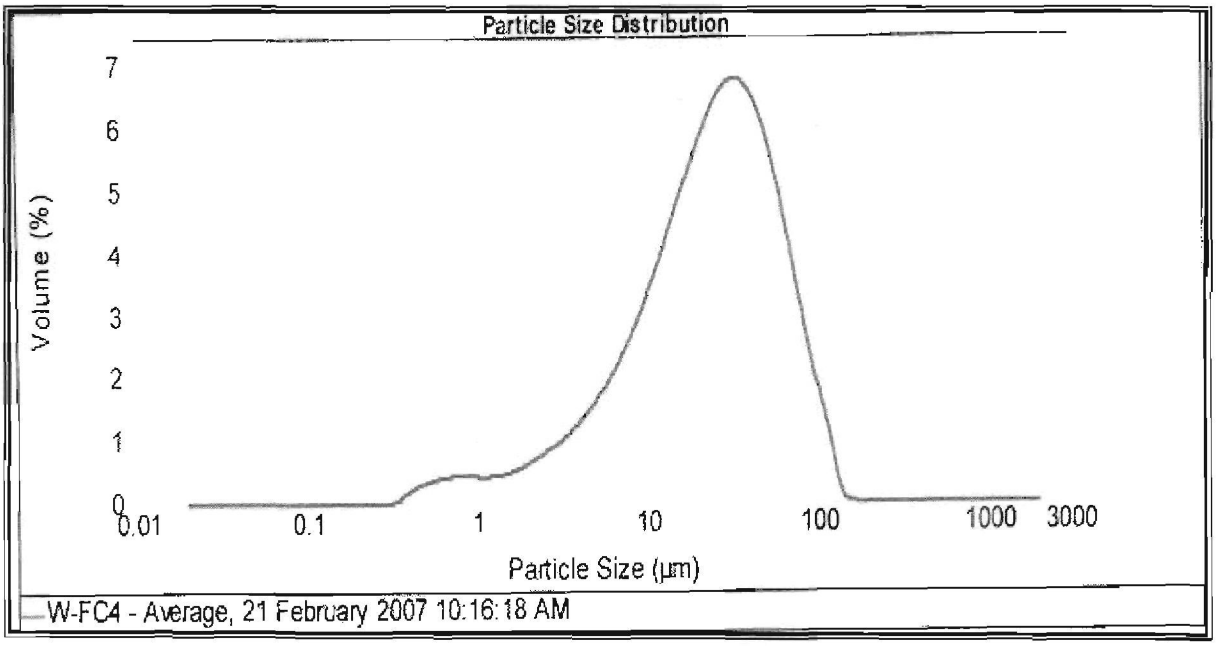


Figure 4.12: Particle size distribution - Waterberg feed coal (120 µm).

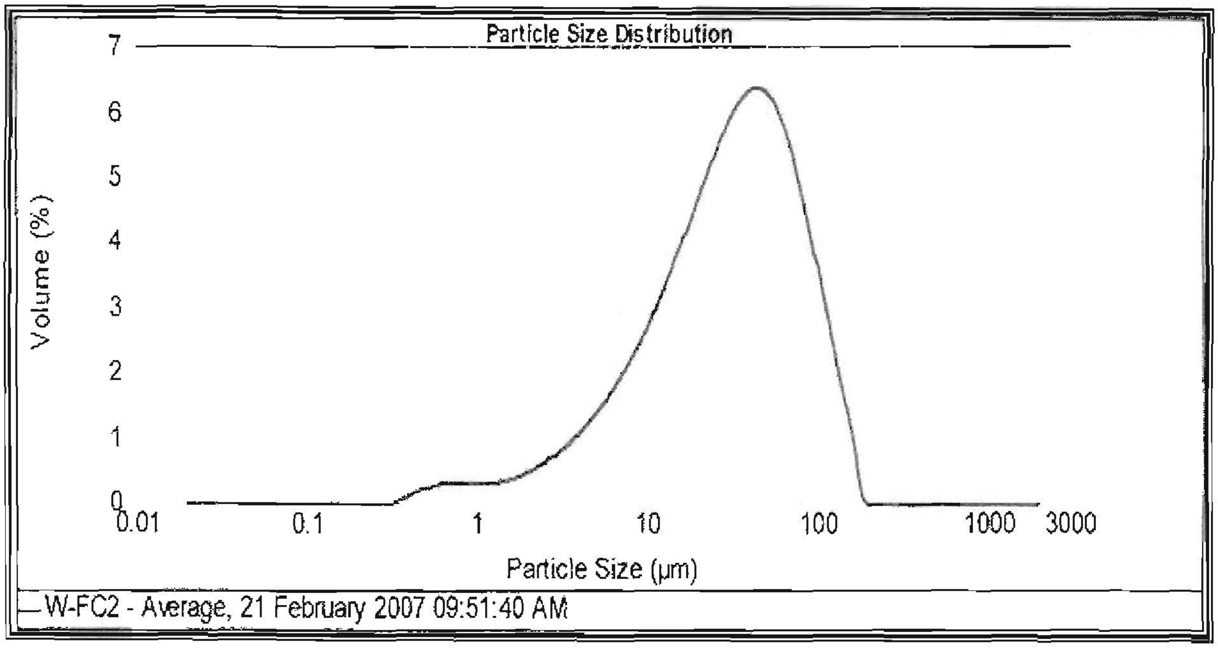


Figure 4.13: Particle size distribution - Waterberg feed coal (200 µm).

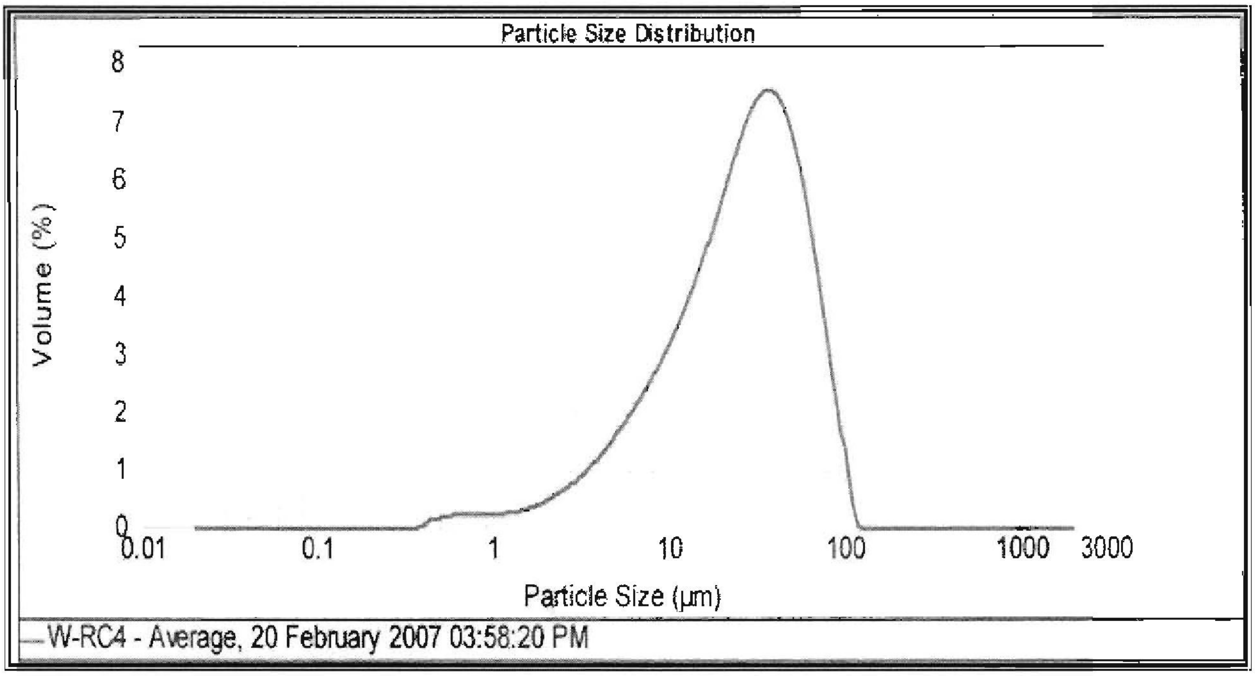


Figure 4.14: Particle size distribution - Waterberg residue coal (120 µm feed coal).

Table 4.23 gives a summary of some of the most important data obtained with the particle size distribution analyses. d(0.5) means that 50% of the particles have a diameter less than or equal to the stated value while D[4,3] is the volume weighted mean.

Table 4.23: Particle size distribution summary.

| Sample | Temp | Particle size | S/C ratio | d(0.5) (μm) | D[4,3] (μm) | Span |
|---|---|---|---|---|---|---|
| **WATERBERG** | | | | | | |
| Feed Coal (120 μm) | | | | 24.6 | 31.0 | 2.5 |
| Feed Coal (200 μm) | | | | 31.8 | 41.1 | 2.7 |
| Residue Coal 1 | 360°C | 120 μm | 10:1 | 26.1 | 31.0 | 2.2 |
| Residue Coal 2 | 360°C | 200 μm | 10:1 | 41.8 | 103.9 | 3.2 |
| Residue Coal 3 | 360°C | 120 μm | 5:1 | 205.5 | 338.4 | 4.1 |
| Residue Coal 4 | 360°C | 120 μm | 10:1 | 26.8 | 31.5 | 2.2 |
| Residue Coal 5 | 360°C | 120 μm | 3:1 | 60.6 | 275.7 | 14.2 |
| Residue Coal 6 | 370°C | 120 μm | 10:1 | 32.9 | 45.9 | 2.3 |
| Residue Coal 7 | 360°C | 120 μm | 10:1 | 32.0 | 72.9 | 2.8 |
| Residue Coal 8 | 350°C | 120 μm | 10:1 | 33.8 | 39.0 | 2.0 |
| **BRANDSPRUIT** | | | | | | |
| Feed Coal (120 μm) | | | | 16.0 | 22.8 | 3.1 |
| Feed Coal (200 μm) | | | | 16.3 | 26.2 | 3.4 |
| Residue Coal 1 | 360°C | 120 μm | 10:1 | 16.6 | 21.0 | 2.5 |
| Residue Coal 2 | 360°C | 200 μm | 10:1 | 16.1 | 22.3 | 2.7 |
| Residue Coal 3 | 360°C | 120 μm | 5:1 | 14.1 | 19.0 | 2.7 |
| Residue Coal 4 | 360°C | 120 μm | 10:1 | 16.9 | 21.4 | 2.5 |
| Residue Coal 5 | 360°C | 120 μm | 3:1 | 23.2 | 145.8 | 22.6 |
| Residue Coal 6 | 370°C | 120 μm | 10:1 | 18.0 | 22.3 | 2.5 |
| Residue Coal 7 | 360°C | 120 μm | 10:1 | 25.8 | 29.7 | 2.1 |
| Residue Coal 8 | 350°C | 120 μm | 10:1 | 15.9 | 20.3 | 2.6 |

From Table 4.23 it can be seen that the largest increases in the d(0.5) and D[4,3] values of the residue coals compared to the feed coals, occur for low solvent/coal ratios. The reason for this may be a large extent of agglomeration taking place at low solvent/coal ratios.

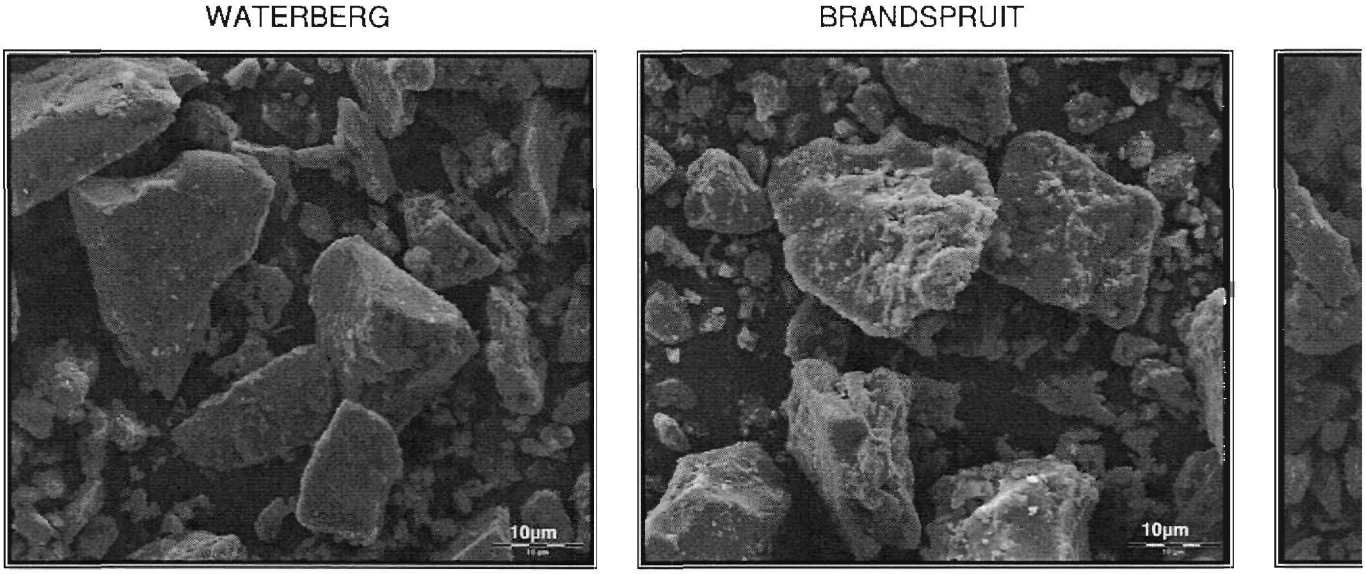
The particle size distribution graphs of the feed coal at 120 μm and 200 μm in Figures 4.12 and 4.13 both show the same bimodal particle size distribution. This bimodal particle size distribution can also be seen in Figure 4.14 for the Waterberg residue coal.

For the Waterberg 120 µm feed coal, 2.24 vol% of the particles is between 0.3 and 1 µm while 97.76 vol% is between 1 and 160 µm. For the Waterberg 200 µm feed coal, 1.62 vol% of the particles is between 0.3 and 1 µm while 98.35 vol% is between 1 and 180 µm. For the Waterberg residue coal in Figure 4.14, 1.17 vol% of the particles is between 0.4 and 1 µm while 98.80 vol% is between 1 and 110 µm. From Figures 4.12 and 4.13 it is clear that there were large quantities of particles present with a particle size much smaller than the desired 120 µm and 200 µm. This can also be seen in the images obtained with the scanning electron microscope (paragraph 4.3.6).

The accuracy of the particle size distribution analysis of the residue coal is questioned however. The reason being that the particle size of the residue coal may not be truly representative of the actual particle size of the residue coal, since the residue coal, obtained as a filter cake, was dried before the analysis was carried out and therefore needed to be crushed.

### 4.3.6 Scanning electron microscope (SEM)

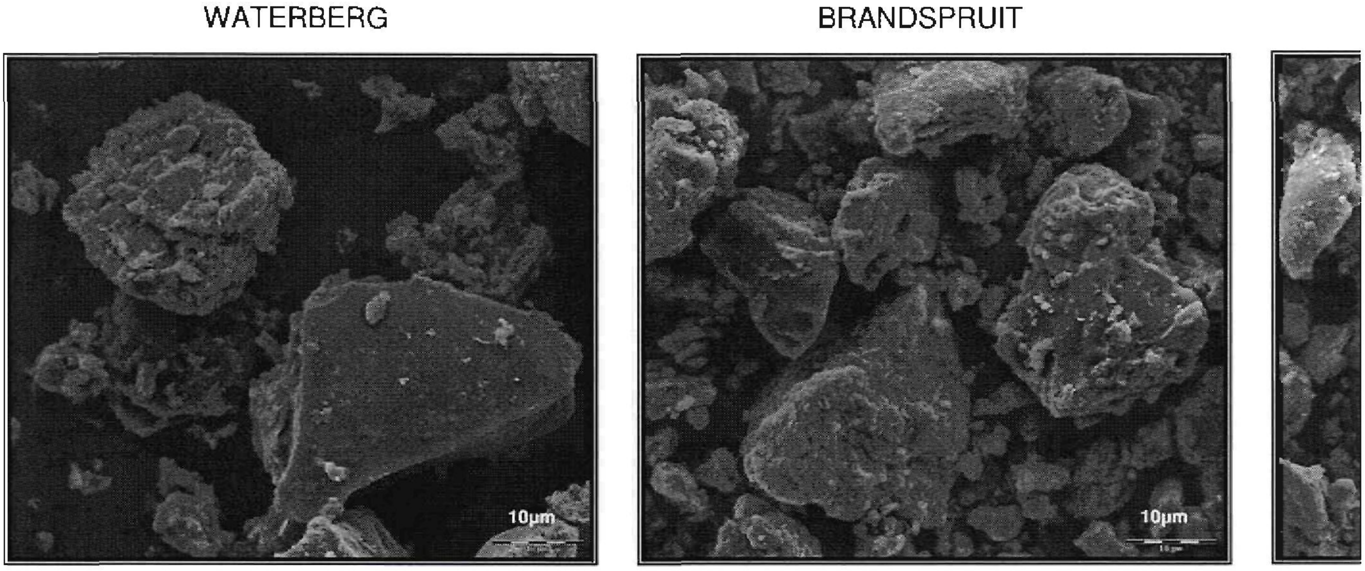
Scanning electron microscope images were taken of the three feed coals as well as of one residue coal of each feed coal. The residue coals used were obtained from experiments with reaction conditions of 360°C, 120 µm particle size and 10:1 solvent to coal ratio. One image of each feed coal is shown in Figure 4.15 and one image of each residue coal in Figure 4.16. The scale bar is 10 µm. More images are available on the CD-ROM. It is rather difficult to make accurate conclusions based on these images. When comparing the feed coals in Figure 4.15, it seems as though the Waterberg and Illionois#6 coals have a smoother surface compared to the rougher-looking surface of the Brandspruit coal. The Waterberg and Illinois#6 feed coals also appear to have sharper edges than the Brandspruit feed coal particles. It is interesting to note the large size distribution that can be seen in the feed coal images. This indicates that there were in fact many particles present with a particle size much smaller than 120 µm, as was also seen with the particle size distribution results. Looking at the residue coal images in Figure 4.16 it can be seen that there is a noticeable difference between the appearance of the feed coal and residue coal particles for all the coals. With the Brandspruit coal there is not so much of a difference between the feed and residue coal particles, however the residue coal particles show some pores that were not noticed in the feed coal particles. In the case of the Waterberg coal, it was noticed that some of the coal particles did not change much while others showed extreme changes in physical appearance. Agglomeration of smaller particles onto larger particles can be seen, while some particles like the one to the left in Figure 4.16, looks like it has been "eaten away" with a "flaky" appearance and rounded off edges compared to the feed coal. With the Illinois#6 coal, the appearance of the residue coal changed a lot compared to the feed coal. Agglomeration of small particles onto larger particles can also be seen and the residue coal particles show a very "flaky" surface compared to the smoother surface of the feed coal. It can therefore be concluded that the coal has undergone certain physical changes during the extraction process.



WATERBERG

BRANDSPRUIT

Figure 4.15: SEM images - Feed coal.



WATERBERG

BRANDSPRUIT

Figure 4.16: SEM images - Residue coal.

### 4.3.7 Pyrolysis- Gas chromatography/mass spectrometry (GC/MS)

Pyrolysis-GC/MS analyses were carried out for the three feed coals. For each coal the 20 peaks with the largest %area were identified and are reported in Tables 4.24-4.26 together with each compound's retention time (RT). A complete set of pyrolysis-GC/MS data for the three feed coals can be seen on the CD-ROM while structure formulas for the compounds presented in Tables 4.24-4.26 can be seen in Appendix F. It should be noted that the identification of the exact chain length of alkanes by the MS was not 100%, as can be concluded from the inconsistencies in the retention times with chain length reported by the GC/MS computer package.

The top 20 peaks accounted for 24% of the total amount of compounds present in the Waterberg feed coal, 17% for the Brandspruit feed coal and 29% for the Illinois#6 feed coal. Cresol is the compound present in the highest concentration in all three feed coals. From Table 4.24 it can be seen that the majority of the compounds are phenolic compounds and the rest alkanes. Table 4.25 shows that the majority of compounds for Brandspruit feed coal are also phenolic compounds while alkanes and acids are also present. For Illinois#6 feed coal, the majority of compounds in Table 4.26 are again phenolic but not so much alkanes are present as with the Waterberg and Brandspruit feed coals.

These results will be compared qualitatively with the GC/MS analyses of the extracts presented in paragraph 4.4.1.

Table 4.24: Pyrolysis-GC/MS - Waterberg Feed coal.

| **WATERBERG – FEED COAL** | | | |
|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** |
| 1. | Cresol | 3.36 | 12.58 |
| 2. | Xylenol | 2.21 | 14.39 |
| 3. | 4-methyl-catechol | 1.70 | 17.45 |
| 4. | Cresol | 1.69 | 12.06 |
| 5. | 3-methyl-1,2-Benzenediol | 1.59 | 16.85 |
| 6. | 3-ethyl-Phenol | 1.26 | 14.85 |
| 7. | Phenol | 1.23 | 10.04 |
| 8. | 4-phenyl-3-Buten-2-one | 1.15 | 20.71 |
| 9. | 1,2-Benzenediol | 1.12 | 15.49 |
| 10. | Trimethyl-Naphthalene | 1.03 | 22.39 |
| 11. | 9H-Fluoren-9-ol | 1.00 | 23.84 |
| 12. | Octadecane | 0.90 | 30.97 |
| 13. | Tetracosane / Octadecane | 0.87 | 31.70 |
| 14. | Eicosane | 0.78 | 32.38 |
| 15. | Heneicosane / Pentadecane | 0.76 | 29.33 |
| 16. | Xylene | 0.75 | 7.02 |
| 17. | Naphthol | 0.75 | 21.66 |
| 18. | Hexadecane | 0.73 | 30.19 |
| 19. | 4-ethyl-catechol | 0.72 | 19.29 |
| 20. | Pentadecane | 0.68 | 21.37 |
| *Total* | | *24%* | |

Table 4.25: Pyrolysis-GC/MS - Brandspruit Feed coal.

| **BRANDSPRUIT – FEED COAL** | | | |
|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** |
| 1. | Cresol | 2.27 | 12.58 |
| 2. | Phenol | 1.92 | 10.03 |
| 3. | Methyl-Benzene | 1.74 | 4.92 |
| 4. | 2-methyl-Phenol | 1.29 | 12.05 |
| 5. | Hexadecanoic acid | 1.22 | 28.01 |
| 6. | 2,4-dimethyl-Phenol | 1.04 | 14.38 |
| 7. | Hexadecane | 0.88 | 30.21 |
| 8. | 1-methyl-Naphthalene | 0.65 | 17.67 |
| 9. | Farnesol | 0.60 | 34.49 |
| 10. | Xylenol | 0.55 | 14.84 |
| 11. | Xylene | 0.54 | 7.03 |
| 12. | 1-Dodecane | 0.54 | 15.39 |
| 13. | 2-methyl-Naphthalene | 0.53 | 17.73 |
| 14. | 2-Propenoic acid | 0.50 | 31.22 |
| 15. | 4-ethyl-Phenol | 0.48 | 14.79 |
| 16. | Tridecane | 0.48 | 23.04 |
| 17. | 1-ethyl-3-methyl-Benzene | 0.45 | 9.59 |
| 18. | 2,4,6-trimethyl-Phenol | 0.45 | 16.86 |
| 19. | Octadecane | 0.45 | 26.09 |
| 20. | 4-methyl-Dibenzofuran | 0.42 | 23.86 |
| *Total* | | *17%* | |

Table 4.26: Pyrolysis-GC/MS - Illinois#6 Feed coal.

| ILLINOIS#6 – FEED COAL | | | |
|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** |
| 1. | Cresol | 5.19 | 12.65 |
| 2. | 1,2-Benzenediol | 2.38 | 15.57 |
| 3. | Phenol | 2.12 | 10.07 |
| 4. | 3-methyl-1,2-Benzenediol | 2.05 | 16.89 |
| 5. | 2,4-dimethyl-Phenol | 1.98 | 14.42 |
| 6. | 4-methyl-catechol | 1.90 | 17.51 |
| 7. | 2-methyl-Phenol | 1.62 | 12.07 |
| 8. | methyl-Benzene | 1.53 | 4.98 |
| 9. | 3-ethyl-Phenol | 1.53 | 14.88 |
| 10. | 4-ethyl-1,3-Benzenediol | 1.05 | 19.33 |
| 11. | 4-ethyl-Phenol | 1.00 | 14.83 |
| 12. | 4-phenyl-3-Buten-2-one | 0.95 | 20.74 |
| 13. | 1,4-dihydro-2,5,8-trimethyl-Naphthalene | 0.87 | 25.11 |
| 14. | 3-methyl-1-Naphthalenol | 0.81 | 23.59 |
| 15. | 2,3-dihydro-1H-Inden-5-ol | 0.79 | 18.54 |
| 16. | Hexadecanoic acid | 0.75 | 28.03 |
| 17. | 2-ethyl-Phenol | 0.74 | 15.43 |
| 18. | 1-Hexene | 0.73 | 3.08 |
| 19. | Chavicol | 0.64 | 18.11 |
| 20. | 4-vinyl-2-methoxy-Phenol | 0.64 | 18.62 |
| *Total* | | *29%* | |

## 4.4 Liquid and volatile extract analyses

In this section, the results of all the analyses that were carried out on the liquid extracts as well as the volatile extracts obtained with the batch extraction experiments, will be given and discussed.

### 4.4.1 Gas chromatography/mass spectrometry (GC/MS)

GC/MS analyses were carried out for the clean residue oil as well as for one liquid extract and one volatile extract of each coal in order to determine the compounds present. The liquid and volatile extracts were obtained from experiments with reaction conditions of 360°C, 120 µm particle size and 10:1 solvent to coal ratio. As with the pyrolysis-GC/MS results, the 20 peaks representing the compounds present in the largest quantities were identified for each mixture analyzed. A summary of these results are given in Tables 4.27-4.30, while detail results of the GC/MS analyses together with chromatographs can be seen on the CD-ROM. Structure formulas of the compounds presented in Tables 4.27-4.30 are shown in Appendix F. The compounds listed in the tables below represent 51-58% of the total compounds present in the solvent as well as in the liquid and volatile extracts, showing that the product distribution of the extracts is much narrower than the product distribution of the pyrolyzed coal. With the Waterberg experiment about 50 ml of volatile extract was obtained, about 30 ml with the Brandspruit experiment and more or less 70 ml with the Illinois#6 experiment. These amounts are in the order of 10% of the estimated amount of solvent+extract in the autoclave at the end of the extraction.

When the GC/MS results of the solvent are compared to those of the three liquid extracts, as given in Tables 4.27-4.30, it can be seen that most of the compounds present in the solvent are also present in the liquid extracts. An obvious reason for this may be that for the liquid extracts that were analyzed, a solvent/coal ratio of 10:1 was used making it difficult to see which compounds were extracted out of the coal. Phenanthrene is the compound present in the largest quantity in the residue oil as well as in all three liquid extracts. Although mostly the same compounds are present in the different liquid extracts, differences in their rank can be observed. Naphthalene for example is the eighth highest peak in the Waterberg liquid extract while it is the seventh highest peak in the Brandspruit liquid extract and the fifth highest in the Illinois#6 liquid extract. Looking at the volatile extracts it can be seen that some of the compounds present in the liquid extracts are also present in the volatile extracts. Naphthalene is the compound present in the largest quantity in all three volatile extracts. Differences in terms of the rank of compounds can be seen between the different volatile extracts. It is also noted that the top 20 peaks of the residue oil and liquid extracts do not contain phenolic compounds as was observed for the pyrolyzed coal while the volatile extracts contain some phenolic compounds.

Table 4.27: GC/MS - Residue oil.

| **RESIDUE OIL** | | | |
|---|---|---|---|
| **Compound** | | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 6.28 | 46.37 |
| 2. | Fluorene | 4.22 | 40.27 |
| 3. | Dibenzofuran | 3.68 | 37.94 |
| 4. | Anthracene | 3.56 | 46.68 |
| 5. | 1-methyl-9H-Fluorene | 2.75 | 44.07 |
| 6. | Fluoranthene | 2.72 | 53.80 |
| 7. | 4-methyl-Dibenzofuran | 2.49 | 42.09 |
| 8. | Naphthalene | 2.33 | 26.80 |
| 9. | 4-methyl-Dibenzofuran | 2.31 | 41.64 |
| 10. | Carbazole | 2.27 | 47.44 |
| 11. | Heptadecane | 2.19 | 57.69 |
| 12. | 2-methyl-9H-Fluorene | 2.10 | 44.61 |
| 13. | Tetradecane | 2.01 | 50.45 |
| 14. | 2-methyl-Naphthalene | 1.98 | 29.80 |
| 15. | Acenaphthene | 1.90 | 36.71 |
| 16. | Tricosane | 1.79 | 59.86 |
| 17. | 1,2-dimethyl-Naphto[2,1-b]furan | 1.72 | 45.27 |
| 18. | Pyrene | 1.61 | 55.03 |
| 19. | Tetracosane | 1.59 | 61.94 |
| 20. | 2-methyl-9H-Fluorene | 1.49 | 44.27 |
| *Total* | | *51%* | |

Table 4.28: GC/MS – Waterberg: Liquid and volatile extracts.

| | **WATERBERG – LIQUID EXTRACT** | | | **WATERBERG – VOLATILE EXTRACT** | | |
|---|---|---|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** | **Compound** | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 6.59 | 46.37 | Naphthalene | 8.87 | 26.82 |
| 2. | Fluorene | 4.21 | 40.26 | Methyl-Naphthalenes | 5.03 | 29.82 |
| 3. | Dibenzofuran | 3.49 | 37.93 | Cresol | 4.23 | 23.53 |
| 4. | Anthracene | 3.36 | 46.68 | Xylenol | 3.05 | 25.62 |
| 5. | 1-methyl-9H-Fluorene | 2.83 | 44.07 | 2-methyl-Phenol | 2.76 | 22.93 |
| 6. | Fluoranthene | 2.81 | 53.80 | Indane | 2.72 | 22.62 |
| 7. | Naphthalene | 2.78 | 26.81 | Methyl-Naphthalenes | 2.67 | 30.29 |
| 8. | 4-methyl-Dibenzofuran | 2.71 | 42.09 | Fluorene | 2.61 | 40.27 |
| 9. | 4-methyl-Dibenzofuran | 2.54 | 41.63 | Dibenzofuran | 2.49 | 37.94 |
| 10. | 2-methyl-Naphthalene | 2.52 | 29.80 | 3,4-dimethyl-Phenol | 2.47 | 26.14 |
| 11. | 1-methyl-Phenanthrene | 2.44 | 50.43 | 1-methyl-Indan | 2.02 | 26.01 |
| 12. | Heptadecane | 2.38 | 57.68 | Phenanthrene | 1.90 | 46.36 |
| 13. | Tricosane | 1.92 | 59.85 | Acenaphthene | 1.90 | 36.72 |
| 14. | Carbazole | 1.88 | 47.43 | 2,4-Dimethylstyrene | 1.80 | 25.73 |
| 15. | Pentadecane | 1.81 | 55.39 | Phenol | 1.78 | 20.61 |
| 16. | Acenaphthene | 1.80 | 36.71 | Dodecane | 1.68 | 27.66 |
| 17. | cis-Stilbene | 1.75 | 44.60 | Biphenyl | 1.60 | 32.50 |
| 18. | Pyrene | 1.72 | 55.03 | Xylene | 1.48 | 16.59 |
| 19. | Tetradecane | 1.53 | 52.99 | 1-methyl-Indan | 1.43 | 24.22 |
| 20. | 2-methyl-Phenanthrene | 1.52 | 50.04 | 4-methyl-Dibenzofuran | 1.42 | 41.63 |
| *Total* | | *53%* | | | *54%* | |

Table 4.29: GC/MS - Brandspruit: Liquid and volatile extracts.

| | **BRANDSPRUIT – LIQUID EXTRACT** | | | **BRANDSPRUIT – VOLATILE EXTRACT** | | |
|---|---|---|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** | **Compound** | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 7.30 | 46.36 | Naphthalene | 8.42 | 26.82 |
| 2. | Fluorene | 4.68 | 40.26 | Methyl-Naphthalenes | 4.36 | 29.82 |
| 3. | Dibenzofuran | 4.16 | 37.93 | 3-methyl-Phenol | 4.21 | 23.54 |
| 4. | Anthracene | 3.85 | 46.67 | Indane | 3.02 | 22.62 |
| 5. | Naphthalene | 3.29 | 26.81 | 2-methyl-Phenol | 2.84 | 22.93 |
| 6. | 1-methyl-9H-Fluorene | 3.05 | 44.07 | Fluorene | 2.55 | 40.26 |
| 7. | 4-methyl-Dibenzofuran | 2.99 | 42.08 | Phenanthrene | 2.36 | 46.36 |
| 8. | Fluoranthene | 2.92 | 53.80 | Dibenzofuran | 2.24 | 37.94 |
| 9. | Methyl-Naphthalenes | 2.84 | 29.80 | Methyl-Naphthalenes | 2.23 | 30.29 |
| 10. | 4-methyl-Dibenzofuran | 2.77 | 41.63 | Xylenol | 2.17 | 25.62 |
| 11. | 1-methyl-Phenanthrene | 2.45 | 50.44 | Phenol | 2.06 | 20.61 |
| 12. | Carbazole | 2.42 | 47.43 | Xylenol | 2.06 | 26.14 |
| 13. | Heptadecane | 2.30 | 57.67 | 1-methyl-Indan | 1.94 | 26.01 |
| 14. | Acenaphthene | 1.97 | 36.71 | Xylene | 1.76 | 16.59 |
| 15. | 2-methyl-9H-Fluorene | 1.95 | 44.60 | 1-Phenyl-1-butene | 1.73 | 25.73 |
| 16. | Tricosane | 1.82 | 59.85 | Dodecane | 1.70 | 27.66 |
| 17. | Pyrene | 1.75 | 55.02 | Acenaphthene | 1.69 | 36.72 |
| 18. | Pentadecane | 1.73 | 55.39 | (1-methyl-1-propenyl)-Benzene | 1.50 | 24.22 |
| 19. | 2-methyl-Phenanthrene | 1.63 | 49.77 | 1-methyl-9H-Fluorene | 1.34 | 44.07 |
| 20. | 2-methyl-Phenanthrene | 1.62 | 50.04 | 4-methyl-Dibenzofuran | 1.33 | 42.08 |
| *Total* | | *57%* | | | *52%* | |

Table 4.30: GC/MS - Illinois#6: Liquid and volatile extracts.

| | **ILLINOIS#6 – LIQUID EXTRACT** | | | **ILLINOIS#6 – VOLATILE EXTRACT** | | |
|---|---|---|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** | **Compound** | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 7.50 | 46.36 | Naphthalene | 8.27 | 26.82 |
| 2. | Fluorene | 4.66 | 40.26 | Methyl-Naphthalenes | 4.72 | 29.81 |
| 3. | Anthracene | 3.89 | 46.67 | Cresol | 3.86 | 23.53 |
| 4. | Dibenzofuran | 3.88 | 37.93 | Phenanthrene | 3.60 | 46.36 |
| 5. | Naphthalene | 3.17 | 26.81 | Fluorene | 3.37 | 40.26 |
| 6. | 1-methyl-9H-Fluorene | 3.10 | 44.07 | Dibenzofuran | 3.02 | 37.94 |
| 7. | 4-methyl-Dibenzofuran | 3.00 | 42.08 | Xylenol | 2.66 | 25.61 |
| 8. | Fluoranthene | 2.99 | 53.80 | Methyl-Naphthalenes | 2.47 | 30.28 |
| 9. | Methyl-Naphthalenes | 2.76 | 29.80 | 2-methyl-Phenol | 2.31 | 22.92 |
| 10. | 4-methyl-Dibenzofuran | 2.70 | 41.63 | Indane | 2.28 | 22.62 |
| 11. | Carbazole | 2.56 | 47.43 | Acenaphthene | 2.10 | 36.71 |
| 12. | 1-methyl-Phenanthrene | 2.56 | 50.43 | 3,4-dimethyl-Phenol | 2.05 | 26.13 |
| 13. | Heptadecane | 2.42 | 57.67 | Anthracene | 2.05 | 46.67 |
| 14. | 2-methyl-9H-Fluorene | 2.00 | 44.60 | 1-methyl-9H-Fluorene | 1.97 | 44.07 |
| 15. | Acenaphthene | 1.93 | 36.71 | 4-methyl-Dibenzofuran | 1.87 | 42.08 |
| 16. | Heneicosane | 1.85 | 59.85 | 4-methyl-Dibenzofuran | 1.60 | 41.63 |
| 17. | Pyrene | 1.83 | 55.02 | 1-phenyl-1-butene | 1.58 | 26.01 |
| 18. | 2-methyl-Phenanthrene | 1.77 | 50.04 | Phenol | 1.47 | 20.61 |
| 19. | Pentadecane | 1.77 | 55.39 | 2,3-dihydro-5-methyl-1H-Indene | 1.38 | 25.73 |
| 20. | 2-methyl-Phenanthrene | 1.73 | 49.77 | Tetradecane | 1.36 | 50.44 |
| *Total* | | *58%* | | | *54%* | |

## 4.4.2 Density

As explained in Chapter 3, the density of the extracts was obtained by distillation and using equation (3.7). In addition to the one extract of each feed coal that was distilled, the solvent was also distilled. Table 4.31 shows the results of the density measurements, while the data used to determine the densities are given in Appendix G.

Table 4.31: Densities of distillation cuts (g/cm$^3$).

| | FRACTION 1 | FRACTION 2 |
|---|---|---|
| Residue oil | 0.95 | 1.03 |
| Waterberg extract | 0.90 | 1.01 |
| Brandspruit extract | 0.89 | 1.02 |
| Illiois#6 extract | 0.89 | 1.03 |

Fraction 1 in Table 4.31 is defined as the petrol fraction cut at 200°C, while fraction 2 is defined as the diesel fraction cut at 350°C. From Table 4.31 it can be seen that the densities of fraction 1 for all three coal extracts are about 5% lower than the density of fraction 1 of the residue oil. No significant change is observed for the density of fraction 2 of the extracts compared to the residue oil. When comparing the densities of fraction 1 in Table 4.31 with the typical petrol density of 0.75-0.78 g/cm$^3$, it is clear that the densities of the extracts are much higher than the required petrol density. Compared to a typical diesel density of 0.8 g/cm$^3$, the densities of fraction 2 in Table 4.31 are also higher. This suggests that the extract product of solvent extraction cannot be added directly to the fuel pool, but requires some additional work-up like hydrogenation before it can be used as a liquid fuel.

## 4.5 Conclusions

From the results of the batch extraction experiments it can be concluded that solvent extraction, using residue oil as solvent, can be used to convert vitrinite-rich South African coal, and with limited success inertinite-rich South African coal, into valuable products. The conclusion can also be made that an industrial solvent such as residue oil can be used in the extraction process to obtain high extraction yields.

For the temperature range investigated in this study, the optimum temperature for Waterberg and Illinois#6 coal was found to be 370°C while no trend was observed for the Brandspruit coal. It was found that the particle size of the feed coal, for the particle size range studied in this investigation, had no effect on the extraction yield of the solvent extraction process. For the range of solvent to coal ratios studied it was found that higher extraction yields were obtained with a 5:1 and 10:1 ratio than a 3:1 solvent/coal ratio. As explained earlier in this chapter, the low extraction yields obtained with a 3:1 solvent/coal ratio may be due to re-adsorption of compounds in the residue oil.

All the analyses carried out on the feed coal, residue oil and extraction products, namely the residue coal and liquid and volatile extracts, showed that there were significant differences between the products and the starting material.

# CHAPTER 5

# CONTINUOUS EXTRACTION AND KINETIC MODEL: A FIRST APPROACH

In this chapter, the results of the continuous extraction experiments will be given in terms of the extraction yields obtained. This chapter also includes a discussion of how the continuous extraction data was used to develop a kinetic model for describing the solvent extraction process. Additionally, the results of the analyses used to characterize the extraction products will also be presented and discussed.

## 5.1 Introduction

The main purpose of the continuous extraction part of this investigation was to develop a continuous experimental setup. Another purpose of the continuous extraction experiments was to obtain kinetical data.

After a lot of troubleshooting, an experimental setup (as described in Chapter 3) was developed that was used to perform continuous extraction experiments (Beukman, 2007; Hattingh, 2007). However, since this was only a first approach, there is plenty of room for improvement of the setup. The procedure used for the continuous extraction experiments was discussed in detail in Chapter 3. To recap, the feed coal is pulverized to 120 µm and mixed with the residue oil in a 10:1 solvent to coal ratio. After being pre-heated to about 40 °C, the coal/solvent slurry is pumped to the reactor from the bottom at the desired flow rate. After the coal/solvent slurry reached the desired reaction temperature in the reactor and approximately two residence times have passed, samples were taken from the volatile extract and liquid extract streams. When the liquid extract product is cooled down it is filtered in the exact same way as the batch extraction filtration to separate the residue coal from the liquid extract.

## 5.2 Extraction yield

The extraction yields obtained with the continuous extraction experiments were calculated in the same way as for the batch extraction experiments using equation (3.5) as discussed in Chapter 3 and demonstrated in Appendix B. Tables 5.1 and 5.2 show the extraction yields obtained for the Waterberg and Brandspruit continuous experiments at the specific operating conditions of temperature and residence time. The residence times were calculated by dividing the volume of the reactor (120 ml) with the volumetric flow rate of the slurry. Note that the extraction yields of the batch extraction experiments, with a residence time of 60 min, are also reported in these tables for comparison purposes. As mentioned in Chapter 3, two to three samples were taken during every experiment, one residence time apart from each other. The average value of these samples were then used to calculate the extraction yields reported in Tables 5.1 and 5.2.

Table 5.1: Extraction yields – Waterberg coal/Residue oil.

| **WATERBERG – EXTRACTION YIELD (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Temperature** | **Residence time (min)** | | | | |
| | 4 | 6 | 12 | 24 | 60 |
| 320°C | -54.9% | -62.3% | -71.6% | -70.2% | |
| 330°C | | -29.0% | -0.5% | | |
| 340°C | | -1.9% | 17.2% | | |
| 350°C | | | | | 43.9% |
| 360°C | | | | | 55.3% |
| 370°C | | | | | 62.9% |

Table 5.2: Extraction yields – Brandspruit coal/Residue oil.

| **BRANDSPRUIT – EXTRACTION YIELD (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Temperature** | **Residence time (min)** | | | | |
| | 4 | 6 | 12 | 24 | 60 |
| 320°C | -46.0% | -98.1% | -28.7% | -69.7% | |
| 330°C | | -92.2% | -22.2% | -65.0% | |
| 340°C | | -77.8% | -12.9% | | |
| 350°C | | | | | 8.5% |
| 360°C | | | | | 12.0% |
| 370°C | | | | | 8.4% |

From Table 5.1 it can be seen that negative extraction yields were obtained for all the Waterberg experiments except for the experiment with a residence time of 12 min at 340°C. Table 5.2 shows that negative extraction yields were also obtained for all the Brandspruit experiments. This can also be explained by the effect of adsorption as was discussed in Chapter 4 for the batch extraction of Brandspruit coal with a 3:1 solvent to coal ratio. The explanation of adsorption being the reason for the negative yields obtained during the continuous extraction experiments is further supported by the results of the ash and volatile matter content, as will be discussed in the proximate analysis section. Still, a distinct pattern can be observed in Tables 5.1 and 5.2 if one looks at the change in extraction yield with temperature and residence time. Due to adsorption dominating at 320°C, it was decided to recalculate the extraction yields for the 330°C and 340°C experiments by taking the 320°C data as reference point instead of the feed coal data. These recalculated extraction yields are reported in Tables 5.3 and 5.4.

Table 5.3: Extraction yields – Waterberg coal/Residue oil (320°C reference point).

| **WATERBERG – EXTRACTION YIELD (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Temperature** | **Residence time (min)** | | | | |
| | 4 | 6 | 12 | 24 | 60 |
| 320°C | | | | | |
| 330°C | | 20.5% | 41.1% | | |
| 340°C | | 37.2% | 51.7% | | |
| 350°C | | | | | 43.9% |
| 360°C | | | | | 55.3% |
| 370°C | | | | | 62.9% |

Table 5.4: Extraction yields – Brandspruit coal/Residue oil (320°C reference point).

| **BRANDSPRUIT – EXTRACTION YIELD (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Temperature** | **Residence time (min)** | | | | |
| | 4 | 6 | 12 | 24 | 60 |
| 320°C | | | | | |
| 330°C | | 3.0% | 5.1% | 2.8% | |
| 340°C | | 10.3% | 12.3% | | |
| 350°C | | | | | 8.5% |
| 360°C | | | | | 12.0% |
| 370°C | | | | | 8.4% |

As with the batch extraction experiments, higher extraction yields were obtained with the Waterberg feed coal than the Brandspruit feed coal. For the Waterberg experiments, an increase in extraction yield with increasing temperature was observed as well as an increase in yield with increasing residence time. The highest extraction yield was obtained at 340°C and residence time of 12 min. The extraction yields obtained with the continuous experiments correlate relatively well with the extraction yields obtained with the batch experiments. For the Brandspruit experiments, an increase in extraction yield with increasing temperature was also observed while an increase in extraction yield with increasing residence time was observed from 6 to 12 min but not from 12 to 24 min at 330°C. However, it should be noted that the corrected extraction yields for Brandspruit coal at 330°C are in the order of the accuracy of the analytical method. The highest extraction yield was obtained at 340°C and residence time of 12 min. The continuous extraction yields also correlate relatively well with the batch extraction yields. Figure 5.1 illustrates the effect of residence time on the extraction yield for the different feed coals and reaction temperatures.

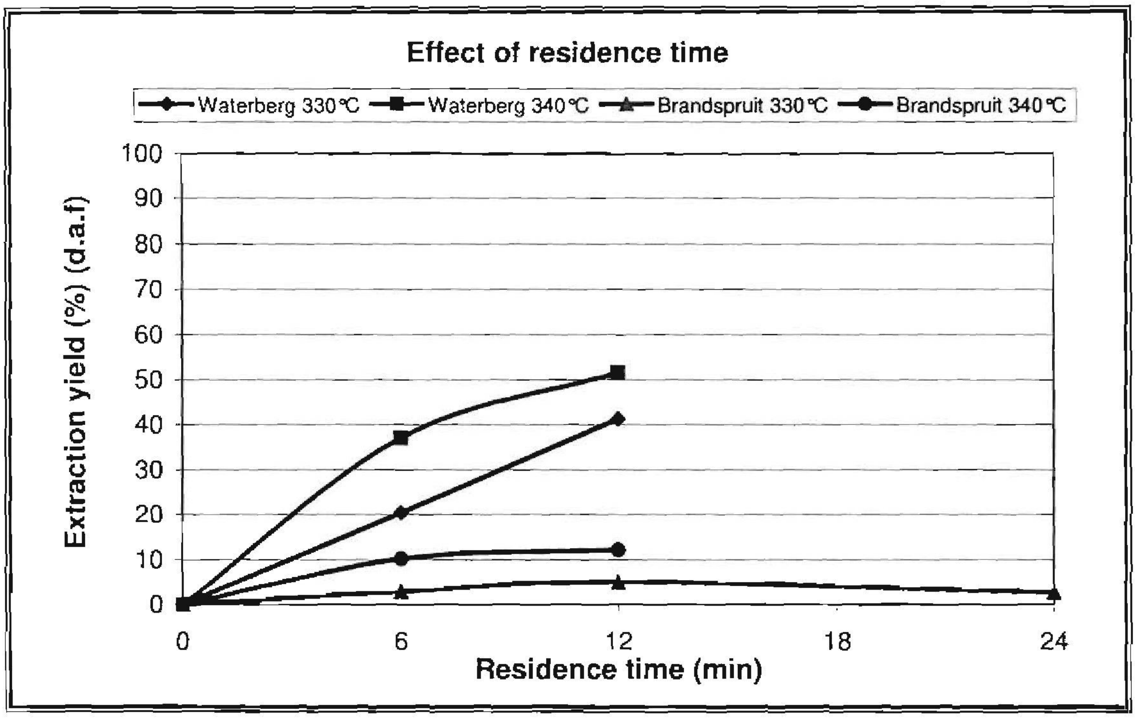


Figure 5.1: Effect of residence time on extraction yield.

As described in Chapter 3, it was not possible to conduct continuous extraction experiments at 340°C and residence time of 24 min due to equipment limitations. The extraction yield for Waterberg coal at 330°C and residence time of 24 min could not be calculated due to insufficient amount of sample available for analysis.

As illustrated in Figure 5.1, the results of the Waterberg coal at different temperatures show an increase in extraction yield with increasing residence time for the residence times investigated. It is also clear from Figure 5.1 that the experiments at 340°C give higher extraction yields than the experiments at 330°C. The results of the Brandspruit coal showed lower extraction yields than the Waterberg experiments.

Due to the limitations of the experimental setup only a small range of temperatures and residence times could be investigated. This should be expanded in order to be able to make more reliable conclusions, while the effect of adsorption should try to be limited by implementing hot filtration or other separation methods, as will be discussed in Chapter 7.

## 5.3 Kinetic model

It was decided to use the shrinking-core model in this study to describe the kinetics of the solvent extraction process. The derivation of this model will be shown in this section, while the determination of the kinetic parameters from the kinetic model will also be presented.

### 5.3.1 Shrinking-core model

The shrinking-core model was derived for the following solvent extraction reaction:

Coal + Residue oil → Residue coal + Coal extract.

The reactor used for the continuous extraction experiments can be treated as a plug-flow reactor (PFR) when the following assumptions are made:

- Isothermal and isobaric reaction conditions.
- The reaction mixture that enters the reactor is perfectly mixed.
- The flow inside the reactor is plug-flow.

The shrinking-core model describes a process where a reaction starts to take place at the outer surface of the particle. As the reaction zone moves inward towards an unreacted core of shrinking size, completely converted material and inert solid is left behind. The following assumptions were made in order to use the shrinking-core model:

- The coal particles are spherical.
- Chemical reaction controlled reactions take place during the solvent extraction process.

According to the shrinking-core model for chemical reaction controlled reactions, the conversion is described by equation (5.1) (Levenspiel, 1999).

$$1-(1-X)^{1/3}=\frac{t}{\tau_f} \tag{5.1}$$

In equation (5.1), $X$ is the conversion, $t$ is the time and $\tau_f$ is defined as the time required for complete conversion or in this case complete extraction. For a continuous process in a plug-flow reactor, equation (5.1) is rewritten as:

$$1-(1-X)^{1/3}=\frac{\tau}{\tau_f} \qquad (5.2)$$

In equation (5.2), $\tau$ is the residence time in a plug-flow reactor. The conversion $X$ in equation (5.2) is given by equation (5.3) and is defined as the extraction yield at specific operating conditions at a given extraction time divided by the maximum or final extraction yield at these conditions.

$$X=\frac{y}{y_f} \qquad (5.3)$$

Substituting equation (5.3) into equation (5.2) results in:

$$1-\left(1-\frac{y}{y_f}\right)^{1/3}=\frac{\tau}{\tau_f} \qquad (5.4)$$

Therefore, by plotting $1-\left(1-\frac{y}{y_f}\right)^{1/3}$ against $\tau$, the time necessary for total extraction ($\tau_f$) can be determined from the inverse slope.

### 5.3.2 Determination of kinetic parameters

In this section, the method for fitting the shrinking-core model is described. In equation (5.4) there are two known variables ($y$ and $\tau$) and two unknown extraction parameters ($y_f$ and $\tau_f$). As explained above $\tau_f=\frac{1}{slope}$ from a plot of $1-\left(1-\frac{y}{y_f}\right)^{1/3}$ against $\tau$. In this investigation values for $y_f$ were assumed and varied until the shrinking-core model fitted the data in the best way. This fit is shown in Figure 5.2. From the graph it can be seen that the shrinking-core model fits the data obtained during the continuous extraction experiments good, except for Brandspruit coal at 330°C and 24 min residence time. However, if this point is left out as was done in Figure 5.2, the remaining two points give a good linear fit. In Table 5.5, the values of $y_f$ as well as $\tau_f$ calculated from the inverse slopes of Figure 5.2, are reported. In Figure 5.2 $\tau$ is represented by τ on the X-axis.

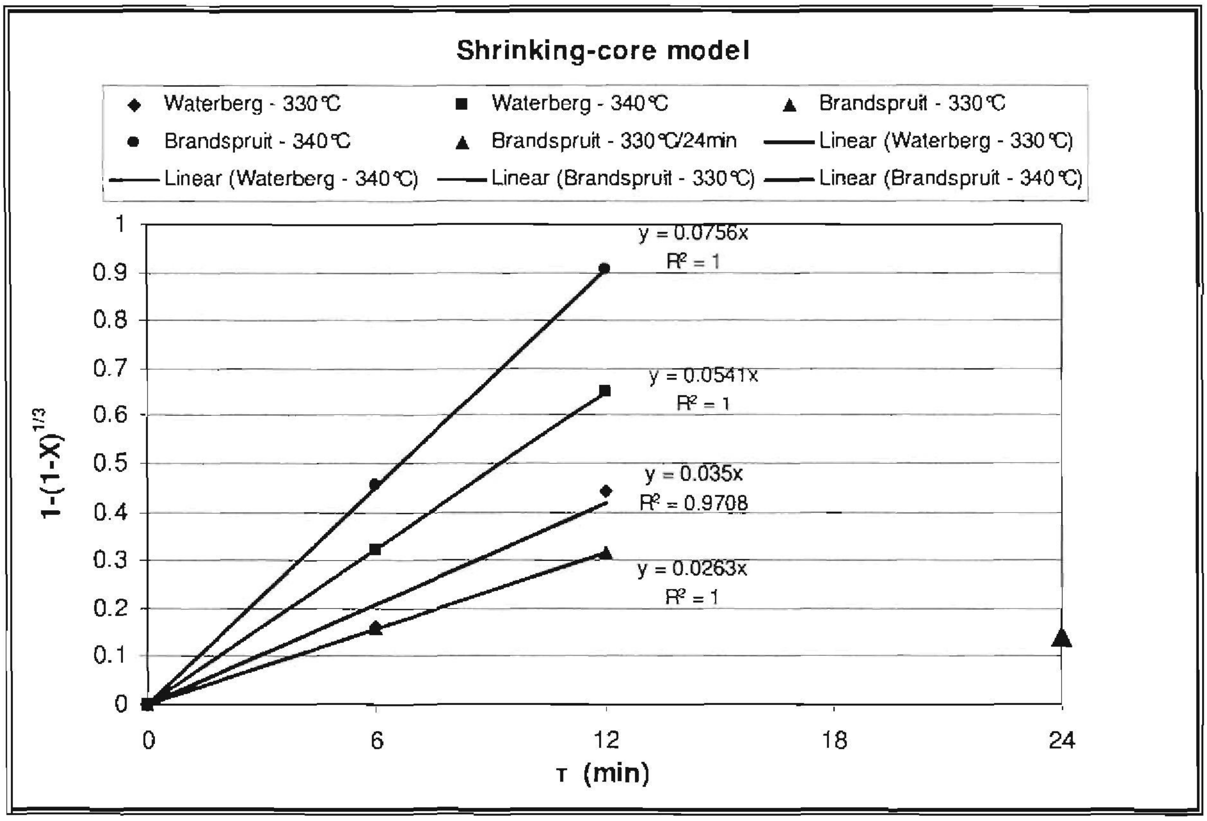


Figure 5.2: Shrinking-core model.

Table 5.5: $y_f$ and $\tau_f$.

| | WATERBERG | | BRANDSPRUIT | |
|---|---|---|---|---|
| | 330°C | 340°C | 330°C | 340°C |
| $y_f$ (%) | 50 | 54 | 8 | 12 |
| $\tau_f$ (min) | 29 | 19 | 38 | 13 |

Table 5.5 shows that 29 min are necessary to reach final extraction for Waterberg coal at 330°C and 18 min at 340°C. For Brandspruit coal 38 min are necessary to reach final extraction at 330°C and 13 min at 340°C.

From the above it can be concluded that the shrinking-core model is a good fit to describe the solvent extraction process, taking into account the number of data available and the data handling procedure.

### 5.3.3 Temperature dependency

The activation energy of the solvent extraction process can be determined using the Arhenius equation given in equation (5.5) (Levenspiel, 1999).

$$k \ = Ae^{-E_{act}/\ RT} \tag{5.5}$$

For the shrinking-core model controlled by chemical reactions it is known that $\tau_f \therefore \frac{1}{k}$ (Levenspiel, 1999). Therefore, the Arhenius equation can be rewritten as:

$$\frac{1}{\tau_f} = Be^{-E_a/\ RT} \tag{5.6}$$

In equation (5.6), $\tau_f$ is the time required for complete extraction, B is the Arhenius constant, $E_a$ is the activation energy, R the gas constant and T the temperature. Equation (5.6) can again be rewritten as:

$$\ln\frac{1}{\tau_f} = \ln B - \frac{E}{R}\cdot\frac{1}{T} \tag{5.7}$$

By plotting $\ln\frac{1}{\tau_f}$ against $\frac{1}{T}$, the activation energy can be obtained from the slope where $-\frac{E}{R} = slope$. This Arhenius plot can be seen in Figure 5.3 where $\tau$ is represented by τ on the Y-axis.

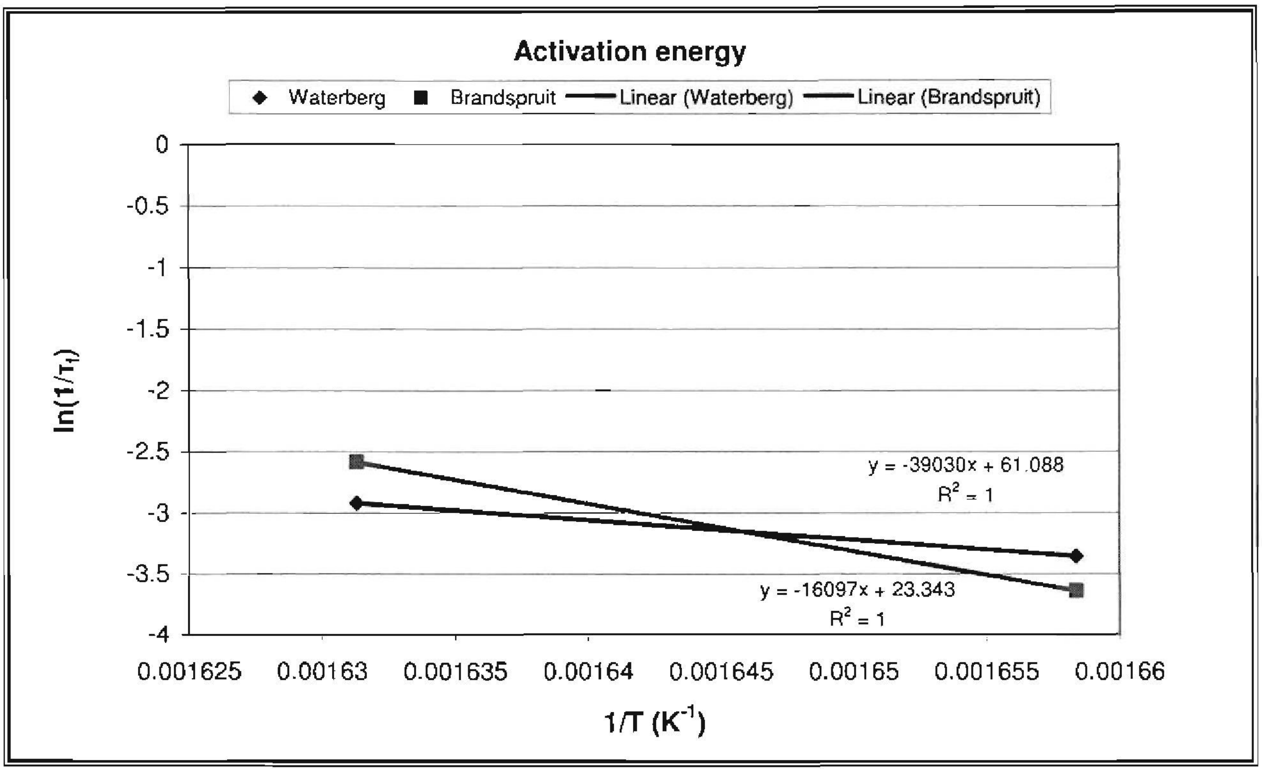


Figure 5.3: Arhenius plot.

From Figure 5.3 the activation energy for Waterberg coal was calculated as 325 kJ/mol and for Brandspruit coal as 134 kJ/mol. It should be remembered that these values may be inaccurate since only two data points were used for the linear fit. To obtain more accurate data more data points at different temperatures should be obtained and an appropriate method should be developed for separating the residue coal from the liquid extract. However, these results compare good with activation energies obtained by Giri and Sharma (2000) for different solvents as reported in Chapter 2. They reported activation energies of 59, 90 and 106 kJ/mol and even though the activation energies obtained in this study are higher, a trend can still be observed and it should also be noted that the activation energies in this investigation were obtained at higher temperatures. It can therefore be concluded that the extraction process with residue oil as solvent is kinetically controlled.

## 5.4 Feed and residue coal analyses

In this section, the results of all the analyses that were carried out on the feed and residue coals will be given and discussed.

### 5.4.1 Proximate analysis

Proximate analyses to determine the moisture, volatile matter (VM), fixed carbon (FC) and ash contents of the feed coals as well as the residue coals obtained during the continuous extraction experiments were done. In Tables 5.6 and 5.7 the volatile matter, fixed carbon and ash contents are reported on a dry basis and are calculated in the same way as the batch proximate analyses. The results as received from SABS can be seen in Appendix H. Where a result is indicated with N/A, insufficient sample was available to complete the analysis.

Table 5.6: Proximate analyses of Waterberg feed and residue coal.

| **WATERBERG – Proximate analysis (wt %)** | | | | |
|---|---|---|---|---|
| **Residence time (min)** | **MOISTURE** | **VM (d.b)** | **FC (d.b)** | **ASH (d.b)** |
| *0 - Feed coal* | *2.9* | *36.3* | *54.9* | *8.9* |
| **320 °C** | | | | |
| 4 – Residue coal | 4.3 | 66.6 | 27.6 | 5.9 |
| 6 – Residue coal | 6.8 | 68.8 | 25.6 | 5.7 |
| 12 – Residue coal | 6.7 | 71.8 | 22.8 | 5.4 |
| 24 – Residue coal | 5.6 | N/A | N/A | 5.4 |
| **330 °C** | | | | |
| 6 – Residue coal | 1.5 | 58.4 | 34.6 | 7.0 |
| 12 – Residue coal | 1.3 | N/A | N/A | 8.8 |
| **340 °C** | | | | |
| 6 – Residue coal | 1.2 | 49.8 | 41.6 | 8.7 |
| 12 – Residue coal | 1.9 | N/A | N/A | 10.5 |

Table 5.7: Proximate analyses of Brandspruit feed and residue coal.

| BRANDSPRUIT – Proximate analysis (wt %) | | | | |
|---|---|---|---|---|
| **Residence time (min)** | **MOISTURE** | **VM (d.b)** | **FC (d.b)** | **ASH (d.b)** |
| *0 - Feed coal* | *5.0* | *22.5* | *52.3* | *25.2* |
| **320 °C** | | | | |
| 4 – Residue coal | 2.2 | 45.0 | 36.3 | 18.7 |
| 6 – Residue coal | 2.1 | 48.0 | 37.5 | 14.5 |
| 12 – Residue coal | 1.5 | 41.8 | 37.5 | 20.7 |
| 24 – Residue coal | 1.9 | 45.6 | 37.9 | 16.5 |
| **330 °C** | | | | |
| 6 – Residue coal | 1.9 | 49.5 | 35.6 | 14.9 |
| 12 – Residue coal | 2.2 | 42.2 | 36.2 | 21.6 |
| 24 – Residue coal | 1.9 | 43.1 | 40.0 | 16.9 |
| **340 °C** | | | | |
| 6 – Residue coal | 1.9 | 43.9 | 40.2 | 15.9 |
| 12 – Residue coal | 1.5 | 39.6 | 37.5 | 22.9 |

In Table 5.6, the proximate analyses of the Waterberg residue coals at 320 °C show an increase in moisture content compared to the feed coal. The moisture content of the Waterberg residue coals at 330 °C and 340 °C as well as the moisture content of all the Brandspruit residue coals, decreased compared to the feed coals. This was also observed for the Waterberg and Brandspruit batch extraction results. As was mentioned before, the moisture content is not very important for the scope of this investigation and is influenced by a number of factors.

The volatile matter content of all the Waterberg and Brandspruit residue coals increased compared to the volatile matter content of the feed coals. This was also observed for the Brandspruit batch extraction experiments while the Waterberg batch extraction experiments showed a decrease in volatile matter for the residue coals. As was explained in Chapter 4 and also earlier with the negative extraction yields obtained during the continuous extraction experiments, it is suspected that adsorption of residue oil compounds occur during the extraction process. This explanation is supported by the increase in volatile matter content. However, it is observed that the volatile matter content increases from the feed coal to the 320°C residue coals whereafter it decreases from the 320°C residue coals to the 330°C residue coals and again from the 330°C residue coals to the 340°C residue coals. This observation suggests that adsorption dominate at 320°C whereafter extraction takes place together with adsorption.

The fixed carbon content of all the Waterberg and Brandspruit residue coals decreased compared to the feed coals as was also observed with the batch extraction experiments.

The ash content of the Brandspruit residue coals decreased compared to the feed coal. The Waterberg residue coals also showed a lower ash content than the feed coal except at 340°C and 12 min residence time where the ash content of the Waterberg residue coal increased. The lower ash content of the residue coals also suggests adsorption taking place. Where the ash content of the residue coals increased it suggests adsorption taking place simultaneously with extraction since the volatile matter content of the residue coals still increased even though the ash content increased.

The results of the volatile matter and ash content, indicating adsorption dominating at 320°C, were the reason for using the 320°C data as reference point in calculating the extraction yields.

### 5.4.2 Ultimate analysis

Ultimate analyses to determine the carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and total sulphur (S) contents of the feed coals as well as the residue coals obtained during the continuous extraction experiments were performed. In Tables 5.8 and 5.9 the ultimate analyses are reported on a dry, ash-free basis and are calculated in the same way as the batch ultimate analyses. The results as received from SABS can also be seen in Appendix H. Again, when a result is indicated with N/A, insufficient sample was available to complete the analysis.

Table 5.8: Ultimate analyses of Waterberg coal.

| **WATERBERG – Ultimate analysis (wt %) (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Residence time (min)** | **C** | **H** | **N** | **O** | **S (Total)** |
| *0 - Feed coal* | *81.6* | *6.0* | *1.6* | *9.6* | *1.1* |
| **320 °C** | | | | | |
| 4 – Residue coal | 86.8 | 6.8 | 2.0 | 3.7 | 0.8 |
| 6 – Residue coal | 87.5 | 6.5 | 2.0 | 3.3 | 0.8 |
| 12 – Residue coal | 86.9 | 6.7 | 1.9 | 2.3 | 0.7 |
| 24 – Residue coal | 89.3 | 7.0 | 1.9 | 1.4 | 0.3 |
| **330 °C** | | | | | |
| 6 – Residue coal | 84.5 | 6.4 | 2.0 | 7.0 | 0.9 |
| 12 – Residue coal | 82.8 | 6.2 | 2.0 | 8.1 | 0.9 |
| **340 °C** | | | | | |
| 6 – Residue coal | 83.9 | 6.3 | 2.0 | 7.4 | 0.9 |
| 12 – Residue coal | 82.9 | 6.0 | 2.0 | 7.9 | 0.9 |

Table 5.9: Ultimate analyses of Brandspruit coal.

| **BRANDSPRUIT – Ultimate analysis (wt %) (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Residence time (min)** | **C** | **H** | **N** | **O** | **S (Total)** |
| *0 - Feed coal* | *80.3* | *4.0* | *2.0* | *12.4* | *1.3* |
| **320 °C** | | | | | |
| 4 – Residue coal | 83.9 | 5.9 | 2.1 | N/A | N/A |
| 6 – Residue coal | 84.8 | 6.2 | 2.1 | 6.1 | 0.8 |
| 12 – Residue coal | 84.6 | 5.7 | 2.2 | N/A | N/A |
| 24 – Residue coal | 85.0 | 4.9 | 1.7 | 7.6 | 0.8 |
| **330 °C** | | | | | |
| 6 – Residue coal | 84.0 | 6.1 | 2.1 | 9.1 | 0.9 |
| 12 – Residue coal | 82.3 | 5.1 | 2.1 | N/A | N/A |
| 24 – Residue coal | 85.2 | 5.8 | 2.2 | 6.1 | 0.8 |
| **340 °C** | | | | | |
| 6 – Residue coal | 85.5 | 5.9 | 2.2 | N/A | N/A |
| 12 – Residue coal | 80.3 | 5.2 | 2.0 | N/A | N/A |

The ultimate analyses results for both the Waterberg and Brandspruit residue coals showed an increase in carbon, hydrogen and nitrogen content while a decrease in oxygen and sulphur content was observed compared to the feed coals. Atomic H/C and O/C ratios were also calculated for the feed and residue coals of the continuous extraction experiments in the same way as explained for the batch extraction experiments. These ratios are reported in Table 5.10.

Table 5.10: Atomic H/C and O/C ratios.

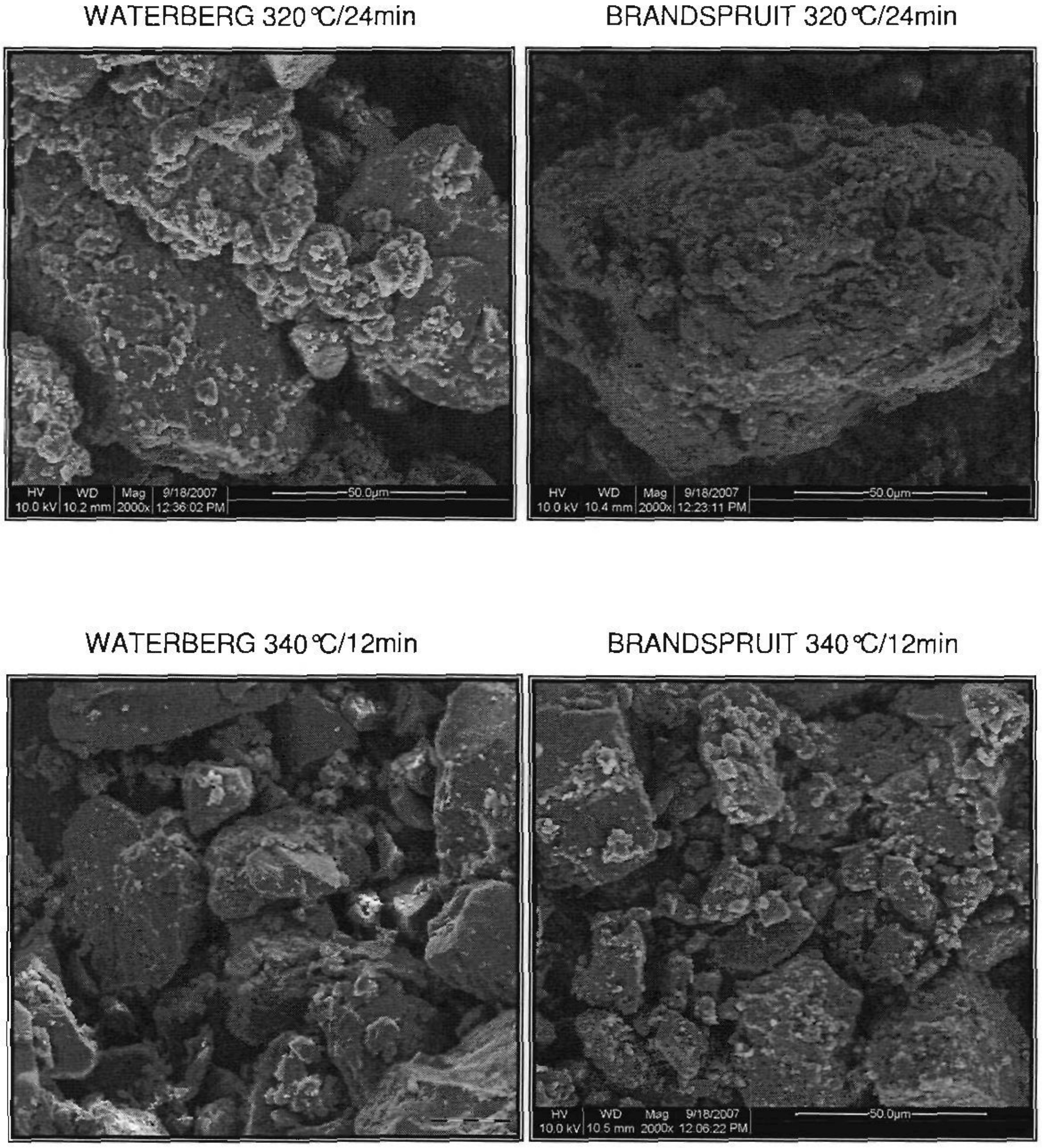
| Temperature | Residence time (min) | WATERBERG | | BRANDSPRUIT | |
|---|---|---|---|---|---|
| | | Residue coal | | Residue coal | |
| | | H/C ratio | O/C ratio | H/C ratio | O/C ratio |
| *Feed coal* | | *0.88* | *0.09* | *0.59* | *0.12* |
| 320°C | 4 | 0.93 | 0.03 | 0.84 | - |
| 320°C | 6 | 0.89 | 0.03 | 0.87 | 0.05 |
| 320°C | 12 | 0.91 | 0.02 | 0.80 | - |
| 320°C | 24 | 0.93 | 0.01 | 0.69 | 0.07 |
| 330°C | 6 | 0.90 | 0.06 | 0.86 | 0.08 |
| 330°C | 12 | 0.90 | 0.07 | 0.74 | - |
| 330°C | 24 | - | - | 0.81 | - |
| 340°C | 6 | 0.90 | 0.07 | 0.82 | - |
| 340°C | 12 | 0.86 | 0.07 | 0.76 | - |

From Table 5.10 it can be seen that the H/C ratio of the Waterberg residue coals are higher than that of the feed coal and that the H/C ratio of the Brandspruit residue coals are much higher than the feed coal's H/C ratio. This increase in H/C ratio of the residue coals again support the explanation of lighter compounds, with higher H/C ratios, being adsorbed by the coal particles.

### 5.4.3 Scanning electron microscope (SEM)

Scanning electron microscope images were taken of the residue coals obtained during the continuous extraction experiments at the different operating conditions. SEM images of the feed coals were presented and discussed in Chapter 4. Only a few images of the residue coals will be presented in this section while all the images can be seen on the CD-ROM.

The images of the residue coals in Figure 5.4 show significant changes compared to the feed coals in Figure 4.16. As was observed for the residue coals of the batch extraction experiments, agglomeration of smaller particles onto larger particles can be seen. The residue coals obtained with the continuous extraction experiments also seem to have rounded off edges and a "flaky" appearance compared to the smoother surface and sharp edges of the feed coals. Figure 5.4 also shows some cracks present in the residue coal particle that were not noticed in the feed coal particles.



WATERBERG 320℃/24min

BRANDSPRUIT 320℃/24min

WATERBERG 340℃/12min

BRANDSPRUIT 340℃/12min

Figure 5.4: SEM images - Residue coal.

## 5.5 Liquid and volatile extract analyses

In this section, the results of all the analyses that were carried out on the liquid extracts as well as the volatile extracts obtained with the continuous extraction experiments will be presented.

### 5.5.1 GC/MS

GC/MS analyses were carried out for the liquid extract after filtration and the liquefied volatile extract obtained during the continuous extraction experiments at 340°C and 12 min residence time. GC/MS analyses for the liquid and volatile extracts obtained during an experimental run at the same conditions with just residue oil were also carried out. This was done to compare the results in order to be able to see which compounds were extracted or adsorbed during the continuous extraction experiments. As with the GC/MS results of the batch extraction experiments, some peaks representing the compounds present in the largest quantities were identified for each mixture analyzed and are summarized in Tables 5.11-5.13 together with their retention times (RT) while the complete GC/MS results can be seen in on the CD-ROM.

Table 5.11: GC/MS – Residue oil: Liquid and volatile extracts (continuous), T=340℃, $\tau$ =12 min.

| **RESIDUE OIL – LIQUID EXTRACT** | | | | **RESIDUE OIL – VOLATILE EXTRACT** | | |
|---|---|---|---|---|---|---|
| **Compound** | | **%Area** | **RT (min)** | **Compound** | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 2.96 | 46.36 | Phenanthrene | 3.68 | 46.36 |
| 2. | Fluoranthene | 2.46 | 53.80 | Naphthalene | 2.93 | 26.81 |
| 3. | Benzofluorene | 1.99 | 57.29 | Fluorene | 2.79 | 40.26 |
| 4. | Heptadecane | 1.98 | 57.68 | Dibenzofuran | 2.44 | 37.93 |
| 5. | Pyrene | 1.83 | 55.03 | 2-methyl-Naphthalene | 2.25 | 29.80 |
| 6. | Anthracene | 1.64 | 46.67 | Anthracene | 2.10 | 46.66 |
| 7. | Tricosane | 1.43 | 59.84 | 4-methyl-Dibenzofuran | 1.91 | 42.08 |
| 8. | Tetracosane | 1.36 | 61.92 | 1-methyl-9H-Fluorene | 1.90 | 44.07 |
| 9. | Methyl-phenanthrene | 1.30 | 50.04 | 4-methyl-Dibenzofuran | 1.76 | 41.63 |
| 10. | Eicosane/Octacosane | 1.29 | 63.91 | 2-methyl-9H-Fluorene | 1.47 | 44.60 |
| 11. | Carbazole | 1.23 | 47.43 | Acenaphthene | 1.37 | 36.71 |
| 12. | Fluorene | 1.18 | 40.26 | Carbazole | 1.36 | 47.43 |
| 13. | Methyl-phenanthrene | 1.13 | 49.77 | Fluoranthene | 1.29 | 53.79 |
| 14. | 1-methyl-9H-Fluorene | 1.10 | 44.07 | 2-methyl-Naphthalene | 1.27 | 30.28 |
| 15. | Pentadecane | 1.07 | 55.38 | Tetradecane | 1.19 | 50.43 |
| 16. | Benz[a]anthracene | 1.04 | 62.34 | Tetradecane/Pentadecane | 1.18 | 47.73 |
| 17. | Benzo[b]naphtho[2,3-d]furan | 1.03 | 56.55 | Methyl-phenanthrene | 1.18 | 50.04 |
| 18. | Methyl-phenanthrene | 0.99 | 49.63 | Heptadecane | 1.17 | 57.67 |
| 19. | Methyl-pyrene | 0.98 | 58.58 | 2-methyl-9H-Fluorene | 1.15 | 44.26 |
| 20. | Methyl-pyrene | 0.97 | 56.76 | Methyl-phenanthrene | 1.10 | 49.77 |
| *Total* | | *29%* | | | *35%* | |

Table 5.12: GC/MS – Waterberg: Liquid and volatile extracts (continuous), T=340°C, $\tau$ =12 min, $d_p$=120 µm.

| **WATERBERG – LIQUID EXTRACT** | | | | **WATERBERG – VOLATILE EXTRACT** | | |
|---|---|---|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** | **Compound** | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 7.36 | 46.35 | Phenanthrene | 3.66 | 46.36 |
| 2. | Fluoranthene | 4.29 | 53.79 | Fluorene | 3.09 | 40.26 |
| 3. | Phenanthrene | 3.60 | 46.67 | Dibenzofuran | 2.42 | 37.93 |
| 4. | Heptadecane | 2.95 | 57.67 | Naphthalene | 2.28 | 26.81 |
| 5. | Pyrene | 2.90 | 55.03 | 1-methyl-9H-Fluorene | 2.19 | 44.07 |
| 6. | Fluorene | 2.62 | 40.26 | 4-methyl-Dibenzofuran | 2.13 | 42.08 |
| 7. | Dibenzofuran | 2.41 | 37.94 | Phenanthrene | 2.09 | 46.67 |
| 8. | Tricosane | 2.31 | 59.84 | 4-methyl-Dibenzofuran | 1.83 | 41.63 |
| 9. | Methyl-phenanthrene | 2.28 | 49.77 | 2-methyl-Naphthalene | 1.80 | 29.80 |
| 10. | Methyl-phenanthrene | 2.26 | 50.04 | 1-methyl-Phenanthrene | 1.77 | 50.44 |
| 11. | 1-methyl-9H-Fluorene | 2.15 | 44.07 | cis-Stilbene | 1.65 | 44.60 |
| 12. | 2-methyl-Fluoranthene/1-methyl-Pyrene | 1.93 | 57.28 | 2-methyl-1,1'-Biphenyl | 1.63 | 40.94 |
| 13. | Methyl-phenanthrene | 1.89 | 49.63 | Acenaphthene | 1.42 | 36.71 |
| 14. | Pentadecane | 1.85 | 55.38 | Carbazole | 1.40 | 47.43 |
| 15. | Tetracosane/Heptadecane | 1.83 | 61.92 | 2-methyl-1,1'-Biphenyl | 1.36 | 41.21 |
| 16. | 1-methyl-Phenanthrene | 1.64 | 50.37 | methyl-9H-Fluorene | 1.33 | 44.27 |
| 17. | 4-methyl-Dibenzofuran | 1.64 | 42.09 | Pentadecane/Tetradecane | 1.19 | 47.73 |
| 18. | 1-methyl-Phenanthrene | 1.64 | 50.40 | 4-methyl-Dibenzofuran | 1.15 | 42.38 |
| 19. | Carbazole | 1.61 | 47.43 | Methyl-phenanthrene | 1.11 | 50.04 |
| 20. | Heneicosane/Octacosane | 1.54 | 63.91 | Heptadecane | 1.10 | 57.67 |
| *Total* | | *51%* | | | *37%* | |

Table 5.13: GC/MS – Brandspruit: Liquid and volatile extracts (continuous), T=340°C, $\tau$ =12 min, $d_p$=120 µm.

| | **BRANDSPRUIT – LIQUID EXTRACT** | | | **BRANDSPRUIT – VOLATILE EXTRACT** | | |
|---|---|---|---|---|---|---|
| | **Compound** | **%Area** | **RT (min)** | **Compound** | **%Area** | **RT (min)** |
| 1. | Phenanthrene | 4.09 | 46.35 | Phenanthrene | 4.45 | 46.35 |
| 2. | Fluoranthene | 3.27 | 53.79 | Fluorene | 3.10 | 40.26 |
| 3. | Pyrene | 2.55 | 55.03 | Naphthalene | 2.89 | 26.80 |
| 4. | 2-methyl-Fluoranthene/1-methyl-Pyrene | 2.45 | 57.28 | Dibenzofuran | 2.58 | 37.92 |
| 5. | Heptadecane | 2.34 | 57.67 | Phenanthrene | 2.51 | 46.66 |
| 6. | Phenanthrene | 2.21 | 46.67 | 2-methyl-Naphthalene | 2.26 | 29.80 |
| 7. | Fluorene | 1.75 | 40.25 | 1-methyl-9H-Fluorene | 2.10 | 44.06 |
| 8. | Methyl-phenanthrene | 1.67 | 50.04 | 4-methyl-Dibenzofuran | 2.08 | 42.08 |
| 9. | Methyl-phenanthrene | 1.59 | 49.77 | 4-methyl-Dibenzofuran | 1.86 | 41.62 |
| 10. | Tricosane | 1.50 | 59.84 | Fluoranthene | 1.68 | 53.79 |
| 11. | Carbazole | 1.45 | 47.43 | cis-Stilbene | 1.52 | 44.59 |
| 12. | Dibenzofuran | 1.36 | 37.93 | 1-methyl-Phenanthrene | 1.44 | 50.44 |
| 13. | 1-methyl-9H-Fluorene | 1.29 | 44.07 | Heptadecane | 1.43 | 57.67 |
| 14. | Tetracosane/Heptadecane | 1.28 | 61.91 | Methyl-phenanthrene | 1.42 | 50.04 |
| 15. | Methyl-phenanthrene | 1.25 | 49.63 | Acenaphthene | 1.38 | 36.70 |
| 16. | 1-methyl-Phenanthrene | 1.23 | 50.37 | Carbazole | 1.36 | 47.43 |
| 17. | 1-methyl-Pyrene | 1.19 | 58.57 | Pentadecane/Tetradecane | 1.29 | 47.73 |
| 18. | Pentadecane | 1.19 | 55.38 | Methyl-phenanthrene | 1.26 | 49.77 |
| 19. | 4-methyl-Dibenzofuran | 1.19 | 42.07 | Pentadecane | 1.23 | 55.38 |
| 20. | Benzo[b]naphtho[2,3-d]furan | 1.13 | 56.54 | methyl-9H-Fluorene | 1.20 | 44.26 |
| *Total* | | *36%* | | | *39%* | |

As can be seen from Tables 5.11-5.13, phenanthrene is the compound present in the largest quantity in all the liquid as well as the volatile extracts. It is observed that most of the compounds present in the liquid and volatile extracts of the clean residue oil are also present in the liquid and volatile extracts obtained during the continuous extraction experiments of Waterberg and Brandspruit coal. However, the rank in which these compounds appear differ. Where the quantity of some compounds increase in the liquid extract it shows that certain compounds were extracted.

# CHAPTER 6

# CONCLUSIONS

---

After completion of the investigation, certain conclusions could be made. These conclusions will be discussed in this chapter.

## 6.1 Batch extraction

Batch extraction experiments were carried out for two South African coals – one a vitrinite-rich coal (Waterberg) and the other an inertinite-rich coal (Brandspruit). A vitrinite-rich American coal (Illinois#6) was used as benchmark. Residue oil was the selected coal-derived industrial solvent used for the extractions.

- The purpose of the batch extraction experiments was firstly to determine if solvent extraction is a possible coal conversion process for South African coals and if high extraction yields can be obtained using an industrial solvent. Based on the high extraction yields obtained using Waterberg coal as feed, it can be concluded that solvent extraction using residue oil as solvent is a possible coal conversion process to convert vitrinite-rich South African coal into valuable products. The high yields obtained using residue oil as solvent and vitrinite-rich Waterberg and Illinois#6 coal as feed, suggested that it is possible to obtain high extraction yields using a coal-derived industrial solvent. This correlates well with the findings of Yoshida *et al.* (2004).

  Smook (2007) suggested that vitrinite-rich coal is better suit for direct coal conversion routes, such as solvent extraction, than inertinite-rich coals. This theory is supported by the high extraction yields obtained in this study for vitrinite-rich Waterberg and Illinois#6 coal compared to inertinite-rich Brandspruit coal. In addition, the research done in this study on Illinois#6 coal correlates good with the results of previous research reported in literature. Miura *et al.* (2001) obtained an extraction yield of 63% for Illinois#6 coal using tetralin as solvent at 350°C for 1 hour, while an extraction yield of 69% was obtained in this study using residue oil as solvent. Okuyama *et al.* (2004) reported an extraction yield of 60% using 1-methylnaphthalene as solvent and Burgess Clifford *et al.* (2007) an extraction yield of 51% using light cycle oil as solvent at 360°C for 1 hour, compared to an extraction yield of 69%-71% obtained in this study with residue oil as solvent.

- Secondly, the batch extraction experiments were used to determine the optimum operating conditions of the solvent extraction process. The extraction temperature (350°C, 360°C and 370°C), particle size of the feed coal (120 µm and 200 µm) and the solvent to coal ratio (3:1, 5:1 and 10:1) were investigated as operating conditions. The effect of these operating conditions was studied based on the extraction yields obtained. For the temperature range investigated in this study, the optimum temperature for Waterberg and Illinois#6 coal was found to be 370°C while no trend was observed for the Brandspruit coal. Okuyama *et al.* (2004) observed the highest extraction yields at 360-380°C and also concluded that the extraction yield increases with an increase in temperature. In this investigate on, an increase in extraction yield with increased temperature was also observed for the Waterberg, and in some extent for the Illinois#6 coal.

  For the particle size range studied in this investigation, it was found that the particle size of the feed coal had no effect on the extraction yield of the solvent extraction process, which correlates with Van Krevelen's (1981) findings.

  For the range of solvent to coal ratios studied it was found that higher extraction yields were obtained with a 5:1 and 10:1 ratio than a 3:1 solvent/coal ratio. As explained in Chapter 4, the low extraction yields obtained with a 3:1 solvent/coal ratio may be due to adsorption of compounds in the residue oil. Griffith *et al.* (2006) also investigated the extraction of coal with 3:1, 5:1 and 10:1 solvent to coal ratios and observed the highest extraction yields with a solvent to coal ratio of 10:1.

- Mass balances were performed for the proximate and ultimate constituents. These balances showed that for all three feed coals most of the moisture reports to the extract while most of the ash in the feed coal reports to the residue coal as was expected. For Waterberg and Illinois#6 coal most of the volatile matter and fixed carbon in the feed coal report to the extract. For Brandspruit coal most of the volatile matter and fixed carbon in the feed coal remains in the residue coal. From these results it can be concluded that the extraction of Waterberg and Illinois#6 coal using residue oil as solvent was successful since most of the volatile matter and fixed carbon in the feed coals report to the extract, while most of the ash in the feed coals report to the residue coal. The extraction of Brandspruit coal using residue oil as solvent had limited success since most of the volatile matter, fixed carbon and ash in the feed coal remain in the residue coal.

- The mass balances of the ultimate constituents showed that most of the carbon, hydrogen, oxygen and sulphur in Waterberg and Illinois#6 feed coal report to the extract while the nitrogen is more or less equally distributed. For the Brandspruit experiments most of the carbon, hydrogen, nitrogen, oxygen and sulphur in the feed coal report to the residue coal which also illustrates the limited success for solvent extraction of Brandspruit coal.

- Atomic H/C and O/C ratios were calculated for the feed coals, residue coals and liquid extracts using the data of the ultimate analyses. The Waterberg and Illinois#6 liquid extracts showed higher H/C ratios and the residue coals lower H/C ratios compared to the feed coals. Half of the Brandspruit extracts had higher H/C ratios and the other half lower H/C ratios than the feed coal, while most of the Brandspruit residue coals showed higher H/C ratios than the feed coal. This indicate that with the Waterberg and Illinois#6 experiments lighter compounds, with higher H/C ratios, were extracted while heavier compounds with lower H/C ratios remained in the residue coal. The increase in H/C ratio of the Brandspruit residue coals may be the result of the coal adsorbing light compounds from the residue oil. These results can be compared with an H/C ratio of 1 for benzene and 2 for alkanes if it is kept in mind that the reported H/C ratios are an average of all the compounds present in the extracts or residue coals.

- Calorific value analyses showed slightly lower calorific values for the residue coals than the feed coals but were still relatively high, indicating the possibility to use the residue coal as boiler fuel for example. In general, the calculated theoretical calorific values based on ultimate analysis were within the accuracy range of ±1.0 MJ/kg from the analytically determined calorific values.

- There was not a very large difference between the porosity of the Waterberg and Illinois#6 feed and residue coals, while the Brandspruit coal showed a significant increase in porosity for the residue coal compared to the feed coal. The mercury intrusion porosimetry showed that the coals consist mainly of macropores. From the porosity measurements it was concluded that no relation could be observed between the extraction yield and the porosity of the residue coal after extraction.

- Particle size distribution analyses showed that the Waterberg feed coal of 120 µm and 200 µm both had a bimodal particle size distribution with about 2 vol% of the particles below 1 µm. This was also observed for the Waterberg residue coal. The particle size distribution also showed that large quantities of particles with a particle size much smaller than the desired 120 µm and 200 µm were present.

- Scanning electron microscope (SEM) images of the feed coals showed that the Waterberg and Illinois#6 coals have a smoother surface compared to the rougher-looking surface of the Brandspruit coal and also appear to have sharper edges. Noticeable differences between the feed coal particles and the residue coal particles were observed. The residue coal particles showed agglomeration of smaller particles onto larger particles, while some particles looked like it had been "eaten away" with a "flaky" appearance and rounded off edges compared to the feed coal. In situ SEM movies of Waterberg coal heated on a hot-stage show that in the absence of a solvent the coal only starts to swell at about 450°C.

- Pyrolysis-GC/MS analyses of the feed coals showed that cresol was the compound obtained in the largest quantity from all three feed coals. Most of the top 20 compounds obtained from all three feed coals were phenolic compounds. However, some differences in the composition of the feed coals were observed.

- GC/MS analyses of the solvent as well as the liquid and volatile extracts showed that most of the compounds present in the solvent are also present in the liquid extracts. Phenanthrene is the compound present in the largest quantity in the residue oil as well as in the liquid extracts, while naphthalene is the compound present in the largest quantity in the volatile extracts. Differences between the different liquid extracts and between the different volatile extracts were observed in terms of the rank of compounds.

- Two distillation cuts, a petrol cut at 200℃ and a diesel cut at 350℃, were obtained for the liquid extracts and used to determine the densities. The petrol fractions had densities of 0.89-0.90 g/cm$^3$ compared to a typical petrol density of 0.75-0.78 g/cm$^3$, while the diesel fractions had densities of 1.01-1.03 g/cm$^3$ compared to a typical diesel density of 0.8 g/cm$^3$. This suggests that the extract product of solvent extraction cannot be added directly to the fuel pool, but requires some additional upgrading, like hydrogenation, before it can be used as a liquid fuel.

## 6.2 Continuous extraction

Continuous extraction experiments were carried out for the same two South African coals used in the batch extraction experiments and also with residue oil as coal-derived industrial solvent. The purpose of the continuous extraction experiments was to develop a continuous experimental setup and to obtain kinetic data which could be used to describe the solvent extraction process.

- It was possible to conduct continuous extraction experiments with the proposed experimental setup. The experimental setup had some limitations however, and only temperatures of 320℃, 330℃ and 340℃ and residence times of 4, 6, 12 and 24 minutes could be investigated. There is a lot of room for improvement of the continuous experimental setup. Negative extraction yields were obtained and together with the results of the analyses, it could be explained by the effect of coal particle adsorbing compounds in the residue oil during the filtration step, which was performed at room temperature. To compensate for the adsorption process, the extraction yields were re-calculated using the 320℃ data as reference point instead of the feed coal data. Extraction yields of 20-52% were then obtained for the Waterberg coal and 3-12% for Brandspruit coal with the highest extraction yield observed at a temperature of 340℃ and residence time of 12 min. In general, an increase in extraction yield with increase in temperature as well as with increase in residence time was.

- The shrinking-core model was used to describe the solvent extraction process and provided a good fit for the experimental data. $\tau_f$, the time needed for complete extraction, was found to be 29 min at 330°C and 19 min at 340°C for Waterberg coal. For Brandspruit coal it was found to be 38 min at 330°C and 13 min at 340°C. It can therefore be concluded that the continuous runs confirmed that the time for the batch experiments (1 hour) was sufficient and that the batch extraction results are therefore valid complete conversion results. Using the Arhenius equation the activation energy for Waterberg coal was determined as 325 kJ/mol and for Brandspruit coal as 134 kJ/mol.

- From the proximate analyses it was observed that the volatile matter content of all the Waterberg and Brandspruit residue coals increased compared to the volatile matter content of the feed coals. This supports the explanation that adsorption of residue oil compounds occur. However, it is also observed that the volatile matter content of the residue coals decreases from 320°C to 340°C. This observation suggests that adsorption dominate at 320°C whereafter extraction takes place together with adsorption.

- The ultimate analyses of both the Waterberg and Brandspruit residue coals showed an increase in carbon, hydrogen and nitrogen content with a decrease in oxygen and sulphur content compared to the feed coals. The H/C ratios of the Waterberg and Brandspruit residue coals are higher than that of the feed coals, again suggesting adsorption of lighter compounds with higher H/C ratios.

- SEM images of the residue coals obtained during continuous solvent extraction showed the same results as for the batch obtained residue coals. Significant differences between the feed and residue coal particles could be observed.

- GC/MS analyses conducted for the liquid and volatile extracts obtained during the continuous extraction experiments as well as for the residue oil, showed that phenanthrene is the compound present in the largest quantity in all the liquid as well as the volatile extracts. It is observed that most of the compounds present in the liquid and volatile extracts of the clean residue oil are also present in the liquid and volatile extracts obtained during the continuous extraction experiments of Waterberg and Brandspruit coal. However, the rank in which these compounds appear differ.

- Finally, most of the results of the continuous extraction experiments are in line with the results of the batch extraction experiments.

# CHAPTER 7

# RECOMMENDATIONS AND OUTLOOK

In this chapter, the outlook of coal solvent extraction will be discussed while some recommendations regarding the practical aspect of the batch and continuous extraction experiments will be made.

## 7.1 Recommendations for future work

### 7.1.1 Batch extraction

As mentioned in Chapter 1, this project was only concerned with the extraction step of the solvent extraction process and since this is a relative new topic in South African coal research, there are a lot of opportunities for future research. Some recommendations for future work on solvent extraction are listed below.

- A major drawback of the batch extraction setup was the long time it took for the coal/solvent slurry to heat up to the desired extraction temperature. A more effective heating system or pre-heating of the coal/solvent slurry or just the solvent may be investigated.

- The investigation of the effect of the extraction temperature on the solvent extraction process can be expanded by expanding the range of temperatures to see if any further trends are observed.

- From literature it was expected that pressure would not have a strong effect on the extraction yield. This assumption should be proven for this experimental setup by performing batch extraction experiments at different pressures.

- An investigation can be launched to find the most effective industrial solvent for the solvent extraction process by testing the extraction capability of different industrial solvents. Another very important factor to make the solvent extraction process economically viable is the recycling of the solvent. It is believed that during the solvent extraction process an internal solvent is produced. In research done by Anderson (1975), it was found that additional solvent was produced during the extraction process which replaced the lost solvent. Residue coal was removed from the liquid product by filtration whereafter the solvent was recovered by vacuum distillation of the filtrate and used in the next extraction step. As the recovered solvent was repeatedly recycled, the identity of the start-up solvent was lost while the composition of the recycled solvent approached the composition of the solvent that was produced during the extraction process. For the solvent recycling to be viable in the extraction process, a sufficient amount of solvent, suitable for dissolving the coal, must be produced during the process.

Miura *et al.* (2004) also investigated the effect of solvent recycling on the extraction yield of Pittsburg#8 coal by using tetralin as solvent in a flow reactor at 350℃ and 100 bar. As can be seen in Figure 7.1, they found that the extraction yield increased with each extraction cycle, with a maximum of 80% in the eighth cycle whereafter it decreased. From these results they concluded that it is possible to apply solvent recycling for effective extraction of coal in order to reduce the amount of solvent needed.

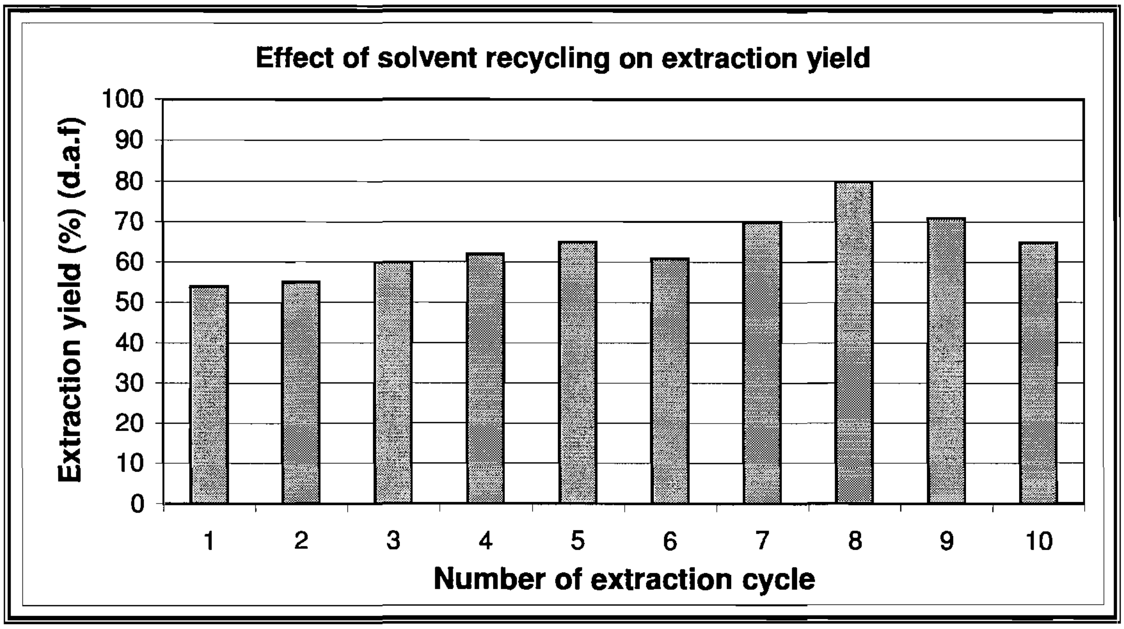


Figure 7.1: Effect of solvent recycling on extraction yield.

- The equipment design for the batch extraction experiments should be improved in order to perform proper mass balances. The measurement and quantification of gaseous products are required for a mass balance and can be achieved by cooling gaseous streams to obtain condensable gasses, followed by a GC analysis of non-condensable gasses. A mass balance will help to verify the reliability of the results.

- More intensive tests can be undertaken to study the quality of the coal extract. In addition, the obtained extraction products can be tested for different applications. Different methods for upgrading the liquid coal extract to a useful product should be investigated. For example, the liquid coal extract can be hydrogenated in the laboratory.

- In addition to the extraction step, the solid/liquid separation step should also be investigated more thoroughly. The effect of hot filtration on the extraction yield is a possible topic to be studied. Burgess Clifford *et al.* (2007) as well as Yoshida *et al.* (2004) observed higher extraction yields when hot filtration, rather than room-temperature filtration, was used. The most effective solid/liquid separation method should also be determined by investigating different possible methods such as vacuum distillation for example which was used in the SRC-II process.

- An area of the extraction process that needs a lot of research is the separation step to recover the solvent from the coal extract and obtain the low-ash product. It should be kept in mind however, that the method used for this separation step has an influence on the type of product that is obtained. The product could either be a liquid, a pitch-like product or a solid. After recovering the residue oil, the starting residue oil composition should be subtracted from the product residue oil composition to aid in performing proper mass balances.

- Operating conditions may influence pyrolysis yields. The pyrolysis-GC/MS analysis may give different results depending on heating rate, particle size, etc. It is therefore recommended that pyrolysis-GC/MS analysis be done at different heating rates to verify the repeatability of the analysis technique.

As can be seen from the above, many research opportunities still exist regarding the solvent extraction of South African coal in order to develop an economical, commercial-scale extraction process. This project was just the first step in showing that it is possible to use solvent extraction to convert vitrinite-rich bituminous South African coal into valuable products.

### 7.1.2 Continuous extraction

As mentioned before there is a lot of room for improvement of the continuous extraction experimental setup. Some recommendations are made here.

- Firstly, the experimental setup should be altered in order to be able to investigate a broader range of residence times and temperatures so that more reliable conclusions can be made. Therefore, a different pump is needed and the heating system should be changed to be able to reach higher temperatures.

- It is also suggested that the continuous extraction experiments should be performed under pressure, e.g 5 bar, as with the batch extraction experiments.
- The reactor configuration of two product outlets should be reconsidered.

- The effect of adsorption could be limited by implementing hot filtration at about 200 °C to prevent compounds being adsorbed or vacuum distillation/evaporation as in the SRC-II process.

## 7.2 Outlook

The outlook for this project will be discussed shortly in this paragraph in terms of the feed coal, the solvent, the extraction process, the residue coal/extract separation step, the liquid product and the proposed commercial-scale extraction process.

*The feed coal*

Vitrinite-rich coals are the best suitable for conversion via solvent extraction when the aim is to obtain high extraction yields. Extraction yields in the order of 60-70% (d.a.f) can be obtained with Waterberg coal under ideal conditions. Although the extraction process can be modelled with the shrinking-core model, the effect of the particle size still has to be assessed. Typically, one would expect that the time for complete extraction would increase with the particle size to the power 2 such that $\tau_f \therefore d_p^2$.

### *The solvent*

A good extraction solvent should:

- Produce a high extraction yield. As the main valuable product aimed for is the liquid extract, a yield above 60% is required.
- Have a low vapour pressure at the extraction temperature.
- Be generated by the extraction process.
- Be used in low solvent to coal ratios.

Residue oil, a coal-derived product rich in poly-aromatic compounds and produced at Sasol Secunda, meets most of these criteria and probably resembles the solvent that will be generated by the extraction process.

### *The extraction process*

The optimum extraction conditions are:

- A temperature of 360-370°C.
- A solvent to coal ratio of 5:1.
- An extraction time in the order of 10 minutes.

### *The residue coal/extract separation step*

The separation of the residue coal from the liquid extract can be achieved in a number of ways:

- Cold filtration and washing with tetrahydrofuran. This method is useful for laboratory studies.
- Hot filtration at 200°C. This method was developed in the SRC-I process as described in Chapter 2. The main objective is to avoid re-adsorption of extracted compounds onto residue coal that seems to be activated by the extraction process (Chapter 4 and 5).
- Distillation of the residue coal/extract slurry. This is an essential part of the SRC-II process as described in Chapter 2. The residue coal/extract slurry is sent to a vacuum tower to be separated into a fuel oil product and a residue which is gasified to produce hydrogen for the process.

In this research, re-adsorption causing decreasing yields at lower solvent to coal ratios, indicate that the residue coal/extract separation is still a major challenge to be tackled.

*The liquid product*

The main product of interest obtained with the solvent extraction process is the liquid extract and can in principle have three applications:

- A solid fuel as in the Hyper-coal or SRC-I process. High-ash coal is converted into a low-ash (<200 ppm) solid fuel that can in principle be used in a more energy efficient gas turbine.
- A clean carbon source for production of carbon fibres and electrodes. However, the size of this market in terms of capacity (Mt/a) and value (M$/a) should be investigated.
- A feedstock for the liquid fuel pool.

*Proposed extraction process*

A proposed solvent extraction process can be seen in Figure 7.2 where the solvent is recycled and the residue coal used to generate heat and hydrogen for the process, while the liquid extract is hydrogenated to produce a liquid fuel.

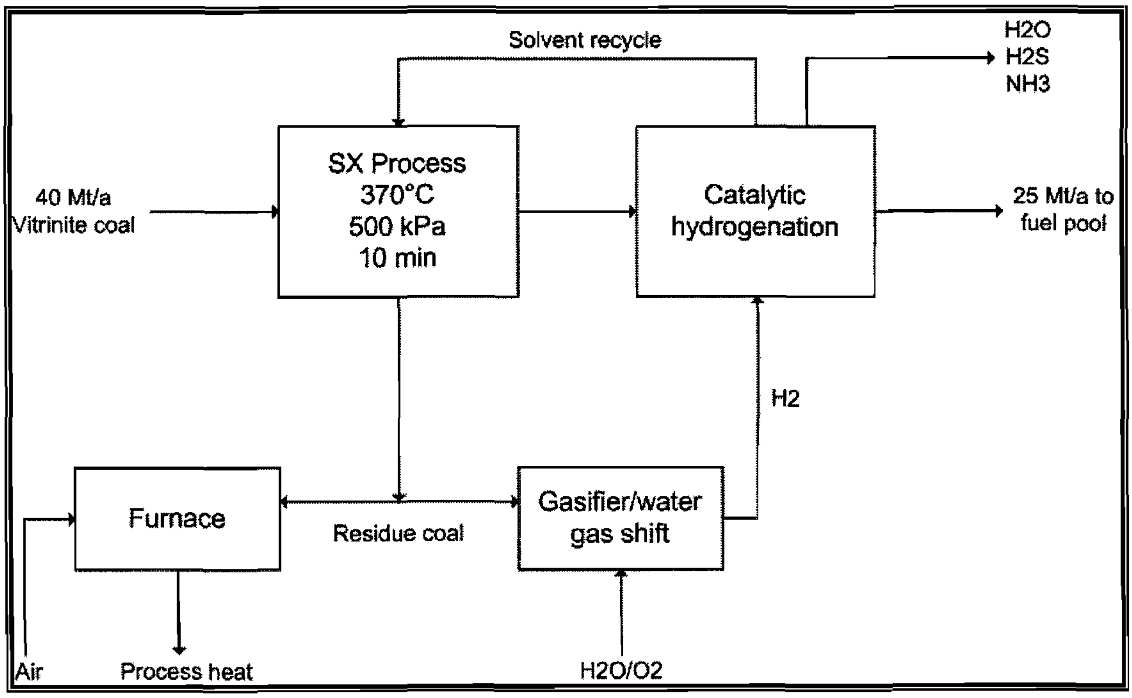


Figure 7.2: Solvent extraction process outlook.

*The benefits*

In order to assess the benefits of coal solvent extraction, it is good to benchmark the process against the existing coal gasification and Fischer-Tropsch technology as they both aim to produce liquid fuels from coal. The main issues for comparison purposes are:

- The yield, expressed as fraction of coal actually converted into fuel
- The capital expenditure
- The $CO_2$ footprint
- The use of utilities
- The technological development

# REFERENCES

ANDERSON, R.P. 1975. Recycling solvent techniques for the SRC process. *Coal processing technology*, 2:130-132.

BEUKMAN, M.T. 2007. The continuous solvent extraction of Waterberg coal. Final year project, Chemical engineering, North-West University. (Unpublished).

BOSSEL, U. 2003. Well-to-wheel studies, heating values, and the energy conservation principle. European Fuel Cell Forum. [Web:] http://www.efcf.com/reports/E10.pdf [Date accessed: 5 June 2007]

BULL, I.D. 2005. Pyrolysis gas chromatography mass spectrometry. Life sciences mass spectrometry facility, Natural environment research council, University of Bristol. [Web:] http://www.bris.ac.uk/nerclsmsf/techniques/pyro.html [Date accessed: 30 May 2007].

BURGESS CLIFFORD, C., SCHOBERT, H.H., ESCALLÓN, M. & GRIFFITH, J. 2007. Effects of coal rank and reaction conditions on production of two-ring compounds for coal-based jet fuel. (Paper presented at International Conference on Coal Science and Technology held in August 2007.) Nottingham, UK.

CHAPMAN, S.K. 1986. Working with a Scanning Electron Microscope. Chislehurst : Lodgemark Press. 113 p.

DADYBURJOR, D.B. & LIU, Z. 2002. Coal liquefaction. (*In* Kirk-Othmer Encyclopedia of Chemical Technology, 6:832-869.)

DEPARTMENT OF TRADE AND INDUSTRY. 1999. Coal liquefaction. [Web:] http://www.dti.gov.uk/files/file18326.pdf [Date accessed: 18 May 2007].

DEPARTMENT OF MINERALS AND ENERGY. 2005. Operating and developing coal mines in the Republic of South Africa. [Web:] http://www.dme.gov.za [Date accessed: 21 May 2007].

DE JAGER, S.G.E. 2006. Internal communication. Sasol Technology, Research and Development, Coal and Syngas Technologies.

ELLINGTON, R.T. 1977. Liquid fuels from coal. New York : Academic Press. 273 p.

ENERGY INFORMATION ADMINISTRATION. 2007. Country analysis briefs: South Africa. [Web:] http://www.eia.doe.gov/ [Date accessed: 21 May 2007].

ENERGY INFORMATION ADMINISTRATION. 2007. International total primary energy consumption and energy intensity. [Web:] http://www.eia.doe.gov/emeu/international/energyconsumption.html [Date accessed: 4 June 2007].

ENGLAND, T., HAND, P.E., MICHAEL, D.C., FALCON, L.M. & YELL, A.D. 1975. Coal preparation in South Africa. Johannesburg : The South African coal processing society. 298 p.

FALCON, R.M.S. & SNYMAN, C.P. 1986. An introduction to coal petrography: Atlas of petrographic constituents in the bituminous coals of Southern Africa. Johannesburg : The Geological Society of South Africa. 106 p.

GIRI, C.C. & SHARMA, D.K. 2000. Mass-transfer studies of solvent extraction of coals in N-methyl-2-pyrrolidone. *Fuel*, 79:577-585.

GIRI, C.C. & SHARMA, D.K. 2000. Kinetic studies and shrinking core model on solvolytic extraction of coal. *Fuel processing technology*, 68:97-109.

GRIFFITH, J.M., BURGESS CLIFFORD, C.E., RUDNICK, L.R., SCHOBERT, H.H. & MARTIN, P.D. 2004. Coal extraction using light cycle oil: A factorial design study of process parameters. *Preprints of papers-American chemical society division of fuel chemistry*, 49(2):627-629.

GRIFFITH, J.M., RUDNICK, L.R. & SCHOBERT, H.H. 2006. Solvent extraction of bituminous coals using light cycle oil. *Preprints of papers-American chemical society division of fuel chemistry*, 51(1):231-237.

HARRISON, J.S. 1975. Coal liquefaction in the U.K. *Coal processing technology*, 2:20-24.

HATTINGH, B. 2007. The continuous solvent extraction of Brandspruit coal. Final year project, Chemical engineering, North-West University. (Unpublished).

HOWARD-SMITH, I. & WERNER, G.J. 1976. Coal conversion technology. New Jersey : Noyes data corporation. 133 p.

KIPPAX, P. 2007. Measuring particle size using modern laser diffraction techniques. Malvern Instruments Ltd. [Web:] http://www.chemie.de/articles/e/61205/ [Date accessed: 30 May 2007].

LARSEN, J.W., GREEN, T.K. & KOVAC, J. 1985. The nature of the macromolecular network structure of bituminous coals. *Journal of organic chemistry*, 50(24):4729-4735.

LEVENSPIEL, O. 1999. Chemical reaction engineering. Wiley. 668 p.

MCMASTER, M & MCMASTER, C. 1998. GC/MS – A practical user's guide. New York : Wiley. 167 p.

MEYERS, R.A. 1982. Coal structure. New York : Academic Press. 340 p.

MIURA, K., NAKAGAWA, H., ASHIDA, R & IHARA, T. 2004. Production of clean fuels by solvent skimming of coal at around 350°C. *Fuel*, 83:733-738.

MIURA, K., SHIMADA, M., MAE, K. & SOCK, H.Y. 2001. Extraction of coal below 350°C in flowing-non-polar solvent. *Fuel*, 80(11):1573-1582, Sep.

MULDER, M. 1996. Basic principles of membrane technology. Dordrecht : Kluwer Academic Publishers. 564 p.

NEAVEL, R.C. 1976. Liquefaction of coal in hydrogen-donor and non-donor vehicles. *Fuel*, 55(3):237-242, July.

NEAVEL, R.C., SMITH, S.E., HIPPO, E.J. & MILLER, R.N. 1986. Interrelationships between coal compositional parameters. *Fuel*, 65:312-320.

OKUYAMA, N., KOMATSU, N., SHIGEHISA, T., KANEKO, T. & TSURUYA, S. 2004. Hyper-coal process to produce the ash-free coal. *Fuel processing technology*, 85:947-967.

RENGANATHAN, K., ZONDLO, J.W., MINTZ, E.A., KNEISL, P. & STILLER, A.H. 1988. Preparation of an ultra-low ash coal extract under mild conditions. *Fuel processing technology*, 18:273-278.

SASOL FACTS. 2007. [Web:] http://www.sasol.com/sasol_internet/downloads/sasolfacts_2007_1180093894888.pdf [Date accessed: 30 May 2007].

SCHMID, B.K. & JACKSON, D.M. 1981. The SRC-II process. *Philosophical transactions of the Royal Society of London. Series A, Mathematical and physical sciences,* 300(1453):129-139, Mar.

SHINN, J.H. 1984. From coal to single-stage and two-stage products: A reactive model of coal structure. *Fuel*, 63(9):1187-1196.

SMOOK, D. 2007. Removal of mineral material from solvent-refined coal by solvent extractions. *Fuel processing technology*, 88(8):795-798, Aug.

STACH, E., MACKOWSKY, M.-TH., TEICHMÜLLER, M., TAYLOR, G.H., CHANDRA, D. & TEICHMÜLLER, R. 1982. Stach's textbook of coal petrology. Berlin : Gebrüder Borntraeger. 535 p.

VAN DER WALT, T.J. 2007. Internal communication. Sasol Technology, Research and Development, Coal and Syngas Technologies.

VAN DYK, J.C., KEYSER, M.J. & COERTZEN, M. 2004. Sasol's unique position in syngas production from South African coal sources using Sasol-Lurgi fixed bed dry bottom gasifiers. (Paper presented at Gasification Technologies Conference.) San Francisco, USA. [Web:] http://www.gasification.org/Presentations/2004.htm [Date accessed: 10 July 2007].

VAN HEEK, K.H. 2000. Progress of coal science in the 20th century. *Fuel*, 79:1-26.

VAN KREVELEN, D.W. 1981. Coal science and technology 3. Amsterdam : Elsevier. 514 p.

VENTER, P.E. 2003. Potential of the Waterberg coalfield. (Presentation by Kumba Coal General Manager at the Limpopo International Investor Conference held in August 2003.) Polokwane. [Web:] http://www.exxaro.com/content/media/presentationsandwebcasts.asp [Date accessed: 20 May 2007].

VORRES, K.S. 2002. Coal. (*In* Kirk-Othmer Encyclopedia of Chemical Technology, 6:703-771.)

WORLD REFINING & FUELS TODAY. 2007. [Web:] www.worldfuels.com [Date accessed: 15 October 2007].

WISE, W.S. 1971. Solvent treatment of coal. London : Mills & Boon. 55 p.

YOSHIDA, T., LI, C., TAKANOHASHI, T., MATSUMURA, A., SATO, S. & SAITO, I. 2004. Effect of extraction condition on "HyperCoal" production (2) – effect of polar solvents under hot filtration. *Fuel processing technology*, 86:61-72.

YOSHIDA, T., TAKANOHASHI, T., SAKANISHI, K., SAITO, I., FUJITA, M. & MASHIMO, K. 2002. The effect of extraction condition on 'HyperCoal' production (1) – under room-temperature filtration. *Fuel*, 81:1463-1469.

ZONDLO, J., STANSBERRY, P., STILLER, A. & KENNEL, E. 2003. (Presentation at The Direct Carbon Fuel Cell Workshop held on 30 July 2003.) Pittsburgh. [Web:] http://www.netl.doe.gov/publications/proceedings/03/dcfcw/zondlo.pdf [Date accessed: 5 July 2007].

# APPENDIX A

# EXPERIMENTAL DATA: BATCH EXTRACTION

In this appendix, the amount of feed coal and residue oil used for each batch extraction experiment as well as the amount of residue coal obtained after drying are reported. Tables A1-A4 show the batch experimental data for the three feed coals with the corresponding operating conditions and in the order the experiments were carried out. In Tables A1-A4 the following holds: EXP = Experiment, TEMP = Temperature, S/C RATIO = Solvent/coal ratio, RO = Residue oil, C = Feed coal and RC = Residue coal.

As mentioned in Chapter 4, the results of the first set of batch extraction experiments with Waterberg as feed coal were not very consistent, so they were treated as a test run and the Waterberg coal experiments were repeated. These test run results are reported in Table A.1.

Table A.1: Batch experimental data - Waterberg coal/Residue oil (Test run).

| EXP | TEMP | PARTICLE SIZE | S/C RATIO | RO (g) | C (g) | RC (g) | YIELD (d.a.f) |
|---|---|---|---|---|---|---|---|
| W1 | 360°C | 120 μm | 10:1 | 497.5 | 50.0 | 23.5 | 46.7% |
| W2 | 360°C | 200 μm | 10:1 | 499.5 | 50.2 | 34.8 | 29.8% |
| W3 | 360°C | 120 μm | 5:1 | 499.5 | 102.6 | 15.4 | -42.9% |
| W4 | 360°C | 120 μm | 10:1 | 499.5 | 50.5 | 29.8 | 33.6% |
| W5 | 360°C | 120 μm | 3:1 | 501.0 | 167.2 | 142.5 | 28.5% |
| W6 | 370°C | 120 μm | 10:1 | 500.9 | 50.9 | 27.3 | 42.7% |
| W7 | 360°C | 120 μm | 10:1 | 500.1 | 50.2 | 38.4 | 36.7% |
| W8 | 350°C | 120 μm | 10:1 | 500.6 | 50.1 | 37.4 | 25.6% |

Table A.2: Batch experimental data - Waterberg coal/Residue oil.

| EXP | TEMP | PARTICLE SIZE | S/C RATIO | RO (g) | C (g) | RC (g) |
|---|---|---|---|---|---|---|
| W1 | 360°C | 120 µm | 10:1 | 499.8 | 49.9 | 21.0 |
| W2 | 360°C | 200 µm | 10:1 | 500.3 | 50.0 | 19.7 |
| W3 | 360°C | 120 µm | 5:1 | 499.2 | 100.0 | 44.8 |
| W4 | 360°C | 120 µm | 10:1 | 500.3 | 50.0 | 19.9 |
| W5 | 360°C | 120 µm | 3:1 | 500.2 | 167.0 | 102.6 |
| W6 | 370°C | 120 µm | 10:1 | 499.8 | 50.0 | 18.3 |
| W7 | 360°C | 120 µm | 10:1 | 499.8 | 50.0 | 20.5 |
| W8 | 350°C | 120 µm | 10:1 | 500.1 | 50.0 | 28.9 |

Table A.3: Batch experimental data - Brandspruit coal/Residue oil.

| EXP | TEMP | PARTICLE SIZE | S/C RATIO | RO (g) | C (g) | RC (g) |
|---|---|---|---|---|---|---|
| B1 | 360°C | 120 µm | 10:1 | 499.5 | 50.2 | 42.8 |
| B2 | 360°C | 200 µm | 10:1 | 500.0 | 51.0 | 43.3 |
| B3 | 360°C | 120 µm | 5:1 | 500.0 | 100.0 | 87.1 |
| B4 | 360°C | 120 µm | 10:1 | 500.5 | 50.0 | 42.5 |
| B5 | 360°C | 120 µm | 3:1 | 499.4 | 167.1 | 166.6 |
| B6 | 370°C | 120 µm | 10:1 | 500.1 | 50.1 | 43.1 |
| B7 | 360°C | 120 µm | 10:1 | 499.5 | 50.0 | 43.2 |
| B8 | 350°C | 120 µm | 10:1 | 499.9 | 49.9 | 43.2 |

Table A.4: Batch experimental data - Illinois#6 coal/Residue oil.

| EXP | TEMP | PARTICLE SIZE | S/C RATIO | RO (g) | C (g) | RC (g) |
|---|---|---|---|---|---|---|
| I1 | 360°C | 120 µm | 10:1 | 499.7 | 50.0 | 15.5 |
| I2 | 360°C | 200 µm | 10:1 | 500.2 | 50.0 | 15.5 |
| I3 | 360°C | 120 µm | 5:1 | 500.3 | 100.0 | 29.8 |
| I4 | 360°C | 120 µm | 10:1 | 499.9 | 50.0 | 15.7 |
| I5 | 360°C | 120 µm | 3:1 | 500.1 | 167.0 | 44.3 |
| I6 | 370°C | 120 µm | 10:1 | 499.9 | 50.0 | 13.8 |
| I7 | 360°C | 120 µm | 10:1 | 500.7 | 50.0 | 16.3 |
| I8 | 350°C | 120 µm | 10:1 | 500.0 | 50.0 | 8.4 |

# APPENDIX B

# YIELD CALCULATIONS AND REPRODUCIBILITY

Examples of the calculations done in order to calculate the extraction yields obtained in the batch as well as the continuous extraction experiments are given in this appendix. Furthermore, an explanation and sample calculation of how the reproducibility of the extraction experiments was determined will be given.

## B.1 Extraction yield

The extraction yield of the extraction experiments, given as a weight percentage, is calculated on a dry ash-free basis using equation (4.4).

$$y = 1 - \frac{Ash_C}{Ash_{RC}} \tag{4.4}$$

The calculation of the extraction yield for the batch Waterberg experiment W1 will be shown as an example. The ash fraction in the feed coal is determined using equation (4.1) and the ash fraction in the residue coal using equation (4.2). The values used in equation (4.1) are obtained from the proximate analysis performed on the feed coal and those for equation (4.2) from the proximate analysis performed on the residue coals.

$$\begin{aligned} Ash_C &= \frac{kg\ ash}{kg\ \ coal\,(d.a.f)} \qquad (4.1) \\ &= \frac{Ash\%}{Volatile\ matter\% + Fixed\ carbon\%} \times 100 \\ &= \frac{9.5}{34.5 + 53.1} \\ &= 0.108 \end{aligned}$$

$$Ash_{RC} = \frac{kg\ ash}{kg\ \ residue\,coal\,(d.a.f)} \tag{4.2}$$

$$= \frac{Ash\%}{Volatile\ matter\% + Fixed\ carbon\%} \times 100$$

$$= \frac{17.9}{30.3 + 50.9}$$

$$= 0.220$$

$$y = 1 - \frac{Ash_C}{Ash_{RC}} \tag{4.4}$$

$$= 1 - \frac{0.108}{0.220}$$

$$= 0.509 \times 100$$

$$= 50.9\%$$

The extraction yields of all batch and continuous experiments are calculated in the same way as illustrated above.

## B.2 Reproducibility

The reproducibility of the batch experimental procedures was determined by repeating an experiment three times at specific operating conditions and using the extraction yields obtained with these experiments. Three experiments for each feed coal at a temperature of 360°C, particle size of 120 µm and solvent/coal ratio of 10:1 were carried out. It was assumed that the reproducibility at these operating conditions would be the same for the procedures carried out at the other operating conditions. For this investigation the reproducibility was reported in terms of the standard deviation. Standard deviation is a measure of how much values differ from the average value. The function STDEVP in Microsoft Excel® was used to calculate the standard deviations and is given by equation (B.1).

$$STDEVP = \sqrt{\frac{\sum (x - \bar{x})^2}{n}} \tag{B.1}$$

In equation (B.1), $x$ is a certain value, $\bar{x}$ is the average value and $n$ the amount of values. The calculation of the standard deviation using the reproducibility data of Waterberg batch extraction experiments in Table B.1 will be shown as an example.

$$STDEVP = \sqrt{\frac{\sum(x-\bar{x})^2}{n}} \tag{B.1}$$

$$= \sqrt{\frac{(50.9-55.3)^2+(57.1-55.3)^2+(57.9-55.3)^2}{3}}$$

$$= 3.1\%$$

The reproducibility data and standard deviations for the batch extraction experiments are reported in Table B.1.

Table B.1: Reproducibility data of batch extraction experiments.

| **Experiment** | **Extraction yield (d.a.f)** | | |
|---|---|---|---|
| | **Waterberg** | **Brandspruit** | **Illinois#6** |
| 1 | 50.9% | 9.7% | 76.3% |
| 4 | 57.1% | 17.4% | 76.0% |
| 7 | 57.9% | 8.8% | 74.6% |
| Average | 55.3% | 12.0% | 68.9% |
| **Standard deviation** | **±3.1%** | **±3.9%** | **±1.6%** |

# APPENDIX C

# PROXIMATE AND ULTIMATE ANALYSES:

# BATCH EXTRACTION

In this appendix, the results of the proximate and ultimate analyses of the feed and residue coals of the batch extraction experiments are reported as were received from SABS. The conversion of these data to dry basis (d.b) or dry, ash-free basis (d.a.f) will also be shown. Furthermore, data obtained from the mass balances done for the proximate and ultimate analyses, which are not reported in Chapter 4, will also be given in this appendix together with a sample calculation of how the mass balances were done. Lastly, sample calculations will be given to show how the H/C and O/C ratios presented in Chapter 4 were determined.

## C.1 Proximate analyses

The proximate analyses reported in Tables C.1-C.3 are as received from SABS, where VM is the volatile matter and FC the fixed carbon content.

Table C.1: Proximate analyses of Waterberg feed and residue coals (SABS).

| EXP | Extraction yield (wt%) (d.a.f) | Waterberg - Proximate analysis (wt %) | | | |
|---|---|---|---|---|---|
| | | MOISTURE | VM | FC | ASH |
| *Feed coal* | | *2.9* | *34.5* | *53.1* | *9.5* |
| W1 | 50.9 | 0.9 | 30.3 | 50.9 | 17.9 |
| W2 | 59.5 | 1.9 | 23.2 | 54.2 | 20.7 |
| W3 | 53.3 | 1.7 | 23.4 | 56.4 | 18.5 |
| W4 | 57.1 | 1.7 | 24.8 | 53.7 | 19.8 |
| W5 | 28.8 | 0.8 | 37.9 | 48.2 | 13.1 |
| W6 | 62.9 | 1.4 | 21.3 | 55.0 | 22.3 |
| W7 | 57.9 | 1.2 | 26.1 | 52.6 | 20.2 |
| W8 | 43.9 | 0.6 | 39.2 | 44.2 | 16.1 |

Table C.2: Proximate analyses of Brandspruit feed and residue coals (SABS).

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Brandspruit – Proximate analysis (wt %)** | | | |
|---|---|---|---|---|---|
| | | **MOISTURE** | **VM** | **FC** | **ASH** |
| *Feed coal* | | *4.3* | *20.7* | *49.9* | *25.2* |
| B1 | 9.7 | 1.4 | 23.9 | 46.8 | 27.9 |
| B2 | 13.3 | 1.3 | 24.3 | 45.5 | 28.9 |
| B3 | 10.2 | 1.5 | 23.9 | 46.8 | 27.8 |
| B4 | 17.4 | 1.2 | 23.1 | 46.1 | 29.6 |
| B5 | -24.3 | 0.6 | 32.3 | 44.9 | 22.2 |
| B6 | 8.4 | 1.1 | 22.3 | 48.4 | 28.2 |
| B7 | 8.8 | 0.9 | 25.0 | 46.4 | 27.8 |
| B8 | 8.5 | 1.4 | 23.0 | 48.2 | 27.4 |

Table C.3: Proximate analyses of Illinois#6 feed and residue coals (SABS).

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Illinois#6 – Proximate analysis (wt %)** | | | |
|---|---|---|---|---|---|
| | | **MOISTURE** | **VM** | **FC** | **ASH** |
| *Feed coal* | | *5.5* | *35.4* | *46.0* | *13.1* |
| I1 | 70.2 | 1.4 | 18.5 | 44.7 | 35.4 |
| I2 | 71.3 | 1.2 | 19.5 | 43.2 | 36.1 |
| I3 | 64.4 | 1.2 | 21.6 | 45.6 | 31.6 |
| I4 | 69.8 | 1.2 | 21.5 | 42.7 | 34.6 |
| I5 | 55.3 | 1.0 | 24.9 | 48.3 | 25.8 |
| I6 | 74.1 | 1.3 | 18.4 | 43.8 | 36.5 |
| I7 | 66.6 | 0.7 | 24.6 | 42.6 | 32.1 |
| I8 | 68.9 | 1.3 | 22.2 | 43.1 | 33.4 |

The volatile matter, fixed carbon and ash contents were converted to dry basis (d.b) using equation (C.1) and are reported in Tables 4.5-4.7. In equation (C.1), $x$ represents the volatile matter, fixed carbon or ash content. The volatile matter content of Waterberg feed coal will be used as a sample calculation.

$$x\%\ (d.b) = \left(\frac{100}{100 - Moisture\%}\right) \times x\% \qquad \text{(C.1)}$$

$$\begin{aligned} Volatile\ matter\%\ (d.b) &= \left(\frac{100}{100 - Moisture\%}\right) \times Volatile\ matter\% \\ &= \left(\frac{100}{100 - 2.9\%}\right) \times 34.5\% \\ &= 35.6\% \end{aligned}$$

## C.2 Proximate analyses: Mass balances

As explained in Chapter 4, mass balances were performed for the moisture, ash, volatile matter and fixed carbon using the proximate analyses data of the feed and residue coals. The amount of feed coal used and residue coal obtained with the batch extraction experiments are known and are reported in Appendix A. Using volatile matter as example, it is known that the amount of volatile matter in the feed coal is distributed between the residue coal and extract. Tables C.4-C.7 show how the proximate constituents are distributed for each coal. To calculate the amount of proximate constituent in the extract, equation (C.2) is used while the volatile matter of the first Waterberg experiment is shown as a sample calculation. In equation (C.2), $x$ represents a specific proximate constituent, $\%x_C$ is the percentage of $x$ in the coal, $\%x_{RC}$ is the percentage of $x$ in the residue coal, C is the amount of feed coal and RC the amount of residue coal. Since the ash balances were calculated on a dry basis, the ash% used were on dry basis while dry, ash-free basis percentages were used for the volatile matter and fixed carbon calculations.

$$x_E\,(g) = C(g) \cdot \%x_C - RC(g) \cdot \%x_{RC} \tag{C.2}$$

$$\begin{aligned} Volatile\ matter_E\,(g) &= C\,(g) \cdot \%Volatile\ matter_C - RC\,(g) \cdot \%Volatile\ matter_{RC} \\ &= 49.9g \cdot 39.4\% - 21.0g \cdot 37.3\% \\ &= 11.8g \end{aligned}$$

## C. PROXIMATE AND ULTIMATE ANALYSES: BATCH EXTRACTION

Table C.4: Moisture balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Moisture (g) | | | Moisture (g) | | | Moisture (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 1.4 | 0.2 | 1.3 | 2.1 | 0.6 | 1.5 | 2.9 | 0.2 | 2.6 |
| 2 | 1.5 | 0.4 | 1.1 | 2.1 | 0.6 | 1.6 | 2.7 | 0.2 | 2.5 |
| 3 | 2.9 | 0.8 | 2.1 | 4.2 | 1.3 | 2.9 | 5.9 | 0.4 | 5.5 |
| 4 | 1.5 | 0.3 | 1.1 | 2.1 | 0.5 | 1.6 | 2.8 | 0.2 | 2.6 |
| 5 | 4.8 | 0.8 | 4.0 | 7.2 | 1.0 | 6.2 | 8.9 | 0.4 | 8.4 |
| 6 | 1.5 | 0.3 | 1.2 | 2.2 | 0.5 | 1.7 | 2.7 | 0.2 | 2.5 |
| 7 | 1.5 | 0.2 | 1.2 | 2.3 | 0.4 | 1.9 | 2.8 | 0.1 | 2.6 |
| 8 | 1.5 | 0.2 | 1.3 | 2.2 | 0.6 | 1.6 | 2.7 | 0.1 | 2.5 |

Table C.5: Ash (d.b) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ash (g) | | | Ash (g) | | | Ash (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 4.9 | 3.8 | 1.1 | 13.2 | 12.1 | 1.1 | 7.2 | 5.6 | 1.6 |
| 2 | 4.9 | 4.2 | 0.7 | 13.5 | 12.7 | 0.8 | 7.1 | 5.7 | 1.4 |
| 3 | 9.8 | 8.4 | 1.4 | 26.1 | 24.6 | 1.5 | 14.3 | 9.5 | 4.8 |
| 4 | 4.9 | 4.0 | 0.9 | 13.1 | 12.8 | 0.2 | 7.0 | 5.5 | 1.5 |
| 5 | 16.4 | 13.5 | 2.8 | 43.9 | 37.2 | 6.8 | 22.7 | 11.6 | 11.1 |
| 6 | 4.9 | 4.1 | 0.8 | 13.4 | 12.3 | 1.1 | 6.6 | 5.1 | 1.5 |
| 7 | 4.9 | 4.2 | 0.7 | 13.1 | 12.1 | 1.0 | 6.9 | 5.3 | 1.6 |
| 8 | 4.9 | 4.7 | 0.2 | 13.0 | 12.0 | 1.0 | 6.9 | 2.8 | 4.0 |

Table C.6: Volatile matter (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Volatile matter (g) | | | Volatile matter (g) | | | Volatile matter (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 19.7 | 7.8 | 11.8 | 14.5 | 14.5 | 0.0 | 21.9 | 4.5 | 17.4 |
| 2 | 19.7 | 5.9 | 13.8 | 14.7 | 15.1 | -0.3 | 21.8 | 4.8 | 17.0 |
| 3 | 39.4 | 13.1 | 26.3 | 28.8 | 29.4 | -0.6 | 43.9 | 9.6 | 34.3 |
| 4 | 19.7 | 6.3 | 13.4 | 14.5 | 14.3 | 0.2 | 21.9 | 5.3 | 16.6 |
| 5 | 65.8 | 45.1 | 20.7 | 49.1 | 69.6 | -20.5 | 72.5 | 15.1 | 57.4 |
| 6 | 19.7 | 5.1 | 14.6 | 14.9 | 13.6 | 1.4 | 21.6 | 4.1 | 17.5 |
| 7 | 19.7 | 6.8 | 12.9 | 14.8 | 15.1 | -0.3 | 21.5 | 6.0 | 15.5 |
| 8 | 19.7 | 13.6 | 6.1 | 14.9 | 14.0 | 0.9 | 21.6 | 2.9 | 18.7 |

Table C.7: Fixed carbon (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fixed carbon (g) | | | Fixed carbon (g) | | | Fixed carbon (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 30.2 | 13.2 | 17.1 | 35.7 | 28.3 | 7.4 | 28.1 | 11.0 | 17.1 |
| 2 | 30.3 | 13.8 | 16.5 | 36.3 | 28.2 | 8.0 | 28.2 | 10.7 | 17.5 |
| 3 | 60.6 | 31.7 | 28.9 | 71.2 | 57.7 | 13.5 | 56.1 | 20.2 | 35.9 |
| 4 | 30.3 | 13.6 | 16.7 | 35.5 | 28.5 | 7.0 | 28.1 | 10.4 | 17.7 |
| 5 | 101.2 | 57.5 | 43.7 | 118.0 | 97.0 | 21.0 | 94.5 | 29.2 | 65.3 |
| 6 | 30.3 | 13.2 | 17.1 | 35.2 | 29.5 | 5.6 | 28.5 | 9.7 | 18.7 |
| 7 | 30.3 | 13.7 | 16.6 | 35.2 | 28.1 | 7.1 | 28.6 | 10.3 | 18.2 |
| 8 | 30.3 | 15.3 | 15.0 | 35.0 | 29.2 | 5.8 | 28.5 | 5.5 | 22.9 |

The values reported as $\%x$ Extracted in Tables 4.8-4.10 is defined as the percentage of $x$ in the feed coal that was extracted during the solvent extraction process and is calculated using equation (4.5).

$$\%x\ Extracted = \frac{C(g)\cdot\%x_C - RC(g)\cdot\%x_{RC}}{C(g)\cdot\%x_C}\times 100 \tag{4.5}$$

In equations (4.5), $x$ represents a specific proximate constituent, $\%x_C$ is the percentage of $x$ in the coal, $\%x_{RC}$ is the percentage of $x$ in the residue coal, C is the amount of feed coal and RC the amount of residue coal. The volatile matter of the first Waterberg experiment will again be used as a sample calculation.

$$\begin{aligned}\%Volatile\ matter\ Extracted &= \frac{C(g)\cdot\%Volatile\ matter_C - RC(g)\cdot\%Volatile\ matter_{RC}}{C(g)\cdot\%Volatile\ matter_C}\times 100\\ &= \frac{49.9g\cdot 39.4\% - 21.0g\cdot 37.3\%}{49.9g\cdot 39.4\%}\times 100\\ &= 60.2\%\end{aligned}$$

It can therefore be said that 60% of the volatile matter that was present in Waterberg feed coal was extracted during the solvent extraction process at the conditions of experiment 1.

## C.3 Ultimate analyses

Tables C.8-C.10 show the carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and total sulphur (S) contents of all the feed and residue coals of the batch extraction experiments as it were received from SABS.

Table C.8: Ultimate analyses of Waterberg feed and residue coals (SABS).

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Waterberg - Ultimate analysis (wt %)** | | | | |
|---|---|---|---|---|---|---|
| | | **C** | **H** | **N** | **O** | **S (Total)** |
| *Feed coal* | | *71.5* | *5.1* | *1.5* | *8.5* | *1.1* |
| W1 | 50.9 | 66.8 | 4.6 | 1.7 | 7.5 | 0.7 |
| W2 | 59.5 | 62.9 | 4.0 | 1.6 | 8.3 | 0.7 |
| W3 | 53.3 | 65.1 | 3.7 | 1.6 | 8.6 | 0.7 |
| W4 | 57.1 | 63.0 | 3.7 | 1.6 | 9.5 | 0.7 |
| W5 | 28.8 | 72.8 | 4.8 | 1.7 | 6.1 | 0.7 |
| W6 | 62.9 | 62.6 | 3.5 | 1.6 | 8.0 | 0.6 |
| W7 | 57.9 | 64.1 | 3.8 | 1.6 | 8.4 | 0.7 |
| W8 | 43.9 | 69.2 | 4.8 | 1.7 | 7.1 | 0.7 |

Table C.9: Ultimate analyses of Brandspruit feed and residue coals (SABS).

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Brandspruit - Ultimate analysis (wt %)** | | | | |
|---|---|---|---|---|---|---|
| | | **C** | **H** | **N** | **O** | **S (Total)** |
| *Feed coal* | | *56.1* | *2.8* | *1.4* | *9.4* | *0.9* |
| B1 | 9.7 | 56.3 | 2.9 | 1.5 | 9.3 | 0.7 |
| B2 | 13.3 | 56.6 | 2.5 | 1.6 | 8.4 | 0.7 |
| B3 | 10.2 | 57.4 | 3.0 | 1.6 | 8.1 | 0.7 |
| B4 | 17.4 | 56.7 | 2.9 | 1.6 | 7.3 | 0.7 |
| B5 | -24.3 | 64.0 | 3.6 | 1.7 | 7.3 | 0.7 |
| B6 | 8.4 | 57.1 | 3.0 | 1.6 | 8.5 | 0.6 |
| B7 | 8.8 | 57.7 | 2.8 | 1.6 | 8.7 | 0.6 |
| B8 | 8.5 | 57.5 | 2.7 | 1.6 | 8.7 | 0.7 |

Table C.10: Ultimate analyses of Illinois#6 feed and residue coals (SABS).

| **EXP** | **Extraction yield (wt%) (d.a.f)** | **Illinois#6 - Ultimate analysis (wt %)** | | | | |
|---|---|---|---|---|---|---|
| | | **C** | **H** | **N** | **O** | **S (Total)** |
| *Feed coal* | | *61.7* | *4.7* | *1.1* | *7.6* | *6.2* |
| I1 | 70.2 | 49.8 | 2.6 | 1.3 | 4.4 | 5.1 |
| I2 | 71.3 | 49.0 | 2.6 | 1.2 | 4.7 | 5.2 |
| I3 | 64.4 | 54.2 | 3.0 | 1.4 | 3.7 | 5.1 |
| I4 | 69.8 | 50.6 | 2.7 | 1.4 | 4.7 | 4.8 |
| I5 | 55.3 | 58.5 | 3.3 | 1.5 | 5.4 | 4.5 |
| I6 | 74.1 | 49.7 | 2.5 | 1.3 | 3.8 | 5.0 |
| I7 | 66.6 | 54.4 | 3.1 | 1.4 | 4.0 | 4.3 |
| I8 | 68.9 | 50.9 | 2.7 | 1.3 | 5.5 | 4.9 |

The ultimate analyses results are reported on dry, ash-free basis (d.a.f) in Tables 4.11-4.13. The data in Tables C.8-C.10 are converted to dry, ash-free basis using equation (C.3) where $x$ represents the C, H, N, O or S content. The carbon content of Waterberg feed coal will be used as a sample calculation.

$$x\%\ (d.a.f) = \left(\frac{100}{100 - Moisture\% - Ash\%}\right) \times x\% \qquad \text{(C.3)}$$

$$\begin{aligned} Carbon\%\ (d.a.f) &= \left(\frac{100}{100 - Moisture\% - Ash\%}\right) \times Carbon\% \\ &= \left(\frac{100}{100 - 2.9\% - 9.5\%}\right) \times 71.5\% \\ &= 81.6\% \end{aligned}$$

## C.4 Ultimate analyses: Mass balances

The mass balances for the ultimate constituents are done in the same way as for the proximate constituents using equation (C.2). The distribution of the ultimate constituents between the feed coal, residue coal and extract is reported in Tables C.11-C.15. The percentage of an ultimate constituent in the feed coal that was extracted during the solvent extraction process was calculated in the same way as for the proximate constituents using equation (4.5) and are reported in Tables 4.14-4.16. A graph of %carbon extracted versus %extraction yield is shown in Figure C.1 where the data for the three coals are treated as a single set of data.

Table C.11: Carbon (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Carbon (g) | | | Carbon (g) | | | Carbon (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 40.7 | 17.3 | 23.5 | 39.7 | 34.1 | 5.6 | 37.9 | 12.2 | 25.6 |
| 2 | 40.8 | 16.0 | 24.8 | 40.3 | 35.1 | 5.2 | 37.9 | 12.1 | 25.7 |
| 3 | 81.6 | 36.6 | 45.0 | 79.6 | 70.6 | 9.0 | 76.0 | 24.0 | 52.0 |
| 4 | 40.8 | 16.0 | 24.8 | 39.8 | 35.1 | 4.7 | 37.8 | 12.4 | 25.4 |
| 5 | 136.3 | 86.8 | 49.5 | 133.3 | 138.1 | -4.8 | 126.3 | 35.4 | 90.9 |
| 6 | 40.8 | 15.0 | 25.8 | 39.6 | 34.8 | 4.8 | 38.0 | 11.0 | 27.0 |
| 7 | 40.8 | 16.7 | 24.1 | 40.2 | 34.9 | 5.3 | 38.0 | 13.2 | 24.8 |
| 8 | 40.8 | 24.0 | 16.8 | 39.8 | 34.9 | 4.9 | 38.0 | 6.6 | 31.4 |

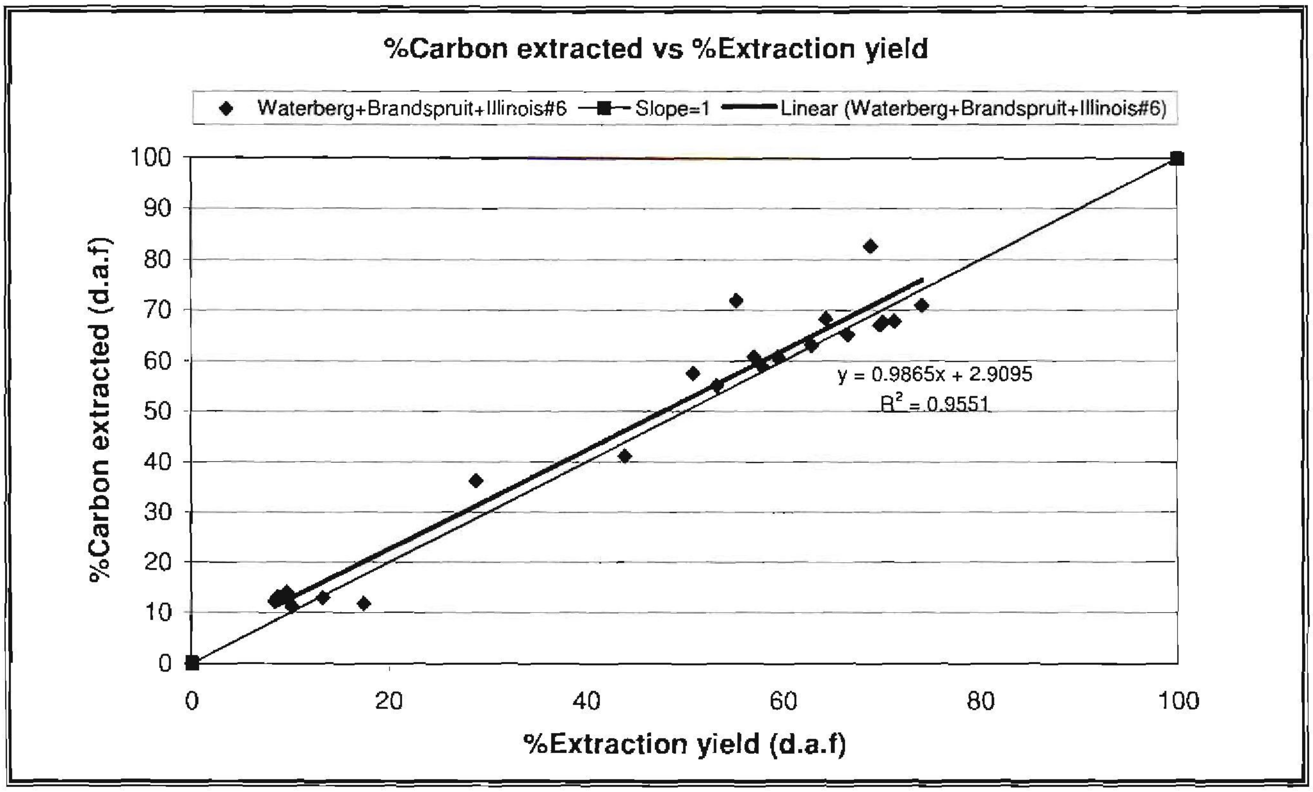


Figure C.1: %Carbon extracted vs. %Extraction yield.

Table C.12: Hydrogen (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Hydrogen (g) | | | Hydrogen (g) | | | Hydrogen (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 2.9 | 1.2 | 1.7 | 2.2 | 1.8 | 0.5 | 2.8 | 0.6 | 2.2 |
| 2 | 2.9 | 1.0 | 1.9 | 2.2 | 1.6 | 0.7 | 3.0 | 0.7 | 2.3 |
| 3 | 5.8 | 2.1 | 3.7 | 3.8 | 3.7 | 0.1 | 5.8 | 1.3 | 4.5 |
| 4 | 2.9 | 0.9 | 2.0 | 1.9 | 1.8 | 0.1 | 3.2 | 0.7 | 2.5 |
| 5 | 9.7 | 5.7 | 3.9 | 6.3 | 7.7 | -0.3 | 9.5 | 2.0 | 7.5 |
| 6 | 2.9 | 0.8 | 2.1 | 1.8 | 1.8 | 0.0 | 2.9 | 0.6 | 2.3 |
| 7 | 2.9 | 1.0 | 1.9 | 1.9 | 1.7 | 0.2 | 2.9 | 0.7 | 2.1 |
| 8 | 2.9 | 1.6 | 1.3 | 1.8 | 1.6 | 0.2 | 2.9 | 0.4 | 2.5 |

Table C.13: Nitrogen (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Nitrogen (g) | | | Nitrogen (g) | | | Nitrogen (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 0.8 | 0.4 | 0.4 | 1.0 | 0.9 | 0.1 | 0.7 | 0.3 | 0.4 |
| 2 | 0.9 | 0.4 | 0.4 | 1.0 | 1.0 | 0.0 | 0.7 | 0.3 | 0.4 |
| 3 | 1.7 | 0.9 | 0.8 | 2.0 | 1.9 | 0.1 | 1.4 | 0.6 | 0.8 |
| 4 | 0.9 | 0.4 | 0.5 | 1.0 | 1.0 | 0.0 | 0.7 | 0.3 | 0.4 |
| 5 | 2.8 | 1.9 | 0.9 | 3.5 | 3.5 | 0.0 | 2.3 | 0.9 | 1.5 |
| 6 | 0.9 | 0.4 | 0.5 | 1.0 | 0.9 | 1.0 | 0.7 | 0.3 | 0.4 |
| 7 | 0.9 | 0.4 | 0.4 | 1.0 | 1.0 | 0.0 | 0.7 | 0.3 | 0.4 |
| 8 | 0.9 | 0.6 | 0.3 | 1.0 | 1.0 | 0.0 | 0.7 | 0.2 | 0.5 |

Table C.14: Oxygen (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Oxygen (g) | | | Oxygen (g) | | | Oxygen (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 4.8 | 1.9 | 2.9 | 6.7 | 5.6 | 1.1 | 4.5 | 1.1 | 3.4 |
| 2 | 4.9 | 2.1 | 2.7 | 6.7 | 5.2 | 1.5 | 4.7 | 1.1 | 3.5 |
| 3 | 9.7 | 4.8 | 4.9 | 13.3 | 9.9 | 3.4 | 9.2 | 1.6 | 7.6 |
| 4 | 4.9 | 2.4 | 2.4 | 6.7 | 4.5 | 2.2 | 4.7 | 1.2 | 3.5 |
| 5 | 16.2 | 7.3 | 8.9 | 21.9 | 15.7 | 6.2 | 16.4 | 3.3 | 13.1 |
| 6 | 4.9 | 1.9 | 2.9 | 7.0 | 5.2 | 1.8 | 4.8 | 0.8 | 3.9 |
| 7 | 4.9 | 2.2 | 2.7 | 6.3 | 5.3 | 1.0 | 4.8 | 1.0 | 3.8 |
| 8 | 4.9 | 2.5 | 2.4 | 6.6 | 5.3 | 1.4 | 4.7 | 0.7 | 4.0 |

Table C.15: Sulphur (d.a.f) balances.

| Exp | WATERBERG | | | BRANDSPRUIT | | | ILLINOIS#6 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sulphur (g) | | | Sulphur (g) | | | Sulphur (g) | | |
| | Coal | Residue coal | Extract | Coal | Residue coal | Extract | Coal | Residue coal | Extract |
| 1 | 0.6 | 0.2 | 0.4 | 0.7 | 0.4 | 0.3 | 4.1 | 1.2 | 2.9 |
| 2 | 0.6 | 0.2 | 0.4 | 0.7 | 0.4 | 0.3 | 3.9 | 1.3 | 2.6 |
| 3 | 1.2 | 0.4 | 0.8 | 1.3 | 0.9 | 0.4 | 7.6 | 2.2 | 5.4 |
| 4 | 0.6 | 0.2 | 0.4 | 0.7 | 0.4 | 0.2 | 3.7 | 1.2 | 2.5 |
| 5 | 2.0 | 0.8 | 1.2 | 2.2 | 1.5 | 0.7 | 12.5 | 2.7 | 9.8 |
| 6 | 0.6 | 0.1 | 0.5 | 0.7 | 0.4 | 0.3 | 3.7 | 1.1 | 2.6 |
| 7 | 0.6 | 0.2 | 0.4 | 0.7 | 0.4 | 0.3 | 3.8 | 1.1 | 2.7 |
| 8 | 0.6 | 0.2 | 0.4 | 0.6 | 0.4 | 0.2 | 3.8 | 0.6 | 3.1 |

## C.5 H/C and O/C ratios

The ultimate analyses were also used to determine the atomic H/C and O/C ratios for the feed coals, residue coals and extracts. The H/C ratios were calculated using equation (C.4) and the O/C ratios using equation (C.5). Waterberg feed coal will be used as a sample calculation.

$$\begin{aligned} H/C\ ratio &= \frac{H\%}{1.0079} \div \frac{C\%}{12.011} \\ &= \frac{5.8\%}{1.0079} \div \frac{81.6\%}{12.011} \\ &= 0.85 \end{aligned} \tag{C.4}$$

$$\begin{aligned} O/C\ ratio &= \frac{O\%}{15.999} \div \frac{C\%}{12.011} \\ &= \frac{9.7\%}{15.999} \div \frac{81.6\%}{12.011} \\ &= 0.09 \end{aligned} \tag{C.5}$$

# APPENDIX D

# CALORIFIC VALUE

In this appendix, the calorific values measured with the bomb calorimeter are reported with an explanation of how these values were converted to dry basis. Furthermore, the reproducibility data will be reported as well as a sample calculation to show how the theoretical calorific values were determined.

## D.1 Analytically measured calorific values

In Chapter 4, the calorific values are reported on dry basis while Table D.1 gives the calorific values of each feed coal and their residue coals as it were obtained from the bomb calorimeter.

Table D.1: Measured calorific values for feed and residue coals.

| **Exp** | **WATERBERG** | **BRANDSPRUIT** | **ILLINOIS#6** |
|---|---|---|---|
| | **CV (MJ/kg)** | **CV (MJ/kg)** | **CV (MJ/kg)** |
| *Feed coal* | *29.8* | *22.7* | *25.4* |
| Exp1 RC | 26.2 | 22.4 | 20.8 |
| Exp2 RC | 25.3 | 22.3 | 22.2 |
| Exp3 RC | 26.3 | 22.1 | 23.4 |
| Exp4 RC | 24.7 | 20.4 | 21.8 |
| Exp5 RC | 30.5 | 24.3 | 24.7 |
| Exp6 RC | 25.2 | - | 25.7 |
| Exp7 RC | 25.6 | 22.0 | 21.9 |
| Exp8 RC | 27.9 | 24.8 | 24.8 |

The values in Table D.1 are converted to dry basis with the same method as for the proximate analyses using equation (C.1) where $x$ in this case represents the calorific value.

## D.2 Reproducibility data

The residue coal of experiment W1 was analyzed five times to check the accuracy of the obtained values. The reproducibility data are reported in Table D.2.

Table D.2: Reproducibility data of calorific value measurements.

| **WATERBERG** | |
|---|---|
| ***Experiment*** | ***Residue coal (MJ/kg) (d.b)*** |
| W1 | 24.9 |
| W1 | 26.8 |
| W1 | 26.2 |
| W1 | 27.6 |
| W1 | 27.5 |
| Average | 26.6 |
| **Standard deviation** | 1.0 |

## D.3 Theoretically determined calorific values

The calorific values of the feed coals and their residue coals were also determined theoretically using equation (3.5). The values used in equation (3.5) are all on dry basis. Waterberg feed coal will be used as a sample calculation.

$$\begin{aligned} Calorific\ value\ (MJ/kg) &= 0.339C + 1.325H - 0.125O + 0.100S - 0.015Ash \qquad (3.5) \\ &= (0.339\times 73.643) + (1.325\times 5.276) - (0.125\times 8.718) + \\ &\quad (0.100\times 1.096) - (0.015\times 9.771) \\ &= 30.8 \end{aligned}$$

This calculated theoretical calorific value is within the accuracy range of ±1.0 MJ/kg from the analytically determined calorific value of 29.8 MJ/kg.

# APPENDIX E

# POROSITY

---

Pore size distribution graphs are presented in this appendix as well as the method used to determine the amount of meso- and macropores present in each sample.

## E.1 Pore size distribution graphs

The data obtained with the Micromeritics AutoPore IV 9500 V 1.07 software were used to construct pore size distribution graphs. These graphs are shown in Figures E.1-E.3, where pore size diameter is plotted against differential intrusion with the pore size diameter on logarithmic scale. In each case the results of the feed coal and its residue coal are plotted on the same graph to illustrate the difference between the feed and residue coals.

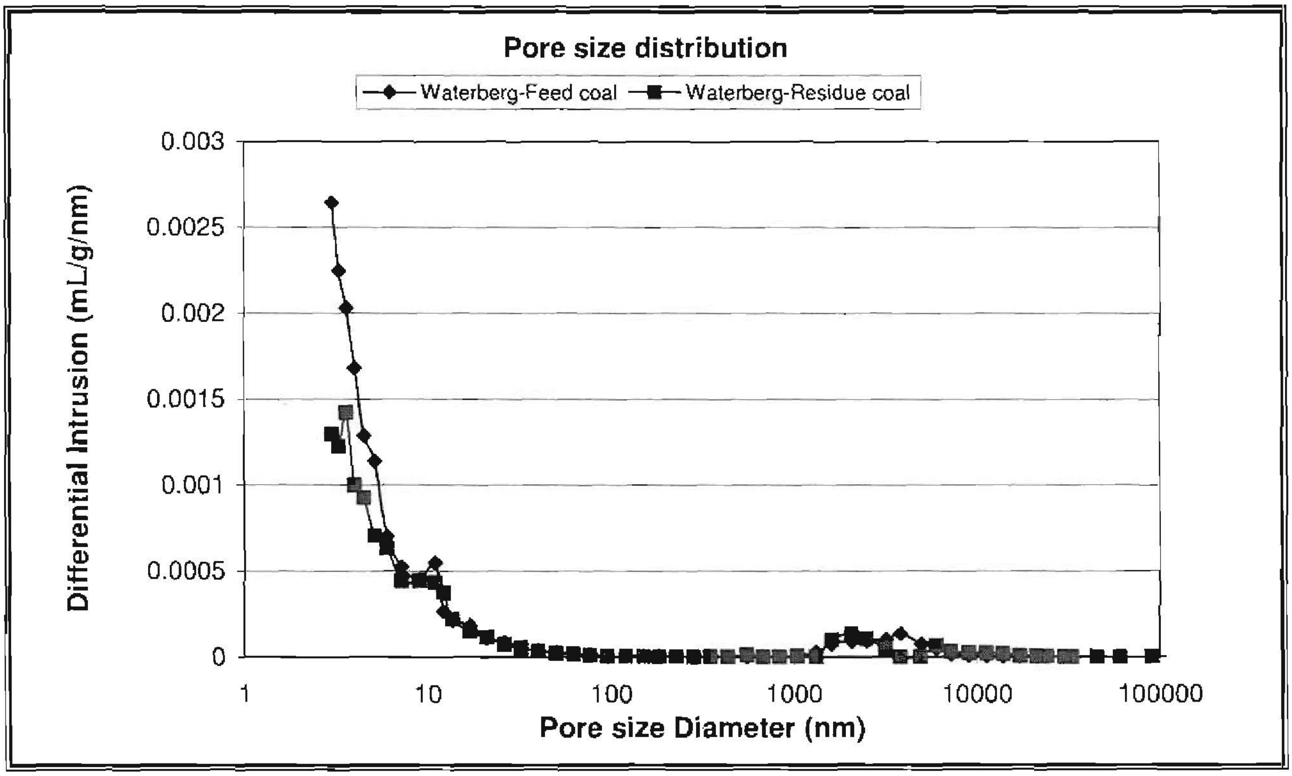


Figure E.1: Waterberg - Pore size distribution.

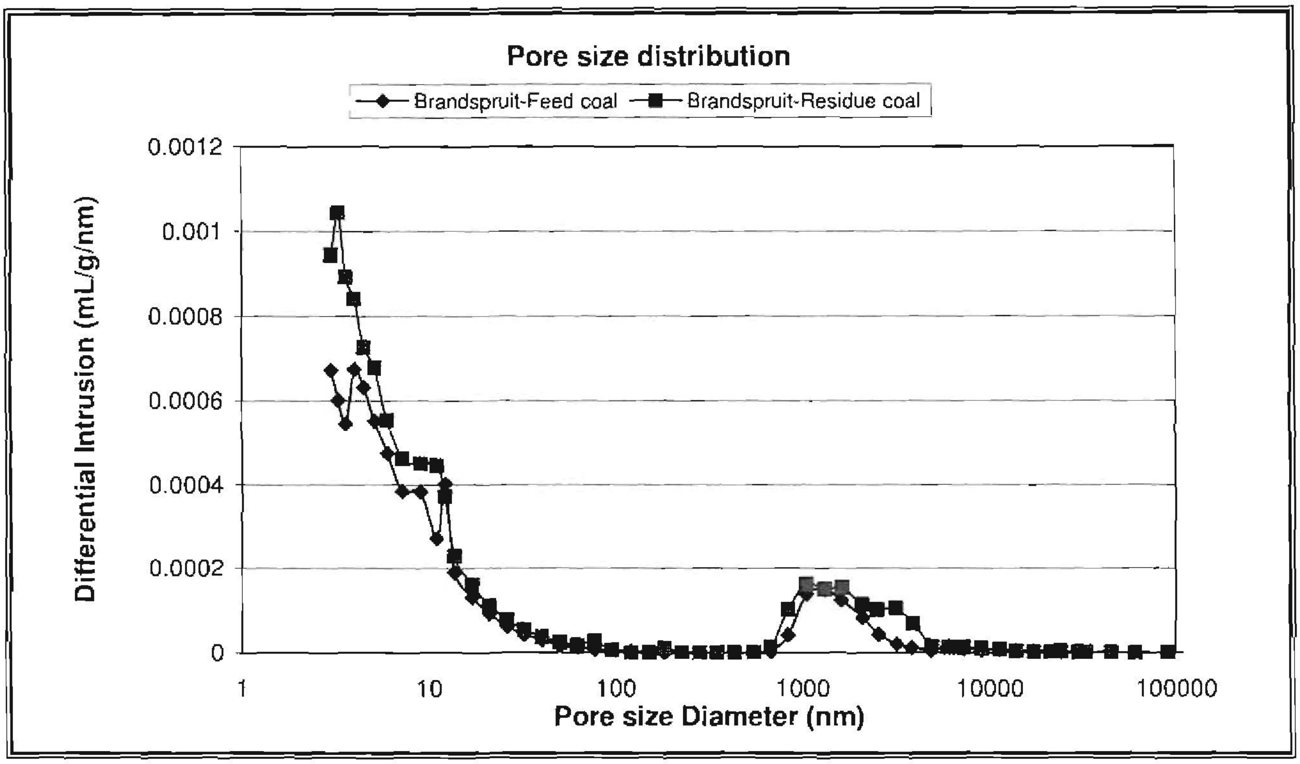


Figure E.2: Brandspruit - Pore size distribution.

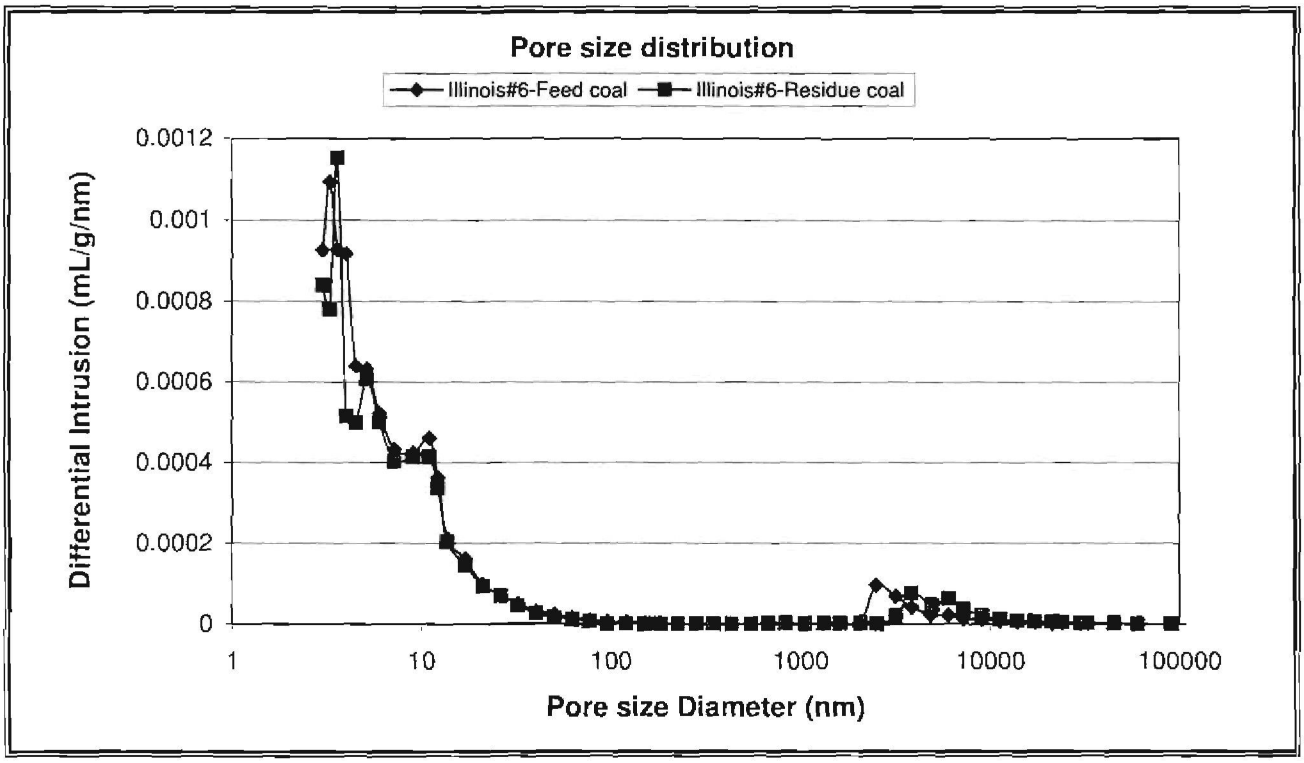


Figure E.3: Illinois#6 - Pore size distribution.

## E.2 Meso- and macropores

The data obtained with the Micromeritics AutoPore IV 9500 V 1.07 software and used to construct the pore size distribution graphs were also used to determine the amount of meso- and macropores present in each coal sample. Equation (E.1) was used for the calculations.

$$Amount\ of\ pores = \sum y_i \times \Delta r_i \qquad \text{(E.1)}$$

In equation (E.1) $y_i$ is the differential intrusion and $r_i$ the pore size diameter. To determine the amount of mesopores, data corresponding to pore size diameters between 2 and 50 nm were used while data corresponding to pore size diameters larger than 50 nm were used to calculate the amount of macropores.

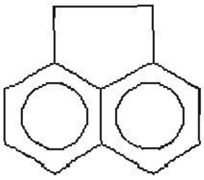
# APPENDIX F

# PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

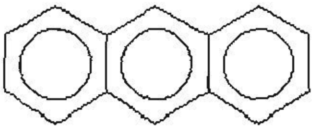
---

In this appendix the structure formulas of the pyrolysis-GC/MS and GC/MS compounds are given.

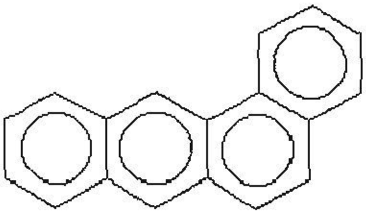
Acenaphthene



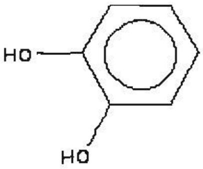
Anthracene



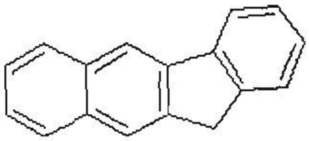
Benz[a]anthracene



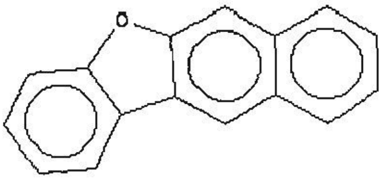
1,2-Benzenediol



Benzofluorene

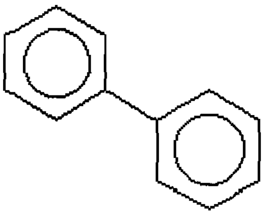


Benzo[b]naphtho[2,3-d]furan

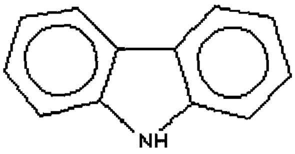


## F. PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

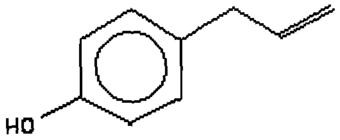
Biphenyl



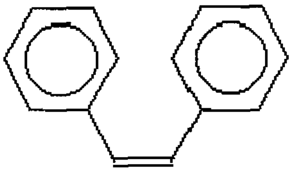
Carbazole



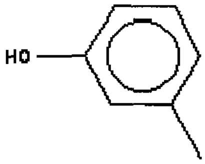
Chavicol



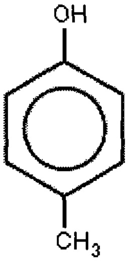
cis-Stilbene



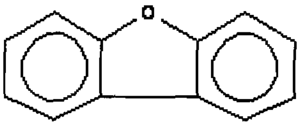
m-Cresol (3)



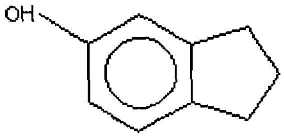
p-Cresol (4)



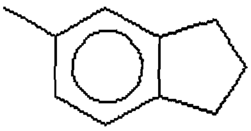
Dibenzofuran



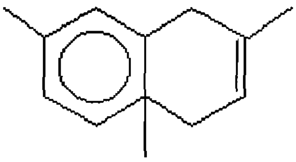
2,3-dihydro-1H-Inden-5-ol



2,3-dihydro-5-methyl-1H-Indene

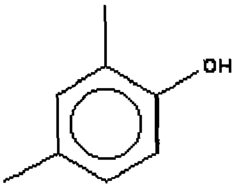


1,4-dihydro-2,5,8-trimethyl-Naphthalene

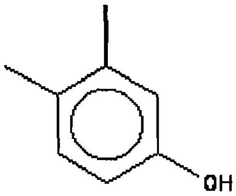


## F. PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

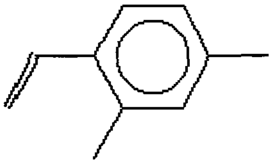
2,4-dimethyl-Phenol



3,4-dimethyl-Phenol

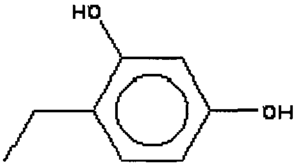


2,4-dimethylstyrene

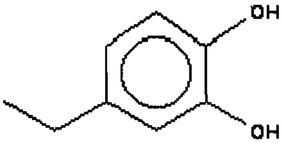


Dodecane (C12H26)

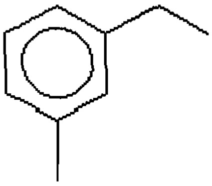
4-ethyl-1,3-Benzenediol



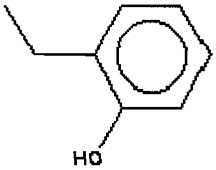
4-ethyl-catechol



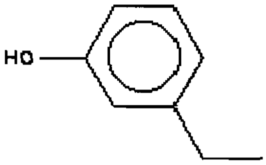
1-ethyl-3-methyl-Benzene



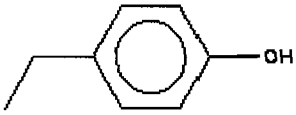
2-ethyl-Phenol



3-ethyl-Phenol



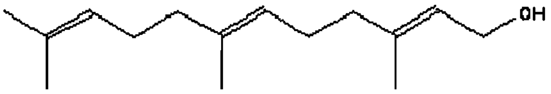
4-ethyl-Phenol



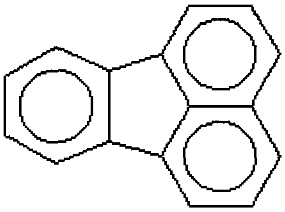
Eicosane (C20H42)

## F. PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

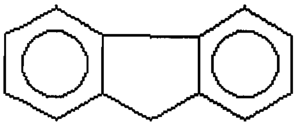
Farnesol (3,7,11-trimethyl-
2,6,10-Dodecatrien-1-ol)



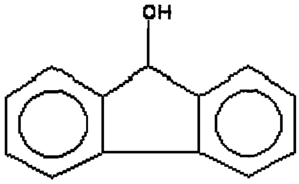
Fluoranthene



Fluorene



9H-Fluoren-9-ol

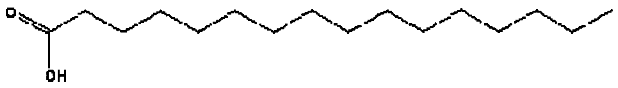


Heneicosane (C21H44)

Heptadecane(C17H36)

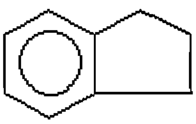
Hexadecane (C16H34)

Hexadecanoic Acid

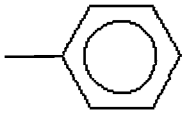


1-Hexene

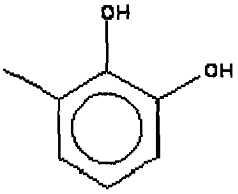
Indane



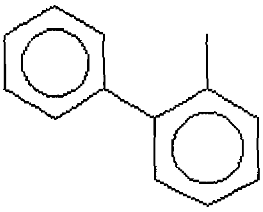
Methyl-Benzene



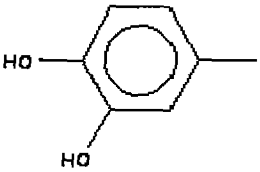
3-methyl-1,2-Benzenediol



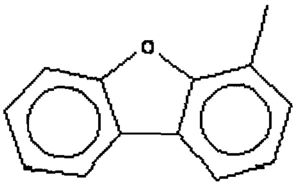
2-methyl-1,1'-Biphenyl



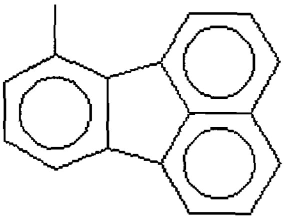
4-methyl-catechol



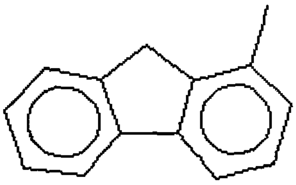
4-methyl-Dibenzofuran



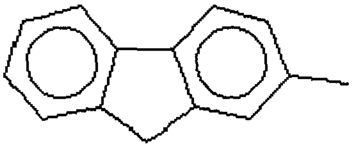
2-methyl-Fluoranthene



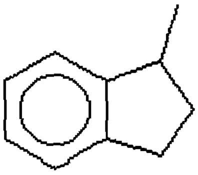
1-methyl-9H-Fluorene



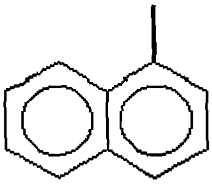
2-methyl-9H-Fluorene



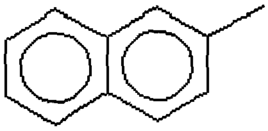
1-methyl-Indan



1-methyl-Naphthalene

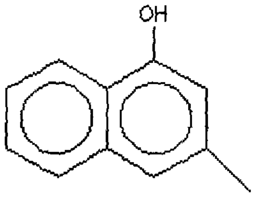


2-methyl-Naphthalene

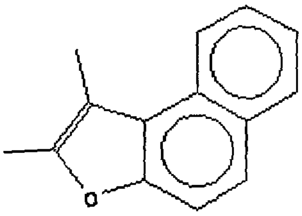


## F. PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

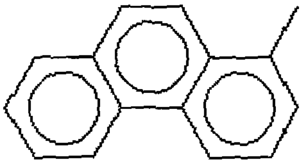
3-methyl-1-Naphthalenol



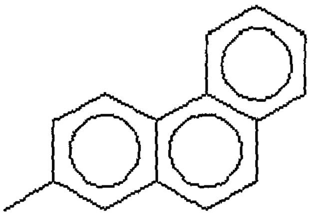
methyl-Naphtho[2,1-b]furan



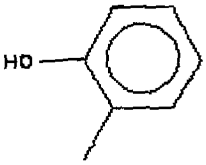
1-methyl-Phenanthrene



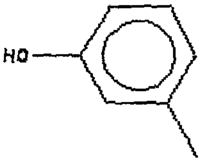
2-methyl-Phenanthrene



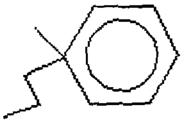
2-methyl-Phenol



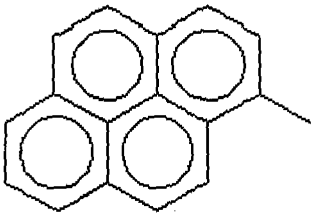
3-methyl-Phenol



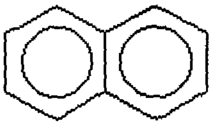
1-methyl-1-propenyl-benzene



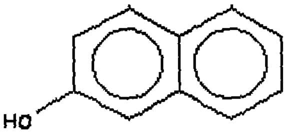
1-methyl-pyrene



Naphthalene



Naphthol



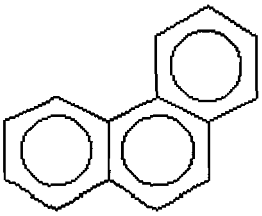
F. PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

Octacosane ($C_{28}H_{58}$)

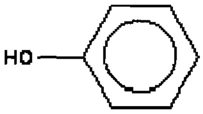
Octadecane ($C_{18}H_{38}$)

Pentadecane ($C_{15}H_{32}$)

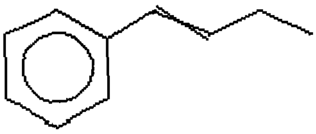
Phenanthrene



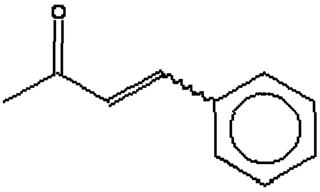
Phenol



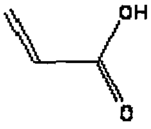
1-phenyl-1-butene



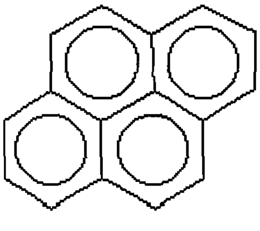
4-phenyl-3-Buten-2-one



2-Propenoic acid



Pyrene



Tetracosane ($C_{24}H_{50}$)

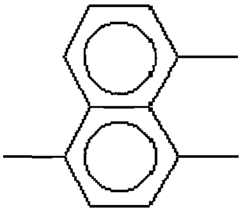
F. PYROLYSIS-GC/MS AND GC/MS COMPOUNDS

Tetradecane (C13H28)

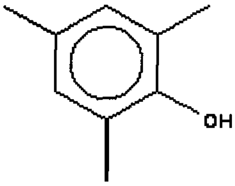
Tricosane (C23H48)

Tridecane (C13H28)

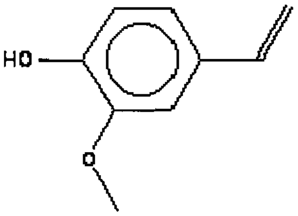
(1,4,5)Trimethyl-Naphthalene



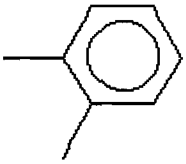
2,4,6-trimethyl-Phenol



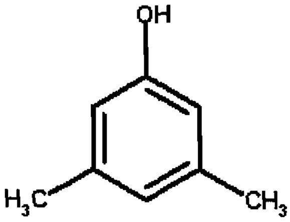
4-vinyl-2-methoxy-Phenol



Xylene (1,2)



Xylenol (3,5)



# APPENDIX G

# DENSITY

---

Table G.1 shows the distillation data of the petrol (200°C) and diesel (350°C) fractions of the solvent as well as a liquid extract of each feed coal. Firstly, the amounts of fraction 1 and fraction 2 obtained during the distillation are reported. A bottoms fraction was also obtained that was not distilled at the specific conditions. In addition, the quantities that were used in equation (3.7) to calculate the densities are also reported.

Table G.1: Distillation data used for density calculations.

| | RESIDUE OIL | W1-EXTRACT | B1-EXTRACT | I1-EXTRACT |
|---|---|---|---|---|
| Starting mass (g) | 500 | 422 | 429 | 444 |
| Total mass of fraction1 (g) | 20 | 100 | 197 | 206 |
| Total mass of fraction2 (g) | 253 | 190 | 131 | 152 |
| ***Fraction 1 (200°C)*** | | | | |
| Mass (g) | 19 | 89 | 86 | 85 |
| Volume (ml) | 20 | 99 | 97 | 95 |
| Density (g/cm$^3$) | 0.95 | 0.90 | 0.89 | 0.89 |
| ***Fraction 2 (350°C)*** | | | | |
| Mass (g) | 249 | 88 | 94 | 96 |
| Volume (ml) | 242 | 87 | 92 | 93 |
| Density (g/cm$^3$) | 1.03 | 1.01 | 1.02 | 1.03 |

# APPENDIX H

# PROXIMATE AND ULTIMATE ANALYSES: CONTINUOUS EXTRACTION

In this appendix, the results of the proximate and ultimate analyses of the feed and residue coals of the continuous extraction experiments are reported as were received from SABS. The conversion of these data to dry basis (d.b) and dry, ash-free basis (d.a.f) was done in the same manner as explained in Appendix C for the batch extraction proximate and ultimate analyses.

## H.1 Proximate analyses

The proximate analyses reported in Tables H.1 and H.2 is as received from SABS, where VM is the volatile matter and FC the fixed carbon content. Where a value is indicated with N/A it means that insufficient sample was available to complete the analysis.

## H. PROXIMATE AND ULTIMATE ANALYSES: CONTINUOUS EXTRACTION

Table H.1: Proximate analyses of Waterberg feed and residue coals (SABS) (Continuous).

| **WATERBERG – Proximate analysis (wt %)** | | | | |
|---|---|---|---|---|
| **Residence time (min)** | **MOISTURE** | **VM** | **FC** | **ASH** |
| *0 - Feed coal* | *2.9* | *35.2* | *53.3* | *8.6* |
| | **320°C** | | | |
| 4 – Residue coal | 4.3 | 63.7 | 26.4 | 5.7 |
| 6 – Residue coal | 6.8 | 64.1 | 23.9 | 5.3 |
| 12 – Residue coal | 6.7 | 67.0 | 21.3 | 5.0 |
| 24 – Residue coal | 5.6 | N/A | N/A | 5.1 |
| | **330°C** | | | |
| 6 – Residue coal | 1.5 | 57.5 | 34.1 | 6.9 |
| 12 – Residue coal | 1.3 | N/A | N/A | 8.7 |
| | **340°C** | | | |
| 6 – Residue coal | 1.2 | 49.2 | 41.1 | 8.6 |
| 12 – Residue coal | 1.9 | N/A | N/A | 10.3 |

Table H.2: Proximate analyses of Brandspruit feed and residue coals (SABS) (Continuous).

| **BRANDSPRUIT – Proximate analysis (wt %)** | | | | |
|---|---|---|---|---|
| **Residence time (min)** | **MOISTURE** | **VM** | **FC** | **ASH** |
| *0 - Feed coal* | *5.0* | *21.4* | *49.7* | *23.9* |
| | **320°C** | | | |
| 4 – Residue coal | 2.2 | 44.0 | 35.5 | 18.3 |
| 6 – Residue coal | 2.1 | 47.0 | 36.7 | 14.2 |
| 12 – Residue coal | 1.5 | 41.2 | 36.9 | 20.4 |
| 24 – Residue coal | 1.9 | 44.7 | 37.2 | 16.2 |
| | **330°C** | | | |
| 6 – Residue coal | 1.9 | 48.6 | 34.9 | 14.6 |
| 12 – Residue coal | 2.2 | 41.3 | 35.4 | 21.1 |
| 24 – Residue coal | 1.9 | 42.3 | 39.2 | 16.6 |
| | **340°C** | | | |
| 6 – Residue coal | 1.9 | 43.1 | 39.4 | 15.6 |
| 12 – Residue coal | 1.5 | 39.0 | 36.9 | 22.6 |

## H.2 Ultimate analyses

Tables H.3 and H.4 show the carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and total sulphur (S) contents of all the feed and residue coals of the continuous extraction experiments as it were received from SABS. N/A again indicates insufficient sample.

Table H.3: Ultimate analyses of Waterberg feed and residue coals (SABS) (Continuous).

| **WATERBERG – Ultimate analysis (wt %) (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Residence time (min)** | **C** | **H** | **N** | **O** | **S (Total)** |
| *0 - Feed coal* | *72.3* | *5.3* | *1.4* | *8.5* | *1.0* |
| **320°C** | | | | | |
| 4 – Residue coal | 78.1 | 6.1 | 1.8 | 3.3 | 0.7 |
| 6 – Residue coal | 76.9 | 5.7 | 1.7 | 2.9 | 0.7 |
| 12 – Residue coal | 78.2 | 6.0 | 1.7 | 2.0 | 0.7 |
| 24 – Residue coal | 79.8 | 6.3 | 1.7 | 1.3 | 0.3 |
| **330°C** | | | | | |
| 6 – Residue coal | 76.2 | 5.8 | 1.8 | 6.3 | 0.8 |
| 12 – Residue coal | 74.0 | 5.6 | 1.7 | 7.2 | 0.8 |
| **340°C** | | | | | |
| 6 – Residue coal | 75.3 | 5.7 | 1.8 | 6.6 | 0.8 |
| 12 – Residue coal | 72.7 | 5.2 | 1.7 | 6.9 | 0.8 |

Table H.4: Ultimate analyses of Brandspruit feed and residue coals (SABS) (Continuous).

| **BRANDSPRUIT – Ultimate analysis (wt %) (d.a.f)** | | | | | |
|---|---|---|---|---|---|
| **Residence time (min)** | **C** | **H** | **N** | **O** | **S (Total)** |
| *0 - Feed coal* | *57.1* | *2.9* | *1.4* | *8.8* | *0.9* |
| **320℃** | | | | | |
| 4 – Residue coal | 66.7 | 4.7 | 1.7 | N/A | N/A |
| 6 – Residue coal | 71.2 | 5.2 | 1.8 | 5.1 | 0.7 |
| 12 – Residue coal | 66.0 | 4.4 | 1.7 | N/A | N/A |
| 24 – Residue coal | 69.6 | 4.0 | 1.4 | 6.2 | 0.7 |
| **330℃** | | | | | |
| 6 – Residue coal | 71.7 | 5.2 | 1.8 | 7.8 | 0.8 |
| 12 – Residue coal | 63.4 | 3.9 | 1.6 | N/A | N/A |
| 24 – Residue coal | 69.5 | 4.7 | 1.8 | 5.0 | 0.6 |
| **340℃** | | | | | |
| 6 – Residue coal | 69.9 | 4.8 | 1.8 | N/A | N/A |
| 12 – Residue coal | 61.6 | 4.0 | 1.6 | N/A | N/A |