Solvent extraction of a bituminous coal using a sweet sorghum bagasse derived solvent

TZ Sehume

orcid.org 0000-0002-3814-8727

Thesis submitted in fulfilment of the requirements for the degree *Doctor of Philosophy in Chemistry* at the North-West University

Promoter:	Prof CA Strydom
Co-promoter:	Prof JR Bunt
Assistant Promoter:	Prof HH Schobert

Graduation July 2019
20441665

“Education is not the learning of facts, but the training of the mind to think.”

–Albert Einstein–

Declaration

I, T.Z. Sehume, hereby declare that this thesis entitled: “***Solvent extraction of a bituminous coal using a sweet sorghum bagasse derived solvent”***, submitted in fulfillment of the requirements for the degree Doctor of Philosophy in Chemistry at the North-West University is my own work and has not been submitted to any other university in whole or in part. Written consent from authors had been obtained for publications where co-authors have been involved.

Signed at Potchefstroom

03 June 2019

T.Z. Sehume

Date

Preface

Thesis format:

The format of this thesis is in accordance with the academic rules of the North-West University, where rule ***A.5.4.2.7*** states: "*Where a candidate is permitted to submit a thesis in the form of a published research article or articles, or as an unpublished manuscript or manuscripts in article format and more than one such article or manuscript is used, the thesis must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis, and integration and with a synoptic conclusion, and the guidelines of the journal concerned must also be included.*"

Rule ***A.5.4.2.8*** states: "*Where any research article or manuscript and/or internationally examined patent is used for the purpose of a thesis in article format to which other authors and/or inventors than the candidate contributed, the candidate must obtain a written statement from each co-author and/or co-inventor in which it is stated that such co-author and/or co-inventor grants permission that the research article or manuscript and/or patent may be used for the stated purpose and in which it is further indicated what each co-author's and/or co-inventor's share in the relevant research article or manuscript and/or patent was.*"

Rule ***A.5.4.2.9*** states: *"Where co-authors or co-inventors as referred to in A.5.4.2.8 above were involved, the candidate must mention that fact in the preface and must include the statement of each co-author or co-inventor in the thesis immediately following the preface."*

Format of numbering and referencing:

The formatting, referencing style, numbering of tables and figures, and general outline of the manuscripts or chapters were changed to ensure uniformity throughout the thesis. The format of manuscripts which have been submitted and/or published adhere to the author guidelines as stipulated by the editor of each journal. The headings and original technical content of the manuscripts were not changed from the submitted and/or published scripts, and minor spelling and typographical errors were corrected therein.

Statement from co-authors

To whom it may concern,

The listed co-authors hereby give consent that **T.Z. Sehume** may submit the following manuscript(s) as part of her thesis entitled: **Solvent extraction of a bituminous coal using a sweet sorghum bagasse derived solvent,** for the degree *Philosophiae Doctor in Chemistry*, at the North-West University:

Thabo Z. Sehume, Christien A. Strydom, John R. Bunt, and Harold H. Schobert. Effectivity of phenol during solvent extraction of a South African bituminous coal at mild conditions. Energy & Fuels **2017**, 31, 13655–13665.

(This letter of consent complies with rules ***A5.4.2.8 and A.5.4.2.9*** of the academic rules, as specified by the North-West University)

Signed at Potchefstroom

CAStrydom

03 June 2019

Christien A. Strydom

Date

03 June 2019

John R. Bunt

Date

Harold H. Schobert

03 June 2019

Harold H. Schobert

Date

List of Publications

Journal articles

Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Effectivity of phenol during solvent extraction of a South African bituminous coal at mild conditions. Energy Fuels **2017**, 31, 13655–13665.

Strydom, C.A.; Sehume, T.Z.; Bunt, J.R.; van Dyk, J.C. 2015. The influence of selected biomass additions on the co-pyrolysis with an inertinite-rich medium rank C grade South African coal. J. South. Afr. Inst. Min. Metall. **2015**, 115, 707–716.

Manuscripts:

Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Bio-oil production from sweet sorghum bagasse via liquefaction using alkaline solutions and identification of phenolic products. Waste and Biomass Valorization, submitted for publication, 2019 (Manuscript number: WAVE-D-19-00223).

Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Solvent extraction of a South African bituminous coal using a model biomass-derived phenolic mixture. S. Afr. J. Chem., submitted for publication, 2019 (Manuscript number: sajc-001855).

Conference proceedings:

Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Schobert. Bio-oil production from sweet sorghum bagasse with alkaline solutions: Extraction of phenols. Presented at 33rd The Sustainable Development of South Africa's Energy Sources, Johannesburg, South Africa, Glenhove Conference Centre, November 29-30, 2017; Session 5, Hybrid Energy. ***(Oral presentation)***

Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Liquefaction of South African bituminous coal using phenol as a solvent. Presented at 33rd Annual International Pittsburgh Coal Conference, Cape Town, South Africa, October 8-12, 2016; Session 24, Clean Coal and Gas to Fuels: New Technologies. ***(Oral presentation)***

Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Liquefaction of South African bituminous coal using phenol as a solvent. Presented at 20th South African Conference on Research in Coal Science and Technology (CST 2015): Latest Research at University and R&D Organizations. Fossil Fuel Foundation Conference, Potchefstroom, South Africa, November 24-25, 2015; Session 2, Bio-fuels. ***(Oral presentation)***

Acknowledgements

The author would like to thank and acknowledge all the individuals' roles and institutions involved in making this project to be successfully completed:

- First and for most, thank, give praise and reverence to God for making all things possible, and also for His grace, blessings, mercy and unconditional love throughout my life;
- My supervisors Professors Christien Strydom, John Bunt, and Harold Schobert for their guidance, encouragement, fruitful discussions, critical criticisms and magnanimous contributions throughout this project;
- Coal Research group for their critical input into this project;
- National Research Fund (NRF) and North-West University for their financial support;
- Dr. David Powell for his assistance in acquiring the Waterberg bituminous coal samples used for this project;
- Dr. Nemera Shargie (Agricultural Research Council, Grain Crops Institute) for his assistance in acquiring the sweet sorghum bagasse used for this project;
- Dr. Frans Marx for his assistance with the ATR-FTIR analysis, and also Dr. Roelf Venter for his assistance with the GC-MS analysis;
- Dr. Henry Ratale for his valuable suggestions and discussions about this project;
- Dr's Lourens Tiedt and Anine Jordaan at the Laboratory for Electron Microscopy for conducting the SEM scans and also for their suggestions;
- Mr. Adrien Brock, Mr. Elias Mofokeng and Mr. Jan Kroeze for their technical assistance with the experimental equipment (autoclave/reactor) and related issues;
- Mrs. Rène Bekker for her assistance with the characterization of some samples, and also Mr. Ian Goodman for his assistance with the apparatus, chemicals, and reagents required for this project;
- Dr. Jean du Toit for language editing of the thesis;
- Colleagues and friends from the Coal Research and Chemical Research Beneficiation Groups for their friendliness, support and valuable contributions;
- Special thanks to my amazing and incredible mother (Dieketseng), brothers (Oupa, Papi, Willy, and Sello), my late father (Thomas) and sister (Ouma) for their unconditional love, patience and moral support;

- Thanks to the Maine family for their care and support, especially with the kids during challenging times experienced throughout this project; and
- Lastly, I thank my very own “fantastic” Sehume family: my better half, pillar of strength and beautiful wife (Thato), and my two energetic and most adorable children (Mpho and Oarabile). Thank you for your love, patience, understanding, resilience and also for your beautiful smiles which revived me throughout the hardships experienced during this project.

Abstract

The aim of the first part of this study was to investigate the extractability of a South African bituminous (Waterberg) coal using phenol as a solvent at 300 °C, 320 °C, 340 °C, and 360 °C and a solvent/coal ratio of 10:1. Secondly, investigate the feasibility of converting biomass into bio-oil via hydrothermal liquefaction and then extract a phenol-rich product from the bio-oil. Lastly, to use a model biomass-derived phenolic mixture to extract or dissolve valuable light products from coal and compare the results to that when phenol is used as a solvent. All of the reactions were conducted inside a high-pressure stainless-steel autoclave system (950 mL capacity, 90 mm diameter and 150 mm height) under inert atmosphere (nitrogen gas). Subsequently, the extraction yields and conversions were obtained. The products were subjected to chemical and physical analyses.

The effectiveness of phenol for coal solvent extraction was investigated in this study. In general, coal solvent extraction using phenol increases as temperature increases, i.e. a low coal conversion of 12% was observed at 300 °C increasing to 50% at 360 °C in this study. From the proximate results, the decrease in the volatile matter of the unreacted coal residues (THFIs) from 44.7 wt. % to 28.5 wt. % daf corresponded with an increase in coal conversion upon an increase in temperature. This decrease in the volatile matter may be an indication of increased depolymerization reactions at higher temperatures. ATR-FTIR results showed that the extracted products had similar spectra to that of the raw coal in terms of similar functional groups. From the ultimate analysis results, the nitrogen and sulphur values of the hexane-soluble products were much lower than those of the coal, suggesting that the formation of oils during phenol extraction has been accompanied by a reduction in heteroatomic content. The oil yield after coal extraction increased from 3% up to 27% with an increase in temperature between 300 °C and 360 °C. The hexane-soluble products contained compounds with a wide range of boiling points (208–615 °C) as determined by SimDis analysis. The largest proportion of the boiling constituents were light vacuum gas oil (23–31 wt. %), distillate fuel oil (16–30 wt. %), heavy vacuum gas oil (18–34 wt. %) and residual oil (3–16 wt. %).

Sweet sorghum bagasse (SSB) was treated with NaOH concentrations of 0.5, 1.0, 3.0 and 6.0 M. The experiments were conducted in a temperature range of 260–320 °C inside an autoclave in using a N_2 atmosphere. It was observed that the bio-oil yield increased with increasing temperature for 0.5–3.0 M NaOH concentrations (5.7–53.2 wt. %). However, the bio-oil yield reduced from 47 to 39 wt. % with increasing temperatures using a concentration of 6.0 M NaOH. The bio-oil yield reached its maximum of 53.2 wt. % at a concentration of 3.0 M NaOH and a liquefaction temperature of 320 °C. This bio-oil yield at 320 °C with 3.0 M NaOH coincides with the highest yield of 40 wt. % total phenols extracted from the bio-oil. The highest variation of phenolic compounds was observed at a temperature of 280 °C and a NaOH concentration of 3.0 M and the compounds were phenol (13.8 wt. % of total liquid products), p-cresol (6.8 wt. %), 4-ethylphenol (10.0 wt. %), 4-isopropylphenol (0.9 wt. %), 2-propylphenol (0.7 wt. %), and 4-ethylguaicol (1.5 wt. %).

The model biomass-derived phenolic mixture, was formulated based on the biomass liquefaction product results, was investigated for its solvent ability for extraction of a South African bituminous coal at temperatures of 300–360 °C. As the temperature increases, the yield of the residues (THFIs) decreases, while the conversion increases. The coal conversions of 14 wt. %, 20 wt. %, 32 wt. % and 37 wt. % were obtained using a model biomass-derived phenolic mixture at 300 °C, 320 °C, 340 °C and 360 °C. The oil yield obtained using a model mixture increased from 1 wt. % up to 17 wt. % (300–360 °C). From the SimDis analysis, the boiling constituents of hexane-soluble fractions (300–360 °C) included distillate fuel oil, light vacuum gas oil, heavy vacuum gas oil and heavy vacuum gas oil fractions which were 14 wt. %, 50 wt. %, and 22 wt. respectively. The phenol and a model biomass-derived phenolic mixture had similar coal conversions between 300 °C and 320 °C (13–20 wt. %). However, coal solvent extraction using phenol resulted in nearly 13 wt. % more than that of a model biomass-derived phenolic mixture at temperatures higher than 320 °C.

The overall conclusion made from this investigation is that the effectivity of phenol-based solvents is characterized significantly by their ability to dissolve or penetrate the coal structure. The results obtained from this study demonstrate that the use of a model biomass-derived phenolic mixture has the potential to solubilize coal. Together with further development, using biomass as a source of mixed phenols could be used to facilitate the production of useful liquids from solvent extraction of South African coals.

Keywords: Coal extraction, bituminous coal, depolymerization, biomass-derived solvent, liquefaction, phenol(s)

Table of Contents

List of Figures

List of Tables

List of Acronyms and Abbreviations

a.d.b.	Air dried basis
d.a.f.	Dry ash free basis
m.m.f.b.	Mineral matter free basis
EDF	Environmental Defense Fund
GTIS	Global Trade Information
OPEC	Organization of the Petroleum Exporting Countries
OECD	Organization for economic cooperation and development
FT	Fischer-Tropsch Synthesis
ARC	Agricultural Research Council
WABP	Weight average boiling point
ISO	International standards of operation
AFROX	Africa Oxygen Limited
DCL	Direct Coal Liquefaction
ICL	Indirect Coal Liquefaction
SSB	Sweet sorghum bagasse
SimDis	Simulated distillation by gas chromatography
SEC	Size-exclusion chromatography
GC-MS	Gas chromatography
ATR-FTIR	Attenuated total reflection infrared spectroscopy
TG	Thermogravimetric analyser
DTG	Derivative thermogravimetric analyser
SEM-EDS	Scanning electron microscopy with environmental scanning electron microscope
XRF	X-ray fluorescence
KF	Volumetric Karl-Fischer analysis
NDF	Neutral detergent fibre
ADF	Acid detergent fibre
ADL	Acid detergent fibre
THFI	Tetrahydrofuran insoluble, unreacted coal residue
THFIS	Tetrahydrofuran soluble
HI	Hexane insoluble, containing pre-asphaltenes + asphaltenes (PAAs)
HS	Hexane soluble, containing oil fraction
HF	Hydro-furan
H/C	Atomic ratio of hydrogen to carbon
°C/min	Degrees Celsius per minute
ΔH	Change in enthalpy
P_i	Internal pressure
PTS	p-Toluene sulphonic acid
Mt	Mega ton
Mtoe	Million tonnes of oil equivalent
bbl/d	barrels of oil per day

Chapter 1

Introduction

Chapter 1 details an account into the current study of research and development of solvent extraction of Permian-aged South African coal. The study investigates the effectiveness of the phenol-based solvents on the extraction of Waterberg bituminous coal. Availability of phenolic compounds from biomass waste is also investigated, which necessitates the need to identify phenolic compounds obtained from alkaline liquefaction of a biomass waste material. Permian-aged South African coal, especially bituminous coal, has not been well studied using solvent extraction processes for the production of chemicals or liquid fuels when compared to North American coals, or coals from other countries. These coals may exhibit different reactivity and behaviour upon reaction with phenol-based solvents during solvent extraction process.

1.1. Introduction and motivation

Coal remains a valuable raw material that is fundamental to the production of fossil fuels. According to the BP Statistical Review of World Energy,[1] South Africa is a developing country, and also has the ninth-largest amount of recoverable coal reserves. Coal provides approximately 72% of the country's total energy needs, and is mostly used for electricity generation, steel manufacturing, petrochemical coal-to-liquids and domestic use.[2] The country has limited reserves of natural gas, renewable energy sources and nuclear energy, which also contribute to the primary energy supply.[1] Oil provides the country with 22% of the energy consumption, followed by natural gas (3%), nuclear (3%), and renewables (less than 1%, primarily from hydro-power). However, coal will remain the most important energy source in the future, due to its low cost and relative abundance. According to EDF,[3] South Africa's dependency on coal for energy supply has lead the country in becoming the biggest emitter of carbon dioxide in Africa (accounting to nearly 50% of emissions) and the 12th largest emitter in the world.

The rapid increase in energy consumption has increased the attention on coal reserves, as energy sources.[4,5] The consequence of this increasing energy demand is a shortage of oil and unstable petroleum prices. To lessen this shortage, production of transportation fuels from coal provides an important alternative to augment petroleum supply beside crude oil.[6,7,8] According to the Total Petroleum and Other Liquids Production,[9] and Oil and Gas Journal,[10] South Africa has limited amounts of proven crude oil reserves (≈15 million barrels) and its crude oil production is very small compared with the largest proven oil reserve countries in Africa such as Nigeria. The country heavily depends on imports to make up for the continuing decline of crude oil as oil fields mature, and with no progress of commercially viable discoveries. South African Revenue Service,[11] as published by Global Trade Information Services (GTIS), reported that the country imported 425 000 barrels of oil per day (bbl/d) of crude oil in 2014. Import of crude oil is mostly from OPEC (Organization of the Petroleum Exporting Countries) countries, namely Saudi Arabia (38%), Nigeria (31 %), and Angola (12%), as illustrated in Figure 1.1. Therefore, there is a need for research and development into carbon-based materials for the production of transportation fuels to meet growing domestic demand for petroleum products, and lessen dependency on crude oil.

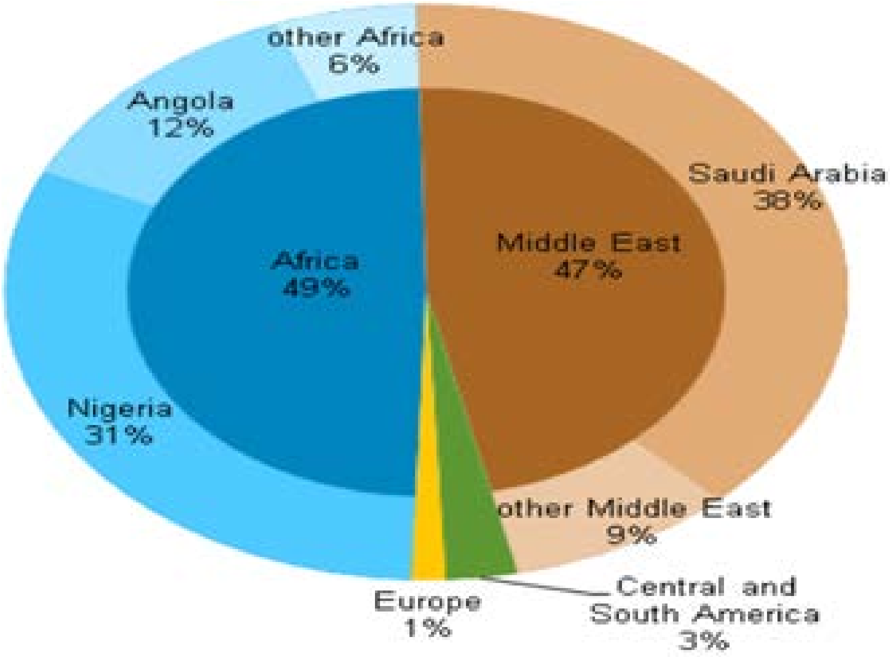


Figure 1.1. South Africa's crude oil and condensate imports, by country of origin in 2014 (Adapted from Global Trade Information[11])

From the literature, coal has been proven to potentially be a useful feedstock for the production of speciality organic chemicals (coal-to-liquids), monomers for aromatic engineering polymers, and carbon materials.[12] However, the chemical industry based on coal conversion depends on technologies available to minimise emissions and lower production costs. The conversion of solid coal into liquid fuels and chemicals has been realised through coal liquefaction (described in detail in **Chapter 2**), namely; (1) pyrolysis, (2) solvent extraction, (3) direct hydrogenation of coal (commonly known as direct liquefaction, DCL), and indirect coal liquefaction (ICL), which is gasification followed by the Fischer-Tropsch synthesis process. In South Africa the ICL process is mostly used.

The gasification process has been around for more than 200 years.[13] This process' main objective is the breakdown of the coal structure with reactive gases (i.e. steam/CO_2) into smallest building blocks, namely synthesis gas ($CO + H_2$), followed by reactions of CO and H_2 to synthesize liquid products under extreme conditions.[5,14] The Sasol gasification technology located in Secunda (South Africa) treats approximately 30 million tons/ annum of coal to synthesis gas, later converted via the Fischer-Tropsch synthesis (FT) process.[14,15] The continuing development of Sasol FT technology has led to successful annual productions of 5 Mt transportation fuels and 2.6 Mt chemicals.[5]

However, in terms of coal-derived chemicals, this process involves high cost of hydrogen (H_2) generation and high levels of carbon dioxide (CO_2) emissions. According to Song et al.,[16] the ICL approach seeks to destroy completely any molecular structural features of the coal. Therefore, this process, despite its technical and economic attractiveness, may not be the best route to use for the production of chemicals that may be derived directly from the macromolecular structure of coal. It is important to consider an alternative process which can utilize coal in a very inexpensive method for the production of chemicals and liquid fuels. Solvent extraction of coal may be considered for production of compounds of interest. This process can also be used as a pre-treatment process for other processes such as DCL.

South African Permian aged coals, typically have minor liptinite contents (<7% by volume) and high mineral matter contents (up to 30%) compared to Carboniferous coals (17–19). Over 95% of South African coal reserves are bituminous, with about 2% being anthracite.[20] The bituminous coal from the Waterberg region is situated north-west of the Karoo basin, and is relatively unexplored compared to other coal from regions such as the Highveld-Witbank region.[2,18,21–23] The dominant maceral in the Waterberg coals is the vitrinite group (up to 90%), decreasing with a depth of formation (60% inertinite at the base of the formation).[21] This coal is characterized as a semi-soft coking coal with ash percentage less than 10%.[2] Permian-aged South African coal, especially bituminous coal, has not been studied well for the production of chemicals using solvent extraction processes, compared to North American coals.[24–26] One reason for the present study is that the obtained results may extend the knowledge of coal-solvent interactions for South African coals, as there is limited literature found for solvent extraction of Permian-aged South African coals with a focus on coal-derived liquids.[27,28]

Extraction of bituminous coal, using an organic solvent, has been a method used in the past to study the composition of coal and possible ways to convert coal into valuable products of potential industrial value.[29–35] The thermal dissolution of coal with solvents offers probably the mildest type of conversion, and it is a process whereby the coal is digested in the solvent. This process can be used to extract the organic part of the coal, extract, and yield a high-ash solid coal residue.[27] The effectiveness of a solvent for coal extraction was found to be directly proportional to its physical properties, usually considered are internal pressure (P_i) and surface tension.[31,36] These quantities are related by a length parameter related to the molecular diameter, such that for most common solvents they stand in the same relative order.

Some of the solvents reported in the literature for coal extraction include: tetralin, benzene, pyridine, toluene, mixed xylenes, creosote oil, and phenols.[31,37] The most preferred solvent is tetralin due to its hydrogen-donating capability. However, it is expensive, which makes it less favourable for commercial applications. Therefore, introducing a low cost effective solvent for coal extraction that can address economy constraints would be beneficial for the industry. Phenols have been reported in early literature to be an effective solvent for coal extraction.[31,38–40] The presence of phenols and other aromatic compounds in biomass-derived solvents (bio-oil) may provide an alternative to petroleum-derived phenols produced industrially from cumene oxidation, and alleviate the pressure to obtain phenol from the direct oxidation of benzene.[41] The study proposes to use a model biomass-derived phenolic compound mixture, to serve as a process vehicle or solvent for coal extraction and production of coal-derived liquid products. Coal-derived liquid products are generally comparable to synthetic crude oil.[42] According to Burgess and Schobert,[12] the value of coal liquids could increase, provided that it is converted directly to specialty chemicals or other value added products, rather than to synthetic crude oil. Therefore, the final product may require to be further refined (via hydrocracking or adding hydrogen over a catalyst) to conform to fuel specifications and high-grade fuel characteristics.

1.2. Hypothesis

Phenols are considered to be effective solvents for coal extraction, and also known to be beneficial for conversion of coal into liquid fuels and chemicals via depolymerization reactions or chemical decomposition. Phenols derived from the bio-oil can substitute “chemically pure” phenol, and promote depolymerization/chemical decomposition of Permian-aged South African bituminous coal at mild reaction conditions without addition of a catalyst or molecular hydrogen, in order to produce value-added precursor and liquid fuels.

1.3. Aims and objectives

The current study seeks to understand the effectiveness of the phenol-based solvent on the extraction of South African Waterberg bituminous coal, with a special focus on the composition of the formed products at mild conditions. In addition, development of a solvent extraction process using a model biomass-derived solvent mixture with coal to produce chemicals and liquid fuels is investigated.

Objectives of this study are summarized as follows:

- Conducting experiments in an autoclave (batch-system) to generate phenol solvent extraction products from bituminous coal under mild conditions, and fractionating the liquid products;
- Determining the changes in the chemical structure of the coal-derived products obtained during the phenol-driven solvent extraction, using techniques such as attenuated total reflection infrared spectroscopy (ATR-FTIR), thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses, scanning electron microscopy (SEM), gas chromatography-mass spectrometry (GC-MS) and simulated distillation by gas chromatography (SimDis GC) analyses (**Chapter 3**). The study seeks to investigate the composition of products produced from solvent extraction of bituminous coal in order to form a basis for comparison to other experiments in **Chapter 5**;
- Conducting extraction of phenolic compounds from bio-oil obtained through liquefaction of indigenous biomass (sweet sorghum bagasse) treated with alkaline solutions at selected temperatures and concentrations (**Chapter 4**);
- Determining the chemical changes of the coal-derived products using a model biomass-derived phenolic compound mixture (based on the results obtained in **Chapter 4**) during solvent extraction of South African bituminous coal (**Chapter 5**). Determining the chemical and physical characterization of the coal-derived products using some of the methods as previously described in **Chapter 3**;
- Comparing the characteristics of the products formed using phenol as surrogate solvent (**Chapter 3**) with a model biomass-derived solvent mixture (**Chapter 5**) for extraction of South African bituminous coal.

1.4. Scope and outline of study

The scope of this investigation is structured in such an approach that it fulfils the aims and objectives of this study as described in the previous section. Figure 1.2 represents a schematic presentation of the outline of the study. The study yielded the first detailed information in relation to the development of a solvent extraction process using Permian-aged South African bituminous coal to produce chemicals and liquid fuels at mild conditions. The experiments were proposed to show the influence of a phenol-based solvent on solvent extraction of bituminous coal. The (washed, low ash yield) Waterberg bituminous coal was ground and milled to a particle size of less than 150 microns. A high-pressure stainless steel autoclave was used to promote solvent extraction of bituminous coal, and for biomass liquefaction reactions. The choice of biomass is based on ease of growth, not competing with the food supply, and a strong possibility to produce high yields of phenols. The main objective of this study was to compare results obtained from solvent extraction of a phenol and that of a biomass-derived solvent as an alternative solvent for extraction of South African bituminous coal. The chemical changes and physical structural changes of the coal during the solvent extraction process were investigated using different analytical instruments. The thesis is divided into six chapters with its relative contents as described in the following sub-section.

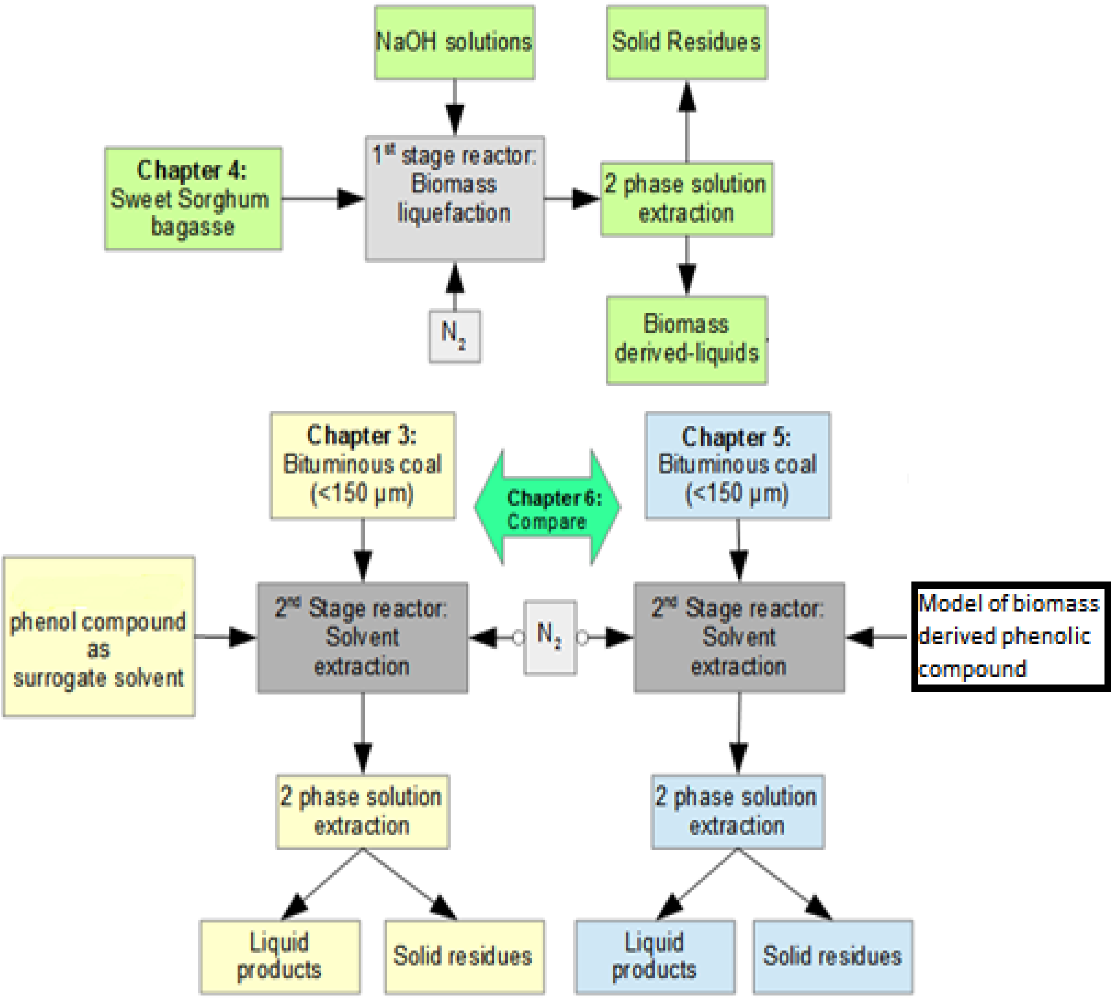


Figure 1.2. Outline of study

1.4.1 Chapter division

Chapter 1 (Introduction): This chapter contains the problem statement, hypothesis, aims, and objectives for the purpose of the current study. An outline of the study is given.

Chapter 2 (Literature Review): This chapter focuses on the available literature, research or publications relating to coal conversion processes. The information from literature pertaining to coal in general (background on coal properties), and the summary of different processes is provided. The chapter is further set to focus on previous studies done on solvent extraction of bituminous coal from other countries.

Chapter 3, **4** and **5**: Results and Discussions: These sections include three chapters in the form of three submitted or published article(s) or manuscripts. These chapters include results obtained from the experimental work.

These chapters describe the following:

Chapter 3 (Article 1): Effectivity of phenol during solvent extraction of a South African bituminous coal at mild conditions. The solvent extraction of a South African Waterberg bituminous coal with relatively low ash content, using phenol, was investigated and is presented in this paper (**Chapter 3**). In this study, an autoclave was used to conduct solvent extraction experiments using phenol as a solvent under mild conditions (without the use of catalyst or hydrogen gas). The physio-chemical properties of the solvent extraction products were investigated, and the results obtained at different temperatures were compared (300, 320, 340 and 360 °C). This was done in order to investigate the potential of phenol as a solvent to extract South African coal at mild temperatures for value-added liquid fuels and add to the general knowledge on the potential utilization of the Permian-aged South African bituminous coals.

Chapter 4 (Manuscript 1): Bio-oil production from sweet sorghum bagasse via liquefaction using alkaline solutions and identification of phenolic products. The bio-oil was produced after treating biomass with various concentrations of sodium hydroxide (NaOH) solutions (0.5, 1, 3 and 6 M) at different temperatures (260, 280, 300 and 320 °C) under inert gas conditions in an autoclave. The method of extraction of phenolic compounds from the bio-oil proceeded as adapted from literature. The resulted residues were characterized using SEM-EDS analysis to show the decreasing carbon content with an increase in the concentration of NaOH solutions. This investigation (**Chapter 4**) was aimed at identifying and quantifying the number of phenols produced using South African indigenous biomass with different concentrations of NaOH solutions. The influence of different concentrations of NaOH solutions on the yield of bio-oils, phenols, and residues was investigated and reported in this chapter.

Chapter 5 (Manuscript 2): Changes in the compositional and structural characteristics of coal during solvent extraction using a model biomass-derived phenolic compound mixture as a solvent. The methods applied in this section were the same as described in **Chapter 3.** The overall objective of this paper (**Chapter 5**) was to determine whether or not phenol can be substituted with a model biomass-derived phenolic mixture for coal extraction, in order to produce valuable products and fuels.

Chapter 6 (Conclusions and Recommendations): This chapter contains important conclusions pertaining to the experimental results, and provide recommendations drawn from this investigation. Possible future studies concerning research and development of solvent extraction of South African coals are listed.

Chapter References

1. BP, Statistical Review of World Energy, Excel workbook of historical data, 2014. https://www.eia.gov/beta/international/analysis.cfm?iso=ZAF (accessed 17.02.2016).
2. Jeffrey, L.S. J. South. Afr. Inst. **2005**, 105, 95–102.
3. EDF (Environmental Defense Fund). 2014. The world's carbon markets: A case study guide to emissions trading. https://www.edf.org/sites/default/files/South-Africa-Case-Study-March-2014.pdf (accessed 18.07.2017).
4. Robinson, K.K. Energies **2009**, 2, 976–1006.
5. Liu, Z.; Shi, S.; Li, Y. Chem. Eng. Sci. **2010**, 65, 12–17.
6. Fletcher, J.; Sun, Q.; Bajura, R.; Zhang, Y.; Ren, X. Coal to clean fuel-The Shenhua investment in direct coal liquefaction. In: 21st Annual International Pittsburgh Coal Conference, September 13–17, Osaka, Japan, 2004.
7. Nolan, P.; Shioman, A.; Rui, H. Eur. Manage. J. **2004**, 22, 150–164.
8. Zhao, L.; Gallagher, K. Energy Policy **2007**, 35, 6467–6477.
9. Total Petroleum and Other Liquids Production. 2014. U.S. Energy Information Administration. http://www.eia.gov/beta/international/rankings/#?prodact=53-1&cy=2014 (accessed 19.02.2016).
10. Oil & Gas Journal, Worldwide look at reserves and production. 2015. http://www.ogj.com/articles/print/volume-112/issue-1/drilling-production/worldwide-look-at-reserves-and-production.html (accessed 19.02.2016).
11. Global Trade Information Services, South African Revenue Service. https://www.eia.gov/beta/international/analysis.cfm?iso=ZAF (accessed 01.04.2015).
12. Burgess, C.E.; Schobert, H.H. Fuel Process. Technol. **2000**, 64, 57–72.
13. Breault, R.W. Energies **2010**, 3, 216–240.
14. Schobert, H.H. 2013. Chemistry of fossil fuels and biofuels. Cambridge University Press, Cambridge, New York, 2013, Chapter 22.
15. Van Dyk, J.C.; Keyser, M.J.; van Zyl, J.W. 2001. Suitability of feedstocks for the Sasol-Lurgi fixed bed dry bottom gasification process, GTC conference, San Francisco, USA, October 7-10, 2001.
16. Song, C.; Schobert, H.H.; Andrésen, J.M. Premium carbon products and organic chemicals from coal, IEA Clean Coal Centre: London, 2005, IEA CCC/98, 1–73.
17. Walker, S. Major coalfields of the world. IEA Coal Research, London, 2000, 131.
18. Cairncross, B.J. Afr. Earth Sci. **2001**, 33, 529–562.

19. Kruszewska, K.J. Int. J. Coal Geol. **2003**, 54, 79–94.
20. Kershaw, J.R.; Taylor, G.H. Technol. **1992**, 31, 127–168.
21. Faure, K.; Willis, J.P.; Dreyer, J.C. Int. J. Coal Geol. **1996**, 29, 147–186.
22. Prevost, X. M. SA coal reserves, after the act. Presented at the Fossil Fuel Foundation 10th Southern African Conference on Coal Science and Technology, Sandton, South Africa, November, 2004, 10-12.
23. Eberhard, A. 2011. The future of South African coal: Market, investment, and policy challenges. Working paper #100; Program on Energy and Sustainable Development: Stanford, 2011, pp 44.
24. Van Niekerk, D.; Pugmire, R.J.; Solum, M.S.; Mathews, J.P. Int. J. Coal Geol. **2008**, 76, 290–300
25. Van Niekerk, D.; Mathews, J.P. Fuel **2010**, 89, 73–82.
26. Van Niekerk, D.; Mitchell, G.D.; Mathews, J.P. Int. J. Coal Geol. **2010**, 81, 45–52.
27. Van Rensburg, E.J. Solvent extraction of South African coal using a low volatile, coal-derived solvent. M.Eng. dissertation at the North-West University, South Africa, 2007.
28. Makgato, M.H.; Moitsheki, L.J.; Shoko, L., Kgobane, B.L.; Morgan, D.L.; Focke, W.W. Fuel Process. Technol. **2009**, 90, 591–598.
29. Asbury, R.S. Ind. Eng. Chem. **1934**, 26, 1301–1306.
30. Parr, S.W.; Hadley, H.F. Fuel **1925**, 4, 31, 49.
31. Kiebler, M.W. 1945. The action of solvents on coal. In “Chemistry of Coal Utilization” (H. H. Lowry. Ed), Wiley and Sons, New York, volume 1: 677-760.
32. Dryden, I.G.C. Fuel **1950***,* 29, 197–207, 221–8.
33. Kröger, C. Erdöl u. Kohle **1956**, 9: 441–6, 516–20, 620–4, 839–43.
34. Stewart, J.J. Coal Extraction. Nova Science Publishers, Inc.: New York, 2011.
35. Speight, J.G. The chemistry and technology of coal, Third edition: Thermal reactivity. CRC Press, 2012, pp 391–422.
36. Kreulen, D. J. W. Fuel **1946***,* 25, 99–108.
37. Darlage, L.J.; Bailey, M.E. Fuel **1976**, 55, 205–210.
38. Illingworth, S.R. Fuel Sci. Pract. **1922**, 1, 213–219.
39. Asbury, R.S. Ind. Eng. Chem. **1936**, 28, 687–90.
40. Kiebler, M.W. Ind. Eng. Chem. **1940**, 32, 1389–1394.
41. Kawser, J.; Ani, F.N. J. Oil Palm Res. **2000***,* 12, 86–94.
42. IEA Clean Coal Center. Review of worldwide coal to liquids Research, D&D activities and the need for further initiatives within Europe, 2009.

Chapter 2

Literature Review

An overview of coal and biomass is presented in this chapter. This is followed by a review of the available coal conversion processes used to produce synthetic fuels and chemicals, with specific focus on the solvent extraction process, which is a method used for the separation of mixtures of compounds with specific solubility in organic solvents.

2.1 Coal

Coal can be found in deposits called seams that originated through the transformation of vegetation that has experienced chemical and physical changes through the coalification process.[1,2] Coal is defined as a sedimentary rock consisting of both organic (maceral) and inorganic (minerals) constituents. This type of rock can be classified as a biological fossil fuel, consisting primarily of carbon, hydrogen, and oxygen with lower amounts of nitrogen and sulphur.[2–4]

2.1.1 Composition

Coal is fundamentally composed of the fossilized remains of plant debris that underwent the coalification process, which consist of organic, mineral (inorganic) and microlithotypes as described below.

2.1.1.1 Organic constituents of coal

Coal compromises of organic materials called macerals, which were formed through chemical and physical changes of plant remains during the coalification process.[5,6] The term “maceral” is used to represent the different organic plant tissue from which coal was originally formed. Macerals have characteristic physical properties that can be observed under an optical microscope.[7,8] The different properties of macerals are summarized in the following sub-sections[9–12]:

2.1.1.1.1 Vitrinite macerals

Vitrinite is a relatively oxygen-rich maceral which formed from the cell wall material and the cell fillings of the woody tissue of plants (trunks, branches, twigs, roots, and leaf tissue). The structure is difficult to determine due to the extreme processes of vitrinization or gelification. This maceral possesses intermediate amounts of hydrogen and volatiles. In low-rank coals, this maceral is readily hydrogenated and liquefied (**Section 2.1.4**). The changes in carbon and volatile matter content with rank are directly related to the amount of light reflecting from the surface of the vitrinite (the higher the carbon content, the higher the reflectance). Vitrinite maceral’s density ranges between 1.27 and 1.80 g/m^3, and the reflectivity varies with the rank of coal.

2.1.1.1.2 Inertinite macerals

Inertinite represents a group of carbon-rich maceral found in bituminous coals derived from plant material that has been strongly altered and degraded in oxidizing conditions in the peat stage of a coal formation. Inertinite macerals are aromatic in structure and have the lowest hydrogen and volatile contents. During carbonization, inertinite macerals are relatively inert and are not preferred for hydrogenation and liquefaction processes (**Section 2.1.4**). Inertinite macerals have the highest reflecting group maceral found in bituminous coals, and their density varies between 1.35 and 1.70 g/cm^3.

2.1.1.1.3 Liptinite (exinite) macerals

Liptinite is a type of maceral which is hydrogen-rich and contains the lowest oxygen content. The liptinite maceral originates from pollen, spores, algae, and decayed leaf matter. It has an aliphatic-aromatic skeleton with aliphatic side chains and oxidizes more rapidly than inertinite and vitrinite. The liptinite maceral is extremely rich in peripheral groups and produces higher yields of volatile matter during carbonization than the other maceral groups. Due to its hydrogen content, this maceral is considered very suitable for the hydrogenation process (**Section 2.1.4**). As coal rank increases further (i.e. mid to high-rank bituminous range), this maceral rapidly increases in reflectance, to a point that it is no longer recognizable and cannot be distinguished from the vitrinite maceral. Liptinite maceral's density varies between 1.18 and 1.25 g/cm^3.

2.1.1.1.4 Microlithotypes (organic + inorganic components)

The organic and inorganic components of coal combine in various associations to form microscopic layers termed microlithotypes which, by definition, are greater than 50 µm in width and containing at least 5% of a maceral group.[11,13] The components may be composed of pure macerals or varying proportions of different macerals. The chemical properties of microlithotypes are very similar to those of the predominating macerals.[10,11]

2.1.1.2 Mineral matter of coal

Coal contains varying amounts of mineral matter (inorganic constituents). The types and concentrations of minerals are different in each coal seam. The minerals can occur as discrete flakes or grains in one of the following physical modes: (1) disseminated tiny inclusions within macerals; (2) layers or partings where fine-grained minerals predominate; (3) nodules, lenticular or spherical concretions; (4) fissures (cleat, fracture fillings and small void fillings); (5) rock fragments, megascopic masses of rock replacements of coal due to faulting, slumping, or related structures.[14,15]

2.1.2 Rank of coal

Coal in different coal seams is described by rank, which is a measure of the degree of coalification that the organic plant sediment has reached in its metamorphosis from peat to a near-graphite-like material.[11,16] It is not directly equated to the carbon content of coal or any other specific coal structure. However, the rank is specified from a knowledge of the proximate analysis and calorific value of coal.[16]

2.1.3 Structure of coal

One of the models describing the structure of coal, describe it as a large cross-linked macromolecular structure, and a complicated network structure of polynuclear aromatic clusters connected by strong bonds.[17–19] Van Niekerk[20] has reported development studies of computational modelling of two Permian-aged South African coal's (vitrinite-rich Waterberg and inertinite-rich Highveld coal) chemical structures. The vitrinite-rich coal model was found to consist of 18,572 atoms and 191 individual molecules, whilst the inertinite-rich coal consist of 14,242 atoms and 158 individual molecules.

2.1.4 Coal conversion procesesses

The conversion of coal into liquid fuels can be produced by the following processes, as discussed below:

2.1.4.1 Devolatilization or thermal degradation (pyrolysis)

The chemistry of the thermal (pyrolytic) decomposition of coal has been a subject for many studies over the past years.[21–27] The pyrolysis process, also known as devolatilization, is defined as the decomposition or thermal degradation of organic material in the absence of a reactive gas such as oxygen.[28–30] This process is considered to occur at temperatures higher than 300 °C in the presence of an inert atmosphere (i.e. nitrogen) to produce gas (i.e. CO_2, low-molecular-weight hydrocarbons with C_1-C_4 and up to C_8 or C_{10}), tar, and char or solid residue.[30] The terms pyrolysis, thermal decomposition, devolatilization, and carbonization are often used interchangeably in the literature due to the similarity of the char chemistry and volatile composition of the coal.[27,30] The term carbonization refers to the process which favours production of char or coke when coal is slowly heated (i.e. low heating rate) at temperatures higher than 500 °C.[25,30] It is important to note that coal pyrolysis is the basic or first step process of coking (carbonization), and the starting reaction of most thermochemical processes such as gasification, as described in **Section 2.1.4.2**.

According to Owen,[31] pyrolysis of coal is a complex process involving a large number of chemical reactions, and the process occurs with the production of gas, liquor (low-molecular-weight liquids), tar (high-molecular-weight liquids), and char (or semi-coke/coke). An increase in temperature during this process can alter the product distribution from the coal depending on the reaction conditions. It is proposed that as the coal particle temperature increases during pyrolysis, the bonds between aromatic clusters in the coal macromolecule break and create lower-molecular-weight fragments that are detached from the coal macromolecule; the larger fragments of this process are often (collectively) known as the metaplast.[30,32,33]

The reaction conditions (i.e. heating rate, particle size, temperature, residence time, and reactor configuration), rank and particle size of the coal are important factors in determining the product distribution, with a special focus on the liquid yield during coal pyrolysis. The yields of liquid products and tar are, to some extent, variable but are greatly dependent mostly on the temperature and rank of coal. The composition of the liquid products and tars from pyrolysis consists of saturated (straight- and branched chain) material, olefins, aromatics, and naphthenes (saturated hydrocarbon ring systems).[4,30] Table 2.1 depicts the influence of temperature on coal pyrolysis products between <350 °C and >1650 °C.

Table 2.1. Events that occur in the various temperature regions of coal pyrolysis (adapted from Speight[30])

Region	Temperature range (°C)	Reactions	Products
	< 350	Mainly evaporation	Water and volatile organics
Low temperature	400–750	Primary degradation	Gas, tar, and liquor
Medium temperature	750–900	Secondary reactions	Gas, tar, and liquor plus additional hydrogen
High temperature	900–1100	Secondary reactions	
Plasma	>1650		Acetylene; carbon black

According to Speight,[30] the pyrolysis behaviour of coal is dependent on experimental conditions and coal type or rank. The low-rank coal (i.e. sub-bituminous and lignite coal) produces relatively high levels of low-molecular-weight gases and very little tar yield during pyrolysis, and also do not exhibit much softening or swelling behavior.[30,34] This non-softening behavior may be due to early crosslinking reactions. In contrast, the high-rank coal (i.e. anthracites and low volatile bituminous coals) produces relatively low levels of both light gases and tar.[30,34] However, the pyrolysis process cannot be controlled so precisely as to obtain only liquids due to high yield of gas.[4]

2.1.4.2 Liquefaction processes

Liquefaction is the conversion of a solid substance into liquid fuels and chemicals. According to Mochida et al.,[35] the primary goal of coal liquefaction is to produce substitutes for petroleum distillate fuels with an atomic ratio (H/C) ranging between 1.8 and 2.5. This process is suited for countries with large reserves of coal and poor petroleum reserves.

2.1.4.2.1 Direct coal liquefaction (DCL)

Direct conversion of coal is also known as hydro-liquefaction due to the importance of hydrogen, and where the liquid yield is the dominant metric.[4,36,37] Two processes need to be distinguished from each other under this process,[38] which include; (1) single-stage direct liquefaction (a process which gives distillation through one reactor or reactor trains in series); and (2) two-stage direct coal liquefaction (a process designed to provide distillate products through two reactors or reactor trains in series). The first stage of a two-stage direct coal liquefaction is to solubilize the coal; this stage can be operated either without a catalyst or with only a low activity disposable catalyst. The resultant heavy liquid products are then hydro-treated in the second stage in the presence of a high activity catalyst to produce additional distillate. The DCL process has its technological root from Germany before the Second World War, invented by Friedrich Bergius in 1913.[4,35] This process was invented in order to fulfil an urgent demand for liquid transportation fuels before and during World War II in Germany, United Kingdom, France, and Japan. The Bergius process involved the use of high pressure at elevated temperatures of 450–500 °C on a low-rank coal (25–32 MPa), bituminous coal (≥ 70 MPa), and used an iron-based catalyst of poor activity.[4,39,40] The product mixture from the Bergius process was fractionated into light oils, middle distillates, and residuum (heavy oil), as shown in Figure 2.1.

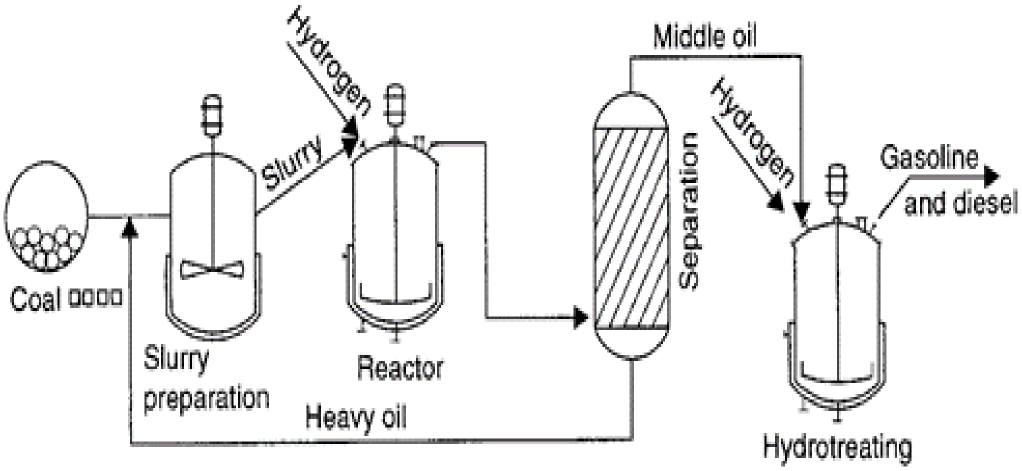


Figure 2.1. A schematic presentation of the Bergius process for direct liquefaction of coal (adapted from Schobert[4])

The middle distillates were the main product and converted coal into gasoline and diesel fuels, whilst the residue was recycled for making coal paste. The middle distillates refer to a general classification of refined petroleum products, which include heating oil, distillate fuel oil, jet aviation fuel, and kerosene.[3]

The reaction mechanism involved in the DCL is a complex sequence of events that are not yet known entirely.[41–43] One of many challenges includes the breakdown of the macromolecule of coal into radicals or resultant fragments and addition of adequate amounts of hydrogen (either as molecular hydrogen and/or via the agency of a hydrogen donor) required to stabilize the radicals into producing liquid products with high hydrogen to carbon (H/C >0.8) ratios.[4,35,44] The DCL process involves the addition of hydrogen to unsaturated hydrocarbons, followed by rearrangement, cracking of bulky molecules, and removal of heteroatoms (i.e. sulphur and nitrogen) to produce lighter and cleaner transportation fuels (gasoline, diesel, and jet), as well as specialty chemicals and carbon-based products.[45] However, insufficient hydrogenation of the resultant radicals or fragments would result in retrogressive reactions between the free radical fragments, which may lead to the formation of solid coke or semi-coke, a group of products chemically stable more so than coal.[43,46] Figure 2.2 shows the general reaction model proposed for the DCL process.

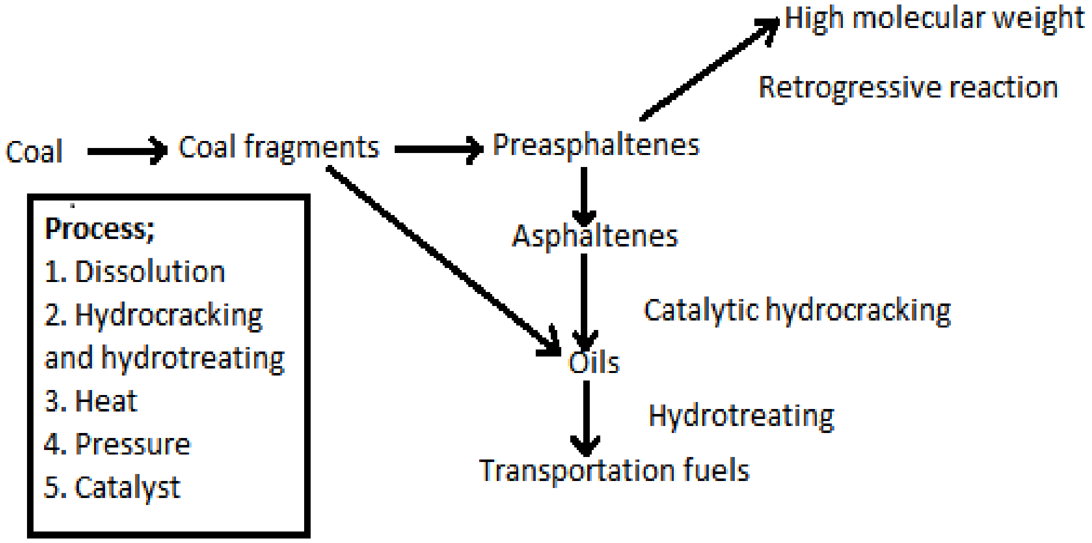


Figure 2.2. General chemistry of DCL process (Adapted from Speight[30])

The yield of the liquid products produced through DCL is influenced by various factors; which include temperature (>400 °C), hydrogen-rich donor solvent (i.e. tetralin), coal type or rank, appropriate catalyst, pressure, and atmosphere.[47,48] Bituminous coals have been considered to be an ideal feedstock for direct liquefaction due to the high yield of liquid products.[49] However, research has shown that lower rank coals (particularly brown coals) were more reactive and required a lower hydrogen pressure for liquid production than bituminous coals.[4,50,51] The DCL process may be an important utilization method for low-rank coals, especially for countries abundant in low-rank coal resources and low petroleum reserves.[52] However, the petrographic composition of coals (whatever the rank) may be an important variable in determining the yield of liquid products from liquefaction.[30,53]

2.1.4.2.2 Indirect coal liquefaction (ICL)

Coal liquefaction technologies were invented in the early 20th century in Germany as mentioned in the previous section, by Bergius (which led to a Nobel Prize in chemistry) in 1931, and by Franz Fischer and Hans Tröpsch in 1923 (a process that was termed as Fischer-Tröpsch synthesis or FTS).[39,54] The ICL process refers to coal that is not converted directly into liquid products. It is realized through a gasification process; (1) which entails conversion of coal to produce gaseous fuel (syngas or synthesis gas), (2) which is catalytically converted to produce liquid fuels and chemicals through Fischer-Tröpsch (FT) synthesis.[3,55–58] The gasification of coal dates back to the 1790s and which later advanced in the 1930s and continuing thereafter, the interest in large-scale gasification shifted to the production of synthesis gas to make substitute natural gas or synthetic liquid fuels.[4] The term coal gasification refers to any process in which coal reacts with a gasifying agent or an oxidizer at high temperatures (>700 °C) to produce synthesis gas and other forms of hydrocarbons. This process occurs inside a reactor vessel containing a biological fossil fuel in the presence of a gasifying agent such as oxygen, carbon dioxide, steam, air, and/or a mixture of two or more, or all of the above mentioned gases under controlled conditions.[3,19,55–57,59] This technology can be used in the following energy systems of potential importance[3]:

1. Production of gaseous fuel for utilization in electricity generation;
2. Production of gaseous fuel for use as chemical feedstock for liquid transport fuel and chemicals;
3. Production of hydrogen gas for fuel cell application;
4. Manufacturing of synthetic or substitute natural gas for utilization as pipeline gas supplies; and
5. Generation of gaseous fuel (low or medium Btu) for industrial purposes.

The fundamentals of the gasification process can be simplified by assuming that coal can be represented by carbon.[4] This representation is done to understand the chemical kinetics that can occur at an appreciable rate until high temperatures are reached inside a reactor vessel under different reaction conditions. At least five reactions are likely to occur during gasification, usually represented as the reactions of carbon with small gaseous molecules as follows[4]:

Combustion: $C + O_2 \leftrightarrow CO_2$ (ΔH: -395 MJ) Reaction (2.1)

Boudouard reaction: $C + CO_2 \leftrightarrow 2\ CO$ (ΔH: 168 MJ) Reaction (2.2)

Carbon-steam reaction: $C + H_2O \leftrightarrow CO + H_2$ (ΔH: 136 MJ) Reaction (2.3)

Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ (ΔH: -32 MJ) Reaction (2.4)

Hydrogenation: $C + 2\,H_2 \leftrightarrow CH_4$ (ΔH: -92 MJ) Reaction (2.5)

2.1.4.3 Solvent extraction

Research and development of an alternative approach for the conversion of coal, besides indirect coal liquefaction and others, to obtain clean liquid transportation fuels and chemical feedstocks for South Africa's fuel market needs to be investigated. Solvent extraction of coal is ideal and known to be effective in producing an ash-free liquid product.[60] The conversion of coal realized through solvent extraction offers an option to convert coal into various types of liquid compounds and hydrocarbons under mild temperatures (<400 °C).[30,61–64] These types of liquid compounds can be used to augment the petroleum supply. The solvent extraction process has always been one of the most commonly used techniques for studying the composition of coal, and it dates back to the 1860s.[65–67] However, the classical period of coal extraction research was between 1910 and 1935, where substantial yields of extracts were obtained.[33,68] Figure 2.3 shows a coal-to-liquids process where coal molecules are dissolved in an organic solvent. However, it should be noted that solvent extraction of coal should not be confused with the principles behind coal cleaning, for example; demineralization of coal through inorganic solvents such as hydrochloric acid (HCl) and hydro-furan (shortened in this thesis as HF).[30]

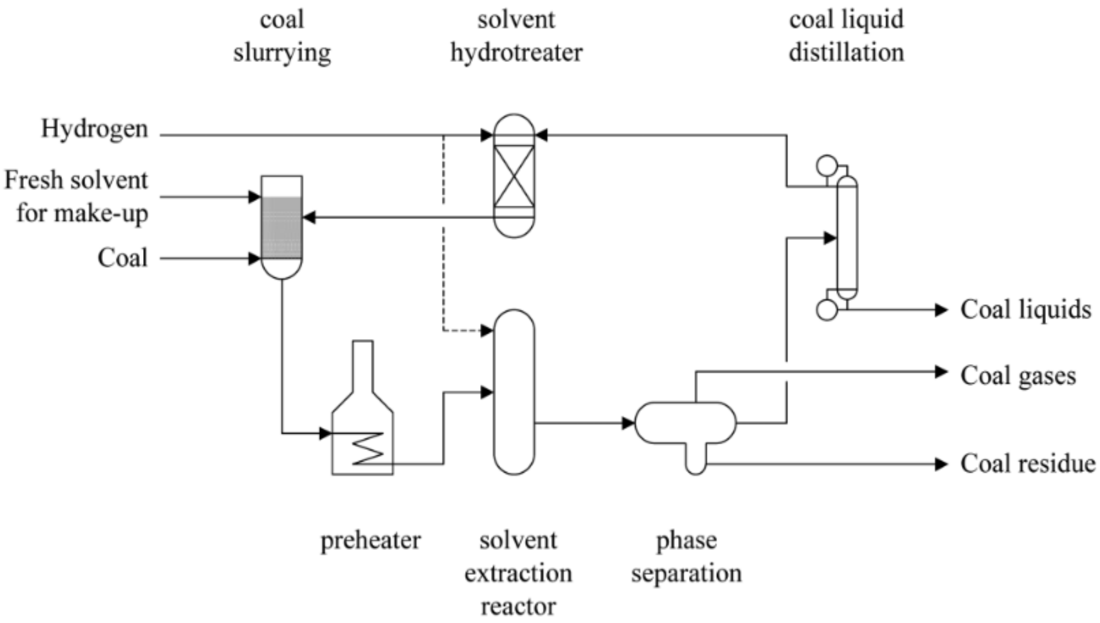


Figure 2.3. The scheme of a generic coal solvent extraction process (Adapted from Hernandez et al.[69])

Solvent extraction occurs through heating coal in the presence of an organic solvent, and usually, in a non-reactive atmosphere. Unlike DCL, it is not common to use a catalyst or a hydrogen atmosphere. The extraction temperatures can vary between 150 and 400 °C, depending on the boiling point of the solvent. If the extraction temperature is high enough to initiate thermal fragmentation of the coal structure, radicals could be stabilized by hydrogen supplied by the solvent or internally from the coal itself.[4,70–72] On a laboratory scale, the extract is often separated into oils, asphaltenes, and pre-asphaltenes as presented in Table 2.2.[73,74] However, the material isolated is not well defined and may not be the same as that isolated in other laboratories.[30,75] The extract can be fractionated to produce a series of fractions based on their solubility or insolubility in different solvents.

Table 2.2. Suggested nomenclature for solvent extraction of coal-derived products (Adapted from Schweighardt and Thames[73])

Separation class name	Solvent type used
Oils (soluble)	pentane
Asphaltenes (soluble)	benzene
benzene insolubles	
Preasphaltenes (soluble)	THF (tetrahydrofuran)
THF insolubles-residue	

The solvent extraction process was divided into four different steps by Jostes and Siebert[76] : (1) the penetration of the solvent into the coal particles; (2) the loosening up of the molecular bindings of the coal substance; (3) the depolymerization of larger molecular aggregations; and (4) the diffusion of bitumens from the coal into the solvent. The role of the solvent is to relax the coal matrix and dissolve soluble molecules from the coal into the bulk solvent phase.[77,78] When a solvent is introduced, swelling occurs in the coal structure due to the disruption of the non-covalent interactions, such as H-bonds in the case of polar solvents and dispersion forces in the case of non-polar solvents. The degree of coal extraction with solvents can be related to the magnitude of swelling resulting from the disruption of non-covalent bonds, and formation of coal-solvent interactions from weaker coal-coal interactions for improvement in extraction yields or selectivity.[79–82] Coal partially dissolves in a number of organic solvents, and dissolution is never complete, and thus, usually requires heating for the thermal degradation or high-temperature solvent extraction reaction to occur. The solvent action on coal is quite complex and requires investigation into its nature as it has been disputed over the years if it is a physical or chemical process.

In general terms, solvents for coal extraction can be grouped into categories based on their effect on coal as described below[4,19,30,83–87] :

I. **Non-specific solvents** extract a small amount (<10 %) of the coal, preferably at low temperatures (<100 °C). The extract is considered to arise from the resins and waxes occluded in the coal matrix, and not typical of the constitution of the coal as a whole. These solvents are low boiling liquids such as methanol, ethanol, benzene, hexane, carbon tetrachloride, acetone, and ether.

II. **Specific solvents** extract between 20% and 40% of the parent coal, preferably at temperatures below 200 °C. The nature of the extract and the parent coal are considered to be similar. Therefore, these solvents are considered to be non-selective in their action on the coal. The most effective solvents are nucleophilic due to the presence of a lone pair of electrons on the nitrogen atom and have high internal pressure. Examples of these types of solvents include pyridine, ethylenediamine, ethanolamine, N-methylpyrrolidone, phenol, quinoline, 1,2-diaminoethane, dimethylformide, and dimethylacetamide.

III. **Degrading or extractive disintegration solvents** extract up to 90% of the coal at high temperatures (>200 °C). The mechanism of solvent action is through the thermal degradation of coal into smaller fragments. After extraction, the solvent can be nearly completely recovered without a change in its chemical form. Examples of these types of solvents include phenanthrene, diphenyl, phenanthridine, and tar oil fractions. However, tar oil fractions do not exactly conform to the definition of degrading solvents since it is not always exact that they are unchanged when recovered from the solution.

IV. **Reactive or extractive chemical disintegration solvents** interact with the coal chemically and are also used in the direct coal liquefaction process due to the importance of hydrogen (**Section 2.1.4.2.1**). The solvents are mostly hydrogen donors; their chemical composition is substantially affected during the process (i.e. actively participate chemically in bond breakage). The smaller coal fragments formed by thermal disintegration are stabilized by hydrogen (donated by the solvent). The temperature for this process is normally high (>300 °C). Hydrogenative extraction plays an important part in the Pott-Broche process in which phenols and cresols are used as solvent media and tetralin as a hydrogen vehicle. Hydroaromatic compounds are known to be good hydrogen-donor solvents, which are converted to their corresponding aromatic counterparts during extraction (i.e. tetralin is converted to naphthalene upon donation of four hydrogen atoms). It should be noted that there can be a clear operational or mechanistic distinction between extractive chemical disintegration and extractive disintegration processes.[88]

V. **Highly-reactive solvents** are more associated with industrial organic chemistry than in coal technology. Also known as super solvents, typically dipolar aprotic solvents, and can dissolve many substances, both polar and non-polar

Furthermore, different solvents can produce different extract yields from the same coal, and higher extraction yields can be expected from mixed solvents (i.e. alcohol-benzene).[4,19] However, other factors such as the influence of coal rank, and extraction conditions contribute towards higher extraction yields. Subsequent subsections discuss these factors with regard to the solvent extraction process.

2.1.4.3.1 Influence of petrography and coal rank on solvent selection

It is reported that there exists a correlation between the coal dissolution in a solvent and coal petrological properties. Thus, it is important to understand the influence of maceral composition during the solvent extraction process.[89] Vitrinites and exinites represent the most extractable portions of the coal, whilst inertinites (i.e. fusinites) tend to dissolve to a much lesser extent.[4,30,90] The success of solvent extraction depends on the dissolution of reactive coal macerals, and coals which exhibit thermoplastic properties such as coking bituminous coals.[91] The stability of the metaplast generated by the coking coals during softening and resolidification, which is emulated in their plastic range, is responsible for the quantity and quality of the extract produced.[88] It was reported that extracting prime coking coals leaves a residue devoid of plastic behavior.[66,92,93] Therefore, the extract must contain the “coking principle”. During the 1930s more investigators came to support the theory that coal extracts are colloidal systems and, thus, that coal itself must be regarded as a solid colloid.[33]

The rank of coal has a considerable influence on the nature and yield of extract produced by solvent extraction.[75,94,95] For example, the solubility of coal in solvents decreases rapidly as the carbon content of the coal increases from 85% up to 89% (daf, dry-ash-free-basis) and is negligible for anthracene (92%-93% w/w carbon). This phenomenon is applicable to all temperatures and types of solvents.[30] Figure 2.4 shows a well-established relationship between the coal rank and the yields of material extractable from coal using specific solvents.

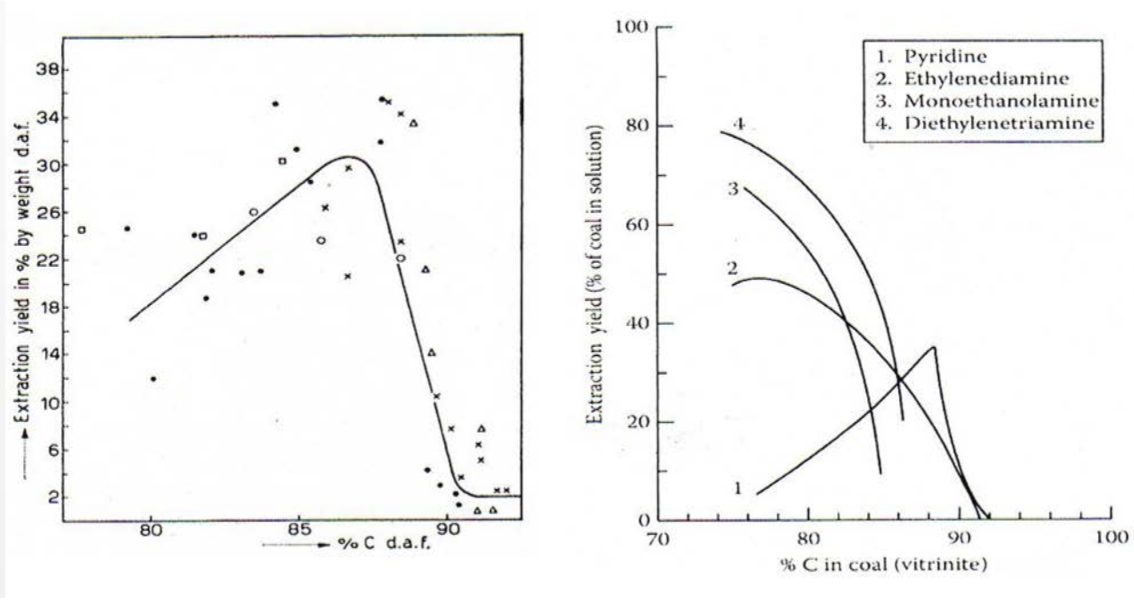


Figure 2.4. Extraction yield in solvent vs coal rank: adapted (a) from Van Krevelen[33]; (b) from Van Krevelen[96]

2.1.4.3.2 Influence of extraction conditions on solvent extraction

The efficiency to extract more out of coal with the use of organic solvents is not solely dependent on petrography or rank of coal, but also on reaction conditions; such as temperature, time, particle size, solvent-to-coal ratio, catalyst(s), pressure and atmosphere.[75,79,97–103] From some of these studies, the extraction yield increases when the particle size of the treated coal is reduced, whilst the solvent-to-coal ratio is increased so that it provides adequate volume for extractable materials. The influence of particle size may be explained by the increased surface of the coal, which facilitates the removal of the compounds with high-molecular-weight compromising the extract.[104] The high molecular-weight constituents of coal are much more difficult to define than the low-molecular-weight constituents insofar as they (1) are difficult, if not possible, to extract with solvents and (2) cannot be “distilled,” either individually or as various compound classes, from coal without the onset of thermal decomposition to low-molecular-weight fragments or, as is often the case, to a carbonaceous residue.[105]

Dryden[98] examined the effect of time on the yield of extract, using bituminous coals of various ranks and primary aliphatic amines as solvents. It was found that the time effect differed according to whether (1) the coal was shaken inside a reactor/autoclave with the solvent at room temperature, or (2) it was extracted near the boiling point of the solvent. The use of high inert gas pressure is beneficial as it keeps the solvent and products in the liquid phase and also delays the evolution of low boiling fractions, and thus, allowing their secondary cracking.[19,93] However, economical consideration dictates the use of low gas pressure. Thus, the use of Friedel-Crafts catalysts was introduced in the 1960s by Herédy and co-workers.[100,106–108]

The yield of the extract was found to increase with time, over the period studied, but no attempt was made to study the data obtained analytically except to point out that the extraction curve was not parabolic.[75] It is known that the initial extraction is very rapid since it is possible that a process of a true physical solution may be accompanied by slow chemical decomposition.[109] However, longer extraction time is sufficient to ensure that the greater part of the dispersible material is extracted. Figure 2.5 shows the influence of extraction time on the extraction yield.

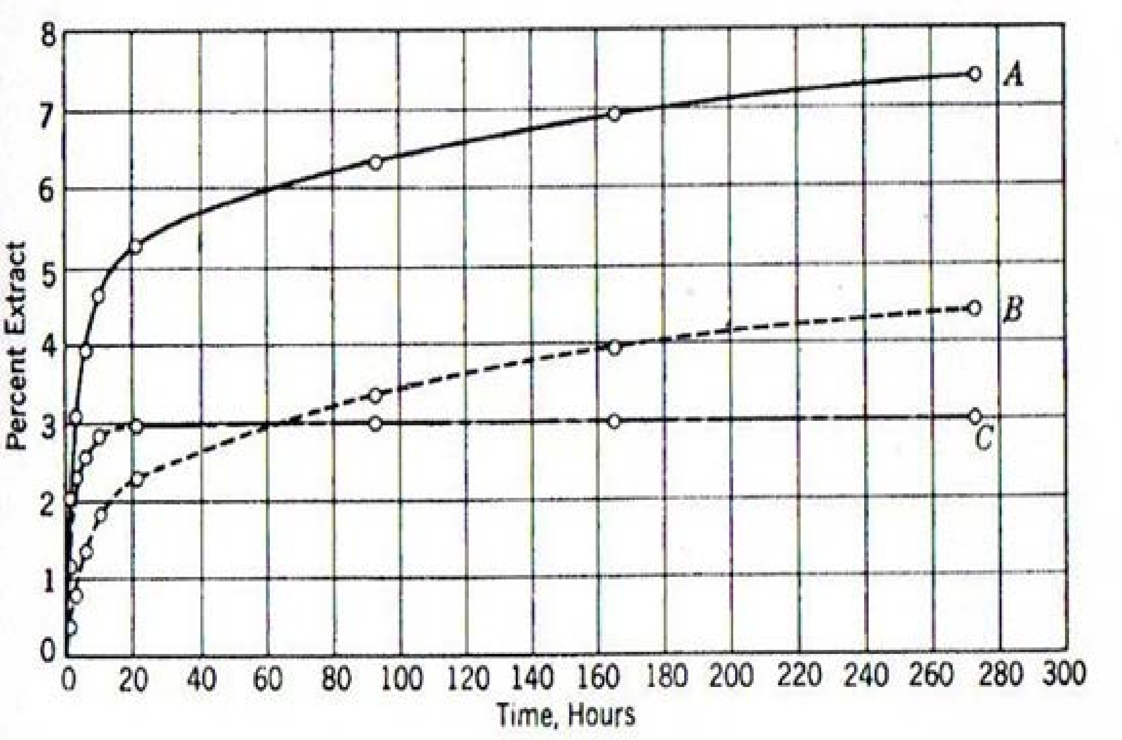


Figure 2.5. Effect of extraction time on yield and composition of extract (adapted from Peters and Cremer[110]): A. Total extract. B. Pentane-insoluble part of extract. C. Pentane-soluble part of extract

As reported by numerous investigators, the effect of temperature is most significant for benzene-type solvents (i.e. above the normal boiling point) and increases the yield of soluble products from the coal.[75,97–99] The temperature is beneficial for rapturing the linkages between aromatic clusters in the macromolecular structure of coal into radical fragments at an elevated temperature. Therefore, it is one of the most predominant factors that affect radical formation, the subsequent free radical reactions and enhance the action of the solvent or its properties, above their critical temperature.[30,48] For instance, at temperatures below those normally required for the thermal decomposition of coal, the yields of extract vary directly with extraction temperature. This effect is usually most pronounced with the non-specific solvents, but it has been noted that ethylenediamine used as solvent can produce from bituminous coal, almost three times as much extract at its boiling point (115 °C) than at room temperature, and also enhances the effect of extraction with other solvents (i.e. N-methyl-2-pyrrolidone).[111] In a series of the primary aliphatic amines the limiting yield, reached in a period of days, has been found to be independent of the method of extraction and depends, to the first order of approximation on the temperature of extraction rather than on the particular amine used.[98] The use of solvents at temperatures above their critical temperatures or boiling points can lead to enhanced yields of extracts due to changes in the solvent properties. Even non-specific solvents (i.e. hydrocarbons) can give yields of extract that are ca. 20% w/w daf.[112–114]

2.1.4.3.3 Influence of solvent type on solvent extraction

The action of a solvent on coal extraction offers a method of treatment (a mild form of chemical conversion) whereby the coal structure may be simplified before a study of its composition.[92,96,97] An effective solvent for coal dissolution must be able to swell or solubilize the coal, penetrate into the macromolecular structure of the coal, separate the organic constituents from inorganics and disperse coal molecules in the solvent to form a low-stability colloidal suspension.[75,115–118] The physical properties of solvents most usually considered are surface tension[119] and internal pressure.[75,120] The extractive capabilities of various solvents have been correlated, amongst other phenomena,[121] with the internal pressure (P_i) of the solvent through the following equation:

$$P_i = (dH_v - RT)/(\frac{M}{r}) \qquad \text{Equation (2.1)}$$

where dH_v is the latent heat of vaporization, R is the gas constant, inconsistent units, T is the temperature (absolute), M is the molecular weight and r is the density. The higher the internal pressure, the greater the solvent action on coal.[30] The relation of extraction yield to an internal pressure at elevated temperatures is approximately linear.[109]

Furthermore, solvents can be classified into donor and non-donor solvents.[48] Typical examples of donor solvents include tetralin, tetrahydrofluoranthene (4HFL), dihydroanthracene (2Han), and common non-donor solvents include decalin, pyrene (PY), fluoranthene (FL), and anthracene (An). Notable among the solvents that have been applied to the solvent extraction of coal include, in increasing effectiveness; naphthalene, tetralin, methyl aniline, aniline, phenol-toluene mixture, pyridine, para-cresol, low boiling tar distillate, ortho-cresol, and phenol.[30,122] However, tetralin and other cycloalkanes are somewhat unusual in that they are capable of transferring hydrogen (group IV, reactive solvents) to the coal or coal fragments during the extraction process, and provide hydrogenation.[123] Some of the solvent pairs are known to enhance the solvent power on the extract far more than the sole use of a single solvent system. The best of such a combination is a mixture of naphthalene, tetralin, and tar phenols as solvents as shown in Figure 2.6. The mechanism of the synergistic effect due to solvent pairing was explained by the increase in the penetration of solvents into coals by coal swelling.[124]

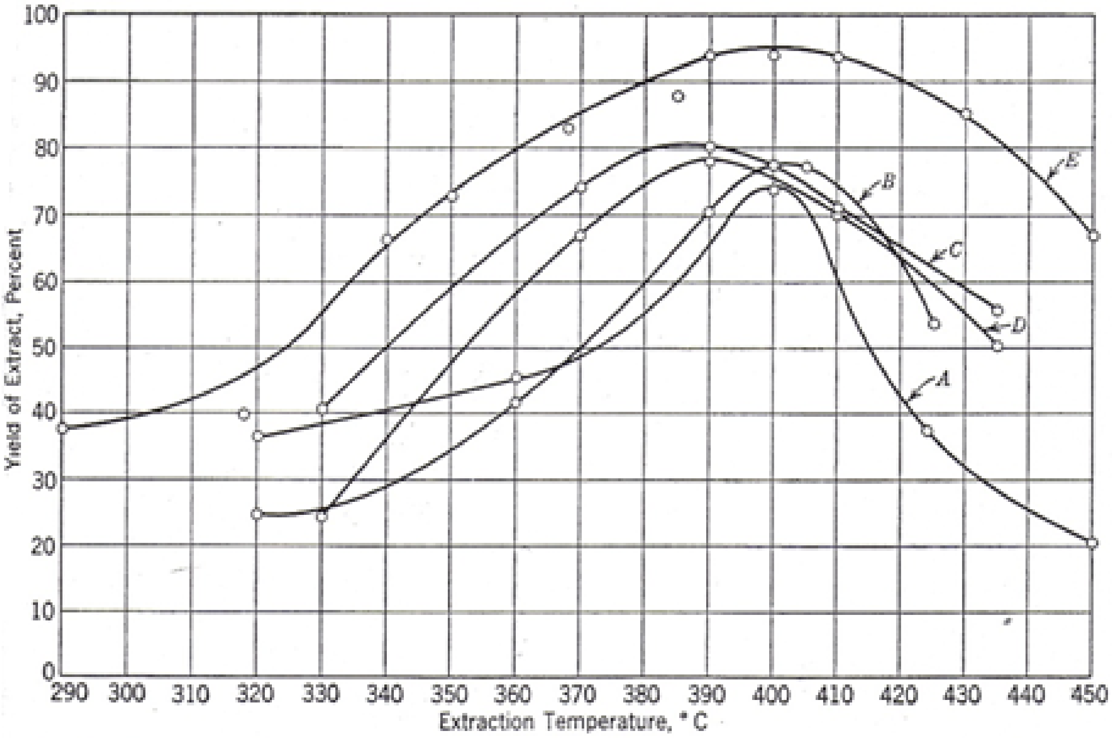


Figure 2.6. Influence of extraction temperature on yield of extract with a mixture of naphthalene, tetralin, and tar phenols as solvents (adapted from Pott et al.[125,126]): A. High-volatile coal 1; B. High-volatile coal 2; C. High-volatile coal 3; D. High-volatile coal 4; E. Brown coal

At higher temperatures (≥ 300 °C) compounds such as phenol, 2-naphthol, anthracene, and phenanthrene are considered to be effective solvents.[4,101] This temperature range also marks the onset of active thermal decomposition of some coals. According to Schobert,[4] an issue at this onset temperature is whether the solvent is dissolving the coal itself, is solubilizing molecular fragments produced by the thermally induced breakdown of the coal structure, or is chemically participating in decomposing the coal structure (the process of solvolysis).

2.1.4.3.4 Depolymerization or chemical decomposition of coal during solvent extraction

According to earlier literature,[76,127–130] it was pointed out that the extraction process involves not only a physical solution of material but also a chemical decomposition or depolymerization of the coal substance. In a true sense, coal is not a polymer, and thus the word depolymerization must be used with caution, and in this context, the term refers to the conversion of coal macromolecule to lower-molecular-weight products.[30] Laboratory work on the extraction of coal by various organic solvents indicates that depolymerization, followed by a colloidal solution, occurs when an appreciable fraction of the coal is dissolved by an organic liquid (i.e. phenol) with a high boiling point, medium dipole, and medium dielectric constant.

Phenols are known to penetrate easily into the micropores of the coal surface because of their affinity to oxygen-containing structures and their promotion of the swelling of coal particles resulting in their fast dissolution.[100] The depolymerization of coal using an organic solvent such as phenol, is a method which, it is claimed, solubilizes coal by cleaving methylene bridges in the coal. Studies with model compounds suggest that the effect of phenol is to facilitate cleavage of carbon-oxygen and carbon-nitrogen bonds.[131,132] Furthermore, the methylene chains joining aromatic groups can be cleaved at the ring and the "free" alkyl group and then alkylate another aromatic substrate[101,133,134]:

$$Ar-(CH_2)_n-Ar' + C_6H_5OH = ArH + HOC_6H_4-(CH_2)_n-Ar \qquad \text{Reaction (2.6)}$$

$$HOC_6H_4-(CH_2)_n-Ar' + C_6H_5OH = HOC_6H_4-(CH_2)_n-C_6H_5OH \qquad \text{Reaction (2.7)}$$

However, there are claims that this particular reaction(s) does not produce the anticipated low-molecular-weight materials as the major products. In addition, the other issue is that depolymerization is reputed to occur when the coal is treated with an iron-based catalyst in the presence of hydrogen.[100,135]

The solvent extraction process is usually enhanced by temperature and with an effective solvent. In non-hydrogenative conditions, it is fairly well known that the most effective solvents for coal at temperatures around 350 °C include aromatic hydrocarbons and their hydroxylated derivatives.[136] Likely, such compounds interact with the coal to facilitate depolymerization and possibly help disperse coal fragments into colloidal suspension as well as dissolving molecular species into a true solution. In this respect, phenol and related compounds differ in their behavior from so-called nonspecific solvents such as benzene or diethyl ether. It is probable that, despite the absence of added catalysts and hydrogen gas, hydrogenation occurs to some extent by transfer of hydrogen atoms from the coal to the solute.[4]

2.1.4.3.5 Summary of previous studies on extraction of bituminous coal

Coal extraction using phenol as a solvent has been reported in the past by a number of investigators as outlined by Kiebler,[75] Stopes and Wheeler,[137] Bakes,[138] and others. In the past, a Soxhlet method was found to be ideal as it is performed at temperatures close to the boiling point of the solvent.[19] However, in some cases, decomposition or oxidation was found to occur based on the recovery of the organic material.

Frazer and Hoffman[139] investigated the effect of various reagents and organic solvents on coal and found that pyridine, aniline, and phenol removed the largest amount of soluble material (extract). A non-coking Illinois coal from Franklin County was used in the solvent extraction. The maximum amount extracted from this coal was 10.87% (calculated on moisture and ash free basis) at about 140 °C. However, the ash content of the extract was abnormally high with the value of 2.16% after distillation of phenol, indicative of oxidation reactions that may have occurred.

In a similar study**,** Parr and Hadley[122] investigated various solvents including phenol in order to separate in unaltered form the fundamental substances of which coal is composed, and also to study its characteristic properties in detail. It was found that the average amount of material extracted from Pocahontas coal was 1.8%. The results varied in the case of Illinois coals ranging from 22% to 39% (coals were reported on an ash and moisture free basis). The amounts of ash in these coals on a dry basis varied between 3.30% and 13.54%. Their preliminary study showed that phenol at >100 °C dissolves certain constituents of coking bituminous coals in their natural state. Furthermore, they concluded that phenol was best suited as an extractive agent due to the larger amount of material extracted from the coal compared to other solvents. In addition, their results showed that the extraction of coal also leaves a residue which has less or none coking tendencies, as the coking constituent of the coal is in the extract. Both the extract and residue were then oxidized. It was found that the extract contained more volatile matter than the residue, but both had the same ultimate analysis results.

Asbury[128] investigated the action of three aromatic solvents on a Pittsburgh seam coal from the Edenborn Mine. The action of heat on coal with solvents has been shown to be the mildest form of pyrolysis. With aniline at 225 °C, tetralin between 250 °C and 400 °C, and phenol at 250 °C and 300°C. The Soxhlet extraction of coal yielding 47%, 85%, and 67% respectively, were obtained with these solvents. Their results showed that the greatest solvent action was observed for tetralin and phenol; since greater action indicates greater dissociating power. Therefore, it was suggested that increased extract yields from these two solvents result from the depolymerization of the coal structure. Kiebler[140] investigated extraction on this coal type extensively with regard to the importance of the nature of various organic solvents in determining the yield between 150 °C and 300 °C. The extraction yield at the following temperatures of 150 °C, 200 °C and 300 °C using phenol as a solvent were 21.0%, 32.1%, and 39.7% respectively. At temperatures between 150 °C and 300 °C, it was observed that the effectiveness of a solvent is, as a first approximation, directly proportional to its internal pressure. The amount of ether insoluble material in the extract, which is related to the degree of thermal depolymerization, shows a similar trend with internal pressure.

Orchin and Storch[141] investigated solvation and hydrogenation of coal at 400 °C with a variety of solvents that suggest a correlation between the degree of coal liquefaction and the chemical structure of the solvent. The authors observed that high boiling aromatic solvents (i.e. naphthalene) liquefy 20–30% of the coal, hydroaromatic solvent (i.e. tetralin) liquefies about 50% of the coal, and hydroaromatic compounds containing a phenolic group (i.e. o-cyclohexylphenol) liquefy more than 80% of the coal. The effectiveness of these solvents in producing coal liquefaction may be due to the hydrogenolysis of some peculiarly susceptible linkages in the coal structure, resulting in the good dispersion of the hydrogen-bonded coal fragments into the solution. In addition, thermal treatment alone does not break these bonds to produce a liquid material; however, if coal is made to consume about 1 to 2% hydrogen, a completely liquid material can be obtained. Overall, solvents containing a hydroxyl group attached to an aromatic ring are recommended for best results. The combination of catalysts (e.g. stannous sulfide and ammonium chloride) with o-cyclohexylphenol as a vehicle is somehow important to orient the hydrogen attack, in order to achieve good results.

The depolymerization of volatile bituminous coal by treatment with phenol-boron trifluoride (Friedel-Crafts catalysts) at 100 °C has previously been reported in detail by Herédy and his collaborators.[100,106–108] The depolymerization of the coal was interpreted as an “aromatic interchange” reaction, involving cleavage of aliphatic-aromatic carbon-carbon linkages and exchange of the aromatic structures with phenol. Imuta and Ouchi[142] reported that the depolymerization reaction may be the most effective and promising methods for investigating the macromolecular structure of coal because it is considered as a mild reaction; whereby the unit of macromolecular structure of coal can be retained without severe degradation. According to Kamiya et al.,[143] phenol may readily solubilize coal fragments; leading to the solvation of oxygen-containing structures among coal fragments by hydrogen bonding with phenol. This observation may result in good dispersion (due to easy penetration into the micro-pores of the coal surface) and dissolution in the solution (resulting from promotion of the swelling of the coal particles). However, the most important role of phenol during depolymerization reactions may be its participation in the scission reaction of ether linkages.

Ouchi and his collaborators studied other catalysts and observed that strong organic acids (i.e. p-toluene sulphonic acid, PTS) and some Friedel-Crafts catalysts were very effective for the depolymerization reaction.[144,145] However, PTS catalysts were found to be better than boron trifluoride because they can be used at higher temperatures up to the boiling point of phenol, so that the reaction can be completed in a shorter period. Extensive depolymerization was observed from their study, and the solubility in pyridine and benzene-ethanol substantially increased, using PTS as a catalyst. However, a study by Larsen and Lee[146] have shown that the efficient “depolymerization” of bituminous coals in hot phenol containing PTS failed to occur or depolymerized coals to a very small extent and that the acid was destroyed during the reaction.

Larsen et al.[147] investigated internal rearrangement of hydrogen during heating of coals (Bruceton and Wyodak) with phenol at 425 °C. It is well reported in the literature that coals can be a good source for hydrogen supply.[148,149] Coals can be solubilized by heating in the presence of the proper solvents with or without a catalyst(s). The process surely involves breaking and rearranging of bonds, and transfer of hydrogen from one place to another within the coal structure.[147] It was found that the hydrogen shuttle in Wyodak coal has a different temperature dependence than does the depolymerization, as Bruceton coal was more easily depolymerized to give soluble products with phenol. King and Stock[131] reported on phenolic compounds with hydrogen donor solvents (i.e. tetralin-d_{12}) during coal dissolution. Phenolic compounds were found to enhance thermal coal dissolution reactions through their influences on the rates of the homolytic cleavage of carbon-oxygen and carbon-nitrogen bonds.[131,132,150,151]

2.1.4.3.6 Importance of solvent extraction

Currently, the main commercial scale operation for coal to liquid fuels in South Africa is via indirect coal conversion.[43,152] However, this process was mainly designed for inertinite-rich coals and is less suited for vitrinite coals such as the Waterberg coal due to the high volatiles and swelling nature of this coal.[153] Therefore, an alternative process needs to be explored in order to overcome this shortcoming. Solvent extraction was developed to produce essentially ash-free coal that could be used as a fuel for turbines, and thereby reducing sulfur emissions.[4,154] The advantage of solvent extraction is that the technology can be integrated into current existing refineries; whereby the remaining coal residues can be used in a thermal conversion process.[20] Thus, it can lead to the development of clean coal technologies and lessen dependency on crude oil for the production of fuels, which are needed for economic stability and growth.[30] For example, the Shenhua DCL project in China is a commercial-scale demonstration project that is the first in the world to implement modern DCL technology for the production of synthetic fuels, and promote the country's capability on research and development of a coal liquefaction process.[43]

2.2 Biomass

Biomass is a sustainable and renewable energy resource that comes from organic materials (i.e. wood, garbage, agricultural and forestry wastes & etc.). This energy source can be used to produce electricity and can be burned as a fuel or converted to liquid biofuels or biogas.[155] Even in the early 21st century, traditional biomass still accounts for 7% of the total global energy demand, amounting to 765 million tonnes of oil equivalents (Mtoe) in 2002, and this is projected to increase to 907 Mtoe by 2030.[156] The chemical composition of biomass is very different from that of coal, oil shales, etc.[29]

Coal can be regarded as a fossilized biomass that had undergone a coalification process (**Section 2.1**).

2.2.1 Composition

Biomass consists of organic and inorganic constituents. The composition of biomass varies among species and is also depend on its environmental conditions.[157]

2.2.1.1 Organic constituents in biomass

The organic-forming elements in biomass include carbon, hydrogen, nitrogen oxygen and sulphur. Biomass consists of high moisture, carbohydrates, alkali, ash and fibrous structures which include cellulose, hemicellulose, and lignin[157–161]:

2.2.1.1.1 Cellulose

Cellulose is a high-molecular-weight (10^6 or more) linear polymer of β-(1→4)-D-glucopyranose units in the $^4C_1$ confirmation. The fully equatorial conformation of β-linked glucopyranose residues stabilizes the chair structure, minimizing flexibility. Glucose anhydride, which is formed through the removal of water (H_2O) from each glucose, is polymerized into long cellulose chains that consist of 5000–10000 glucose units. The basic repeating unit of the cellulose polymer consists of two anhydride units, called a cellobiose unit. Cellulose degradation temperature occurs in the range of 240–350 °C to produce anhydrocellulose and levoglucosan.

2.2.1.1.2 Hemicellulose

Hemicellulose (also known as polyose) is a second chemical constituent of biomass. This constituent is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid, and galacturonic acid residues. In contrast to cellulose, hemicellulose has lower molecular weights than cellulose, and the number of repeating saccharide monomers is only approximately 150, compared to the number in cellulose (5000–10000). Hemicellulose degradation temperatures occur in the range of 200–260 °C, giving rise to more volatiles, fewer tars, and fewer chars than cellulose. Most hemicellulose do not yield significant amounts of levoglucosan.

2.2.1.1.3 Lignin

The third major component of biomass is lignin, which is an amorphous cross-linked resin with no exact structure. Lignin is the main binder for the agglomeration of fibrous cellulosic components while also providing a shield against the rapid microbial or fungal destruction of the cellulosic fibers. It is a three-dimensional, highly branched, polyphenolic substance that consists of an irregular array of variously bonded hydroxy- and methoxy- substituted phenylpropane units. These three general monomeric phenylpropane units exhibit the p-coumaryl, coniferyl, and sinapyl structures. The physical and chemical properties of lignin differ, depending on the extraction or isolation processes used to isolate them. The degradation temperatures for lignin occur over a wider temperature range of 300–900 °C.

2.2.1.2 Inorganic constituents in biomass

Thermal conversion of biomass can lead to small quantities of inorganic mineral residues in the ash. The ash consists of non-biodegradable carbon found in biomass.[157] The most commonly found mineral constituents for woody biomass include oxides, silicates, carbonates, sulfates, chlorides, and phosphates.[162] Some portions from the organic-forming elements also occur in inorganic matter, whilst part of the inorganic-forming elements are also present in organic matter, similar to coal.[163]

2.2.2 Utilization of biomass

Agricultural waste or grass is classified under second generation biomass feedstock. Sweet sorghum (Sorghum Bicolor L Moench) is a hardy crop that can be grown very successfully on marginal land.[164,165] According to Marx et al.,[166] a single crop of sweet sorghum can be grown in six months to produce grain with a high starch yield and stalks that are rich in sugar syrup and lignocellulosic constituents. Biomass can be thermally treated to produce gas, char, and pyrolytic tar (also known as bio-oil or biomass-derived pyrolysis oils) depending on the conversion processes (i.e. thermal and bio-chemical conversion). Bio-oils are characterized as dark brown, free-flowing organic liquids that are comprised of highly oxygenated compounds.[167–170] The presence of oxygen is the main reason for the difference in the properties and behaviour between hydrocarbon fuels and bio-oils.[167] Bio-oils are formed by the rapid and simultaneous depolymerization and fragmentation of cellulose, hemicellulose, and lignin with an increase in temperature.[29] Chemically, the bio-oil is a complex mixture of water, phenolics, aldehydes, ketones and other carboxylic acids.[171] The chemistry of bio-oils can be manipulated by changing the thermal conditions of the process or by conducting pyrolysis in the presence of catalysts.[29]

However, biomass utilization has been regarded as a low-technology solution for renewable energy and is slow to generate public enthusiasm or investor funding for projects in most organizations for economic cooperation and development (OECD) countries.[172] Biomass represents a renewable and alternative source for the production of low sulphur and low nitrogen containing fuels and chemicals.[161] The highly oxygenated biomass-derived pyrolysis oils can be utilized for the production of valuable oxygenated chemicals, such as phenols (phenol or hydroxy-benzene and its derivatives) and sugars, which have a better market opportunity if the materials are economically separated and purified.[158,173,174]

2.2.3 Extraction of chemical compounds from biomass

The extraction of phenols from biomass via a different process is well documented in the literature.[175,176] However, phenols could also be extracted from the bio-oil obtained through pyrolysis of biomass.[161,177,178] The liquefaction process plays a crucial role in conversion of biomass, where the preferred products are mostly liquids that may be used as fuels or chemicals.[177] The bio-oils from waste biomass such as agricultural waste may be more carbon friendly (provided that land use is also considered) when compared to petroleum feedstock, and are renewable as previously mentioned.[167]

There are techniques currently used for extraction of phenols from pyrolytic oil obtained via a pyrolysis route. The traditional method for phenols recovery includes liquid-liquid extraction of pyrolytic oils with different solvents.[161,178–180] Based-catalyzed thermochemical treatment of biomass in the presence of a solvent is used to increase the amount of organic soluble phenol derivatives in the oil phase.[161] The type and concentration of base added changes the composition of the phenol derivatives. For this study it was decided to investigate the process at four concentrations of NaOH to identify the different products formed. Since the pyrolytic oil has a relatively high water content and high viscosity, the liquid-liquid extraction method has great potential to improve the quality, stability, and separation of the pyrolytic oil into different chemicals groups compared to other techniques.[180] These other separation techniques include ion-exchange and silica gel column chromatography, ultrasonic and microwave radiation, distillation, adsorption over activated carbons and polymeric and inorganic adsorbents, membrane pervaporation and membrane-solvent extraction.[181–184]

2.2.4 Co-utilization of coal and biomass

The energy sector has a major challenge of providing energy at an affordable price and simultaneously protecting the environment.[185] Increasing concerns arising from the emissions (i.e. NOx, SOx and volatile organic compounds) that are due to coal conversion technologies (i.e. combustion) and gradual depletion of the fossil fuel reserves, which has led to the co-utilization of coal and a renewable energy source (biomass) to meet future energy demands. The co-utilization of biomass and coal provide an opportunity for the production of liquid fuels and chemicals.[186] There is an interest in research and development for an inexpensive biomass-derived solvent to be used as a medium or vehicle during coal solvent extraction reactions for the production of valuable chemicals and liquid fuels. Both coal and biomass are essential ingredients in the production of specialist products needed to sustain energy demand, especially for countries with poor petroleum reserves.

2.3 Summary of chapter

The solvent extraction process has been discussed for coal conversion. A great part of the earlier literature has been reported mostly for bituminous coals; with the studied experimental parameters involved in the solvent extraction or liquefaction of coal, mostly from other countries. The experimental parameters influence solvent extraction behavior. However, some of that influence may be overcome by increasing processing severity or the use of catalysts. These routes may be counterproductive in reducing operating expenses for commercial applications.[94,187] For the purpose of this current study, the extent of conversion of a Waterberg bituminous coal to produce solvent extraction products at mild conditions was investigated using an organic solvent (phenol) and a model biomass-derived solvent. These solvents have not yet been reported in the literature for the extraction of South African bituminous coal. The nature of coal, extraction temperatures and the chemical action of the solvent are considered to be crucial for their role during solvent extraction, as reported in the literature. The effects of other coal extraction conditions have not been considered, nor was an attempt made to investigate reaction conditions or kinetics that might lead to optimum conversions in subsequent chapters.

Chapter References

1. Vorres, K.S. Coal. In Kirk-Othmer Encyclopedia of Chemical Technology 6, 2004, 703-771.
2. Miller, B.G. (M.S). Coal Energy Systems, Academic Press, New York, 2005, Chapter 1.
3. Lee, S. Gasification of coal. In: Lee, S., Speight, J.G., and Loyalka, S. K. (Editors). Handbook of alternative fuel technologies. CRC Press, New York, 2007.
4. Schobert, H.H. 2013. Chemistry of fossil fuels and biofuels. Cambridge University Press, Cambridge, New York, 2013, Chapter 22.
5. Green, T.; Kovac, J.; Brenner, D.; Larsen, J.W. In *Coal Structure*, Meyers, R. A. (Editor). Academic Press, San Diego, CA, 1982, pp 199.
6. Bunt. J.R. A new dissection methodology and investigation into coal property transformational behaviour impacting on a commercial-scale Sasol-Lurgi. PhD Dissertation. University of North West: Potchefstroom. South Africa, 2006.
7. Unsworth, J.F.; Gough, H. J. Microsc. **1989**, 156, 313–326.
8. Wagner, N.J.; Joubert, J. 2005. Enhanced understanding of the carbon conversion process during gasification as determined petrographically. *Presentation* at the 11th Coal Science & Technology Conference, Johannesburg, South Africa, Fossil Fuel Foundation of Africa, CD-ROM.
9. Grainer, L.; Gibson, J. Cal utilization: Technology, Economics and Policy, Graham and Trotman, 1981, pp 1–30.
10. Stach, E.; Mackowsky, M.-T.H.; Teichmüller, M.; Taylor, G.H.; Chandra, D.; Teichmüller, R. Stach's textbook of Coal Petrology. Third revised and enlarged edition, Berlin: Gebruder Borntraeger, 1982, pp 535.
11. Falcon, R.M.S.; Snyman, C.P. An introduction to coal petrography: Atlas of petrographic constituents in the bituminous coals of Southern Africa. Johannesburg: The Geological Society of South Africa, 1986, pp 106.
12. Borrego, A.G.; Alvorez, D.; Menndez, R. Energy Fuels **1997**, 43, 702–761.
13. Taylor, G.H.; Teichmuller, M.; Davis, A.; Diessel, C.F.K.; Littke, R.; Robert, P. Organic petrology, Berlin, Gebrüder Borntraeger, 1998, pp 704.
14. Harvey, R.D.; Ruch, R.R. Mineral matter in Illinois and other U.S coals. In mineral matter and ash in coal. K.S. Vorres (ed.). Washington, D.C., ACS Symposium Series 301, 1986, Chapter 2.
15. Speight, J.G. Handbook of coal analysis, John Wiley and Sons Inc. Publications, New Jersey, 2005, pp 1–215.

16. Smith, K.L.; Smoot, L.D.; Fletcher, T.H.; Pugmire, R.J. The structure and reaction processes of coal. Plenum Press, New York and London, Plenum Press, 1994, Chapter 2.
17. Berkowitz, N. An introduction to coal technology, Academy Press, Inc., New York, 1994.
18. Pinto, F.; Gulyurtlu, I.; Lobo, L.S.; Cabrita, I. Fuel **1999**, 78, 629–634.
19. Kabe, T.; Ishihara, A.; Qian, E. W.; Sutrisna, I.P.; Kabe, Y. Coal and coal-related compounds: structures, reactivity and catalytic reactions. Studies in surface science and catalysis series, 150. Elsevier, Amsterdam, 2004, 269–309.
20. Van Niekerk, D. Structural elucidation, molecular representation and solvent interactions of vitrinite-rich and inertinite-rich South African coals. PhD Thesis. The Pennsylvania State University. The Graduate School Department of Energy and Mineral Engineering, USA, 2008.
21. Howard, H.C. In chemistry and of coal utilization, Supplementary volume, H.H. Lowry (Ed). John Wiley & Sons, Inc., New York, 1963, Chapter 9.
22. Howard, J.B. Fundamentals of coal pyrolysis and hydro-pyrolysis. John Wiley & Sons, Inc., New York, 1981, Chapter 12.
23. Howard, J.B. In chemistry and of coal utilization. Second supplement volume, M.A. Elliot (Ed.). John Wiley & Sons, Inc., New York, 1981, Chapter 12.
24. Jones, W.I. J. Inst. Fuel **1964**, 37, 3–11.
25. Gavalas, G.R.; Cheong, P.H-K.; Jain, R. Ind. Eng. Chem. Fundam. **1981**, 20, 113-122.
26. Galavas, G.R. Coal pyrolysis. Coal Science and Technology 4, *Coal Pyrolysis.* Elsevier, Amsterdam the Netherlands, 1982.
27. Hayhurst, A.N.; Lawrence, A.D. Combust. Flame **1995**, 100, 591–604.
28. Dermibas, A.; Arin, G. Energy Sources **2002**, 24, 471-482.
29. Mohan, D.; Charles Pittman, C.U.; Steele, P.H. Energy Fuels **2006**, 20, 848–889.
30. Speight, J.G. The chemistry and technology of coal, Third edition: Thermal reactivity. CRC Press, 2012, pp 391-422.
31. Owen, J. Proceedings. Residential Conference on Science in the use of coal. Institute of Fuel, London, U.K., 1958, pp C34.
32. Fletcher, T.H.; Grant, D.M.; Pugmire, R.J. Preprint, Am. Chem. Soc., Div. Fuel Chem. **1991**, 36, 250–257.
33. Van Krevelen, D.W. Coal: Typology, Chemistry, Physics and Constitution. Coal Science and Technology 3. Amsterdam, Oxford, New York, 1981, Chapter XIV.

34. Solomon, P. R.; Serio, M. A.; Deshpande, G. V.; Kroo, E. Energy Fuels **1990**, 4, 42–54.
35. Mochida, I.; Okuma, O.; Yoon, S-H. 2014. Chem. Rev. **2014**, 114, 1637–1672.
36. Lee, S. Alternative fuels. Taylor & Francis. Washington, DC, 1996, Chapter 4.
37. Rahman, M.; Adesanwo, T.; Gupta, R.; de Klerk, A. Energy Fuels **2015**, 29, 3649–3657.
38. Paul, P.F.M.; Romey, I.; Imarisio, G. Synthetic fuels from coal: Status of the technology. Graham & Trotman Ltd, Kluwer Academic Publishers Group, 1988, pp 119–201.
39. Dadyburjor, D.; Liu, Z.; 2004. Coal liquefaction. In: Kirk-Othmer Encyclopedia of Chemical Technology. vol. 6, fifth ed., Wiley-Interscience, Wiley, Hoboken, New Jersey, 2004, pp 832–869.
40. IEA Clean Coal Center. 2009. Review of worldwide coal to liquids Research, D&D activities and the need for further initiatives within Europe.
41. Chakrabartty, S.K. Preprints. Division of Fuel Chemistry. J. Am. Chem. Soc. **1981**, 26, 10–15.
42. Meyers, R.A. (Ed). Coal Handbook, Marcel Dekker Inc., New York, 1981.
43. Liu, Z.; Shi, S.; Li, Y. Chem. Eng. Sci. **2010**, 65, 12–17.
44. Yan, J.; Bai, Z.; Li, W.; Bai, J. Fuel **2014**,136, 280–286.
45. Comolli, A.G. Prepr. Symp. Am. Chem. Soc., Div. Fuel Chem. **1999**, 44, 300–305.
46. Li, X.; Hu, S.; Jin, L.; Hu, H. Energy Fuels **2008**, 22, 1126–1129.
47. Whitehurst, D.D.; Mitchell, T.O.; Farcasiu, M. Coal liquefaction: The chemistry and technology of thermal processes. Academic Press, Inc., New York, 1980.
48. Shui, H.; Cai, Z.; Xu C. Energies **2010**, 3: 155–170.
49. Akash, B.A. 2013. Thermochemical liquefaction of coal. IJEE **2013**, 5, 51–60.
50. Storch, H.H.; Golumbic, N.; Anderson, R.B. The Fischer Tropsch and related synthesis. John Wiley & Sons, Inc., New York, 1951.
51. Wu, W.R.K., and Storch, H.H. Bulletin No. 633. United States Bureau of Mines, Washington, DC, **1968**.
52. Yu, J.; Tahmasebi, A.; Han, Y.; Yin, F.; Li, X. Fuel Proc. Technol. **2012**, 106, 9–20.
53. Gagarin, S.G.; Krichko, A.A. Fuel **1992**, 71, 785.
54. Schulz, H., 1999. Applied Catalysis **1999**, 186, 3–12.
55. Littlewood, K. Prog. Energy Combust. Sci. **1977**, 3, 35–71.
56. Van Heek, K.H., and Mühlen, H-J. Aspects of coal properties and constitution important for gasification. Fuel **1985**, 64, 1405–1414.

57. Kristiansen, A. Understanding coal gasification, IEACR/ 86. IEA Coal Research, London, 1996, 12–50.
58. Speight, J.G. Synthetic Fuels Handbook: Properties, Processes, and Performance. McGraw-Hill, New York, 2008.
59. Speight J.G. The Chemistry and Technology of Coal. Second Ed., Marcel Dekker: New York, 1994, Chapter 21, pp 611–620.
60. Okuyama, N.; Komatsu, N.; Shigehisa, T.; Kaneko, T.; Tsuruya, S. Hyper-coal process to produce the ash-free coal. Fuel Process. Technol. **2004**, 85, 947–967.
61. Crussard, L. Ann. Mines **1931**, 19, 248.
62. Pertierra, J.M. Anales fis. Y quim. (Madrid) **1931**, 29, 663
63. Pertierra, J.M. Fuel **1934**, 13, 23.
64. Kreulen, D.J.W. Chem. Weekblad **1934**, 31, 104, 630, 663, 758, 761.
65. Frémy, E. Compt. Rend. **1861**, 52, 114.
66. De Marsilly, C. Ann. Chim. et phys. **1862**, 66, 167.
67. Bedson, P.P. J. Soc. Chem. Ind. (London) **1899**, 15, 739.
68. Van Krevelen, D.W.; Schuyler, J. Coal Science: Aspects of Coal Constitution. Elsevier Science Publishers, Amsterdam, 1957, Chapter V.
69. Hernandez, M.R.; Murcia, C.F.; Gupta, R.; de Klerk, A. Solvent-coal-mineral interaction during solvent extraction of coal*.* Energy Fuels **2012***,* 26, 6834–6842.
70. Petrakis, L.; Gandy, D.W. Fuel **1981**, 60, 1017–1021.
71. Neavel, R.C. In: Coal Science. Volume I. (Gorbaty, M.L.; Larsen, J.W.; Wender, I., eds.) Academic Press: New York, 1982, pp 1–21.
72. Burgess, C.; Huang, L.; Martin, S.; Tomic, J.; Schobert, H.H. Proceedings, 9th International Conference on Coal Science **1997**, 3, 1373–1376.
73. Schweighardt, F.K.; Thames, B.M. J. Am. Soc. **1978**, 50, 1381-2.
74. Herod, A.A.; Ladner, W.R.; Snape, C.E. *Phil. Trans. R. Lond. Series A*, **1981**, 300, 3–14.
75. Kiebler, M.W. In chemistry of coal utilization: The action of solvents on coal, H.H. Lowry (Ed.) John Wiley & Sons, Inc., New York, 1945.
76. Jostes, F.; Siebert, K. Oel, Kohle, Erdoel, Teer **1938**, 14, 777–83.
77. Onal, Y.; Kadim, C. Fuel Process. Technol. **1997**, 53, 81–97.
78. Murcia, C.F.; Hernandez, R.M.; Gupta, R.; De Klerk, A. Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem. **2011**, 56, 304–305.
79. Van Krevelen, D.W. Coal Science: Aspects of coal constitution. Elsevier, Amsterdam, the Netherlands, 1957, Chapter 5.

80. Larsen, J.W.; Green, T.K.; Kovac, J. J. Org. Chem. **1985**, 50, 4729–4735.
81. Renganathan, K.; Zondlo, J.W. Fuel Sci. Technol. Int. **1993**, 11, 677–695.
82. Hu, H.; Sha, G.; Chen, G. Fuel Process. Technol. **2000**, 68, 33–43.
83. Pott, A.; Broche, H. Glückauf **1933**, 69, 903.
84. Oele, A.P.; Waterma, H.I.; Goedkoop, M.L.; van Krevelen, D.W. Fuel **1951**, 30, 169.
85. Wise, W.S. Solvent treatment of coal. London: Mills & Boon, 1971, pp 55.
86. Stiller, A.H.; Sears, J.T.; Hammack, R.W. Coal extraction process. US Patent 4, **1981**, 272–356.
87. Williams, J.M.; Vanderborgh, N.E.; Walker, R.D. In Coal Science and Chemistry, A. Volborth (Ed.). Elsevier, Amsterdam, the Netherlands, 1987, pp 435.
88. Stansberry, P.G. Characterization of coal solvent extraction processes using petrographic chemical, and physical methods. Final report, DOE Award Number DE-FC26-98FT40350, 2004.
89. Rahman, M.; Samanta, A.; Gupta, R. Fuel Process. Technol. **2013**, 115, 88–98.
90. Bürküt, Y.; Suner, F.; Nakhla, F.M. Thermal properties of coal. In Coal: Resources, Properties, Utilization, Pollution, O. Kural (Ed). Istanbul Technical University, Istanbul, Turkey, 1994, Chapter 6.
91. Mitchell, G.D. Direct coal liquefaction, in: Suàrez-Ruiz, I., and Crelling, J.C. (Eds.). Applied coal petrology: The role of petrology in coal utilization. Academic Press is an imprint of Elsevier, 2008, Chapter 6.
92. Burgess, M.J.; Wheeler, R.V. J. Chem. Soc. **1911**, 99, 649.
93. Brown, H.R.; Waters, P.L. Fuel **1966**, 45, 41.
94. Fisher, C.H.; Sprunk, G.C.; Eisner, A.; O'Donnell, H.J.; Clarke, L.; Storch, H.H. U.S. Bureau of Mines Tech. **1942**, 642, 151.
95. Vorres, K.S. Users' handbook for the Argonne premium coal sample program. Argonne National Laboratory, Argonne, IL; National Technical Information Service, United States Department of Commerce, Springfield, VA, 1993.
96. Van Krevelen, D.W. Fuel **196*5*,** 44, 229–242.
97. Asbury, R.S. Ind. Eng. Chem. **1934**, 26, 1301–1306.
98. Dryden, I.G.C. Fuel **1951***,* 30, 145–8.
99. D'yakova, M.K.; Surovtseva, V.V. Zhur. Priklad. Khim. **1955**, 28, 65–70.
100. Herédy, L.A.; Neuworth, M.B. Fuel **1962***,* 41, 221–231.
101. Larsen, J.W.; Urban, L.; Lawson, G.; Lee, D. Fuel **1981**, 60, 267.
102. Gorin, E.G. Fundamentals of coal liquefaction: Chemistry of coal utilisation, 2nd supplementary volume, ed. Elliott, M., John Wiley & Sons, 1981, Chapter 27.

103. Larsen, J.W.; Shawver, S. Energy Fuels **1990**, 4, 74–77.

104. Juettner, B.; Howard, H.C. Ind. Eng. Chem. **1934***, 26*, 1115.

105. Davidson, R.M. Molecular structure of coal. Report No. ICTIS/TRO8. International energy Agency, London, U.K., 1980.

106. Herédy, L.A.; Kostyo, A.E.; Neuworth, M.B. Fuel **1963**, 42, 182.

107. Herédy, L.A.; Kostyo, A.E.; Neuworth, M.B., 1964. Fuel **1964**, 43, 414.

108. Herédy, L.A.; Kostyo, A.E.; Neuworth, M.B. Fuel **1965**, 44, 125.

109. Dryden, I.G.C. Fuel **1950**, 9, 197–207.

110. Peters, K.; Cremer, W. Angew. Chem. **1934**, 47, 576–8.

111. Pande, S.; Sharma, D.K. Energy Fuels **2002**, 16, 194-204.

112. Bartle, K.D.; Martin, T.G.; Williams, D.F. Fuel **1975**, 54, 226–235.

113. Whitehead, J.; Williams, D.F. J. Inst. Fuel **1975**, 48, 182.

114. Williams, D.F. Indian J. Chem. **1975**, 10, 20.

115. Brink, A. Solvent refined coal and coal hydrocracking: in Annual School on Chemicals from Coal, South Transvaal Section of the South African Chemical Institute, Potchefstroom University, 1976, 124–136.

116. Marzec, A.; Juzwa, M.; Betlej, K; Sobkowiak, M. Fuel Process. Technol. **1979**, 2, 35–44.

117. Loison, R.; Foch, P.; Boyer, A. Coal in general. In: Coke quality and production, London: Butterworths, 1989.

118. Onal, Y.; Ceylan, K. Fuel Process. Technol. **1997**, 53, 81–97.

119. Kreulen, D.J.W. Fuel **1946**, 25, 99–108.

120. Pertierra, J.M. Anales fis. Y quìm. (madrid) **1941**, 37, 58–68.

121. Given, P.H. In Coal Science, M.L. Gorbaty, J.W. Larsen, and I. Wender (Eds.). Academic Press, Inc., New York, 1984, Vol 3, pp 63.

122. Parr, S.W.; Hadley, H.F. The analysis of coal with phenol as a solvent. Illinois University, Urbana, Exp. Sta. 1914, Bulletin No. 76, pp 3-41.

123. Clarke, J.W.; Rantell, T.D.; Snape, C.E. Fuel **1984***,* 63, 1476–1478.

124. Iino, M.; Matsuda, M. Bull. Chem. Soc. Jpn. **1984**, 57, 3290.

125. Pott, A.; Broche, H.; Nedelmann, H.; Schimtz, H.; Scheer, W. Glückauf **1933**, 69, 903–12

126. Pott, A.; Broche, H.; Nedelmann, H.; Schimtz, H.; Scheer, W. Fuel **1934**, 13, 91-5, 125-8, 154-7.

127. Agda, G.; Hubertus, R. Braunkohlenarch **1936**, 46, 3–30.

128. Asbury, R.S. Ind. Eng. Chem. **1936**, 28, 687–90.

129. Gillet, A.C. Brennstoff-Chem. **1936**, 17, 421–9.

130. Storch, H.H. Nature of solvent or vehicle. (Lowry, H.H. Ed.), In Chemistry of Coal Utilization: Supplementary volume, John Wiley and Sons, Inc., New York, 1963, Chapter 38.

131. King, H.H.; Stock, L.M. Fuel **1982**, 61, 1172–1174.

132. Bockrath, B.C. In: Coal Science, Volume 2. (Gorbaty, M.L.; Larsen, J.W.; Wender, I., eds.) Academic Press: New York, 1983, pp 65–124.

133. Mastral-Lamarca, A.M. In Coal sciences and chemistry (Volborth, A. Ed.). Elsevier, Amsterdam, the Netherlands, 1987, pp 289.

134. Sharma, D.K. Fuel **1988**, 67, 186.

135. Wang, H.P.; Lo. R.; Sommerfeld, D.A.; Huai, H.; Pugmire, R.J.; Shabtai, J.; Eyering, E.M. Fuel **1992**, 71, 723.

136. Berkowitz, N. An introduction to Coal Technology, Academic Press, Inc., New York, 1979, Chapter 7.

137. Stopes, M.C.; Wheeler, R.V. Fuel **1924**, 3, 63, 356, 439.

138. Bakes, W.E. D.S.I.R. Fuel Res. Tech. **1933**, Pap. No. 37

139. Frazer, J.C.W.; Hoffman, E.J. U.S. Bur. Mines ***1912**, Technical Paper*, 5, 5–20.

140. Kiebler, M.W. Ind. Eng. Chem. **1940**, 32, 1389–1394.

141. Orchin, M.; Storch, H.H. Ind. Eng. Chem. **1948**, 40, 1385–1389.

142. Ouchi, K.; Imuta, K. Fuel **1973**, 52, 171.

143. Kamiya, Y.; Sato, H.; Yao, T. Fuel **1978**, 57, 681–685.

144. Ouchi, K.; Imuta, K.; Yamashita, Y. Fuel **1965**, 44, 29–38.

145. Ouchi, K.; Imuta, K.; Yamashita, Y. Fuel **1973**, 52, 156.

146. Larsen, J.W.; Lee, D. Fuel **1983**, 62, 918–923.

147. Larsen, J.W.; Sams, T.L.; Rodgers, B.R. Fuel **1981**, 60, 335.

148. Collins, C.J.; Raaen, V.F.; Benjamin, B.M.; Kabalka, G.W. Fuel **1977**, 56, 107.

149. Raaen, V.F.; Roark, W.H. Fuel **1978**, 57, 650–1.

150. Schlosberg, R.H. Chemistry of coal conversion. Exxon Chemical Company, Linden, New Jersey, 1985, 307–312.

151. Trewhella, M.J.; Grint, A. Fuel **1988**, 67, 1135–1138

152. Van Dyk, J.C.; Keyser, M.J.; van Zyl, J.W. Suitability of feedstocks for the Sasol-Lurgi fixed bed dry bottom gasification process, GTC conference, San Francisco, USA, 7-10 October, 2001.

153. Smook, D. Fuel Process. Technol. **2007***,* 88*,* 795–798.

154. Renganathan, K.; Zondlo, J.W.; Mintz, E.A.; Kneisl, P.; Stiller, A.H. Fuel Process. Technol. **1988**, 18, 273–278.

155. EIA, 2007. https://www.eia.gov/energyexplained/?page=biomass_home (accessed 19.11.2017).

156. World Energy Outlook 2004. International Energy Agency, Paris, 2005, Chapter 7.

157. McKendry, P. Bioresour. Technol. **2002**, 83, 37–46.

158. Soltes, E. J.; Elder, T. J. Pyrolysis. In Organic Chemicals from Biomass; Goldstein, I. S., Ed.; CRC Press: Boca Raton, FL, 1981, pp 63-95.

159. Jenkins, B.M., Bakker, R.R., Wei, J.B. Biomass Bioenergy **1996**, 10, 177–200.

160. McCarthy, J.; Islam, A. Lignin chemistry, technology, and utilization: a brief history. In Lignin: Historical, Biological and Materials Perspectives; Glasser, W. G., Northey, R. A., Schultz, T. P., Eds.; ACS Symposium Series 742; Am. Chem. Soc.: Washington, DC, 2000, pp 2-100.

161. Amen-Chen, C.; Pakdel, H.; Roy, C. Bioresour. Technol. **2001**, 79, 277–299.

162. Raveendran, K.; Ganesh, A.; Khilart, K.C. Fuel **1995**, 74, 1812–1822.

163. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. Fuel **2010**, 89, 913–933.

164. Mastrorilli M.; Katerji N.; Rana G. European J. Agron. **1999**, 11, 207–15.

165. Vasilakoglou, I.; Dhima, K.; Karigiannides, N.; Gatsis, T. Field Crops Res. **2011**, 120, 38–46.

166. Marx, S.; Ndaba, B.; Chiyanzu, I.; Schabort, C. Biomass Bioenergy **2014**, 65, 145–150.

167. Czernik, S.; Bridgwater, A. V. Energy Fuels **2004**, 18, 590–598.

168. Peacocke, G.V.C.; Russel, P.A.; Jenkins, J.D.; Bridgwater, A.V. Biomass Bioenergy **1994**, 7, 169–178.

169. Peacocke, G.V.C.; Madrali, E.S.; Li, C.-Z.; Guell, A.J.; Kandiyoti, R..; Bridgwater, A. V. Biomass Bioenergy **1994**, 7, 155–167.

170. Peacocke, G.V.C.; Russel, P.A.; Bridgwater, A.V. Biomass Bioenergy **1994**, 7, 147–154.

171. Piskorz, J.; Scott, D.S.; Radlien, D. Composition of oils obtained by fast pyrolysis of different woods. In Pyrolysis Oils from Biomass: Producing analyzing and upgrading; American Chemical Society: Washington, DC, 1988, pp 167-178.

172. Mousdale, D.M. Biofuels: Biotechnology, chemistry, and sustainable development. CRC Press, Taylor & Francis Group, NW, 2008, Chapter 2

173. Connor, M.A.; Piskorz, J. Workshop report: chemicals from biomass. In: Bridgewater, A.V. (Ed.), Advances in Thermochemical Biomass Conversion. Blackie, New York, 1994, pp. 1502–1504.

174. Murwanashyaka, J.N., Pakdel, H., Roy, C. Sep. Purif. Technol. **2001**, 24, 155–165.

175. Wojtkowski, P.W. U.S. Patent 4, **1986**, 605,790.

176. Hames, B.R. U.S. Patent 6, **2004**, 719,908.

177. Patel, R.N.; Bandyopadhyay, S.; Ganesh, A. Energy **2011**, 36, 1535–1542.

178. Žilnik, L.F.; Jazbinśek, A. Sep. Purif. Technol. **2012**, 86, 157–170.

179. Amen-Chen, C.; Pakdel, H.; Roy, C. Biomass Bioenergy **1997**, 13, 25.

180. Wei, Y.; Lei, H.; Wang, L.; Zhu, L.; Zhang, X.; Liu, Y.; Chen, S.; Ahring, B. Energy Fuels **2014**, 28, 1207–1212.

181. Chriswell, C.D.; Chang, R.C.; Fritz, J.S. Anal. Chem. **1975**, 47, 1325.

182. Schabron, J.F.; Hurtubise, R.J.; Silver, H.F. Anal. Chem. **1979**, 51, 1426.

183. Busca, G.; Berardinelli, S.; Arrighi, L. J. Hazard. Mater. **2008**, 160, 265–288.

184. Ince, A.E.; Sahin, S.; Sumnu, G. J. Food Sci. Technol. **2014**, 51, 2776–2782.

185. Kumar, A.; Kumar, N.; Baredar, P.; Shukla, A. Renew. Sust. Energ. Rev. **2015**, 45, 530–539.

186. Liu, W.; Wang, J.; Bhattacharyya, D.; Jiang, Y.; De Vallance, D. Energy **2017**, 141, 76–86.

187. Alpert, S.B.; Wolk, R.H. Liquefaction processes. In chemistry of coal utilization (Eliott, M.A., Ed.) 2nd supplement, Wiley & Sons, New York, 1981, Chapter 28, 1919-1990.

Chapter 3

Effectivity of phenol during solvent extraction of a South African bituminous coal at mild conditions

Thabo Z. Sehume, *Christien A. Strydom, John R. Bunt and Harold H. Schobert*

In this chapter, the extraction yields and all the results of the analyses that were obtained from the extraction of bituminous coal using phenol as a solvent at mild conditions are reported herein.

The content of this paper was published in Energy & Fuels **2017**, 31, 13655–13665.

Abstract

Solvent extraction of a South African bituminous coal was carried out under mild conditions (<400 °C) with a holding time of 20 min and an initial nitrogen (N_2) pressure of 6 MPa. Thermal degradation of coal with phenol results in the depolymerization of the coal, yielding coal-derived liquids and insoluble residues. The effectiveness of phenol for solvent extraction of coal between 300–360 °C was investigated with a focus on the quality of the coal-derived liquids. It was found that an increase in temperature from 300 °C to 360 °C, resulted in an increase in the conversion and yields of both oil and gas, and a reduction in the intermediate components (pre-asphaltenes + asphaltenes, PAAs). The conversion and extraction yields of hexane-soluble (HS) oils were 49.5% (daf) and 26.3% (daf) respectively for thermal depolymerization reactions at 360 °C. It seems that the extraction process dissolves molecular fragments of the coal as the infrared spectra of the coal and the extraction products are similar. The SimDis results of the coal-derived liquids (300–360 °C) indicated that the samples consisted of light vacuum gas oil (23–31 wt. %), distillate fuel oil (16–30 wt. %), heavy vacuum gas oil (18–34 wt. %) and residual oil (3–16 wt. %). These results show the potential of phenol as a solvent to extract South African bituminous coal at mild temperatures for value-added liquid fuels and add to the general knowledge of the potential utilization of the Permian-aged South African bituminous coals.

3.1. Introduction

South Africa is a developing country with abundant coal reserves, but a limited amount of crude oil reserves.[1] The production of fuels from coal provides an important alternative for petroleum supply other than from crude oil. Coal can be converted into liquid hydrocarbons via coal liquefaction; including pyrolysis, solvent extraction, direct coal liquefaction, and indirect coal liquefaction.[2] The country heavily relies on indirect coal liquefaction, i.e. coal gasification followed by the Fischer-Tröpsch process where the liquid products are formed to augment the petroleum supply.[3] However, this process involves high production costs and poses a negative impact on the environment, such as unwanted gaseous emissions (e.g. carbon dioxide).[4,5]

More research and development in alternative technology, which can convert solid coal into liquid fuels and chemicals, is needed. In this regard, solvent extraction offers an alternative for liquid fuels supply, as the solvent has a pronounced effect on the yields of coal-derived liquids. Coal liquefaction by solvent extraction occurs through heating coal in the presence of a solvent, and usually, in a non-reactive atmosphere. Unlike direct coal liquefaction, it is not common to use a catalyst or a hydrogen atmosphere. The extraction temperatures can vary between 150 and 400 °C, depending on the choice of solvent. If the extraction temperature is high enough to initiate thermal fragmentation of the coal structure, radicals could be stabilized by hydrogen supplied by the solvent or internally from the coal itself.[6–9] On a laboratory scale, the extract is often separated into oils, asphaltenes, and pre-asphaltenes, as in direct liquefaction. In a commercial operation, the liquid stream would likely be distilled into different boiling-range cuts comparable to petroleum distillates. The solid remaining after extraction is char or semi-coke. In the past, researchers have studied a wide range of coals with an equally wide variety of coal sizes, temperatures, times, and solvents.[10–17] Studies have been done mostly on bituminous coal from countries other than South Africa for coal extraction or liquefaction products. The Northern Hemisphere bituminous coals are geologically older (Carboniferous) than the Permian aged South African coals; and therefore, have somewhat different chemical structures and thus reactivities due to their different petrographic compositions. However, various other factors can also influence the reactivity of coal.[18–20] The present study is the first reported exploration of coal-phenol interactions for South African coals. The bituminous coal is preferred on the basis that it is amenable for liquefaction reactions due to a higher yield of hydrocarbon products.[2]

The study of solvent extraction of coal at 200–400 °C in an inert atmosphere was first reported by Harger[10] and Illingthworth.[11] The extraction of coals with various solvents were mostly conducted using Soxhlet apparatus and analytical methods, which include nuclear magnetic resonance (NMR), infrared spectroscopy, and gas chromatography. It was thought that there was a correlation between the amount of coal that would dissolve in a number of solvents (i.e. phenol), and the degree of oxidation and decomposition or depolymerization of the coal substance at mild temperatures. The soluble products from coal extraction (extracts or bitumen) consist of a mixture of organic substances ranging from low-molecular-weight compounds to highly complex molecules and colloids.[14]

According to a study by Illingworth,[11] bituminous coal yielded 1% of extract at 184 °C after a 24-hour extraction with liquid phenol, which increased to 6% soluble in phenol after the coal was heated to 400 °C out of contact with air. Pew and Withrow[21] conducted atmospheric Soxhlet extractions of bituminous coal (Pittsburgh No. 8 Seam, Ohio) with a number of solvents, including phenol, in air and carbon dioxide. The extraction yields using phenol were found to be around 44% in air and carbon dioxide respectively. Other authors have studied the degradation of coal in phenol under hydrogen pressure (80 atmosphere) in an autoclave at 250, 300, 350, 375, 400 and 420 °C.[22,23] The conclusion drawn from their research is that depolymerization rather than decomposition occurs at high temperatures in the presence of solvents as they observed small amounts of hydrocarbon gases in the gaseous products at these temperatures. In this paper, the term ‘depolymerization’ indicates the breaking down of the macromolecular structure of the coal by cleavage of relatively labile bridges such as polymethylene chains or heteroatom chains, producing fragments that resemble the parent coal in composition and structure. The term ‘decomposition’ indicates extensive thermal disintegration of the coal structure with cleavage of numerous stable covalent bonds, including dealkylation of aromatic ring systems and loss of heteroatomic functional groups.

Kiebler[24] evaluated the influence of a variety of organic solvents at 150 to 300 °C on the yields of extracts from Pittsburgh seam coal inside small stainless-steel bombs. This study showed that phenol is a better solvent for Pittsburgh seam coal than pyridine at the same temperature; as extraction yields were in the range of 21% to 40% (150–300 °C). A variety of solvents were evaluated by Orchin and Storch[25] for their ability to extract coals. Their studies showed that hydroxy-aromatic solvents containing a phenolic group were superior to those without one, regarding the degree of extraction. Solvents such as α-naphthol, p-cyclohexylphenol and o-phenylphenol could extract 80%, 58%, and 15% respectively of Pittsburgh seam coal at their boiling points.[26] During extraction of high-rank coal with a solvent containing one or more rings with a hydroxyl group attached to an aromatic ring, it was generally thought that the higher the boiling point, the better the extraction. However, the correlation with the boiling point was found to extend only to hydroxy-aromatic solvents, such as naphthol.[25–27] Some studies on coal extraction use the presence of phenolic groups in the extraction products to assess the extent of decomposition or extraction of the parent coal.[28] Care should thus be taken when coal decomposition is followed through monitoring phenolic groups, in cases where phenol is used as the extraction medium.

Other authors reported on depolymerization of coal in hydrogen-rich environments (i.e. solvent or gas), and also in the presence of catalysts, such as Friedel-Crafts catalysts; to elucidate the involvement and importance of phenols in thermal decomposition of coals.[29–31] Herédy and Neuworth[29] studied the solubility of coal (Pittsburgh Seam coal) when treated with boron trifluoride (BF_3) as catalyst and phenol as solvent at 100 °C. They observed phenol-soluble extracts of more than 60% of the coal, and this provided evidence for aromatic interchange reactions, involving cleavage of aliphatic-aromatic linkages and exchange of the aromatic structures with phenol. Darlage and Bailey[32] studied the depolymerization reactions of coal in the presence of a catalyst in a variety of phenolic and non-phenolic solvents using high-volatile bituminous coal (Pond Creek seam, Kentucky).

The effectiveness of solvents, obtained from sources such as biomass, during solvent extraction of South African bituminous coals are of interest. Phenolic compounds may be extracted from biomass and could provide the needed phenols for coal solvent extraction or coal liquefaction. Before considering the phenolic compounds from biomass as a source of solvent for coal solvent extraction, the effectiveness of phenol as a solvent to extract liquids from South African bituminous coal should be investigated. The solvent extraction of a South African Waterberg bituminous coal with relatively low ash yield, using phenol, was investigated and is presented in this paper. An autoclave was used to conduct solvent extraction experiments using phenol as the solvent at mild conditions. The detailed physico-chemical properties of the solvent extraction products were determined and the results obtained using phenol as solvent at different temperatures were compared (300, 320, 340 and 360 °C).

3.2. Experimental Section

3.2.1 Materials

South African Waterberg bituminous coal (medium rank-B) was supplied by Exxaro Resources Limited, South Africa. The coal was pulverized to less than 150 µm and stored in a desiccator flushed with N_2 gas (high purity: 99.999%) obtained from Africa Oxygen Limited (AFROX, South Africa) for further analyses and subsequent solvent extraction experiments. The samples were oven-dried at 80 °C for 24 h to reduce the moisture content, before the solvent extraction experiments. The phenol (purity ≥ 89.0% and impurities ≈10%, water), used as the solvent in all solvent extraction experiments, was supplied by Sigma-Aldrich, South Africa. Solvents used for the series of extraction of liquefied products include tetrahydrofuran (THF) and n-hexane supplied by Merck Chemicals (Pty) Ltd, South Africa.

3.2.2 Coal solvent extraction experiments using a single solvent system

The experimental procedure followed for the solvent extraction of bituminous coal is shown schematically in **Figure 3.1**. A stainless-steel high-pressure autoclave system (950 mL capacity, 90 mm diameter and 150 mm height) was used for solvent extraction experiments under N_2. Coal (20 g) and 200 g of phenol were introduced together into the autoclave at ambient temperature. The air was displaced by N_2, and the autoclave sealed and tested for leaks with N_2, before being pressurized with N_2 to a fixed initial pressure of 6 MPa. To ensure that phenol, remains in the liquid phase, the pressure of 6 MPa was used. The autoclave was then heated to a specific temperature (either 300, 320, 340, 360 °C), and maintained at the specific temperature for 20 min. The temperature was measured inside the autoclave using a thermostat. A heating rate of approximately 4 °C/min was used, and the stirring rate was kept constant at 300 rpm. At the end of the desired reaction period, the autoclave was cooled to ambient temperature using an electric fan. The autoclave was depressurized through a gas meter. The solid-liquid mixture (consisting of coal residue, extract, and solvent) was removed from the autoclave and weighed (to calculate the yield of gaseous products) and then vacuum filtered to separate the solid residue from the liquid phase. The extraction procedure was repeated more than three times for reproducibility of results.

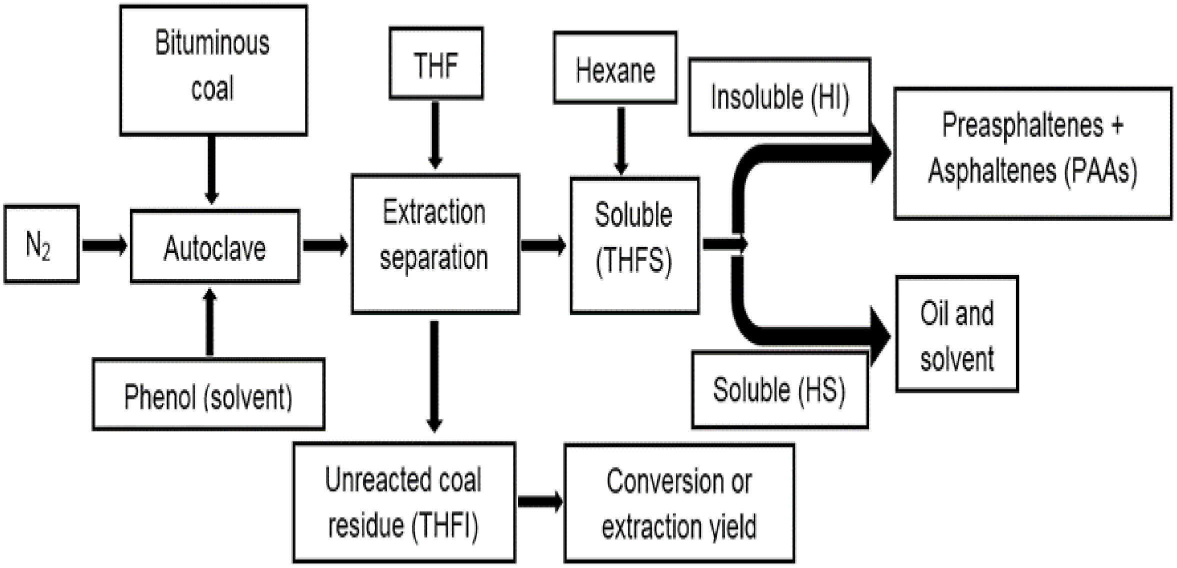


Figure 3.1. Solvent extraction procedure using phenol as solvent

A series of extractions were carried out on the liquid mixture using a reflux system with two solvents at 85 °C for 1 h, as previously described in the literature[33,34] and presented in **Figure 3.1**. The procedure involves the extraction with tetrahydrofuran (THF) and n-hexane in sequence to separate the products. The THF-insoluble part of the liquid residue was labelled THFI and represents the unreacted portion of the coal. The THF-soluble part of the liquid residue (THFS) was further extracted with hexane, and the hexane-insoluble part of this extraction step (HI) was labelled PAAs, as it contains a combination of pre-asphaltenes and asphaltenes as intermediate products. The hexane-soluble (HS) product contains the oil part of the product. All the product yields were calculated on a dry ash free basis (daf).[35,36] The unreacted coal residues (THFI) and PAA products were washed with a low boiling point organic solvent (acetone), to remove the residual solvent. The solvent extraction products were dried under vacuum at 80 °C for 24 h.

3.2.3 Characterization of samples

The proximate analysis was performed using a U-Therm TGA, and ultimate analysis results were obtained using a CE 440 analyzer. Each sample was repeatedly characterized and averages used. The characterization of samples and a petrographic analysis were carried out at the Council for Geoscience (South Africa). The petrographic analysis was conducted using a Leica DM600 microscope with Carl Hilgers motorized system and according to the ISO 7404-2 method.

Pyrolysis experiments were carried out in an SDQT600 thermogravimetric analyzer to study the thermal behavior of the samples. Approximately 12 mg of the sample (coal or PAAs) was heated in a nitrogen environment with a flow rate of 75 mL/min from ambient temperature up to 900 °C at a heating rate of 4°C/min. The weight loss (TG curves) and weight loss rates (DTG curves) were obtained as a function of temperature.

The organic functional groups in the liquefaction products and raw bituminous coal were characterized by infrared analysis in the region 400 to 4000 cm^{-1} at ambient temperature using an FTIR spectrometer (Bruker ALPHA's Platinum ATR) single reflection diamond ATR module.

The composition of the gaseous products was analyzed using an Agilent 7890 GC equipped with a GS-GASPRO column (60 m x 0.32 mm), a flame ionization detector (FID) and a thermal conductivity detector (TCD) to determine C_1 to C_4 hydrocarbon products (methane, ethane, propane, butane and carbon dioxide).

Simulated distillation analysis was carried out using an HP 5890 GC in accordance with the ASTM D2887 method. The analysis was carried out on a high-temperature GC-FID system fitted with an ARX 2887 Restek column (10 m x 0.53 mm x 0.53 µm). The HS products were prepared by dissolving approximately 200 mg of the sample in 2 mL dichloromethane (CH_2Cl_2) followed by injection of approximately 0.2 μL of the sample into the GC column. Samples were injected at an initial temperature of 40 °C, heated at 15 °C/min to 600 °C and held isothermally at 600 °C for 10 min.

The conversion of coal during coal solvent extraction using phenol as the solvent was calculated as follows (all values indicated are in weight %):

Conversion or extraction yield, % = [coal charged – unreacted coal residue (THFI)/ daf coal] x 100%. (1)

The yield of pre-asphaltenes and asphaltenes (PAAs, HI) is defined by:

PAAs, % = [(Hexane insoluble material, THF soluble) / daf coal] x 100%. (2)

The oil part of the extracted products (HS) is obtained by difference:

Oil, % = [Conversion – (PAAs) – G] x 100%. (3)

where daf coal is the weight of the dry, ash-free coal. G is the yield of gaseous products obtained after coal solvent extraction (obtained by mass balance). The conversion or extraction yield and intermediate products yields (PAAs) were determined gravimetrically on the basis of solvent-free dried residues. The PAAs yields are reported together due to their similar solubility in THF.[35]

3.3. Results and Discussion

3.3.1 Characterization of samples

The proximate, ultimate, X-ray fluorescence (XRF) and petrographic results for the washed bituminous coal are summarized in Table 3.1. The petrographic results show that the vitrinite and inertinite are the main maceral components of this coal sample with values of 52.8% and 29.4% respectively (Table 3.1). The results of the proximate and ultimate analyses of the extraction products (HS) and the unreacted coal residues (THFIs) are summarized in Table 3.2. The carbon contents of the THFI and PAA samples lie within ±1% of the value for the parent coal. The nitrogen contents of these two products are also close to that of the parent coal. The sulphur contents of the THFI and PAAs are consistently somewhat lower than the value for the coal sample. This observation agrees with a possible loss of sulphur gases from the coal at temperatures ≤300 °C. The hydrogen contents of THFI and PAAs are lower than for the coal sample, in agreement with the lower values of the atomic H/C ratios. The main reason appears to be an internal redistribution of the available hydrogen in the coal in conjunction with the formation of the HS products. These HS products, or oils, have hydrogen contents and H/C ratios higher than the coal, reflecting the redistribution of hydrogen. It is especially noteworthy that the nitrogen and sulphur contents of the HS products are much lower than those of the parent coal, suggesting that the formation of oils during phenol extraction has been accompanied by a reduction in heteroatomic content.

Table 3.1. Proximate, ultimate, XRF and petrographic results for the coal sample

Chemical properties	Standard methods used	Coal
Proximate analysis (wt.%, ad)[a]		
Inherent Moisture	ISO11722	3.1
Volatile matter	ISO 562	34.2
Ash	ISO 1171	10.9
Fixed carbon	By difference	51.8
Ultimate analysis (wt.%, daf)[b]	ISO 29541	
Carbon		80.9
Hydrogen		5.5
Nitrogen		1.9
Sulphur	ISO 19579	1.3
Oxygen	By difference	10.4
H/C (Atomic ratio)		0.82
XRF (wt.%)	ASTM D4326	
Fe_2O_3		8.7
MnO		0.1
Cr_2O_3		0.1
V_2O_5		0.2
TiO_2		2.6
CaO		1.4
K_2O		1.0
P_2O_5		0.1
SiO_2		62.3
Al_2O_3		20.4
MgO		0.8
ZnO		1.1
SO_3		1.1
Petrographic analysis (vol. %, m.m.f.b.)	ISO 7404-2	
Vitrinite		52.8
Liptinite		3.5
Reactive semifusinite		6.7
Total inertinite		29.4
Visible mineral matter		7.5
Vitrinite reflectance		0.6

***a** ad: air-dried basis.
***b** daf: dry-ash-free basis.

Table 3.2. Proximate and ultimate analyses of coal solvent extraction products (unreacted coal residues (THFIs), HS and PAAs)

Product	Chemical Properties	Standard methods	300 °C	320 °C	340 °C	360 °C
THFI	Proximate analysis (wt.%, air-dry basis)					
	Moisture	ISO11722	2.0	2.1	2.8	2.6
	Volatile Matter	ISO 5621	44.7	43.0	31.7	28.5
	Ash	ISO 1171	10.2	10.5	18.5	20.6
	Fixed Carbon	By difference	43.1	44.4	47.0	48.3
	Ultimate analysis (wt.%, dry-ash-free basis) ISO 29541					
	Carbon		79.1	79.0	82.9	82.2
	Hydrogen		5.1	4.8	5.1	4.8
	Nitrogen		1.6	1.6	1.9	2.0
	Sulphur	D4239-14	0.9	0.9	1.0	1.1
	Oxygen	By difference	13.3	13.7	9.1	9.9
	H/C (Atomic ratio)		0.77	0.73	0.74	0.70
HS	Proximate analysis (wt.%, air-dry basis)					
	Moisture	ISO11722	9.7	9.7	9.7	9.7
	Volatile Matter	ISO 5621	90.3	90.3	90.3	90.3
	Ash	ISO 1171	-	-	-	-
	Fixed Carbon	By difference	-	-	-	-
	Ultimate analysis (wt.%, dry-ash-free basis) ISO 29541					
	Carbon		83.7	85.7	81.9	84.0
	Hydrogen		7.0	7.3	6.8	6.9
	Nitrogen		0.2	0.2	0.2	0.1
	Sulphur	D4239-14	0.2	0.2	0.2	0.2
	Oxygen	By difference	8.9	6.6	10.9	8.8
	H/C (Atomic ratio)		1.00	1.02	1.00	0.99
PAAs	Proximate analysis (wt.%, air-dried basis)					
	Moisture	ISO11722	1.7	2.2	2.1	2.2
	Volatile Matter	ISO 5621	56.2	57.1	54.0	55.5
	Ash	ISO 1171	0.9	0.8	0.9	0.9
	Fixed Carbon	By difference	41.2	39.9	43.0	41.4
	Ultimate analysis (wt.%, dry-ash-free basis) ISO 29541					
	Carbon		80.1	80.8	81.3	81.8
	Hydrogen		5.1	5.2	5.1	5.1
	Nitrogen		2.0	1.9	2.0	1.8
	Sulphur	D4239-14	0.7	0.7	0.8	0.7
	Oxygen	By difference	12.1	11.4	10.8	10.6
	H/C (atomic ratio)		0.76	0.77	0.75	0.75

3.3.2 Coal conversion as a function of temperature and product distribution

Figure 3.2 shows the conversions and distributions of the solvent extraction products of the bituminous coal using phenol as a solvent under N_2 at 300–360 °C. However, the solvent extractions were not conducted at conditions (i.e. without catalyst) that had necessarily been shown to maximize conversions. The temperature range of 300 °C to 360 °C was chosen to investigate the influence of temperature on yields obtained at mild conditions, for two reasons. Firstly, there is a broad consensus in the literature that the main thermal decomposition of coal starts at temperatures of about 350–375 °C.[10,11,37] The investigation focuses on temperatures below the main decomposition temperature of coal. Secondly, previous investigators have found this a useful temperature range for studying extraction of South African coals with other solvents.[38,39] It was observed that the coal conversion (as defined earlier) increases as temperature increases, i.e. a low coal conversion of 12% was observed at 300 °C increasing to 50% at 360 °C (Figure 3.2). This trend is expected because it is consistent with general experience in high-temperature solvent extraction.[40,41] An increase in conversion with temperature has also been found in systems using tar phenols as the solvent.[40,41] The conversion of approximately 50% at 360 °C is consistent with other results for solvent extraction of bituminous coals of nearly 80% carbon content at 360 °C.[40,41] The conversion increased from 22% to 34% between 320 °C and 340 °C during coal solvent extraction.

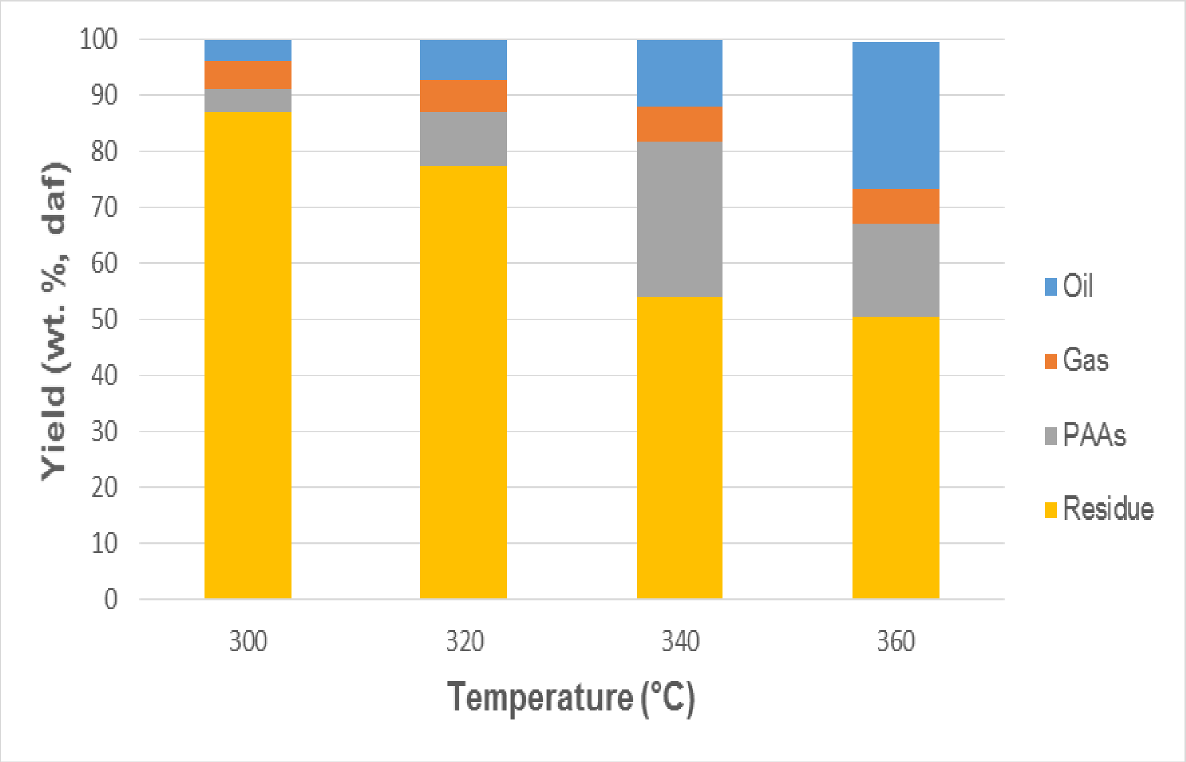


Figure 3.2. Coal conversion and extraction product distribution using phenol as solvent

The decrease in the volatile matter (THFI, Table 3.2) as a function of extraction temperature (from 43 wt. % to 31.7 wt. % daf) occurs in the range 320–340 °C, precisely where the biggest increase in conversion is observed in Figure 3.2. Previous studies indicated that the conversion of coal under mild operating conditions during solvent extraction can be influenced by the nature of the solvent and depolymerization reactions.[14,23,42] The phenol liquefied coal extraction yields in this study obtained between 300 °C and 360 °C correlates well with previously reported results for bituminous coal, which were reported to be in the range between 15% and 56%.[21,24,26,32,40,41,43]

3.3.3 The effect of temperature on gas yields during solvent extraction

Figure 3.3 shows the gas and hydrocarbon yields progressively increases with rising temperature. The average strength of the hydrogen bonds was found to decrease above 230 °C for some bituminous coals during coal pyrolysis.[44] The components of the gas likely represent molecular fragments that were weakly bonded (thermally labile) in the macromolecular coal structure, as Speight[45] suggested for gaseous compounds evolved at 200–375 °C. Since there is no significant increase in gas yield between 320 °C and 360 °C, this early decomposition must account for most of the weakly bonded structures in this coal. The small amount of hydrocarbon gases produced is evidence of depolymerization reactions in high-temperature solvent extraction.[22,23]

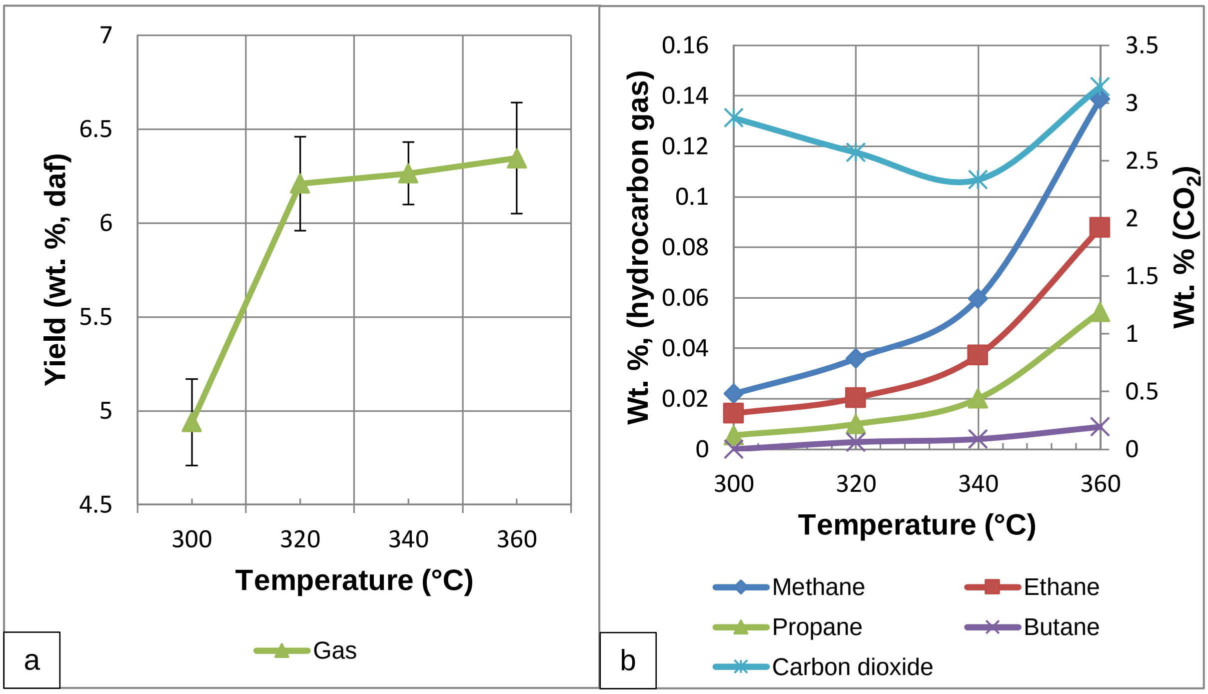


Figure 3.3. Gas yields (a) and GC-FID analysis (b) of gases during solvent extraction

3.3.4 The effect of temperature on PAAs during solvent extraction

The yield of PAAs increases with increasing temperature, to a maximum value of 28% at 340 °C (Figure 3.4). Above 340 °C the PAAs yield decreases to 17%. At temperatures up to at least 340 °C, but below 360 °C, the PAAs yield parallels the conversion as a function of temperature. This behavior shows that, up to at least 340 °C, that the effect of temperature is to increase conversion without significantly shifting the proportion of PAAs produced. Thus, increasing the temperature simply provides “more of the same,” regarding the major product of extraction, without changing the nature of the extraction process or changing the chemistry of the extraction process. This effect of temperature on PAA yield from the extraction of other bituminous coals in this temperature range has not yet been reported in literature. Somewhere in the temperature range between 340 °C and 360 °C a major change occurs, because the PAAs yield at 360 °C is much lower than would have been anticipated from all the results obtained up to 340 °C. The change in yield suggests that some thermal or chemically induced breakdown of the PAAs begins in this temperature range. The critical temperature of phenol is approximately 421 °C, so the effect observed was not as a result of the supercritical nature of phenol.

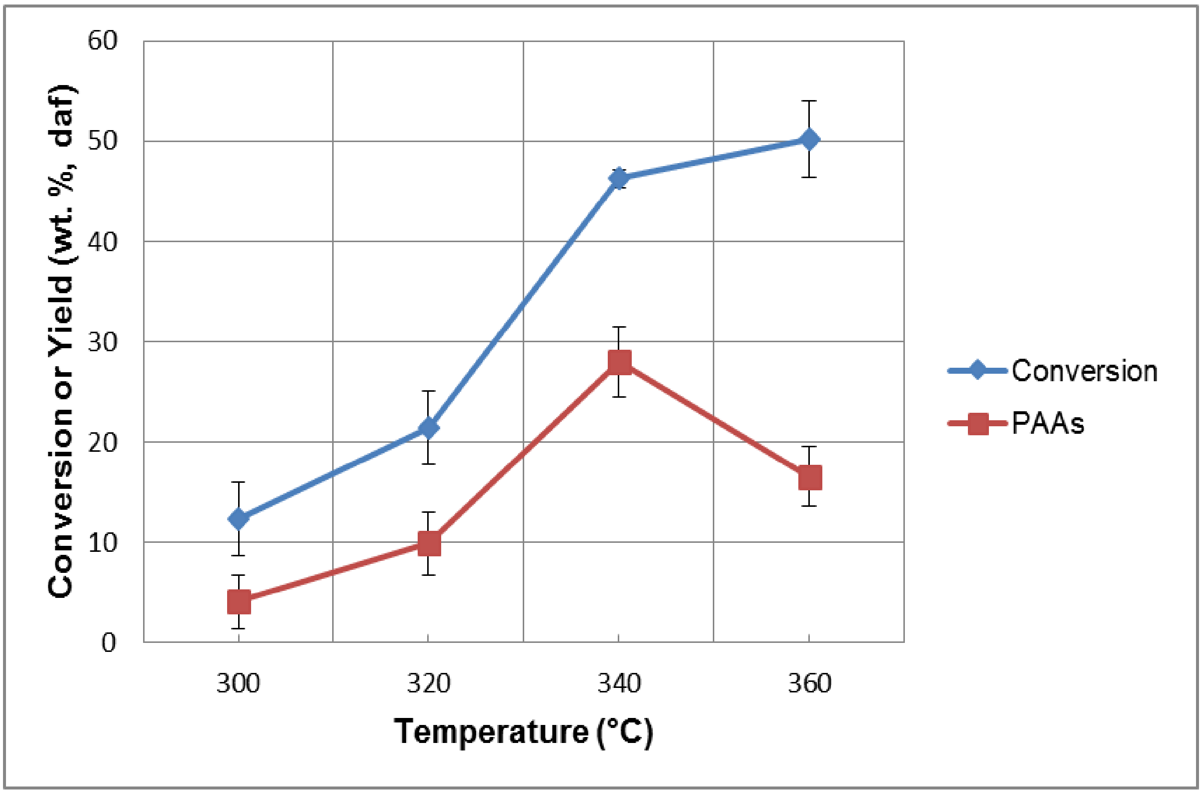


Figure 3.4. Coal conversion and yield of PAAs during solvent extraction

3.3.5 The effect of the temperature during solvent extraction

The effect of the temperature during solvent extraction with the use of phenol as the solvent for the enhancement of the oil yields (HS fractions) is shown in Figure 3.5. The oil yield increased from 3% to 27% with an increase in temperature between 300 °C and 360 °C. The most significant increase in oil fraction occurred when the extraction temperature was raised from 340 °C to 360 °C. This observation corresponds with the large drop in yield of PAAs with the same temperature increase. Since the gas yield is approximately constant as a function of temperature, an increase in conversion and a drop in PAAs yield necessarily becomes an increase in oil yield. Though there is a small increase in conversion as the temperature increases from 340 °C to 360 °C, the increased oil yield corresponds almost exactly with the decreased PAAs yield. This observation is a good indication that the “extra” oil yield is due to the breakdown of PAAs. Increasing the extraction temperature from 340 °C to 360 °C, the conversion increases by approximately 3% (roughly 47% to 50%). In this same range, PAAs yield drops by approximately 11% (roughly 28% to 17%). The oil yield increases by roughly 15% (12% to 27%). The increase in oil yield is thus numerically accounted for by the slight increase in conversion plus the large decomposition of the PAAs. At 360 °C (Figure 3.5), oils represented more than half of the total products (≈56%), and about 62% of the total liquid products (i.e., oils + PAAs).

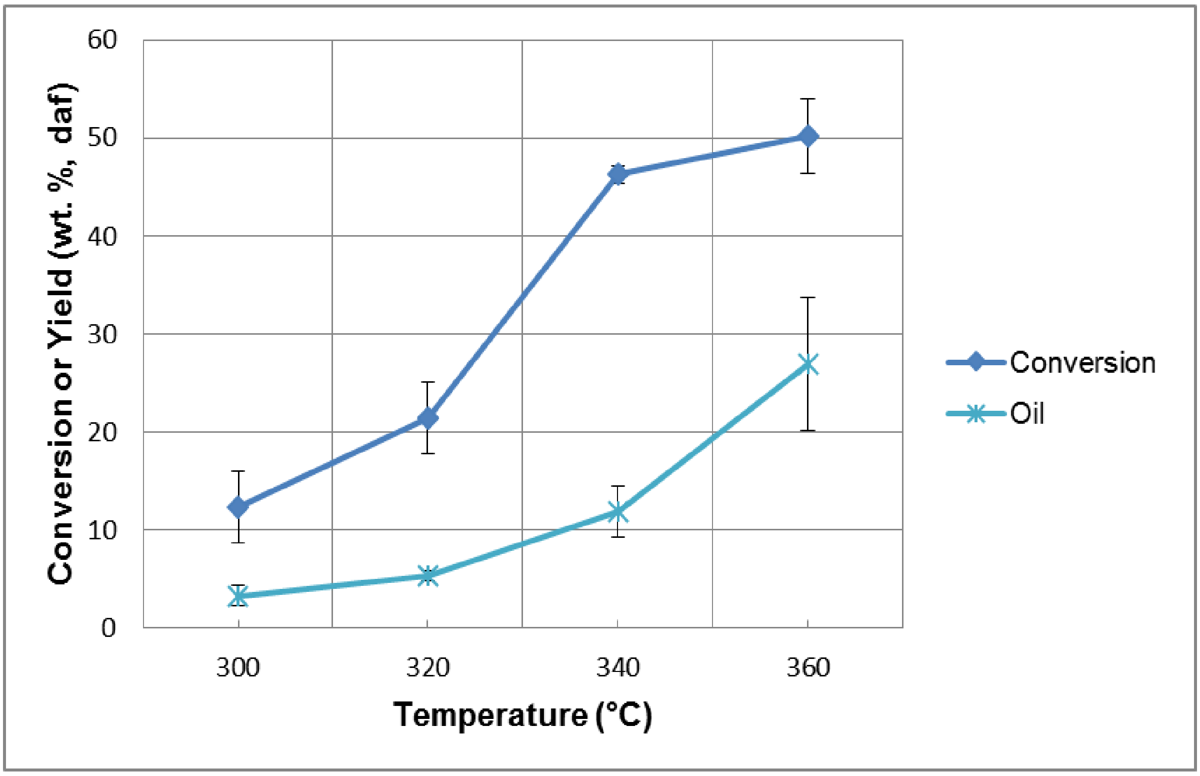


Figure 3.5. Coal conversion and oil yields during solvent extraction

The temperature is crucial for the cracking of the coal macromolecular structure for the radical formation and increased reaction product yields during coal solvent extraction. All extraction temperatures used in the present study were above the boiling point of phenol at atmospheric pressure (182 °C) markedly increases the yield of soluble products from coal as reported in the literature.[25–27]

3.3.6 Pyrolysis of coal and PAAs during TGA test

Figure 3.6 (a-b) shows the TGA and DTG analysis of the coal and HI (PAAs) at a slow heating rate of 4 °C/min and at higher temperatures. The TGA curves show that the raw coal and the PAAs had approximately 64 wt. % of reacted residues, and emission of volatile matter of approximately 36 wt. % at the end of the pyrolysis (up to 900 °C). As coal pyrolysis progresses between 300 and 360 °C, the volatile matter content is significantly lower in those regions than observed for conversion from extraction temperatures as seen in Figure 3.4. This observation suggests little thermal breakdown of the coal structure occurred in these temperature ranges. The influence of thermal degradation on the behavior of the coal and PAAs are investigated without the presence of the solvent. As expected, the weight losses of both samples increased with increasing pyrolysis temperature.

The DTG analysis of the original coal shows a single peak with maximum mass loss rate at approximately 430 °C (Figure 3.6b). However, the PAAs show two maxima peaks at approximately 220 °C and 450 °C respectively. The peak at 450 °C was also observed for the unreacted coal. However, the height of the peak at 450 °C is lower for the PAA sample than for the corresponding peak from the unreacted coal. The latter thus seems to correspond to the peak with maximum temperature at 430 °C for the coal sample. The weight loss of PAAs started at the initial temperature of approximately 140 °C, and the softening temperature of asphaltenes and preasphaltenes has been reported to occur at 140 and 150 °C respectively.[46] The components of the PAAs could include some species originally present in the coal and dissolved during the extraction process.

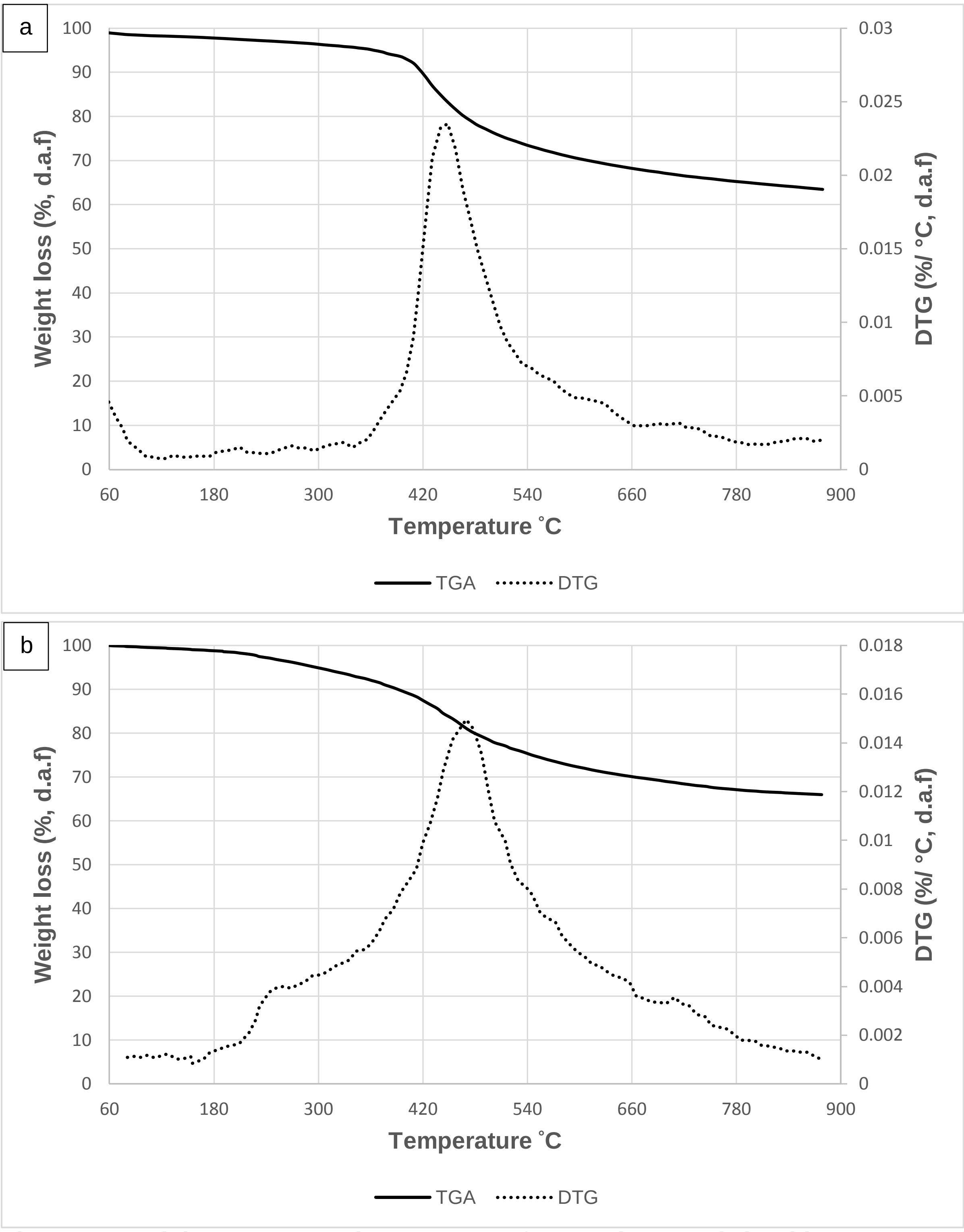


Figure 3.6. Weight loss TGA and DTG curves of pyrolysis at 4 °C/min without solvent a) raw bituminous coal and b) PAAs

TGA results (Figure 3.6a and 3.6b) suggest that interactions occur between the coal and phenol as noted by a small difference in the pyrolysis behavior of the raw coal without solvent between 300-360 °C. This observation is corroborated by Rappoport and Khudyakova,[22,23] who reported that depolymerization, rather than decomposition, occurs at high temperatures in the presence of a solvent due to small amounts of volatiles from the coal pyrolysis between the range 300-360 °C.

The solvent extraction chemistry may be compared to that of pyrolytic conditions with no solvent present, as found in coking reactions, whereby an increase in conversion is related to hydrogen depletion of the coal residue to form coke.[37] Carbonization of coals in closed systems under inert gaseous conditions, generally results in an increase in coke and gas yields, with a decrease in tar yields. According to studies by Geng *et al.*[47], Fischer assay analysis of the Shenmu bituminous coal sample was conducted between 460 °C and 580 °C. The process produced a semi-coke, oil and gas with contents of 75–80%, 8–10%, 2–9% respectively. The oil and gas yields from the coal sample reached 9.24 and 5.24 wt. % respectively at the optimum temperature of 520 °C. The observed extent of conversion of the Waterberg bituminous coal to produce solvent extraction products at mild temperatures depends both on temperature, and on the chemical action of the solvent. To summarize, conversion increases with increasing temperature, from 12% at 300 °C to 50% at 360 °C. Up to 340 °C, the yield of PAAs as a function of temperature parallels the temperature dependence of conversion. Between 340 and 360 °C, a drop in PAA yield was observed. A corresponding increase in oil yield was shown suggesting that chemical interactions, such as further depolymerization of PAAs, occur and start to become important at 340 °C.

3.3.7 ATR-FTIR Spectroscopy

Figure 3.7 shows FTIR spectra of the unreacted coal residues (THFIs) and the raw coal sample, and Figures 3.8 and 3.9 show the FTIR spectra of the coal solvent extraction products obtained at the selected temperatures. The wavenumbers of the main functional groups in raw coal and solvent extracted products were between 3500–2800 cm^{-1}, as well as between 1700 and 1000 cm^{-1}. From Figure 3.7, the spectra for the raw coal and unreacted coal residues (THFIs) are similar, especially the O-H (3500–3200 cm^{-1}), C-H aromatic (3200–2900 cm^{-1}) and aliphatic C-H (2919–2841 cm^{-1} and approximately 1400 cm^{-1}) stretching modes. The peaks observed in the 1700–1430 cm^{-1} range correspond to C=C bending and C=C stretching vibrations for aromatic ring (cyclic) structures.[48] The stretching vibration of C-O is found in the range 1200–1000 cm^{-1}. The broad band at 3200 cm^{-1} may belong to the OH vibration in water, phenol, alcohol and carboxyl groups. The spectra of the THFIs, HS fractions and pre-asphaltenes and asphaltenes (PAAs, HI) indicate that more hydrogen bonding occurs than for raw coal, as a high-intensity broad band of O-H stretching vibrations is observed with increasing temperature. These results show that some of the weaker hydrogen bonds in the raw coal are broken during solvent extraction at mild temperatures between 300 °C and 360 °C. The ATR-FTIR spectra (Figure 3.7–9) indicate that the extracted products display similar spectra to that of the raw coal. This observation is fairly well known in liquefaction and solvent extraction literature, as shown, by results obtained on coal of approximately 80% carbon content by Ouchi et al.[49] The SEM image of the coal showed structural changes after solvent extraction at specific temperatures where the coal residues were characterized by porous structures that are due to the release of volatiles during thermal treatment (Appendix A.1).

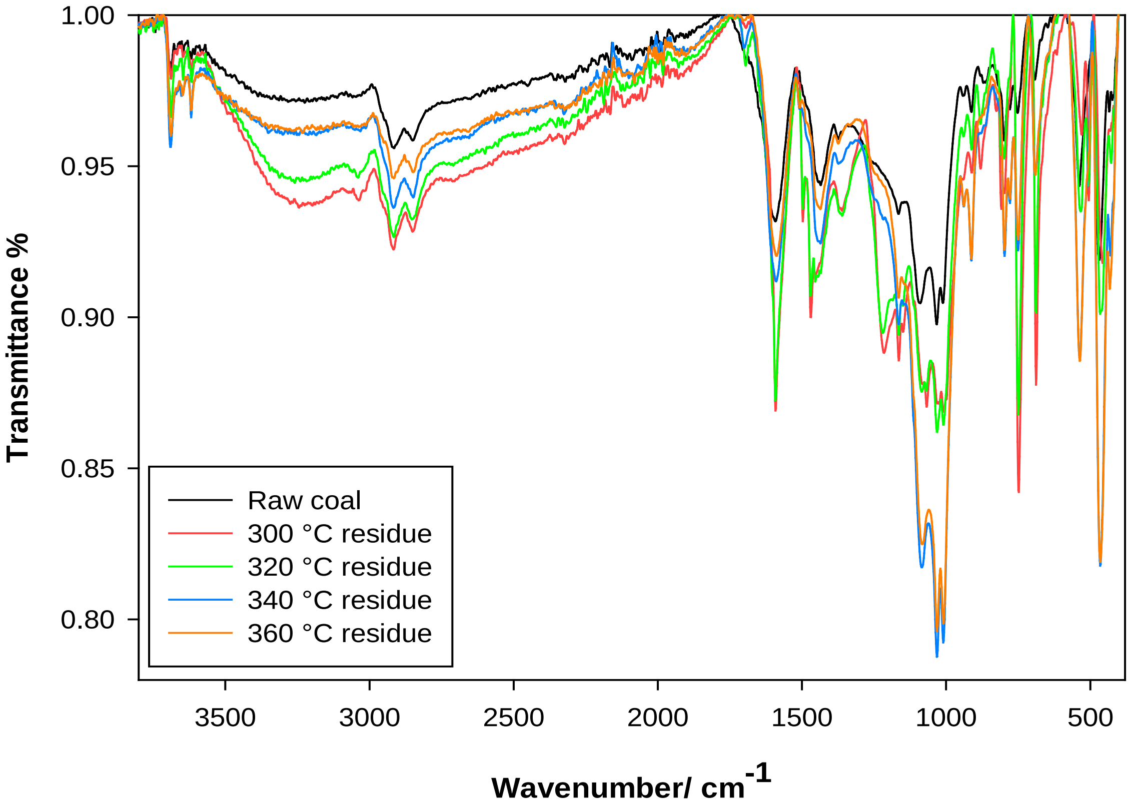


Figure 3.7. Infrared spectrum of coal sample and unreacted coal residues (THFIs) after coal solvent extraction at temperatures between 300 °C and 360 °C using phenol as solvent

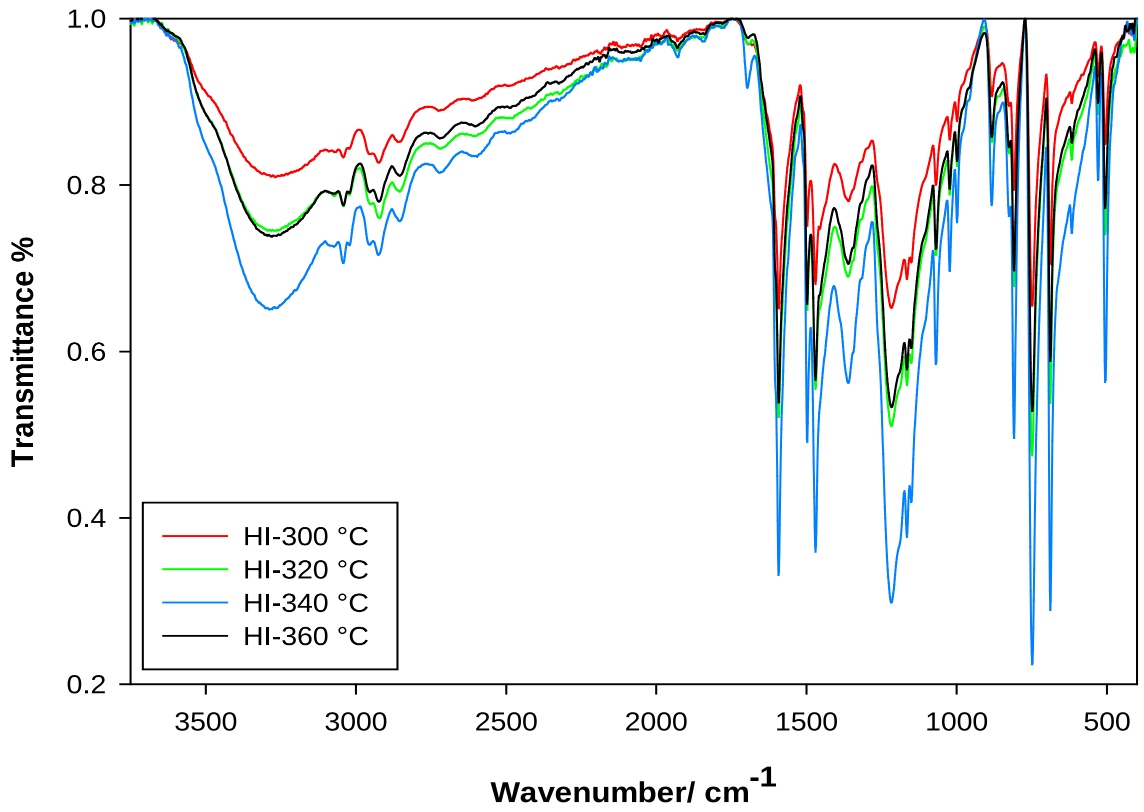


Figure 3.8. Infrared spectrum of hexane-insoluble products (PAAs) after coal solvent extraction at temperatures between 300 °C and 360 °C using phenol as solvent

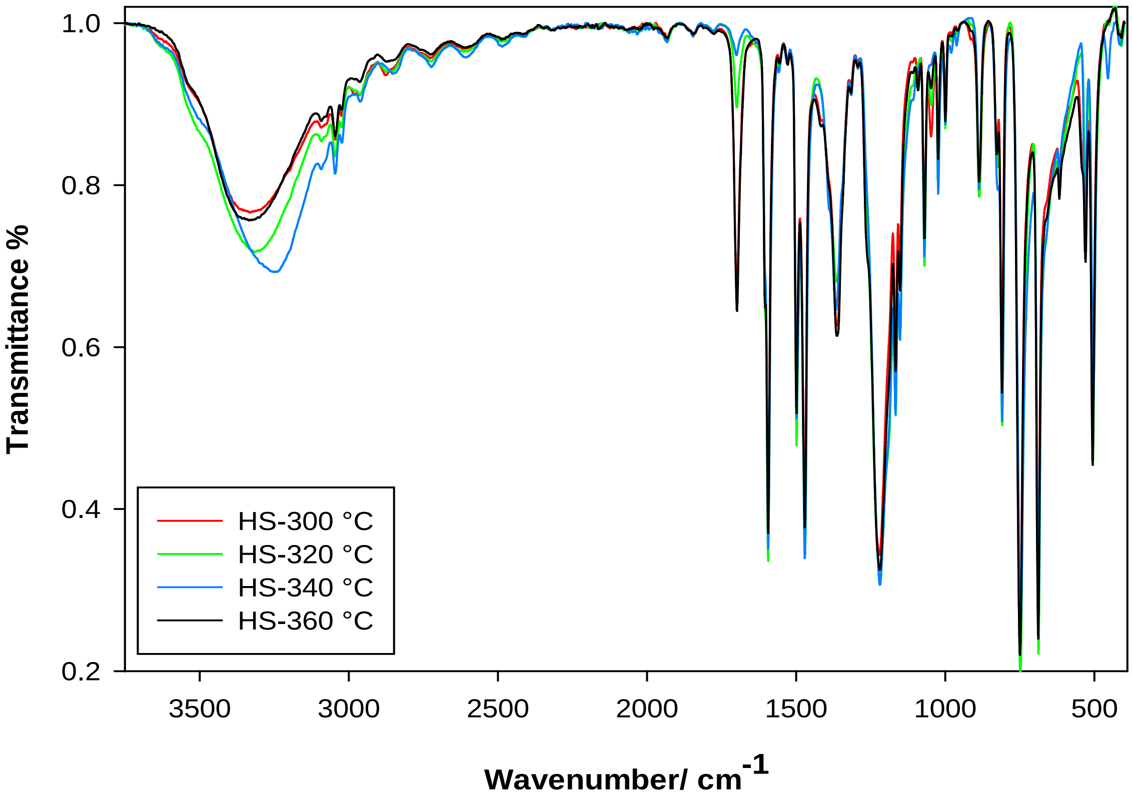


Figure 3.9. Infrared spectrum of the HS products after coal solvent extraction at temperatures between 300 °C and 360 °C using phenol as solvent

3.3.8 SimDis GC analysis

To compare the coal-derived liquids to crude oil as a potential refinery feedstock, coal liquids obtained from this study were further characterized. The boiling point range distributions for the HS fractions at different temperatures are shown in Figure 3.10. Evaluation of the boiling point curves for the samples have been determined on a phenol-free basis due to the hindrance of the phenol peak that masks other peaks. The lightest compounds (i.e. naphtha) with a boiling point distribution of 79–191 °C were co-eluted with the solvent elution peak as inferred from the excessive broadening of the solvent boiling point peak.[50]

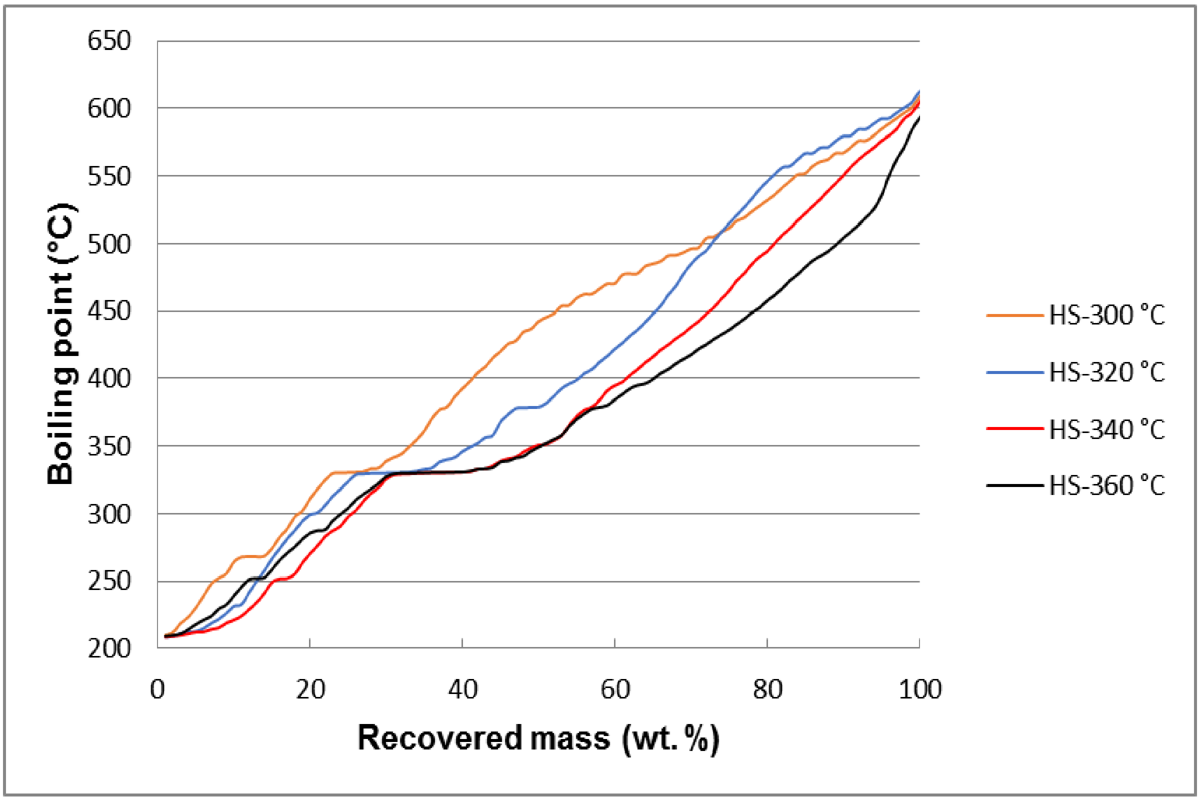


Figure 3.10. Distillation curves of liquefied products (HS) as determined by SimDis analysis

From Figure 3.10, it is observed that the HS fraction generated at 300 °C yielded the highest boiling point distribution with regard to constant recovered mass, followed by HS's generated at 320, 340 and 360 °C. However, at 500 °C and above, this trend is no longer observed as shown in Figure 3.10. The liquefied product (HS) contains compounds with a wide range of boiling points (208–615 °C). Table 3.3 summarizes the boiling point range distributions of samples that were fractionated into distinct sections following a cut fraction classification system developed for crude oil refining.[51,52] The HS fractions generated at different temperatures contained compounds confined to high boiling point ranges (277–615 °C). Extraction temperature has little effect on the number of products in the kerosene distillation range (191–277° C), as shown in Table 3.3. The boiling fraction of distillate fuel oil and light vacuum gas oil increases with an increase in temperature. However, vacuum gas oil decreases with rising temperatures. The largest proportion of the boiling constituents were light vacuum gas oil (23–31 wt. %), distillate fuel oil (16–30 wt. %), heavy vacuum gas oil (18–34 wt. %) and residual oil (3–16 wt. %). It is important to note that kerosene, distillate fuel oil, and light vacuum gas oil fractions show increasing amounts of recovered mass (in HS) at higher temperatures. This highlights the importance of thermal cracking in the chemical transformation of coal with phenol as the solvent to produce synthetic fuel. If the extraction temperature is high enough to initiate thermal fragmentation of the coal structure, depolymerization reactions can also be facilitated. The 191–566 °C distillation cut point represents constituents that can meet the requirements for production of fuels that can augment South African petroleum supply. The boiling point fractions of the solvent extraction products (HS) generated at different temperatures closely resemble that taken from commercial values for IS petroleum.[53,54] Thus, the boiling point fractions of the HS products indicate the use of the HS products for downstream refining of diesel and synthetic oil. Table 3.3 shows that there is a decreasing trend of mass recovered (12–3 wt. %) in residual oils of samples with increasing temperature, which indicates that most of the constituents are distillable at higher temperatures. According to the GC-MS results (Appendix A.2), these results showed that the main products in phenol extraction were alkyl substituted mono-aromatics, polyaromatics, and heterocyclic organic compounds.

Table 3.3 Boiling point distributions for the different HS fractions based on crude oil fractions

Boiling fraction/ definition	Boiling Range (°C)	Unit	HS-300 °C	HS-320 °C	HS-340 °C	HS-360 °C
Medium naphtha	79–121	wt.%	–	–	–	–
Heavy naphtha	121–191	wt.%	–	–	–	–
Kerosene	191–277	wt.%	14.0	15.0	20.0	17.0
Distillate fuel oil	277–343	wt.%	16.0	23.0	26.0	30.0
Light vacuum gas oil	343–455	wt.%	23.0	27.0	26.0	31.0
Heavy vacuum gas oil	455–566	wt.%	34.0	18.0	19.0	18.0
Residual oil	>566	wt.%	12.0	16.0	8.0	3.0
Total	–	wt.%	99.0	99.0	99.0	99.0
Initial boiling point	–	°C	209.8	208.6	208.6	209.2
Average boiling point (WABP)	100–550	°C	424.6	403.0	380.7	371.6
Final boiling point	–	°C	615.4	615.6	612.4	600.6

The average boiling point of the hydrocarbon constituents of the samples were calculated using Eq. (4). This equation estimates the weight average boiling point (WABP) using the method outlined by Worman and Green[55], and Kegler[56]:

$$\mathrm{WABP} = \frac{T_1 + T_2 + T_3 + T_4 + T_5}{5} \qquad (4)$$

where temperature (T_i) refers to the weight percentage of distilled fractions 1 to 5 obtained at temperature cut-points corresponding to 10, 30, 50, 70 and 90 wt.%. The respective calculated values are summarized in Table 3. It is noted that the HS generated at 300 °C has the highest WABP (424.6 °C). The WABP for other samples (403.0–371.6 °C) decreased with an increase in the maximum temperature at which extraction with phenol was conducted. This trend is proportional to the increase in the amounts of light lower boiling constituents (distillate fuel oil and light vacuum gas oil) as summarized in Table 3.

3.4. Conclusions

Solvent extraction of South African coal using phenol as a solvent was investigated. The study revealed the potential of phenol as a solvent for solvent extraction and showed that an increase in temperature increased the solvent extraction products derived from the coal. The increased yields suggest that thermal degradation of coal with phenol resulted in the depolymerization of the coal structure. The distribution of solvent extraction products showed the maximum oil yield of 27%, with the optimal conversion of 50% at 360 °C under 6 MPa N_2 initial pressure. The yields of PAAs reached a maximum value of 28% at 340 °C, then decreased to 17% at 360 °C. The change in yield at around 340 °C suggests that chemically induced breakdown of PAAs into further oil and gas during solvent extraction of coal begins in this temperature range.

The ATR-FTIR spectra of the extraction products are similar to the spectrum of the parent coal. This similarity suggests that the extraction process dissolves molecular fragments that are also present in the coal structure.

From SimDis results, the boiling point fractions of the coal-derived products are considered to be suitable for downstream refinement to petroleum as the boiling point constituents for light vacuum gas oil are between 23 wt.% and 31 wt.%. The present paper shows that South African bituminous coal can be used for solvent extraction at mild temperatures to obtain value-added liquid fuels from coal that can augment the petroleum supply.

Acknowledgements

The North-West University is acknowledged for partial funding of this research project. The assistance by Dr. Daniel van Niekerk (Sasol) with SimDis analysis is highly appreciated. We are grateful to Dr. David Powell from Exxaro for the supply of coal used in this paper. The work presented in this paper is based on research financially supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa (Coal Research Chair Grant No. 86880, UID85643, Grant No. TP1208137225). Any opinion, finding, conclusion, or recommendation expressed in this material is that of the author/s, and NRF does not accept any liability in this regard.

Chapter References

1. BP, Statistical Review of World Energy, Excel workbook of historical data, 2014. https://www.eia.gov/beta/international/analysis.cfm?iso=ZAF (accessed 17.02.16).
2. Akash, B.A. Int. J. of Thermal & Environmental Engineering **2013**, 5, 51–60.
3. Liu, Z.; Shi, S.; Li, Y. Chem. Eng. Sci. **2010**, 65, 12–17.
4. Larson, E.; Tingjin, R. Energy Sustain. Dev. **2003**, 7, 79–102.
5. Zhou, W.; Zhou, B.; Chen, D.; Zhao, F.; Fei, W. Energy **2011**, 36, 6559–6566.
6. Petrakis, L.; Gandy, D.W. Fuel **1981**, 60, 1017-1021.
7. Neavel, R.C. In: Coal Science. Volume I. (Gorbaty, M.L.; Larsen, J.W.; Wender, I., eds.) Academic Press, New York, 1982, pp 1-21.
8. Burgess, C.; Huang, L.; Martin, S.; Tomic, J.; Schobert, H.H. Proceedings, 9th International Conference on Coal Science **1997**, 3, 1373-1376.
9. Schobert, H.H. Chemistry of Fossil Fuels and Biofuels. Cambridge University Press: Cambridge, 2013, Chapter 22.
10. Harger, J. J. Soc. Chem. Ind. **1914**, 33, 389–393.
11. Illingworth, S.R. Fuel Sci. Pract. **1922**, 1, 213–219.
12. Asbury, R.S. Ind. Eng. Chem. **1934**, 26, 1301–1306.
13. Lowry, H.H. J. Inst. Fuel **1937**, 10, 291–301.
14. Kiebler M.W. The action of solvents on coal; In “Chemistry of Coal Utilization” (H.H. Lowry. Ed), Wiley, New York, 1945, pp 677–760.
15. Lowry, H.H.; Rose, H.J. U.S. Bur. Mines **1947**, Inform*. Circ*. No. 7420, 12.
16. Pilipetzs, M.G.; Kuhn, E.; Friedman, S.; Storch H.H. U.S. Bur. Mines **1949**, Rept. Invest. 4546.
17. D’yakova, M.K. Academy of Science of the U.S.S.R. **1957**, 86.
18. Van Niekerk, D.; Pugmire, R.J.; Solum, M.S.; Painter, P.C.; Mathews, J.P. Int. J. Coal Geol. **2008**, 76, 290–300.
19. Van Niekerk, D.; Mathews, J.P. Fuel **2010**, 89, 73–82.
20. Van Niekerk, D.; Mitchell, G.D.; Mathews, J.P. Int. J. Coal Geol. **2010**, 81, 45–52.
21. Pew, J.C.; Withrow, J.R. Fuel **1931**, 10, 44–47.
22. Rappoport, I.B.; Khudyakova, A.D. J. Appl. Chem. (U.S.S.R.) **1939**, 12, 759–766.
23. Rappoport, I.B.; Khudyakova, A.D. Chem. Abs. **1940**, 34, 3051.
24. Kiebler, M.W. Ind. Eng. Chem. **1940**, 32, 1389–1394.
25. Orchin, M.; Storch, H.H. Ind. Eng. Chem. **1948**, 40, 1385–1389.
26. Golumbic, C.; Anderson, J.B.; Orchin, M.; Storch, H.H. Bur. Mines **1950**, Report of investigation No. 4665, 12.

27. Orchin, M.; Golumbic, C.; Anderson, J.E.; Storch, H.H. U.S. Bur. Mines **1951**, Bull., No. 505, 15.
28. Butala, S.J.M.; Medina, J.C.; Hulse, R.J.; Bartholomew, C.H.; Lee, M.L. Fuel **2000**, 79, 1657–1664.
29. Herédy, L.A.; Neuworth, M.B. Fuel **1962**, 41, 221–231.
30. Herédy, L.A.; Kostyo, A.E.; Neuworth, M.B. Fuel **1965**, 44, 125–133.
31. Ouchi, K.; Imuta, K.; Yamashita, Y. Fuel **1973**, 52, 156–157.
32. Darlage, L.J.; Bailey, M.E. Fuel **1976**, 55, 205–210.
33. Park, Y.; Mochida, I. Carbon **1989**, 27, 925–929.
34. Mochida, I.; Yozo, K.; Cha, K.; Fumitaka, W.; Yukio, S. Carbon. **2000**, 38, 305–328.
35. Guo, Z.; Bai, Z.; Bai, J.; Wang, Z.; Li, W. Fuel Process. Technol. **2011**, 92, 119–125.
36. Yan, J.; Bai, Z.; Li, W.; Bai, J. Fuel **2014**, 136, 280–286.
37. Hernández, M.R.; Murcia, C.F.; Gupta, R.; de Klerk, A. Energy Fuels **2012**, 26, 6834–6842.
38. Van Rensburg, E. J. Solvent extraction of South African coal using a low volatile, coal-derived solvent. M.Eng. dissertation at the North-West University, South Africa. 2007.
39. Makgato, M.H.; Neomagus, W.J.P.; Everson, R.C.; Schobert, H.H. Production of liquid fuel precursors from South African vitrinite-rich coal by direct liquefaction. International Conference on Coal Science & Technology (ICCS&T), 9–13 October 2011, Oviedo, Spain.
40. Pott, A.; Brosche, H.; Nedelmann, H.; Schimdtz, H.; Scheer, W. Glückauf **1933**, 69, 903–12.
41. Pott, A.; Brosche, H.; Nedelmann, H.; Schimdtz, H.; Scheer, W. Fuel **1934**, 13, 91–5, 125–8, 154–7.
42. McNeil, R.I.; Cronauer, D.C. Fuel Process. Technol. **1984**, 9, 43–52.
43. Larsen, J.W.; Sams, T.L.; Rodgers, B.R. Fuel **1981**, 60, 335–341.
44. Miura, K.; Mae, K.; Li, W.; Kusakawa, T.; Morozumi, F.; Kumano, A. Energy Fuels **2001**, 15, 599–610.
45. Speight, J.G. The Chemistry and Technology of Coal. Marcel Dekker: New York, 1994; Chapter 12.
46. Barraza, J.; Muñoz, N.; Barona, L. Rev. Fac. Ing. Univ. Antioquia N. º70 **2014**, 99–107.
47. Geng, C.; Li, S.; Yue, C.; Ma, Y. J. Energy Inst. **2016**, 89, 725–730.
48. Painter, P.C.; Snyder, R.W.; Starsinic, M.; Coleman, M.M.; Kuehn, D.W.; Davis, A. Appl. Spectrosc. **1981**, 35, 475–4
49. Ouchi, K.; Imuta, K.; Yamashita, Y. Fuel **1965**, 44, 29–38.
50. Dulaurent, A.; Dahan, L.; Thiébaut, D.; Bertoncini, F.; Espinat, D. Oil Gas Sci. Technol. – Rev. IFP **2007**, 62, 33–42.

51. Giles, H.N. Significance of tests for petroleum products, 7th ed.; Rand, S.J., Ed.; ASTM International: West Conshohocken, PA, 2003; pp 51–62.
52. Gary, J.H.; Handwerk, G.E.; Kaise, M.J. Petroleum Refining Technology and Economics, Fifth Edition, CRC Press, 2007.
53. Villalanti, D.C.; Raia, J.C.; Maynard, J.B. High-temperature simulated distillation applications in petroleum characterization. In Encyclopaedia of Analytical Chemistry. http://onlinelibrary.wiley.com/doi/10.1002/9780470027318.a1819/full, 2016 (accessed 05.01.16).
54. Lee, K.H. Journal of Analytical and Applied Pyrolysis **2012**, 94, 209–214.
55. Worman, J.C.; Green, L.E. Anal. Chem. **1965**, 37, 620–1621.
56. Kegler, W.H. Control of feedstock for delayed coking. US Patent 4,043,898, August 23, 1977.

Chapter 4

Bio-oil production from sweet sorghum bagasse via liquefaction using alkaline solutions and identification of phenolic products

Thabo Z. Sehume, *Christien A. Strydom, John R. Bunt and Harold H. Schobert*

In this chapter, the bio-oil was produced after treating biomass with various concentrations of sodium hydroxide (NaOH) solutions (0.5, 1, 3 and 6 M) at different temperatures and the results are reported herein.

Abstract

In order to investigate the feasibility of converting biomass into bio-oil, the effect of an alkaline treatment during biomass liquefaction was studied. Sweet sorghum bagasse (SSB) was treated with NaOH concentrations of 0.5, 1.0, 3.0 and 6.0 M. The experiments were conducted in a temperature range of 260–320 °C in N_2. The results showed that the alkaline treatment affected the product distribution of SSB liquefaction. The highest yield of bio-oil (53.2 wt. %) and phenols extracted (≈40.0 wt. %) were obtained at a reactor temperature of 320 °C and NaOH aqueous solution of 3.0 M. The bio-oil fractions and extracted phenols were characterized by attenuated total reflection Bruker Fourier Transform Infra-Red spectrometry (ATR-FTIR) and gas chromatography-mass spectrometry (GC-MS). The ATR-FTIR results indicated the presence of carboxyl, ketone, ester and aromatic ring structures in the bio-oils. The absorption intensities of all the bio-oils at 1100 cm^{-1} (primary alcohols) substantially decreased with an increase in temperature and NaOH concentration. At a given reaction temperature, the use of 3.0 and 6.0 M NaOH resulted in the extraction of more identifiable phenol derivatives than were obtained with the lower concentrations of NaOH. These results suggest that a temperature of 320 °C and a NaOH concentration of 3.0 M yields the best results of the four temperatures tested, and also that alkaline treatment is feasible for liquefaction and extraction of phenols from the bio-oil.

4.1 Introduction

Biomass is a renewable energy source that is considered to be more carbon dioxide (CO_2) friendly (if land use change is added to the mass balance) than coal and has the potential to substitute or be co-utilised with fossil fuels as an energy source and for the production of chemicals through different processes.[1–3] Lignocellulosic biomass is composed of carbohydrates (cellulose and hemicellulose), lignin and other components (proteins, lipids, and inorganic materials).[2,4] Lignin is composed of phenyl-propane units, which are a rich source of phenols upon thermal degradation.[5] One of the desirable products that can be produced from biomass is bio-oil. This bio-oil is produced through liquefaction (i.e. thermal, hydrothermal or by the use of solvents).

Liquefaction of biomass materials occurs through a sequence of structural and chemical changes, which involve at least the following steps[6,7]: (1) cracking and reduction of polymers such as lignin and lipids; (2) hydrolysis of cellulose and hemicellulose to glucose; (3) hydrogenolysis of organic compounds; (4) reduction of amino acids; (5) new molecular rearrangements through dehydration and decarboxylation; and (6) hydrogenation of functional groups. Hydrothermal liquefaction can liquefy biomass with any level of moisture content and it also leads to high biomass conversion and relatively pure products.[8,9] According to Gollakota and Kishore,[10] hydrothermal liquefaction of biomass is the thermochemical conversion of biomass into liquid fuels by processing the biomass in a hot, pressurized water environment for sufficient time to break down the solid bio-polymeric structure to mainly liquid components. Generally, the hydrothermal processing conditions include a temperature range of 250–370 °C and pressure starting from 4 up to 22 MPa. This method is ideal for the production of valuable chemicals at a low operating temperature and with a low tar yield compared to the pyrolysis process.[10,11] However, at high biomass to solvent ratios, the hydrothermal process tends to behave similarly to the pyrolysis process.[8] The high operating temperatures of pyrolysis (400–1000 °C) can lead to recombination or cross-linking reaction between various molecular fragments, resulting in tar which is difficult to degrade further.[11] High temperatures are not usually suited for the production of liquid products both in terms of operational cost and liquid oil yield.[8]

Solvents can extract biomass components and enhance the dissolution of biomass fragments during the hydrothermal treatment of biomass.[8] Biomass liquefaction through the use of various solvents has been described in the literature.[12] Karagoz et al.[13–15] carried out low temperature (<280 °C) liquefaction in water and investigated the effects of treatment conditions, including catalysts, temperature and reaction time. Water can act as both a reactant and reaction medium between 220 °C and 300 °C.[9] As a reactant, water facilitates hydrolysis reactions and rapidly degrades the polymeric structure of biomass to water-soluble products.[16,17] It has been reported that an aqueous solution of NaOH can directly and quickly dissolve lignocellulosic biomass at lower temperatures.[18–20] NaOH can be an effective agent for both delignification and solubilization of lignocellulosic materials.[21] Lignin usually plays a negative role in the chemical utilization of biomass; thus, it must be modified, partially degraded, or completely removed depending on the end uses of the final products.[22] Kim et al.[23] reported that the alkaline reagents interact primarily with lignin and suggested that they are more efficient for lignin removal. Li et al.[18] investigated the dissolution of wheat straw with an aqueous NaOH/urea solution (NaOH: urea: H_2O=10:9:81 wt. %). The aqueous NaOH/urea solution is reported to be capable of dissolving complex macromolecules with high efficiency by destroying the cellulose-hemicellulose-lignin network and the hydrogen bonds in the cellulose.[18] The addition of aqueous alkaline solutions assisted the enhanced swelling of cellulose, collapsed the crystalline structure, and reduced the degree of polymerization (DP).[24] It was observed that for cellulose with low to moderate degree of polymerization, the maximum solubility occurs with 8–10% sodium hydroxide solution.[22] Isogai and Atalla[25] investigated cellulose dissolution in aqueous NaOH particularly focusing on the effects of crystalline form and molecular weight. They suggested that the long-range order in solid cellulose, that is, a dimension over 100 nm, is the determining factor preventing cellulose dissolution in caustic soda solutions. Generally, alkaline or alkali/urea based solvent systems are well suited for dissolution of cellulose at low temperatures.[22,25]

The production and extraction of valuable chemicals, such as phenols, from the bio-oil obtained through low-temperature liquefaction of agricultural biomass is less investigated when compared to woody biomass obtained through the pyrolysis process (>400 °C). Phenols are generally formed by dehydration, isomerization, and cyclization reactions.[26] Amen-Chen et al.[27] reported an optimum extraction procedure using a NaOH solution of 2 M while determining the effect of pH on the recovery of phenols. We chose to focus our work only on the lignin component of the biomass, and on the phenols that are known to be derived from lignin. This choice was made because we were interested in using biomass as a source of mixed phenols that could subsequently be used to facilitate the production of useful liquids from South African coals. It has been reported that 6-ring sugars (from cellulose fractions) can also contribute towards the formation of phenolic derivatives during hydrothermal liquefaction.[28]

4.2 Experimental Section

4.2.1 Materials and reagents

The sweet sorghum bagasse which was used in this study was supplied by the Agricultural Research Council, Grain Crops Institute (Potchefstroom, South Africa). The biomass feedstock was air dried for a week and pulverized to obtain a particle size of <1.5 mm. Sodium hydroxide (NaOH) with a purity of 99.87% was supplied by CC Imelmann (Pty) Ltd (South Africa). Hydrochloric acid (HCl) and chloroform were supplied by Associated Chemical Enterprises (ACE) and Minema, South Africa. Nitrogen (purity ≥ 99.999%) gas cylinders were obtained from Africa Oxygen Limited (Afrox) (South Africa). Phenols standards were purchased from Industrial Analytical (Pty) Ltd (South Africa) and were used without further purification. These samples include phenol (CAS 108-95-2), guaiacol (CAS 90-05-1), 4-ethylphenol (CAS 123-07-9), 2-methoxy-4-methylphenol (CAS 93-51-6), 4-ethylguaiacol (2785-89-9), 4-methylphenol (CAS 106-44-5), 4-isopropylphenol (CAS 99-89-8), 2-propylphenol (CAS 644-35-9), 4-n-propylphenol (CAS 645-56-7) in methanol; certified reference material of the standard solution is summarized in Appendix B.2.

4.2.2 Alkaline treatment of biomass and liquefaction process

Raw biomass samples (20 g) were mixed with aqueous solutions of NaOH of various concentrations (200 mL) in the liquefaction reactor. The treatment process is aimed at producing a phenolic-rich bio-oil fraction (which includes water and organics). Four NaOH concentrations were prepared (0.5, 1.0, 3.0 and 6.0 M) to determine the effect of concentration on the bio-oil yield.

All experiments were conducted in a stainless steel high-pressure autoclave (Figure 4.1) (volume 950 mL), which was charged with the biomass and the solvent (NaOH solution) to the ratio of 1:10. The reactor was sealed and flushed with a carrier gas (N_2). The autoclave was pressurized and heated up to the desired temperature in an N_2 atmosphere (initial cold pressure of 0.5 MPa) at a heating rate of 4 °C/min. Biomass sample was liquefied, with one of the alkaline aqueous solutions, at reaction temperatures of 260, 280, 300 and 320 °C, whilst magnetically stirring the mixture at 300 rpm, and with a holding time of 30 min at each specified maximum temperature (±4 °C). The temperature range chosen (260-320 °C) in this study is in the active region for major devolatilization of the biomass. The effect of residence times on hydrothermal liquefaction has been explored by other authors.[13,29] According to Boocock and Sherman,[30] longer residence times suppresses the bio-oil yield except for very high biomass to water ratios. Yan et al.[9] concluded that a reaction time of 30 min is sufficient to liquefy sugarcane bagasse in water and obtain the highest heavy oil and total oil yields.

4.2.3 Characterization of products

After each run, the autoclave was cooled to ambient temperature by employing an electric fan and then depressurized. The solid-liquid mixture was removed from the autoclave, weighed and then vacuum-filtered to separate the liquids and the solid residues (SRs). The liquid product consisted of the bio-oil (BO) and aqueous products. The liquid product was neutralized (pH≈ 7) with 1 M HCl solution. This liquid product was separated into two layers (organic and inorganic phases) using chloroform. Then the evaporation of the chloroform followed by using a rotary evaporator at nearly 70 °C to obtain the bio-oil product. The yields of SRs (Y_{SRs}) and the BO (Y_{BO}) to SSB on a dry and ash-free basis, respectively; i.e., $Y_R = M_G/M_{SSB,\ daf}$ and $Y_{BO} = M_{BO}/M_{SSB,\ daf}$. The yield of the non-condensable gaseous products (Y_G) was obtained by difference; i.e., $Y_G = 1 - Y_R - Y_{BO}$. As the major interest of this study was mostly based on the bio-oil production, the aqueous phase and gaseous products were not analyzed.

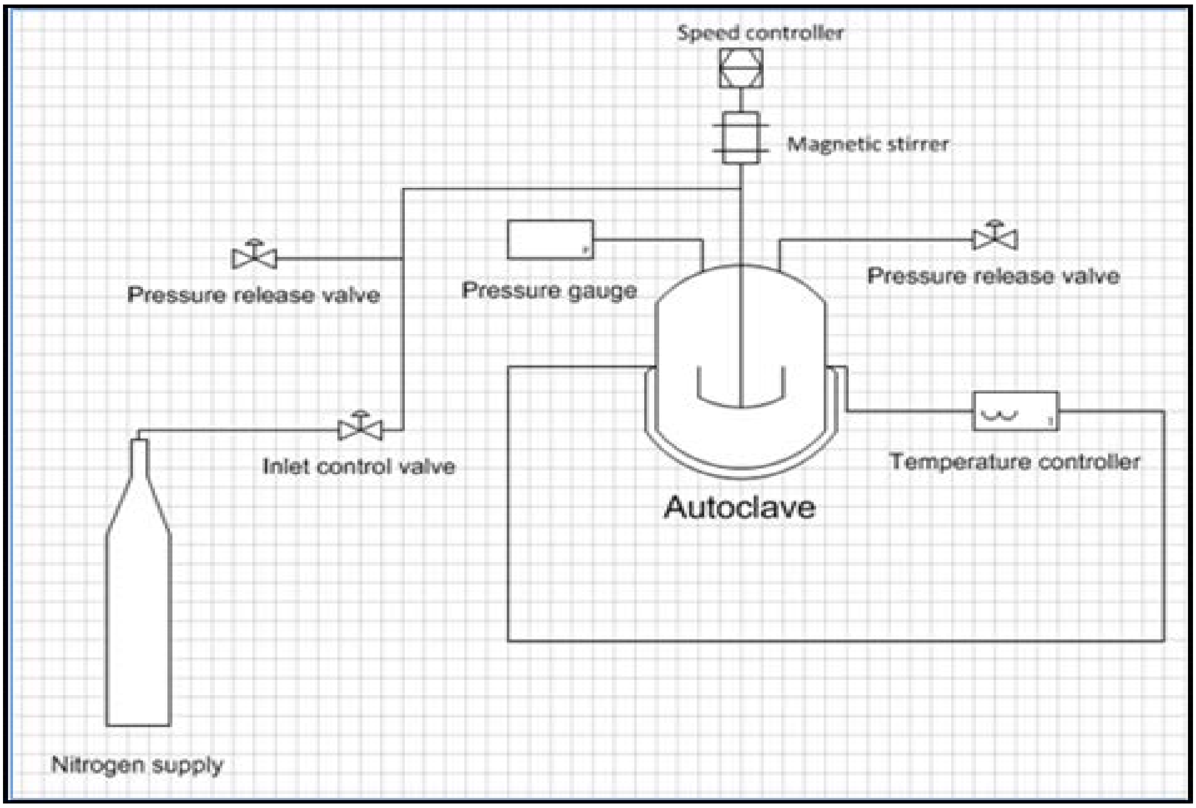


Figure 4.1 Schematic diagram of the high-pressure autoclave system

4.2.3.1 Characterization of biomass

The characterization of sweet sorghum bagasse (SSB) was carried out at the Agricultural Research Council (ARC, South Africa), Irene laboratories, using methods summarized in Table 4.1.

4.2.3.2 Aqueous phase content

The aqueous phase contents in the liquefaction liquid streams were determined using a volumetric Karl–Fischer (KF) titration method utilizing a Metrohm automatic titration instrument according to the IP438 method.[31] The organic contents in the liquid mixture were measured by mass balance. The measurements of each sample were made at least in triplicate.

4.2.3.3 Ultimate analysis

The ultimate analysis of the raw biomass feedstock was carried out using an Elemental Vario El cube elemental analyzer, according to the ASTM 29541 method,[32] in order to determine the contents of carbon, hydrogen, and nitrogen. The oxygen and sulphur contents (grouped together) were subsequently calculated by difference.

4.2.3.4 ATR-FTIR analysis

Samples were analyzed using an attenuated total reflection Bruker Fourier Transform Infra-Red spectrometer (ATR-FTIR) with an ALPHA's Platinum ATR single reflection diamond ATR module, at ambient temperature in the region of 400 to 4000 cm^{-1}. Infrared spectroscopy was used to elucidate the effect of the liquefaction process on the functional groups of bio-oils that were obtained at different temperatures and concentrations.

4.2.4 GC-MS analysis of phenols

The chemical compositions of the extracted phenolic compounds from the bio-oils were characterized by GC-MS using an Agilent 6890N gas chromatograph coupled with an Agilent 5975 mass detector. The GC was equipped with an Agilent 19091S column (30 m length, 0.25 mm diameter, 0.25 µm film). An injector split ratio of 10:1 and an inlet temperature of 250 °C were chosen. The program selected for the oven temperature was 35 °C for 2 min, then the temperature was increased with 5 °C/min to 320 °C, after which the last temperature was held for 10 min. The extracted phenolic compounds were quantified by GC-MS. Calibration curves were established using an internal standard consisting of identified phenols.

4.2.5 Liquid-liquid (ℓ-ℓ) extraction of phenols from the bio-oil

Solvent extraction is generally used to get higher concentrations of phenols from the bio-oil.[33] The steps followed during the extraction procedure were as reported in the literature and are illustrated in Figure 4.2.[34,35] The steps were:

(1) Mix 5 g of the bio-oil sample with an aqueous NaOH solution (2.5 M) in a 1:3 ratio by volume and magnetically stir the mixture for 5 min for the transformation of phenols;

(2) The extraction of phenols was conducted at a pH near 5 by adding drops of HCl solution (32 vol. %);

(3) The extraction of phenols from the aqueous phase was done with a volumetric ratio of bio-oil sample to ethyl acetate of 1:5 to form two distinct phases that were magnetically stirred in a closed system for 1 h;

(4) The fraction soluble in ethyl acetate was concentrated to a volume of approximately 5 mL using a rotary evaporator (the colour of the ethyl acetate solution changed from a colourless to an orange-brown liquid consisting of phenols), and was analyzed by gas chromatography-mass spectrometry (GC-MS) analysis to verify the identification and quantification of phenols.

The extraction procedure for each sample was repeated three times, and the average values were used to represent concentrations of phenols at each specific experimental condition.

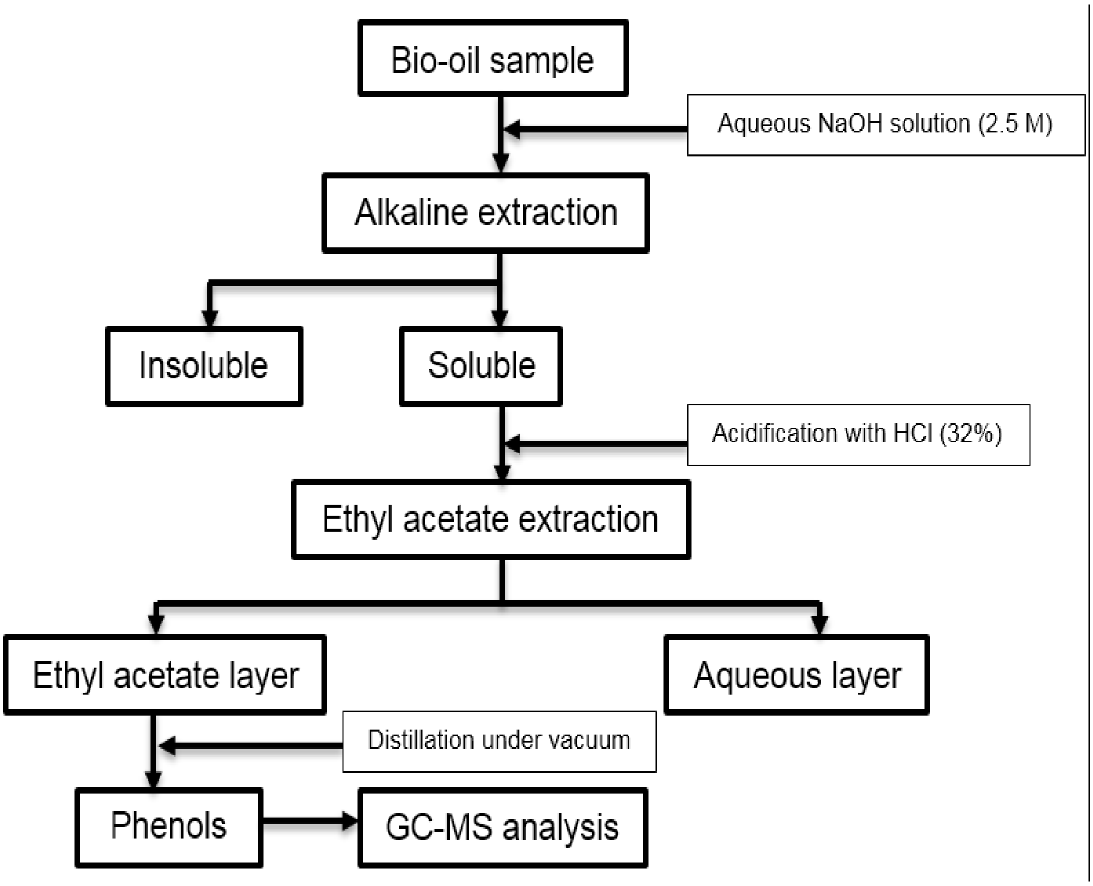


Figure 4.2. ℓ-ℓ extraction scheme of phenols from a bio-oil sample

4.2.6 SEM-EDS (Scanning electron microscopy with energy-dispersive X-ray spectroscopy) of SSB and solid residues (SRs)

Surface morphologies of the raw biomass and solid residues were observed using scanning electron microscopy (SEM, Quanta FEG 250 field emission gun (FEG) with environmental scanning electron microscope (ESEM) capabilities. The precision of the instrument with regard to the closeness of agreement between randomly selected individual measurements was ±0.1%.

4.2.7 Thermogravimetric analysis

The pyrolysis behaviour of biomass and solid residues was studied by thermogravimetric analysis (TGA, SDTQ600). Samples of approximately 12 mg were analyzed. Thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles of both the untreated biomass and the solid residues were obtained using a heating rate of 20 °C/min. Tests were conducted over the temperature range of 40–1200 °C under a nitrogen flow of 75 mL/min.

4.3 Results and Discussion

4.3.1 Chemical analysis of SSB

The chemical composition of the sweet sorghum bagasse (SSB) is summarized in Table 4.1. The characterization of the SSB corroborates the studies conducted by Mafu et al.,[32] using the same biomass feedstock. SSB has a low ash content (4.6 wt. %), high oxygen + sulphur content (44.5 wt. %) and H/C ratio of 1.57 (Table 1). Cellulose is generally the largest fraction followed by hemicellulose, lignin, and ash; SSB followed this trend as observed in the literature.[36,37]

Table 4.1. The properties of sweet sorghum bagasse (SSB)

Analysis	Method	Unit	Value
Inherent moisture	SANS 5925	wt.%	5.8
Ash	ASTM 048	wt.%	4.6
Volatile matter	ISO 1171	wt.%	72.3
Fixed carbon	By difference	wt.%	17.3
NDF (neutral detergent fibre)	ASTM 060	wt.%	61.8
ADF (acid detergent fibre)	Not SANAS accredited	wt.%	38.6
ADL (acid detergent lignin) [a]	Not SANAS accredited	wt.%	8.9
Total non-structural carbohydrates		wt.%	15.3
Residual sugars		wt.%	27.0
Gross energy	ASTM 053	MJ/kg	17.0
Cellulose [b]	-	wt.%	29.8
Hemicellulose [c]	-	wt.%	23.2
Ultimate analysis (dry-ash free basis)	ISO 29541		
Carbon		wt.%	48.2
Hydrogen		wt.%	6.3
Nitrogen		wt.%	1.0
Oxygen + Sulphur	By difference	wt.%	44.5
H/C (atomic ratio)			1.57

* Note: [a] lignin = ADL, [b] Cellulose = ADF-ADL, [c] Hemicellulose = NDF-ADF

* ADL value was assumed to be the total lignin mass % in the biomass

4.3.2 Effects of temperature and concentration of NaOH on product distribution

The effects of temperature and concentration of NaOH on the yields of SSB liquefaction products are shown in Figure 4.3 (a-d). By using concentrations of 0.5–6.0 M NaOH and temperatures between 260 and 320 °C, the yields of bio-oil, solid residue and gas were obtained (Figure 4.3). Generally, the temperature is known to have an increasing effect on both the yields of liquids and gases due to the extended biomass fragmentations with an increase in temperature.[8] It was observed that the bio-oil yield increased with increasing temperature for 0.5–3.0 M NaOH concentrations (5.7–53.2 wt. %). However, the bio-oil yield reduced from 47 to 39 wt. % with increasing temperatures using a concentration of 6.0 M NaOH. This observation suggests that a further increase in NaOH concentration (>3.0 M) will inhibit bio-oil formation at higher temperatures. The bio-oil yield reached its maximum of 53.2 wt. % at a concentration of 3.0 M NaOH and a liquefaction temperature of 320 °C. This maximum yield is corroborated by literature where the temperature for hydrothermal liquefaction is reported as around 300 °C and higher for compact biomass feedstock.[8,29,38]

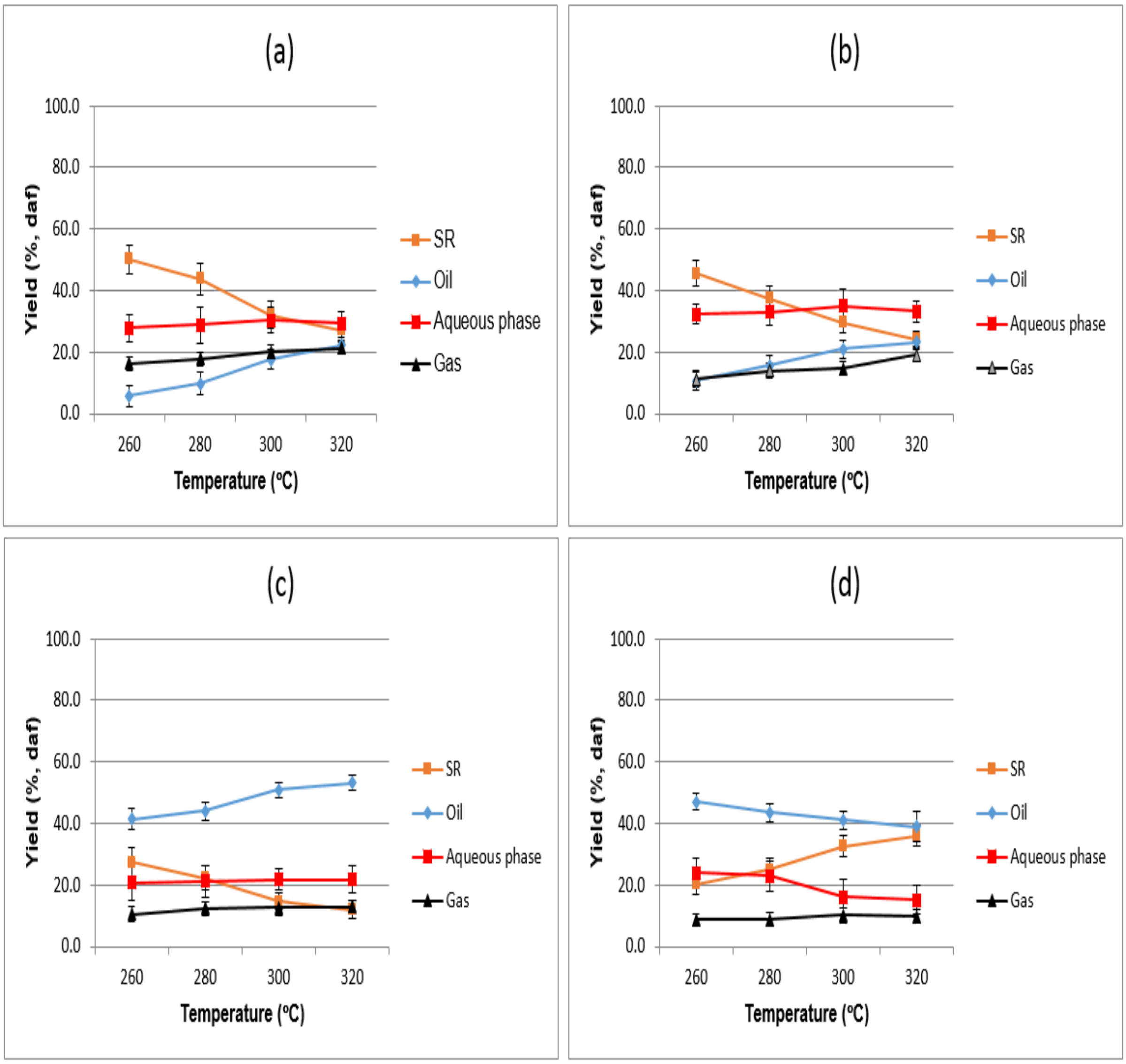


Figure 4.3. The product distribution after biomass liquefaction at different temperatures between 260 and 320 °C and NaOH concentrations of (a) 0.5 M; (b) 1.0 M; (c) 3.0 M; (d) 6.0 M. SR indicates solid residue

The effect of the biomass to water ratio during liquefaction of *C. lanceolate* in water without alkali treatment was studied by Qu et al.[29] They reported a maximum yield of heavy oil of 24 wt. % at 320 °C. Karagöz et al.[39] reported the liquefaction of sawdust in the presence of an alkaline solution (K_2CO_3) where the total oil yield was observed to be 3.7%, 7.6% and 8.5% at 180 °C, 250 °C, and 280 °C respectively. Zhou et al.[40] converted algae into bio-oil by hydrothermal liquefaction at temperatures of 220–320 °C. They found that at a moderate temperature of 300 °C with 5 wt. % Na_2CO_3 the liquefaction led to the highest bio-oil yield of 23 wt. %. These results indicate that temperature has an effect on the bio-oil yields, and also the treatment of biomass with alkaline treatment. Liu and Zhang[11] also reported that the product distribution is strongly affected by the solvent type. Consequently, considering the bio-oil yield obtained from this study, NaOH concentration of approximately 3.0 M NaOH and a temperature of 320 °C led to a high yield of bio-oil.

Increasing the liquefaction temperature from 260 to 320 °C for the 0.5–3.0 M NaOH treatments resulted in a decrease in the yields of the solid residues (Figure 4.3 a–c, denoted as SR). The decrease in solid residues indicates an increase in thermal decomposition of biomass to liquid and/or gaseous products with increasing temperature as also observed by other authors.[41] The reduction in the solid residues' yields also suggests that the presence of NaOH facilitated the collapse of intramolecular and intermolecular hydrogen bonds in the SSB structure, as well as the reduction and cracking reactions of macromolecules.[17] However, by using 6.0 M NaOH between 260 °C and 320 °C, the yield of solid residues increased (Figure 3 d). Alkaline hydrolysis of polysaccharides in biomass is caused by depolymerization reactions beginning at the ends of the polysaccharide chains, a process referred to as "peeling." [42] The so-called peeling of cellulose shows a strong dependence on OH^- concentration; most importantly, the reaction is significantly reduced in concentrated OH^- solutions.[43] An additional factor possibly affecting the observed increase in solid residue formation in 6M NaOH lies in the known dependence of alkali-induced cleavage of glycoside linkages on hydroxide ion concentration.[42] The rate of hydrolysis of various glycosides at first increases with increasing OH^- concentration, but eventually levels off at high concentrations.[44] This behaviour is known to affect hydrolysis of phenyl glucosides,[45] from which we infer that a reduced rate of alkali attack on these linkages could allow for increased amounts of competing reactions, such as recombination or cross-linking reactions, leading to an increased yield of solid residue. With SSB, 6M NaOH may be above the concentration at which a reduction of polysaccharide peeling and a slowing of phenol glucoside hydrolysis become significant. Although we did not study the further processing of the solid residues as part of this present work, we suggest that they could provide an alternative, parallel material for additional extraction of phenolic compounds apart from the bio-oil fractions.

4.3.3 ATR-FTIR spectra of bio-oil fractions

The quality and quantity of any bio-oil constituents are strongly dependent on the properties of the feedstock, production method, and operating conditions. The structural and chemical changes in bio-oils produced by aqueous NaOH treatment of SSB were investigated using infrared spectroscopy. Figure 4.4 (a-d) shows the ATR-FTIR spectra of the bio-oils. The ATR-FTIR spectra are similar, except for a few band positions. The strong and broad peak at 3290 cm^{-1} can be assigned to the O-H stretching vibrations of phenolic, water and alcohol moieties in the bio-oils.[17] The high intensity at 3290 cm^{-1} for bio-oil obtained at 3 M NaOH

(260–320 °C) may be indicative of a notable increase in concentration for extracted phenols (see Section 4.3.4). The bio-oil fractions show weak stretching vibrations of C-H at 2934 cm^{-1}, caused by cycloparaffin or cycloalkane structures.[46] The weak absorption at 2969 cm^{-1} can be due to the C-H stretching vibration in the aromatic rings or due to methyl groups. According to Li et al.,[17] the absorption bands between 3000 and 2900 cm^{-1} are due to symmetrical and asymmetrical C-H stretching vibrations of methyl and methylene groups. It can be seen that the peak caused by C-H groups (≈ 2900 cm^{-1}) is significantly reduced from the bio-oils produced with 3.0 M NaOH solutions at the different temperatures. Table B.3–B.6 also shows the distribution of the chemical composition of bio-oils obtained at different temperatures and NaOH concentrations.

The absorption observed in the 1700–1500 cm^{-1} range corresponds to aromatic C=C bending and C=O stretching vibrations, which indicates the presence of carboxyl, ketone, ester, and aromatic ring (likely derived from lignin) structures in the bio-oils.[47–49] The high-intensity bands at around 1500 and 1600 cm^{-1} are characteristic bands which show aromatic ring vibrations,[50] that could represent structures derived from lignin. The absorption band at approximately 1380 cm^{-1} corresponds to aliphatic CH_3 groups. This observation could be explained by the increased amount of ethyl- or propylphenol produced when the NaOH concentration was increased, as also observed in the GC-MS analysis (see Section 4.3.4). According to Fan et al.,[47] the absorption bands between 1200 and 1050 cm^{-1} correspond to C-O stretching vibrations in the phenolic hydroxyl group and secondary and primary alcohols respectively. However, the absorption intensities of the bio-oils at near 1100 cm^{-1} (primary alcohols) substantially decreased with an increase in temperature and NaOH concentration, especially for bio-oil obtained at 3 M and 6 M NaOH. Liu and Zhang,[11] reported that the peaks between 1000 cm^{-1} and 600 cm^{-1} were from the out-of-plane vibrations of methyl or other alkyl constituents on the aromatic group.

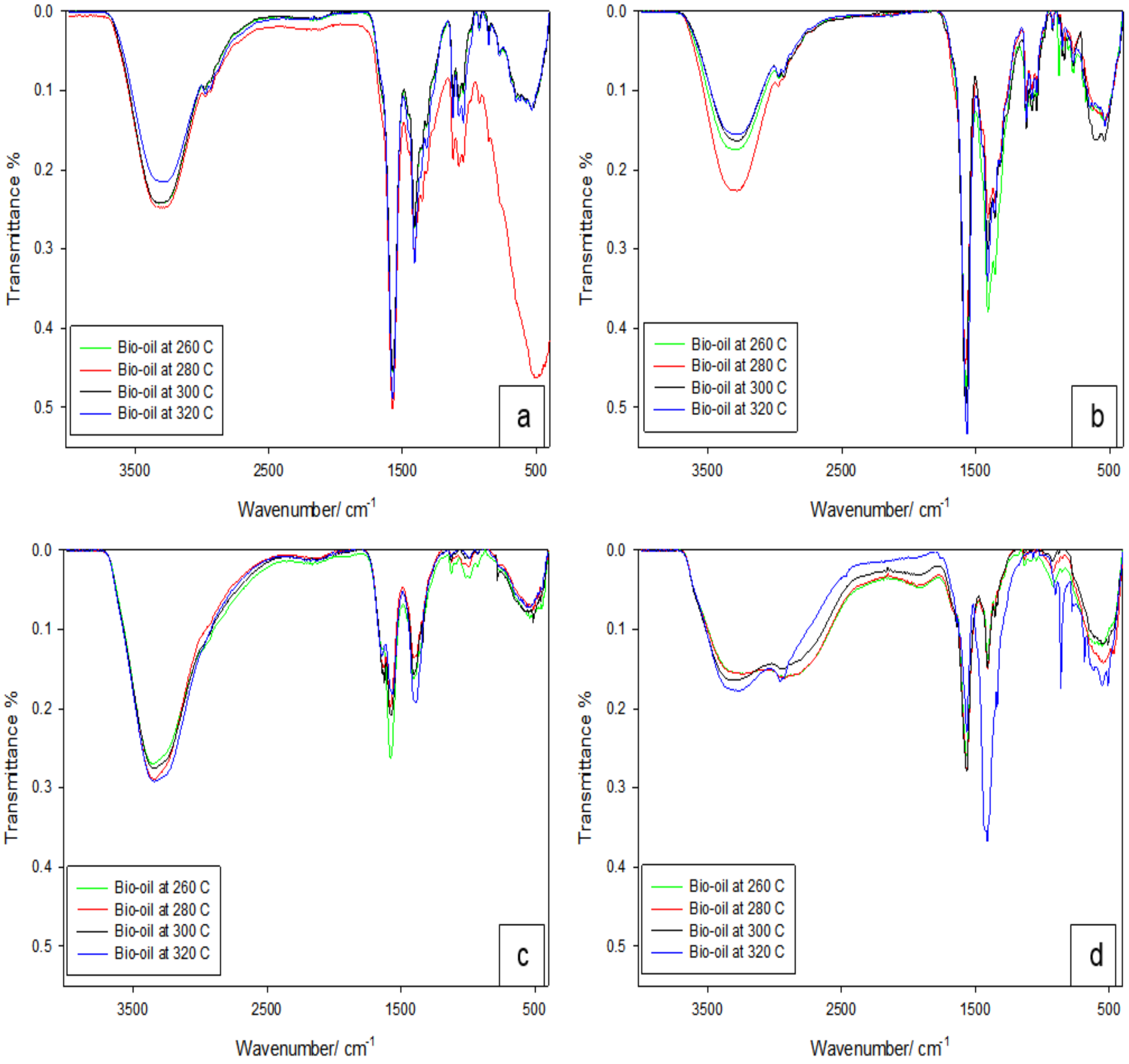


Figure 4.4. ATR-FTIR spectra of bio-oil fractions from liquefaction at temperatures between 260 and 320 °C and NaOH concentrations of (a) 0.5 M; (b) 1.0 M; (c) 3.0 M; (d) 6.0 M

4.3.4 GC-MS analysis of phenols extracted by ethyl acetate from the bio-oil fractions

Table 4.2 summarizes the quantitative measurements of the principal phenolic species obtained through the ℓ-ℓ extraction method of bio-oil fractions produced from the liquefaction of SSB using NaOH solutions at different concentrations (0.5–6.0 M). It should be noted that these phenolics are not strictly derived from lignin, as the lignin content of the SSB was 8.9 wt. % (Table 4.1). This is corroborated by phenolic extractions which were less than 8.9 wt. % observed for 0.5–1.0 M NaOH solutions (Table 4.2). However, this study suggests that phenols could also be derived from hydrolysis of phenyl glucoside and related compounds.[51]

The composition of the phenolic fractions became considerably more complex with higher NaOH solutions. In this study, the most consistent and abundant phenolic species obtained throughout each run were phenol (3.1–17.3 wt. %) followed by 4-ethylphenol (0.6–14.0 wt. %). The highest yield, 17.3 wt. % and 14.0 wt. %, respectively, of phenol and 4-ethylphenol were obtained from bio-oil produced at 320 °C and 3.0 M NaOH. As it can be expected (Table 4.2), the highest concentration of phenols obtained coincides with the highest bio-oil yield produced, at 320 °C with 3.0 M NaOH (see Section 4.3.2).

Table 4.2 shows a change in the phenolic fractions produced at the various temperatures and NaOH concentrations. For all experiments at 260 °C or 280 °C, regardless of the molarity of the NaOH solution used, the products detected by GC-MS are dominated by phenol. For example, with 1.0 M NaOH at 280 °C, 83% of all the identified products are accounted for by phenol itself. However, for temperatures of 300 °C or 320 °C, phenol accounts for less than half of the total identified products, regardless of molarity of NaOH (e.g. 30% at 300 °C, 6 M NaOH). At a given reaction temperature, the use of 3.0 or 6.0 M NaOH resulted in the extraction of more identifiable phenol derivatives than that was obtained with the less concentrated NaOH solutions. For example, at 280 °C, 1.0 M NaOH extracted three compounds, whereas 3.0 M NaOH extracted eight compounds. Along with this, it was only the 3.0 and 6.0 M NaOH solutions that extracted propylated derivatives (i.e., propyl- or isopropylphenols) at any temperature. These results suggest that the phenolic fractions after ℓ-ℓ extraction increase with increasing NaOH concentrations. This is corroborated by Amen-Chen et al.[27] who stated that a high pH value is required for complete extraction of phenols from the oil matrix. The extraction of phenols from the water phase with polar organic solvents was studied,[52,53] and the distribution coefficients at a high dilution at room temperature for some phenolate solutes between water and some polar organic solvents obtained are reported in the literature.[52,54] For example, Žilnik and Jazbinšsek[54] reported that the distribution coefficients of all phenolic components reach high values at low water to bio-oil ratios and that the values are decreasing with increasing water to bio-oil ratio up to a maximum.

The increased yield of alkylated phenols as a percentage of total phenols, with respect to the observation of propylated phenols at a concentration of 3.0 M and 6.0 M, reflect a solubility effect. The propylated compounds, in particular, are much less soluble in water than phenol itself or 4-ethylphenol. The conversion of the larger alkylated phenols to their corresponding sodium alkylphenolate derivatives enhances the solubility of these sodium salts to a point where they will dissolve and appear among the extraction products. The variety of phenolic species can be explained by the complexity of the structure of lignin and the experimental conditions.[34]

Table 4.2. GC-MS analysis results of the phenolic fractions after the ℓ-ℓ extraction of bio-oil prepared at different temperatures and NaOH concentrations

0.5 M NaOH at 260 °C	**Average wt. %**	**1.0 M NaOH at 260 °C**	**Average wt. %**
Phenol	3.10 ± 0.43	Phenol	7.14 ± 0.33
Guaiacol	0.84 ± 0.11	4-Ethylphenol	0.78 ± 0.13
0.5 M NaOH at 280 °C	**Average wt. %**	**1.0 M NaOH at 280 °C**	**Average wt. %**
Phenol	3.81 ± 0.25	Phenol	6.43 ± 0.71
Guaiacol	0.90 ± 0.03	p-Cresol	0.62 ± 0.02
–	–	4-Ethylphenol	0.70 ± 0.03
0.5 M NaOH at 300 °C	**Average wt. %**	**1.0 M NaOH at 300 °C**	**Average wt. %**
Phenol	5.23 ± 0.07	Phenol	6.04 ± 0.12
Guaiacol	1.41 ± 0.25	p-Cresol	1.41 ± 0.35
4-Ethylphenol	0.68 ± 0.01	4-Ethylphenol	1.43 ± 0.43
p-Cresol	2.88 ± 0.42	–	–
4-Ethylguaiacol	0.57 ± 0.05	–	–
0.5 M NaOH at 320 °C	**Average wt. %**	**1.0 M NaOH at 320 °C**	**Average wt. %**
Phenol	4.54 ± 0.33	Phenol	3.91 ± 0.58
p-Cresol	0.85 ± 0.16	p-Cresol	0.85 ± 0.07
4-Ethylphenol	0.52 ± 0.04	4-Ethylphenol	0.76 ± 0.10
3.0 M NaOH at 260 °C	**Average wt. %**	**6.0 M NaOH at 260 °C**	**Average wt. %**
Phenol	11.60 ± 1.00	Phenol	9.01 ± 1.39
Guaiacol	7.27 ± 1.31	p-Cresol	10.17 ± 1.85
4-Ethylphenol	9.63 ± 1.04	4-Ethylphenol	9.47 ± 1.28
Creosol	1.58 ± 0.26	Creosol	0.87 ± 0.10
4-Isopropylphenol	0.90 ± 0.13	4-Isopropylphenol	0.85 ± 0.08
2-Propylphenol	0.52 ± 0.02	2-Propylphenol	0.44 ± 0.04
4-Ethylguaiacol	5.41 ± 1.03	4-Ethylguaiacol	1.61 ± 0.31
3.0 M NaOH at 280 °C	**Average wt. %**	**6.0 M NaOH at 280 °C**	**Average wt. %**
Phenol	13.76 ± 0.19	Phenol	9.14 ± 0.96
p-Cresol	6.81 ± 0.07	p-Cresol	7.88 ± 0.90
Guaiacol	3.96 ± 0.09	4-Ethylphenol	10.00 ± 0.67
4-Ethylphenol	10.00 ± 0.29	4-Isopropylphenol	1.03 ± 0.14
Creosol	0.65 ± 0.04	2-Propylphenol	0.44 ± 0.02
4-Isopropylphenol	0.94 ± 0.05	4-Ethylguaiacol	0.46 ± 0.02
2-Propylphenol	0.66 ± 0.14	–	–
4-Ethylguaiacol	1.49 ± 0.41	–	–
3.0 M NaOH at 300 °C	**Average wt. %**	**6.0 M NaOH at 300 °C**	**Average wt. %**
Phenol	14.50 ± 1.13	Phenol	8.64 ± 1.00
p-Cresol	4.90 ± 0.33	p-Cresol	9.18 ± 1.13
4-Ethylphenol	10.72 ± 0.98	4-Ethylphenol	9.83 ± 0.78
4-Isopropylphenol	0.91 ± 0.08	4-Isopropylphenol	0.75 ± 0.05
2-Propylphenol	0.74 ± 0.23	4-Propylphenol	0.75 ± 0.02
3.0 M NaOH at 320 °C	**Average wt. %**	**6.0 M NaOH at 320 °C**	**Average wt. %**
Phenol	17.27 ± 0.86	Phenol	11.33 ± 0.89
p-Cresol	7.34 ± 0.81	p-Cresol	11.41 ± 0.96
4-Ethylphenol	13.95 ± 1.56	4-Ethylphenol	11.87 ± 1.02
4-Isopropylphenol	1.34 ± 0.09	4-Isopropylphenol	0.90 ± 0.09
2-Propylphenol	1.28 ± 0.19	4-Propylphenol	1.24 ± 0.17

4.3.5 SEM/EDS analysis of SSB and SRs

Figure 4.5 (a-e) shows the micrographs of the SSB and SRs (solid residues) produced at 320 °C during liquefaction. It is evident that significant changes to the surface of the solid residues had occurred with the treatment of NaOH aqueous solutions. Figure 4.5 (a) shows that the untreated SSB displays a fibrous structure. It also shows the intact plant cell walls, with ordered surfaces, that are compacted and highly fibrillar structured. Figure 4.5 (b)-(e) show the solid residues after NaOH treatment, which exhibit changes to the fibrillar structures compared to the untreated biomass as observed in Figure 4.5 (a). SEM images of NaOH treated SSB, as shown in Figure 4.5 (b)-(d) exhibit loose, rough and porous surface structures with cracks. This may be due to the removal of some lignocellulosic components and other surface impurities which resulted in surface roughness with increasing alkali concentrations (Figure 4.5 b–d). The NaOH treatment of the SSB usually attacks the linkages in cellulose, hemicellulose, and lignin by the partial dissolution of hemicellulose and lignin leading to the exposure of the skeleton structure of cellulose.[17,49] The SEM image of SSB treated with 6.0 M NaOH (Figure 4.5 (e)) indicates a large structural change unlike those observed in Figure 4.5 (a)-(d). The structures appear more crystalline and irregularly loose-shaped, with rough surfaces. The surface morphological changes of the SRs from the liquefaction suggest that the NaOH treatment significantly altered the physical structure of the SSB, thereby creating favourable conditions for the subsequent liquefaction reactions.

The elemental analysis of the SSB and SRs was carried out by SEM equipped with the EDS technique. The SEM/EDS analysis results are given in Table 4.3 for the untreated SSB and SRs produced at 320 °C during liquefaction. The SEM/EDS analysis gave 50.2 wt. % carbon and 44.3 wt. % oxygen for the raw SSB. These values obtained from the surface analysis (Table 3) compare favourably with those obtained from a bulk composition for the untreated SSB (see Table 4.2, 48.2 wt. % for carbon and 44.5 wt. % for oxygen + sulphur on dry ash free basis) for high degree precision, especially for SEM/EDS.[55] The carbon content of the SRs gradually reduced from 72.8 to 27.0 wt. % with increasing temperature and NaOH concentrations (0.5–6.0 M). The elemental composition of the liquefaction solid residues (SR's) also shows the decrease in carbon content (63.2 up to 16.3 wt. %, d.b.) with increasing temperature and NaOH concentrations (Appendix B.1). The SR contains a modest amount of mineral matter (based on the 4.6% ash, Table 4.1), which does not dissolve appreciably, or even dissolve at all, in the aqueous NaOH. By the time we get to an SR that is 27% C, a large fraction of the SR is original or slightly altered mineral matter. Thus biomass resulted in significant changes in fibre morphology were most of the organic fraction is destroyed with increasing alkali concentrations.

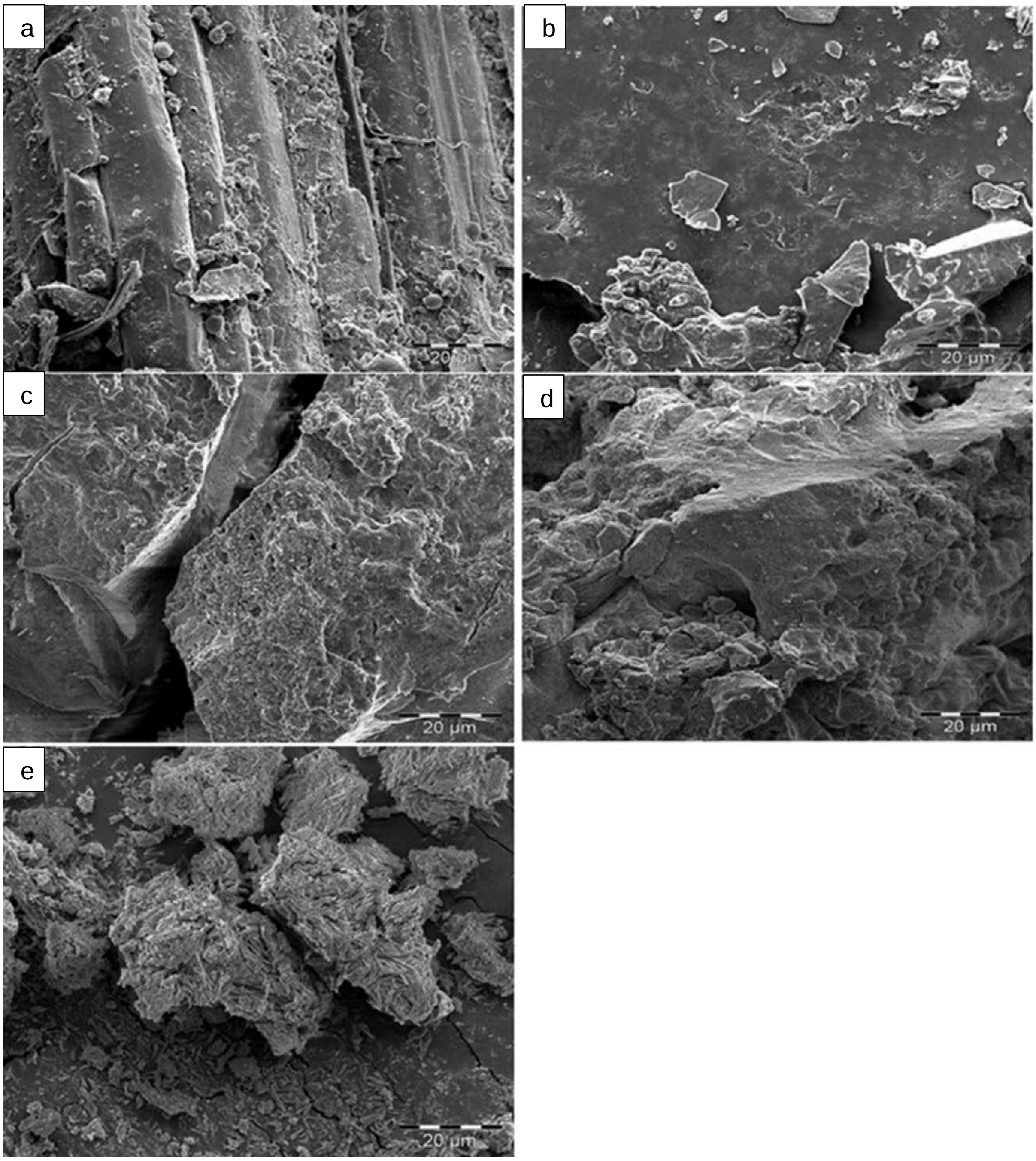


Figure 4.5. Scanning electron graphs of (a) raw SSB and SRs obtained with NaOH aqueous solutions of (b) 0.5 M, (c) 1.0 M, (d) 3.0 M, and (e) 6.0 M at 320 °C

Table 4.3. SEM-EDS normalized semi-quantitative elemental analysis results

	SSB	0.5 M NaOH	1.0 M NaOH	3.0 M NaOH	6.0 M NaOH
Element	wt. %	wt. %	wt. %	wt. %	wt. %
C	50.2	72.8	55.3	47.6	27.0
O	44.3	20.9	30.9	31.4	43.2
Na	–	1.1	6.3	4.5	25.5
Mg	0.5	0.7	1.6	5.0	1.1
Al	–	–	0.1	0.2	–
Si	0.4	1.8	3.0	3.8	–
P	0.1	0.1	0.4	1.8	–
Cl	0.9	0.9	0.2	–	1.7
K	3.2	0.2	0.4	–	0.3
Ca	0.4	1.0	1.4	4.8	0.4
Cr	–	–	–	0.3	0.3
Fe	–	0.4	0.4	0.6	0.5
Total	100.0	99.9	100.0	100.0	100.0

4.3.6 Thermal properties of SSB and SRs

The thermal degradation properties of the untreated SSB and liquefaction-solid residues were investigated by thermogravimetric analysis to obtain an understanding of their thermal behaviour during pyrolysis. Figure 4.6 (a) shows the thermal degradation of the untreated SSB and the liquefaction solid residues obtained with different NaOH concentrations. Generally, all the lignocellulosic biomass are mainly composed of cellulose, hemicellulose, and lignin.[2] From Figure 4.6 (b), it follows that the untreated SSB degraded through the following steps as also reported in the literature:[2,56] a weight loss at 50–120 °C, which is attributed to loss of moisture and light volatiles; and the weight loss from 125–380 °C, which is attributed to the decomposition of hemicellulose and cellulose (with peaks at 200 °C and 330 °C on the DTG curves). Furthermore, a weight loss from 330–760 °C, which is attributed to the decomposition of lignin. The loss of weight as a function of increasing temperature is particularly steep in the region of 260-320 °C for the untreated SSB. From Figure 4.6 (a), more than 30 wt. % of the SSB was lost when the temperature reached 320 °C during pyrolysis. As pyrolysis progresses between 280 and 320 °C, the volatile matter content is significantly lower in those regions than observed for liquefaction temperatures of SSB as seen in Section 4.3.2. This observation suggests the great influence of NaOH treatment without solvent.

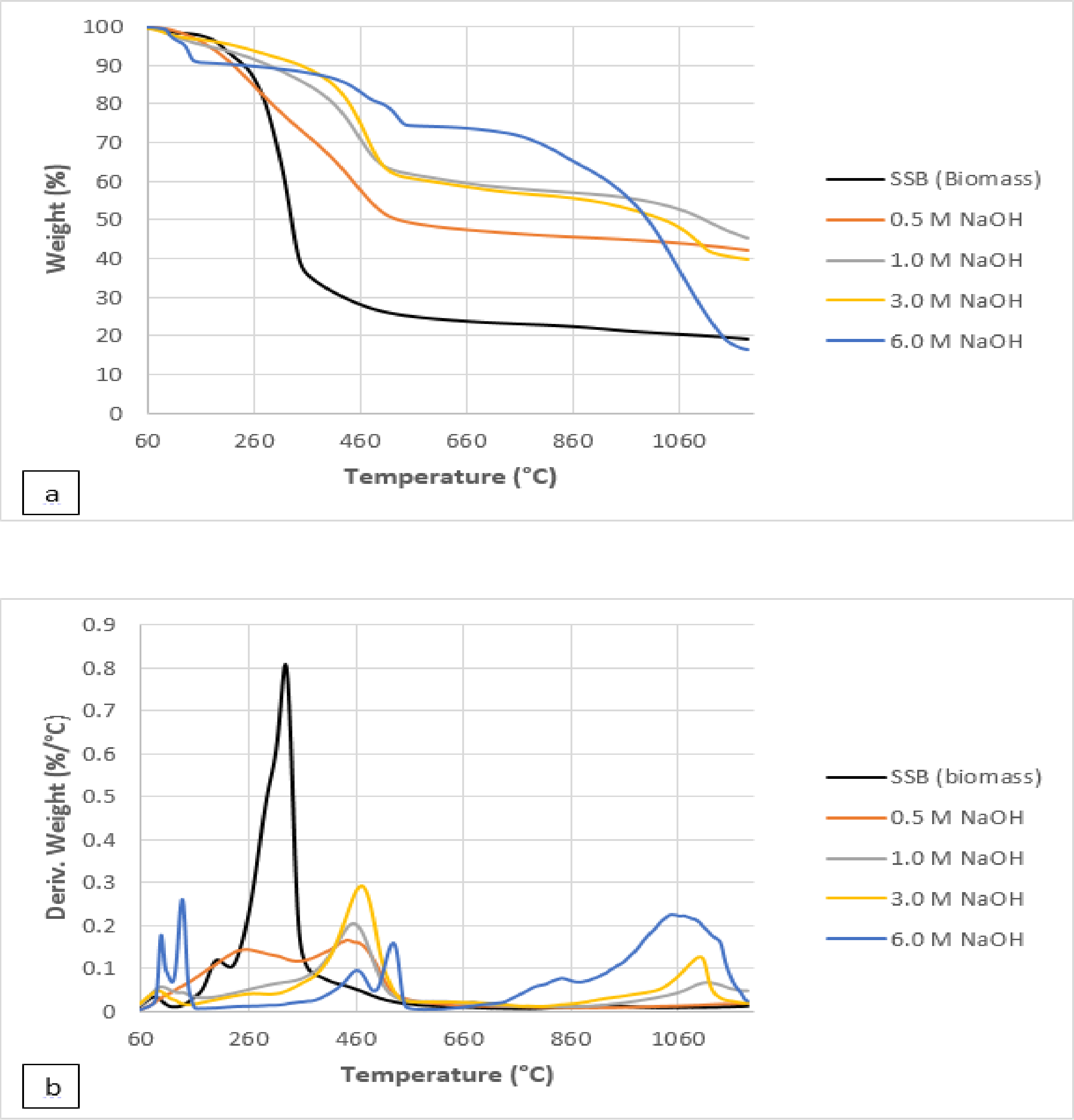


Figure 4.6. TGA curves of SSB and solid residues from liquefaction prepared at 320 °C and different NaOH concentrations, (a) TG analysis, (b) DTG analysis.

In contrast to the degradation of the untreated SSB, the solid residues degraded through one more step, based on the peak intensity, starting from 0.5 M NaOH. The DTG peaks of the decomposition of hemicellulose and cellulose in the range of 125–380 °C gradually disappeared with increasing NaOH concentrations for liquefaction-solid residues as shown in Figure 4.6 (b). Similar trends were also reported by Li et al.[17] and Cunha et al.[57] for sugarcane bagasse alkaline hydrolysis. The DTG analysis also showed thermal decomposition of lignin in the SRs between 317 °C and 560 °C (Figure 4.6 b). The results reported in this study suggest that lower alkaline treatment was effective in reducing the lignocellulosic structures in the residues at lower temperatures. The DTG curve of the SR obtained after the treatment with 6.0 M NaOH indicates that the decomposition of lignin took place in two different temperature ranges and thus steps, in contrast to the treatment with ≤3.0 M NaOH, which showed a single peak in this temperature range (DTG_{max}) temperatures appeared at approximately 476 °C and 540 °C for the residue after treatment with 6.0 M NaOH at 320 °C). This observation accorded well with the SEM results for a high concentration of phenolate-crystal structures (Figure 4.6 e). The TG curves indicate a significant difference between the 0.5 – 3.0 M NaOH residues and the 6 M NaOH residue (Figure 4.6 a). The remaining mass after treatment with 0.5 – 3.0 M NaOH are all around 40%, while the remaining mass after treatment with 6 M NaOH which is much lower at below 20%, indicating that the treatment may have degraded the lignin in the biomass. This observation is consistent with a notable increase in yield of phenols extracted with more than 3.0 M NaOH solutions discussed earlier (see Section 4.3.4, GC-MS results).

4.4 Conclusions

The SSB was treated with alkaline solutions during liquefaction at different concentrations and temperatures. The treatment of SSB with 3.0 M NaOH at 320 °C was found to be more effective when compared with other experimental conditions as it produced high yields for the bio-oil production (53.2 wt. %), and the subsequent extraction of phenols (40.0 wt. %). The GC-MS results show that the phenolic fractions after ℓ-ℓ extraction increased with increasing NaOH concentrations. At a given reaction temperature, the use of higher concentrated NaOH solutions (≥3 M) resulted in the extraction of more identifiable phenol derivatives than that was obtained with the less concentrated NaOH solutions. It was only with NaOH solutions (≥3 M) that propylated derivatives (i.e., propyl- or isopropylphenols) were extracted at any of the experimental temperatures. The ATR-FTIR and SEM/EDS results showed increased changes in chemical composition and structures of the liquefaction products with an increase in the concentration of NaOH. The ATR-FTIR results also corroborate the GC-MS results that increased amounts of ethyl- or propylphenol were produced when the NaOH concentration was increased. The increased yield of alkylated phenols (as a percentage of total phenols), with respect to the observation of propylated phenols at a concentration of ≥3.0 M (GC-MS results), may reflect a solubility effect. The propylated compounds, in particular, are much less soluble in water than phenol itself or 4-ethylphenol. The conversion of the larger alkylated phenols to their corresponding sodium alkylphenolate derivatives may enhance the solubility of these sodium salts to a point where they may dissolve and appear among the extraction products. At the lower NaOH concentrations of 0.5 and 1.0 M, the maximum yield occurs at 300 °C. But, at 3.0 and 6.0 M NaOH, the maximum yield occurs at 320° C. Furthermore, at the two higher molarities, the total phenol yield at any temperature is higher by about a factor of 5 to 10 relative to the results at the lower molarities.

From the SEM/EDS results, the carbon content of SRs gradually reduced from 72.8 to 27.0 wt. % with increasing temperature and NaOH concentrations (0.5–6.0 M). In contrast, the oxygen (O) and sodium (Na) percentages of SRs show a gradual relative increase after liquefaction with increasing NaOH concentrations. The TGA results of the SRs between 125 °C and 380 °C are consistent with an effective reduction of the amounts of hemicellulose and cellulose by the aqueous NaOH treatment. These results showed that the alkaline treatment with a concentration higher than 6.0 M may lead to solubilization of all the lignocellulosic materials. Alkaline liquefaction at concentrations of lower than 3.0 M NaOH degrade completely hemicellulose and cellulose, and lignin partially. The extraction of phenols from bio-oil fractions, produced by using concentrations of 0.5–6.0 M NaOH on SSB, was found to be feasible and effective at relatively low temperatures. Therefore, the liquefaction of the SSB with NaOH at lower temperatures is promising for the production of valuable and useful chemicals.

As explained in the Introduction, the present study focused on the production of mixed phenols from this biomass, because of our specific interest in using this product in a subsequent processing step with coal. We hope that other workers will be stimulated the study of the products arising from the cellulose and hemicellulose treated with hot aqueous sodium hydroxide, which will surely yield other useful chemicals from biomass.

Conflict of interest

The authors declares no conflict of interest.

Acknowledgements

The authors thank Dr. Roelf Venter for GC-MS analysis, and Dr. Nemera Shargie from the Agricultural Research Council, Grain Crops Institute, for the supply of sweet sorghum bagasse. The work presented in this paper is based on research financially supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa (Coal Research Chair Grant No. 86880, UID115228, Grant No. TP1208137225). Any opinion, finding, conclusion, or recommendation expressed in this material is that of the authors(s), and the NRF does not accept any liability in this regard.

Chapter References

1. Czernik, S.; Bridgewater, A.V. Energy Fuels **2004,** 18, 590–598**.**
2. Mohan, D.; Pittman, C.U.; Steele, P.H. Energy Fuels **2006**, 20, 848–889.
3. Bridgwater, A.V. 2012. Biomass Bioenergy. **2012**, 38, 68–94.
4. Kim, T.H. Pretreatment of lignocellulosic biomass. In: Yang, S.T., El-Enhasy, H.A. Thingchul, N., Martin, Y. (Eds.). Bioprocessing Technologies in Integrated Biorefinery for Production of Biofuels. Biochemicals, and Biopolymers from Biomass. Wiley, New York, USA, 2013, pp 91–109.
5. Amen-Chen, C.; Pakdel, H.; Roy, C. Bioresource. Technol. **2001**, 79, 227–299.
6. Chornet, E.; Overend, R.P. Fundamentals of Thermochemical Biomass Conversion, Elsevier, New York, 1985.
7. Demirbas, A. Energy Sources **2004**, 26, 715–730.
8. Akhtar, J.; Amin, N.A.S. Renew. Sust. Energ. Rev. **2011**, 15, 1615–1624.
9. Yan, X.; Ma, J.; Wang, W.; Zhao, Y.; Zhou, J. BioResources **2018**, 13, 997–1018.
10. Gollakota, A.R.K.; Kishore, N. Renew. Sust. Energ. Rev. **2018**, 81, 1378–1392.
11. Liu, Z.; Zhang, F–S. Energy Convers. Manag. **2008**, 49, 3498–3504.
12. Yip, J.; Chen, M.; Szeto, Y.S.; Yan, S. Bioresour Technol. **2009**, 100, 6674–6678.
13. Karagoz, S.; T. Bhaskar, T.; Muto, A.; Sakata, Y.; Oshiki, T.; Kishimoto, T. Chem. Eng. J. **2005**, 108, 127–137.
14. Karagoz, S.; Bhaskar, T.; Muto, A.; Sakata, Y.; Uddin, M.A. Energy Fuels **2004**, 18, 234–241.
15. Karagoz, S.; Bhaskar, T.; Muto, A.; Sakata, Y. J. Chem. Technol. Biotechnol. **2005**, 80, 1097–1102.
16. Kumar, S. Hydrothermal treatment for biofuels: Lignocellulosic biomass to bioethanol, biocrude, and biochar, Ph.D. Dissertation, Auburn University, Auburn, AL, 2010.
17. Ju, Y.-H.; Huynh, L.-H.; Kasim, N. S.; Guo, T.-J.; Wang, J.-H.; Fazary, A. E. Carbohyd. Polym. **2011**, 83, 591–599.
18. Singh, S.P.; Chouhan, A.P. Afr. J. Basic and Applied Sciences **2014**, 6, 19–24.
19. Li, Z.; Cao, J.; Huang, K.; Hong, Y.; Li, C.; Zhou, X.; Xie, N.; Lai, F.; Shen, F.; Chen, C. Bioresour. Technol. **2015**, 177, 159–168.
20. Li, X.; Ye, J.; Chen, J.; Yu, J.; Ding, M.; Hong, J. Fiber. Polym. **2015**, 16, 2368–2374.
21. Janker-Obermeier, I.; Sieber, V.; Faulstich, M.; Schieder, D. Ind. Crop. Prod. **2012**, 39, 198–203.
22. Wang, Y. Cellulose fiber dissolution in sodium hydroxide solution at low temperature: Dissolution kinetics and solubility improvement. Thesis, PhD in the Department of

Chemical and Biomolecular Engineering, Georgia Institute of Technology, December, 2008.

23. Kim, J.S.; Lee, Y.Y.; Kim, T.H. Bioresour. Technol. **2016**, 199, 42–48.
24. Fan, L.T.; Lee, Y.H.; Gharpuray, M.M. Adv. Biochem. Eng. **1982**, 23, 157–187.
25. Isogai, A.; Atalla, R.H. Cellulose **1998**, 5, 309–319.
26. Chen, Y.; Ren, X.; Wei, Q.; Guo, J. Bioresour. Technol. **2016**, 221, 477–484.
27. Amen-Chen, C.; Pakdel, H.; Roy, C. Biomass Bioenergy **1997**, 13, 25–37.
28. Xu, J.; Xie, X.; Wang, J.; Jiang, J. Green Chem. **2016**, 18, 3124–3138.
29. Qu, Y.; Wei, X.; Zhong, C. Energy **2003**, 28, 597–606.
30. Boocock, D.G.B.; Sherman, K.M. Can. J. Chem. Eng. **2009**, 63, 627–33.
31. Speight, J.G. Handbook of petroleum product analysis (2nd edition), John Wiley & Sons, Inc., Hoboken, New Jersey, 2015.
32. Mafu, L.D.; Neomagus, H.W.J.P.; Everson, R.C.; Carrier, M.; Strydom, C.A.; Bunt, J.R. Bioresour. Technol. **2016**, 202, 192–197.
33. Patel, R.N.; Bandyopadhyay, S.; Ganesh, A. Energy **2011**, 36, 1535–1542.
34. Li, J.; Wang, C.; Yang, Z. J. Anal. Appl. Pyrol. **2010**, 89, 218–224.
35. Mantilla, S.V.; Manrique, A.M.; Gauther-Maradei, P. Waste Biomass Valori. **2015**, 6, 371–383.
36. Drummond, A.R.F.; Drummond, I.W. Ind. Eng. Chem. Res. **1996**, 35, 1263–8.
37. Bridgwater, A.V. J. Anal. Appl. Pyrol. **1999**, 51, 3–22.
38. Zhang, L.; Li, C.J.; Zhou, D.; Zhang, S.C.; Chen, J.M. J. Anal. Appl. Pyrol. **2013**, 35, 1349–1357.
39. Karagoz, S.; Bhaskar, T.; Muto, A.; Sakata, Y. Bioresour. Technol. **2006**, 97, 90–8.
40. Zhou, D.; Zhang, L.; Zhang, S.; Fu, H.; Chen, J. Energy Fuels **2010**, 24, 4054–61.
41. Pidtasang, B.; Udomsap, P.; Sukkasi, S.; Chollacoop, N.; Pattiya, A. J. Ind. Eng. Chem. **2013**, 19, 1851–1857.
42. Lai, Y.Z. Chemical degradation. In: Wood and Cellulosic Chemistry. (Hon, D.N.S.; Shiraishi, N., eds.) Marcel Dekker, Inc.: New York, 1991; Chapter 10.
43. Lai, Y.Z.; Ontto, D.E. J. Appl. Polym. Sci. **1979**, 23, 3219–3225.
44. Lai, Y.Z. Carbohydr. Res. **1972**, 24, 57–65.
45. Lai, Y.Z.; Ontto, D.E. Carbohydr. Res. **1979**, 75, 51–59.
46. Wang, Y.; Wang, H.; Lin, H.; Zheng, Y.; Zhao, J.; Pelletier, A.; Li, K. Biomass Bioenergy **2013**, 59, 158–167.
47. Fan, S.P.; Zakaria, S.; Chia, C.H.; Jamaluddin, F.; Nabihah, S.; Liew, T.K.; Pua, F.L. Bioresour. Technol. **2011**, 102, 3521–3526.
48. Agrawalla, A.; Kumar, S.; Singh, R.K. Bioresour. Technol. **2011**, 102, 10711–10716.
49. Bagewadi, Z.K.; Mulla, L.S.; Ninnekar, H.Z. 3 Biotech **2016**, 6, 101.

50. Singh, R.; Balagurumurthy, B.; Prakash, A.; Bhaskar, T. Bioresour. Technol. **2015**, 178, 157–165.
51. Yu, Y; Lou, X; Wu, H. Energy Fuels **2008**, 22, 46–60.
52. Won, K.W.; Prausnitz, J.M. J. Chem. Thermodyn. **1975**, 7, 661–670.
53. Lo, T.C.; Baird, M.H.; Hanson, C. Handbook of solvent extraction. Wiley Interscience, New York, 1983, Chapters 18.5, 21, 23.
54. Zilnik, L.F.; Jazbinsek, A. Sep. Purif. Technol. **2012**, 86, 157–170.
55. Newbury, D.E.; Ritchie, N.W.M. Scanning **2013**, 35, 141–168.
56. Munir, S.; Daood, S.S.; Nimmo, W.; Cunliffe, A.M.; Gibbs, B.M. Bioresour. Technol. **2009**, 100, 1413–1418.
57. Cunha, J.A.; Pereira, M.M.; Valente, L.M.M.; de la Piscina, P.R.; Homs, N.; Santos, M.R.L. Biomass Bioenergy **2011**, 35, 2106–2116.

Chapter 5

Solvent extraction of a South African bituminous coal using a model biomass-derived phenolic mixture

Thabo Z. Sehume, *Christien A. Strydom, John R. Bunt and Harold H. Schobert*

In this chapter, the extraction yields and all the results of the analyses that were obtained from the extraction of bituminous coal using a model biomass-derived phenolic mixture as a solvent at mild conditions are reported herein.

Abstract

A model biomass-derived phenolic mixture was investigated for its solvent ability for extraction of a South African bituminous coal at temperatures of 300–360 °C. The coal contained vitrinite (52.8%), inertinite (29.4%), reactive semifusinite (6.7%) and liptinite (3.5%). A previous study indicated that pure phenol gave the highest extraction yield of 49.5 wt. % (daf) for the specific bituminous coal at 360 °C, with an oil yield of 26.3 wt. % (daf). The phenolic products produced from sweet sorghum bagasse via an alkaline liquefaction process were identified and reported earlier and a model biomass-derived phenolic mixture was formulated, evaluated and results used in this study. The model solvent mixture gave an extraction yield of 37.1 wt. % (daf) and oil yield of 16.9 wt. % (daf) at 360 °C. This solvent mixture was found to be less effective for high extraction yields when compared to phenol at mild temperatures. This observation could be due to phenol being a better hydrogen carrier than the solvent mixture during internal redistribution of the available hydrogen in the coal. The infrared spectroscopy results of the coal and extraction products obtained using the model mixtures compared to pure phenol showed similar functional groups. Data from the simulated distillation curves of the coal-derived products obtained using a model biomass-derived phenolic mixture showed comparable chemical characteristics to those obtained by phenol. However, there were differences in the average boiling point (WABP) of HS fractions (300–360 °C) obtained using these solvents. The results obtained from this study demonstrate that the use of a model biomass-derived phenolic mixture has the potential to depolymerize coal and produce high-value chemicals from coal.

5.1. Introduction

South Africa relies on its abundant coal reserves to meet much of its energy demand. Coal provides 79% of the country's total energy needs.[1,2] The country's synthetic liquid fuel production contributes 40% to the total liquid fuel demand. The remaining 60% is sourced from the refining of imported crude oil.[1,3] The production of liquid transportation fuels synthesized from coal provides an important alternative solution to augment the petroleum supply, thus reducing the dependency on imported petroleum and helping to relieve strained refinery capacity.[4–6] Sasol runs an indirect liquefaction process for the production of liquid fuels and chemicals from coal. The indirect coal liquefaction facility in South Africa produces approximately 160,000 barrels of crude oil equivalent a day.[1,7] However, the currently favoured approach to producing synthetic liquid fuels, coal gasification followed by the Fischer-Tropsch process, poses challenges.[8] For example, this includes the by-product of this process, namely carbon dioxide (CO_2), a greenhouse gas associated with global warming.[9] Furthermore, a large amount of hydrogen is used for coal processing through coal liquefaction, which raises cost and energy consumption.[10] In this study, we examine the potential of solvent extraction for coal conversion. This process is an alternative coal conversion process that can produce coal-derived liquids without hydrogen and also at lower temperatures.

Coal extraction with an appropriate solvent can be used to study the composition, structure of coal and also as a conversion process to produce value-added products from coal. The solvent extraction process and explanation of the terms used to describe the process (i.e. decomposition and depolymerization) was summarized by Sehume et al.[11] In general, solvent extraction represents the treatment of coal with a solvent(s) to dissolve some components of the coal, at temperatures between 200 and 400 °C.[11,12] The extensive experiments, using phenol as a solvent, for solvent extraction of coal date back to 1920s.[13,14,15] This approach was found to be ideal as it is performed at temperatures close to the boiling point of the solvent for higher extraction yields.[12] It was reported that repeated extraction at increasingly higher temperatures leads to a continuous increase in extract yield.[16] The change in the extract yield has been related to the chemical nature of the solvent at higher temperatures.[17,18] According to Berkowitz,[19] at temperatures below ≈350 °C, the solvent potency may depend on the ability of the solvent to swell, peptize, and promote coal depolymerization; and the most effective solvents are aromatics and hydroxylated aromatics (i.e. phenol, naphthalene, α- and β-naphthols, phenyl phenols, anthraces, or phenanthrene). Orchin and Starch[20] evaluated a variety of solvents for their ability to extract coals and showed that hydroaromatic solvents containing a phenolic group were superior to those without one. In addition, the presence of a phenolic OH usually leads to high extraction, but not always. However, these authors did not state at which conditions phenolic OH will not lead to high extraction yields. Aromatic compounds, such as naphthalene, cresol, diphenyl, or o-phenylphenol, have been reported in the literature of being able to dissolve 20–30% of the coal at 400 °C.[21] Other studies have shown that coal extraction with a single solvent in the system can be limited depending on factors, such as extraction yield and solvent swelling.[18,21–23] Coal extraction with some of the solvent mixtures can lead to high yields of extract.[16,18,22–24] The influence of the mixed solvents was explained by the increase in the penetration of solvents into coals by coal swelling.[25] Kuznetnov[18] have reported a coal extraction yield of 30–40% using a solvent mixture (1:1) of tetralin–phenol, and naphthalene-phenol, quinoline-phenol. Miura and Mae[24] reported a high coal extraction yield with carbolic oil (composed of phenolic compounds), as an extraction solvent. They reported that the role of this solvent is to dissociate hydrogen bonds between coal structures, namely, the physical effect rather than the chemical effect.[26] Aida et al.[23] extracted coal with supercritical water–phenol mixtures near 400 °C. They observed that the extraction yield increased as the ratio of phenol–water was increased, showing a maximum of 70% at a water-phenol ratio of 4.5:0.5 and then reduced to 50-55% for phenol. Recently, Sehume et al.[11] showed that phenol has the potential to extract up to 50 wt. % (daf) of a South African bituminous coal at a temperature of 360 °C. It was of interest to investigate a renewable energy source material (i.e. derived from biomass) that can produce phenolic-rich compounds that could subsequently be used to facilitate the production of useful liquids from South African coals.

Sehume et al.[27] identified the phenolic compounds obtained from a sweet sorghum bagasse biomass sample, which was subjected to liquefaction using an alkaline treatment method at low reaction temperatures. The main phenolic compounds produced at a temperature of 280 °C and a NaOH concentration of 3.0 M were phenol (13.8 wt. % of total liquid products), p-cresol (6.8 wt. %), 4-ethylphenol (10.0 wt. %), 4-isopropylphenol (0.9 wt. %), 2-propylphenol (0.7 wt. %), and 4-ethylguaicol (1.5 wt. %). The model biomass-derived phenolic mixture was formulated based on the constituents as in the above-mentioned phenolic extraction results. We report in this paper on the utilization of a model biomass-derived phenolic mixture as a solvent for the bituminous coal in comparison to the use of phenol.

5.2. Experimental Section

5.2.1 Materials

South African bituminous coal (Waterberg) was supplied by Exxaro Resources Limited (South Africa).[11] Sample sizes of less than 150 µm were used in this investigation. A model biomass derived-phenolic mixture was based on the prominence of phenolic species identified in a previous study.[27] A solution of phenol (purity ≥ 89.0% and impurities ≈10%, water) was supplied by Sigma-Aldrich (South Africa). The following phenol derivatives' were purchased from Minema Chemicals (South Africa); p-Cresol (99%), 4-ethylphenol (99%), 4-isopropylphenol (98%), 2-propylphenol (97%), and 4-ethylguaicol (98%). The phenols were mixed prior to the solvent extraction and used without further purification. The weight ratio of the phenol: p-cresol: 4-ethylphenol: 2-propylphenol: 4-isopropylphenol: 4-ethylguaicol was 4:2:3:0.3:0.2:0.5. N_2 (high purity, 99.999%) was supplied by Africa Oxygen Limited (AFROX, South Africa). Tetrahydrofuran (THF) and n-hexane were purchased from Merck Chemicals (Pty) Ltd, South Africa.

5.2.2 Solvent extraction process and characterization of products

All experiments were conducted in a stainless steel high-pressure autoclave as described by Sehume et al.[11] The autoclave was charged with a weight ratio of 1:10 coal to solvent (model biomass-derived phenolic mixture). Larry and Bailey[28] also investigated solvent effects in depolymerization of coal using coal: phenol ratio of 1:10. The reactor was sealed and flushed with N_2. The autoclave was pressurized and heated to the reaction temperature in an N_2 atmosphere (initial cold pressure of 0.5 MPa) at a heating rate of 4 °C/min. The coal solvent extraction process was performed at reaction temperatures of 300, 320, 340 and 360 °C, whilst magnetically stirring the mixture at 300 rpm. The autoclave was held for 20 min at each specified maximum temperature (±4 °C), and then cooled down to room temperature using an electric fan. The product mixtures (solid and liquid) were vacuum filtered and the gases produced were calculated according to mass balance. A series of extractions were carried out on the filtered liquid (after solvent extraction) using a reflux system with two solvents at 85 °C for 1 h, as described in a previous study.[11] The THF-insoluble part of the liquid residue was labelled THFI and represents the unreacted portion of the coal. The THF-soluble part of the liquid residue (THFS) was further extracted with hexane, and the hexane-insoluble part of this extraction step (HI) was labelled PAAs, as it contains a combination of preasphaltenes and asphaltenes. The hexane-soluble (HS) product contains the oil part of the product.

5.2.3 Characterization of coal and extraction products

Proximate analyses were performed using a U-Therm TGA thermogravimetric analyzer, and ultimate analyses of the coal and solvent extraction products were carried out using an Elemental Vario El cube elemental analyzer, according to the ASTM 29541 method.[11] The oxygen content was calculated by difference. Each sample was characterized three times and the averages were used. The petrographic analysis was conducted by the Council for

Geoscience (South Africa) using a Leica DM600 microscope with a Carl Hilgers motorized system, according to the ISO 7404-2 method.

The model biomass-derived phenolic mixture was characterized by GC/MS using an Agilent 6890N gas chromatograph coupled with an Agilent 5975 mass detector. The GC was equipped with an Agilent 19091S column (30 m length, 0.25 mm diameter, 0.25 µm film). The split ratio was 1/15 at an inlet temperature of 250 °C. The initial program selected for the oven temperature was 30 °C for 2 minutes then ramped at 5 °C/min to 320 °C and held for 10 min. The National Institute of Standards and Technology (NIST) library was used for peak identification.

Samples were analyzed using an attenuated total reflection Bruker Fourier Transform Infra-Red spectrometer (ATR-FTIR) with an ALPHA's Platinum ATR single reflection diamond ATR module, at ambient temperature in the region of 400 to 4000 cm^{-1}. Infrared spectroscopy was used to elucidate the effect of the solvent extraction process on the functional groups of the products that were obtained at different temperatures.

The pyrolysis behaviour of the coal and PAAs was studied by thermogravimetric analysis (TGA, SDTQ600). Samples of approximately 12 mg were analyzed. Thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles of both the coal and the solid residues were obtained using a heating rate of 4 °C/min. Tests were conducted over the temperature range of 60–900 °C under a nitrogen flow of 75 mL/min.

Simulated distillation (SimDis) analyses were carried out using an HP Model 5890 GC system, in accordance with the ASTM D2887 method. The analysis was carried out on a high-temperature GC-FID system that has been fitted with an ARX 2887 Restek column (10 m × 0.53 mm × 0.53 µm). This process was followed by the injection of ~0.2 µL of the fractions into the GC column. The distillation curves were determined on a solvent-free basis.

The overall percentage conversion or extraction yield of coal during the solvent extraction, using a model biomass-derived phenolic mixture as the solvent, was calculated according to the equation (all values indicated are weight percentages):[11]

Conversion or extraction yield (wt. %) = [coal charged – unreacted coal residue (THFI)/ daf coal] x 100%. (1)

The yield of pre-asphaltenes and asphaltenes (PAAs, HI) is defined by:

PAAs (wt. %) = [(Hexane insoluble material, THF soluble) / daf coal] x 100% (2)

where daf coal is the weight of the dry, ash-free coal.

The oil part of the extracted products (HS) is obtained by difference:

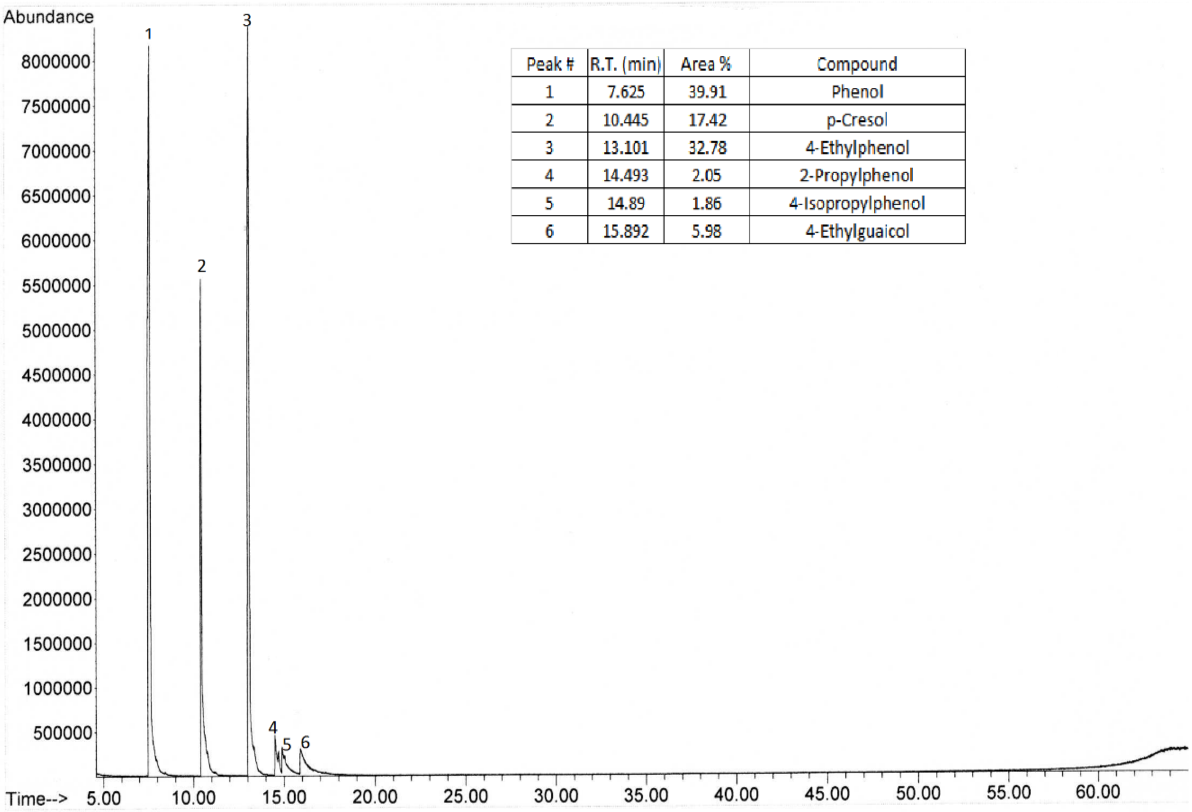
oil (wt. %) = [Conversion – (PAAs) – G] x 100% (3)

where G is the yield of the gaseous products obtained after the coal solvent extraction (obtained by mass balance). The conversion or extraction yield and intermediate products yields (PAAs) were determined gravimetrically, based on the solvent-free dried residues.

5.3. Results and Discussion

5.3.1 GC-MS (semi-quantitative) analysis of the model biomass-derived phenolic mixture

The GC-MS analysis was performed on the model biomass-derived phenolic mixture prior to solvent extraction and the results are shown in Figure 5.1. The area percentages of the phenolic compounds were 39.91, 17.42, 32.78, 2.05, 1.86 and 5.98 % for phenol, p-cresol, 4-ethylphenol, 2-propylphenol, 4-isopropylphenol, and 4-ethylguaicol respectively (Figure 5.1).



Peak #	R.T. (min)	Area %	Compound
1	7.625	39.91	Phenol
2	10.445	17.42	p-Cresol
3	13.101	32.78	4-Ethylphenol
4	14.493	2.05	2-Propylphenol
5	14.89	1.86	4-Isopropylphenol
6	15.892	5.98	4-Ethylguaicol

Figure 5.1. GC-MS spectrum of the model biomass-derived phenolic mixture

5.3.2 Characterization of Samples

The elemental analysis, X-ray fluorescence (XRF) and maceral composition results as reported earlier for the coal are summarized in Table 5.1.[11] The proximate and ultimate analyses shows that the coal compromises of 34 wt. % (ad) volatile matter, 50 wt. % (ad) fixed carbon and 81 wt. % (daf) carbon content. The most abundant oxides in the ash were SiO_2 (62.3%), Al_2O_3 (20.4%) and Fe_2O_3 (8.7%) contributing up to 91.4% of the total ash composition (Table 5.1). In most bituminous coals a portion of the SiO_2 may be present as free quartz; however, much or all of the SiO_2 is likely present in clays. All of the Al_2O_3 will be in clays or similar minerals. Probably most or all of any Fe_2O_3 are due to the oxidation of pyrite, FeS_2, during the ashing process. The petrographic constituents of this coal decreased in the order vitrinite (52.8%), inertinite (29.4%), reactive semifusinite (6.7%), and liptinite (3.5%).

In Table 5.2, the results from the proximate analysis of the unreacted coal residues (THFIs) and the extraction products (PAAs) after the solvent extraction treatment are summarized. The results show that the ash percentages of THFIs increased from 10.4 and 14.2 wt. % with increasing extraction temperatures between 300 °C and 360 °C. The inorganic materials in the coal are largely or completely un-extracted, while the amount of organic substance extracted increases with temperature. Therefore, inevitably the ash yield will increase as observed in this study. The ash percentage trend is also similar to the results obtained through the use of pure phenol (10.4 wt. % up to 20.6 wt. %).[11] The volatile matter contents of approximately 45 wt. % and ash percentages of approximately 0.3 wt. % of the PAAs remain constant at the various experimental temperatures for the solvent extraction process reported in this study. The nitrogen and sulphur contents of THFIs (300–360 °C) were somewhat lower than that observed for the coal. In general, the ultimate analysis characterization results of THFIs and PAAs using a model biomass-derived phenolic mixture are similar to results obtained in a previous study using pure phenol.[11]

Table 5.1. Proximate ultimate, XRF and petrographic results for the coal.[11]

Chemical properties	Standard methods used	Coal
Proximate analysis (wt.%, ad)[a]		
Inherent Moisture	ISO11722	3.1
Volatile matter	ISO 562	34.2
Ash	ISO 1171	10.9
Fixed carbon	By difference	51.8
Ultimate analysis (wt.%, daf)[b]	ISO 29541	
Carbon		80.9
Hydrogen		5.5
Nitrogen		1.9
Sulphur	ISO 19579	1.3
Oxygen	By difference	10.4
H/C (Atomic ratio)		0.82
Dilatation	SANS 6072	
Softening temperature (°C)	397	
Temperature of maximum contraction (°C)	501	
Maximum contraction (%)	27	
XRF (wt. %)	ASTM D4326	
Fe_2O_3	8.7	
MnO	0.1	
Cr_2O_3	0.1	
V_2O_5	0.2	
TiO_2	2.6	
CaO	1.4	
K_2O	1.0	
P_2O_5	0.1	
SiO_2	62.3	
Al_2O_3	20.4	
MgO	0.8	
ZnO	1.1	
SO_3	1.1	
Petrographic analysis (vol. %, m.m.f.b.)	ISO 7404-2	
Vitrinite	52.8	
Liptinite	3.5	
Reactive semifusinite	6.7	
Total inertinite	29.4	
Visible mineral matter	7.5	
Vitrinite reflectance	0.6	

***a** ad: air-dried basis.

***b** daf: dry-ash-free basis.

* Note – Gieseler fluidity and some values from dilatation were not determined due to sample size.

Table 5.2. Proximate and ultimate analyses of coal solvent extraction products using a model biomass-derived phenolic mixture and phenol[11] (unreacted coal residues (THFIs) and PAAs)

Product	Chemical Properties	Standard methods	300 °C	300 °C[11]	320 °C	320 °C[11]	340 °C	340 °C[11]	360 °C	360 °C[11]
THFIs	Proximate analysis (wt.%, air-dry basis)									
	Moisture	ISO11722	1.8	2.0	2.2	2.1	2.6	2.8	2.6	2.6
	Volatile Matter	ISO 5621	39.9	44.7	38.3	43.0	35.9	31.7	32.3	28.5
	Ash	ISO 1171	10.4	10.2	11.3	10.5	12.3	18.5	14.4	20.6
	Fixed Carbon	By difference	47.9	43.1	48.2	44.4	49.2	47.0	50.7	48.3
	Ultimate analysis (wt.%, dry-ash-free basis) ISO 29541									
	Carbon		77.9	79.1	81.3	79	81.9	82.9	82.2	82.2
	Hydrogen		5.1	5.1	5.3	4.8	5.3	5.1	5.1	4.8
	Nitrogen		1.6	1.6	1.5	1.6	1.4	1.9	1.6	2.0
	Sulphur	D4239-14	1.2	0.9	1.1	0.9	1.1	1.0	1.2	1.1
	Oxygen	By difference	14.2	13.3	10.8	13.7	10.3	9.1	9.9	9.9
	H/C (Atomic ratio)		0.79	0.77	0.78	0.73	0.78	0.74	0.74	0.70
PAAs	Proximate analysis (wt.%, air-dried basis)									
	Moisture	ISO11722	2.6	1.7	3.2	2.2	3.4	2.1	2.4	2.2
	Volatile Matter	ISO 5621	45.5	56.2	46.5	57.1	45.9	54.0	46.9	55.5
	Ash	ISO 1171	0.3	0.9	0.2	0.8	0.3	0.9	0.3	0.9
	Fixed Carbon	By difference	51.6	41.2	50.1	39.9	50.4	43.0	50.4	41.4
	Ultimate analysis (wt.%, dry-ash-free basis) ISO 29541									
	Carbon		80.7	80.1	81.8	80.8	81.1	81.3	80.9	81.8
	Hydrogen		5.4	5.1	5.5	5.2	5.3	5.1	5.3	5.1
	Nitrogen		1.5	2.0	1.3	1.9	1.3	2.0	1.4	1.8
	Sulphur	D4239-14	0.7	0.7	0.7	0.7	0.7	0.8	0.6	0.7
	Oxygen	By difference	11.7	12.1	10.7	11.4	11.6	10.8	11.8	10.6
	H/C (atomic ratio)		0.8	0.76	0.81	0.77	0.78	0.75	0.79	0.75

5.3.3 Coal conversion as a function of temperature and product distribution

Figure 5.2 shows the coal conversion and overall product distribution after solvent extraction at 300–360 °C using a model biomass-derived phenolic mixture. As the temperature increases, the yield of the residue (THFIs) decreases, while the conversion increases. Using pure phenol as a solvent the same trend was observed.[11] Figure 5.2 shows the coal conversions of 14 wt. %, 20 wt. %, 32 wt. % and 37 wt. % using a model biomass-derived phenolic mixture at 300 °C, 320 °C, 340 °C and 360 °C. The yield of the solid residues (THFIs) during the solvent extraction decreased from 86 to 63 wt. % (daf) when treated between 300 °C and 360 °C. Pew and Withrow[29] reported approximately 43.6 wt. % extract and 63.8 wt. % residue after solvent extraction of a Pittsburgh No. 8 seam coal using phenol in an atmosphere of carbon dioxide. Kiebler[30] observed extracts of 39.7, 40.4 and 49.1 wt. % for Pittsburgh seam coal with phenol, m-cresol and o-phenyl phenol, respectively. However, their results showed that the solvents which gave the greatest yield of extract were appeared to be most affected by oxidation, based on a high material balance (>100%). Fieldner and Ambrose[21] reported that compounds, such as cresol, diphenyl, or o-phenylphenol, could only dissolve 20–30% of the coal. Larry and Bailey[28] observed extraction yields of 32 wt. % and 36 wt. % daf for phenol/o-cresol and phenol/catechol solvent mixtures in the presence of a catalyst (sulphuric acid), respectively, using high-volatile bituminous coal from the Pond Creek seam. Some of these results corresponded with the conversion yield of nearly 37 wt. % obtained at 360 °C. However, this value was lower than that obtained in the experiments where pure phenol was used as a solvent, where conversion of nearly 50 wt. % was observed.[11] The effectivity of a solvent is characterized significantly by their physico-chemical properties, which determine the extent to dissolve or penetrate coal structure.[25] According to the literature, phenol can readily give up a hydrogen atom to form a phenoxy radical.[31] The phenoxy radicals are capable of abstracting a hydrogen atom from a donor site in the coal, regenerating phenol. Therefore, phenol may serve as a good hydrogen carrier, whilst alkyl-substituted phenols were found to be undesirable due to the formation of benzylic radicals resulting in incorporation of the alkyl phenol into the coal structure.[32]

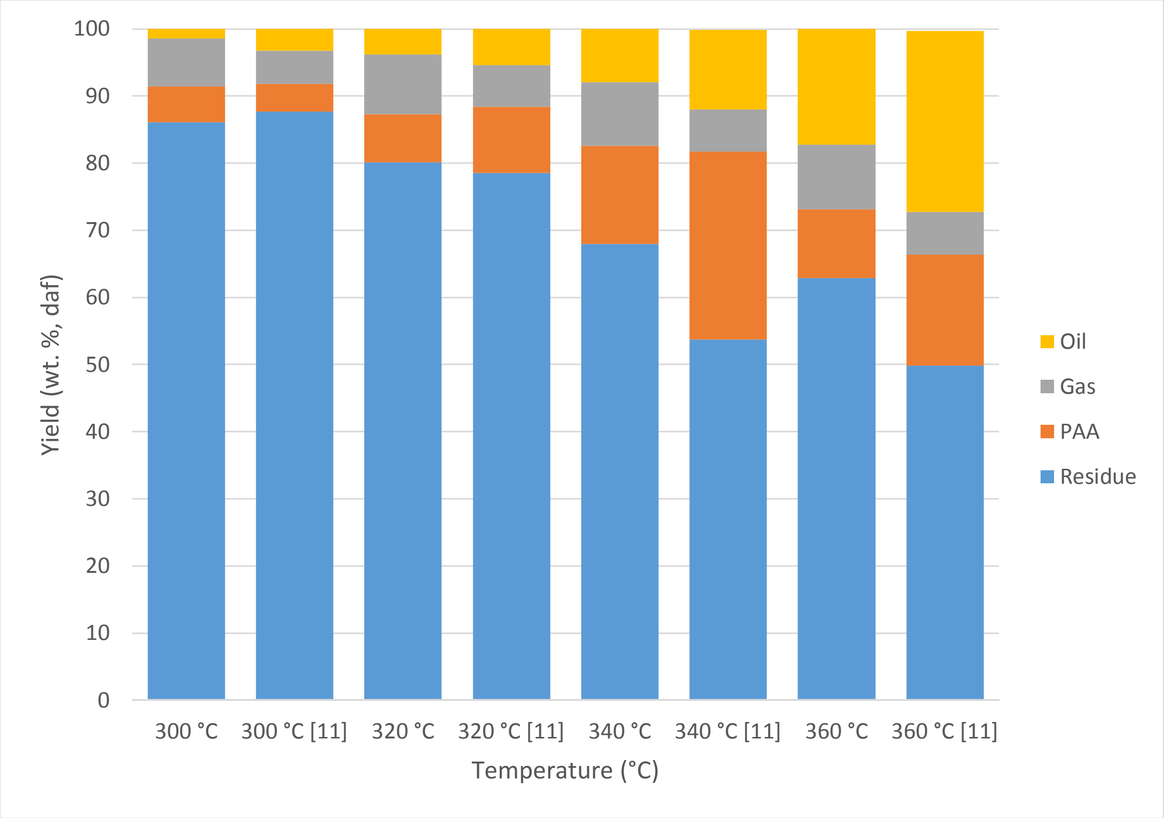


Figure 5.2. Coal conversion and extraction product distribution using a biomass-derived phenolic mixture and phenol.[11]

5.3.4 The effect of temperature on gas yields during solvent extraction

The gaseous product yields obtained after coal solvent extraction at temperatures of 300–360 °C through mass balance are shown in Figure 5.3. The temperature range above 250 °C has been reported to mark the onset of the active thermal decomposition of bituminous coal.[19,33] As it can be seen from Table 5.1 (dilatation results) the coal used in this study begins to soften at about 397 °C. The results show that gaseous products progressively increased with increasing temperature (7–9.6 wt. %). Similar trends were also reported for coal extraction using phenol as a solvent (300–360 °C).[11] However, the gaseous yields of the present study, using a model biomass-derived phenolic mixture, were slightly more than that obtained in a previous study using phenol, where the yields were 4.9, 6.2, 6.3 and 6.4 wt. % at 300, 320, 340 and 360 °C.[11] It is more likely that the gaseous products can be due to gases that could have been chemisorbed onto the coal surface, apart from the gases resulted from the thermal rupture of the labile bonds in the coal structure.

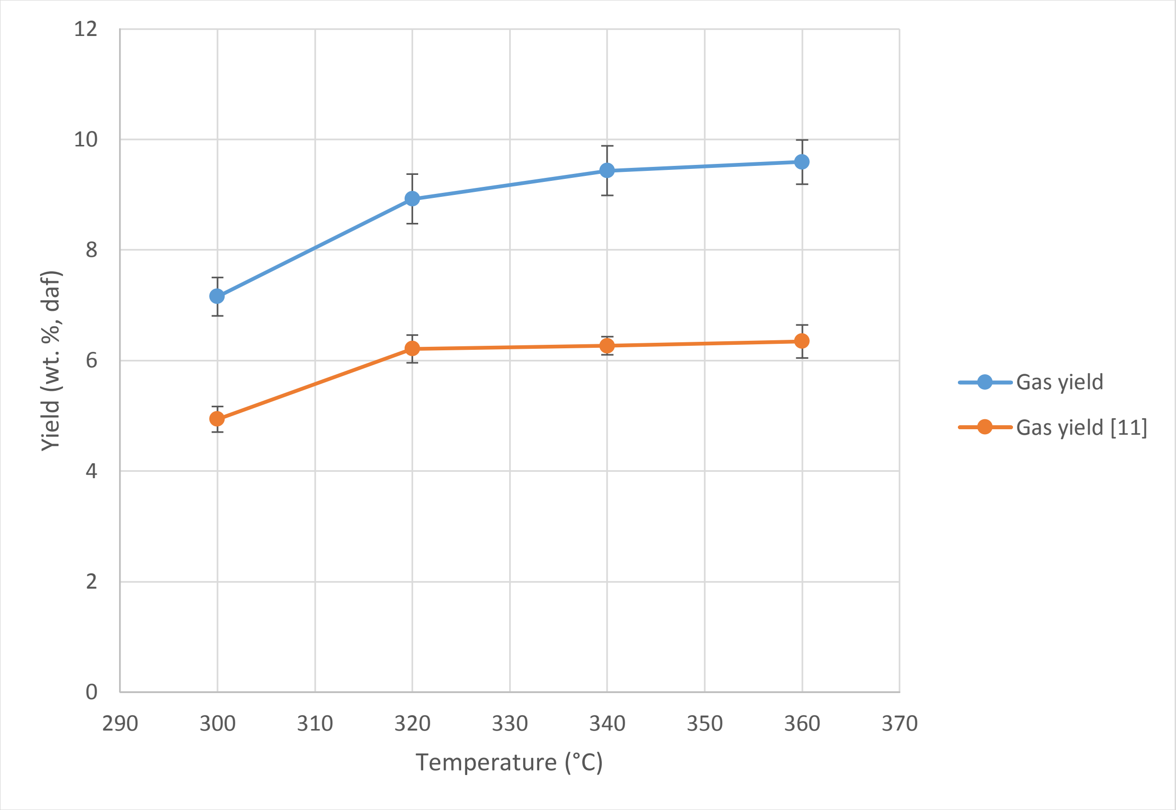


Figure 5.3. Gaseous products after solvent extraction using a model biomass-derived phenolic mixture and phenol.[11]

5.3.5 The effect of temperature on PAAs during solvent extraction

Figure 5.4 shows the effect of temperature on the conversion of coal and PAAs during the coal extraction process using a model biomass-derived phenolic mixture. It can be seen from Figure 5.4 that the conversion increased from 14 to 37 wt. % with increasing reaction temperatures (300–360 °C). The PAAs are an intermediate product in coal extraction or liquefaction which can be further converted to oil and/or gases.[34,35] PAAs were grouped together as one fraction due to the similarity in their dissolving ability in THF and n-hexane.[35] The yield of PAAs slowly (4–7 wt. %) increased as the temperature increased between 300 °C and 320 °C which is in the range of the thermal decomposition of the coal.[11] Between 320 °C and 340 °C, the PAAs yields increased, which also parallels the increasing conversion as a function of temperature in this temperature range. In the present study, the yield of PAAs (15–10 wt. %) slowly decreased with increasing temperature between 340 °C and 360 °C. This drop in the PAAs yield in this temperature range corresponds with an increase in the oil yield as a function of temperature (see below Section 5.3.6). Similar trends were also reported for coal extraction using phenol at this temperature range.[11] The PAAs obtained using a model biomass-derived phenolic mixture displayed the same thermal behaviour during pyrolysis (Appendix C.1).

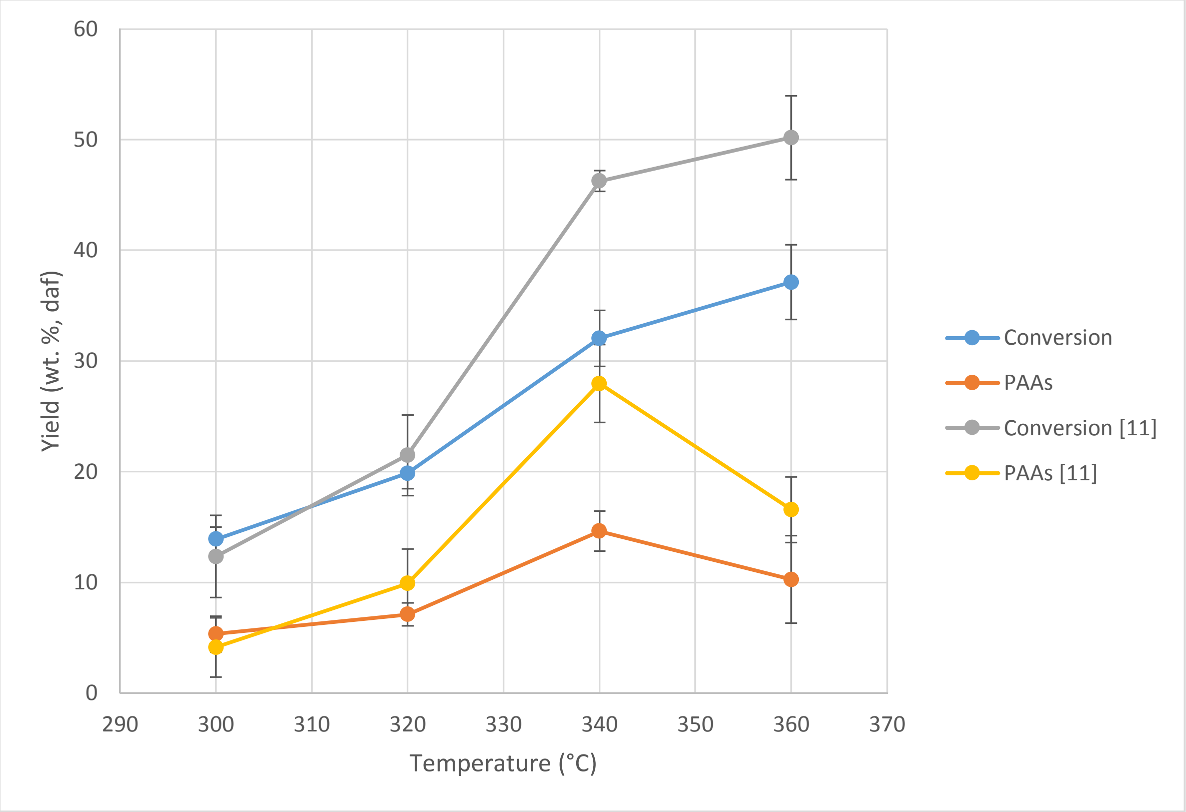


Figure 5.4. Coal conversion and PAAs yields using a model biomass-derived phenolic mixture and phenol.[11]

5.3.6 The effect of the temperature on oil yield during solvent extraction

The effect of temperature on the yield of oil after solvent extraction using a model biomass-derived phenolic mixture is shown in Figure 5.5. As shown earlier, an increase in the PAAs yield is coupled with higher coal conversions. The same trend is also observed with oil yields as coal is converted into solvent extraction products. From these results (Figure 5.5), it can be seen that an increase in temperature also increased oil yields (300–360 °C). The oil yield in this temperature range increased from 1 wt. % to 17 wt. % and with the most significant change observed above 320 °C. The oil yield increased by nearly 5 wt. % between extraction temperatures of 340 °C to 360 °C, whilst the conversion increased by nearly 5 wt. %. The oil yield observed at 360 °C using phenol as a solvent was higher, at 27 wt. %, than the 17 wt. % observed in this study using the biomass-derived phenolic mixture.[11] The higher oil yields observed for pure phenol as a solvent are a result of phenol being a better hydrogen carrier during depolymerization of coal as compared to alkyl-substituted phenols, thus leading to higher coal extractions.

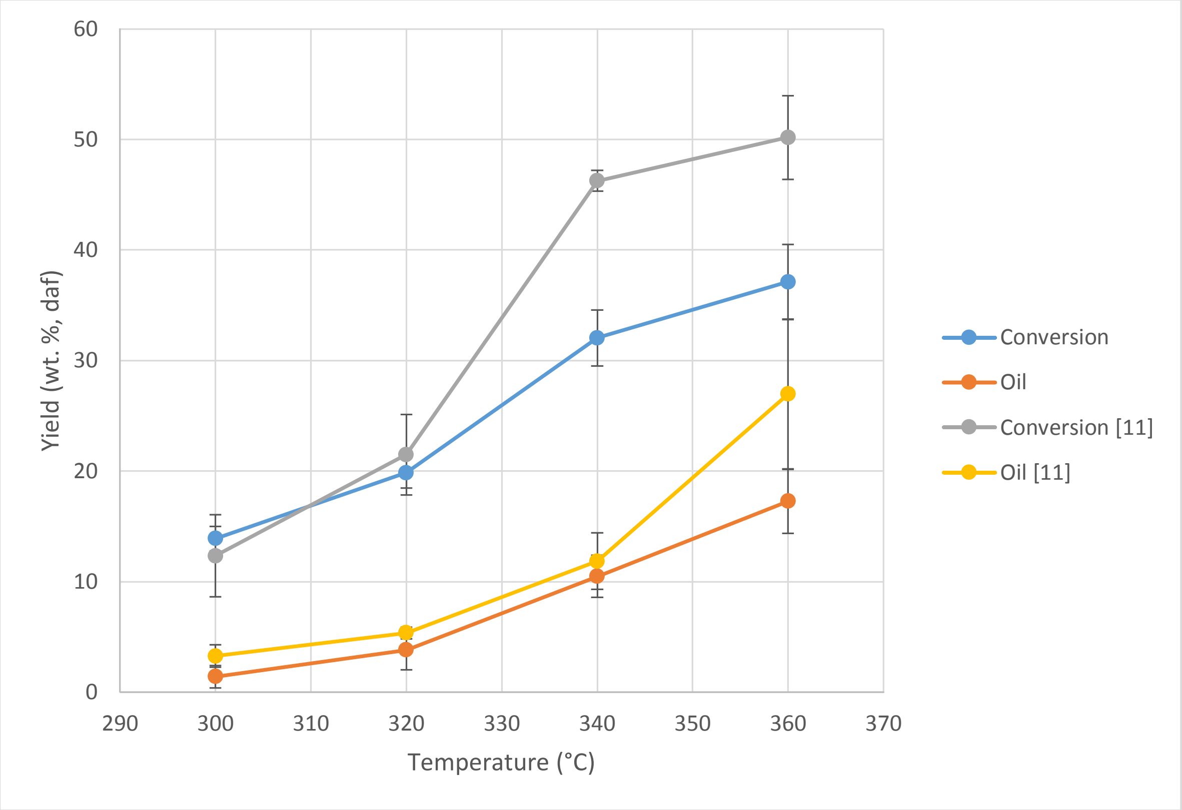


Figure 5.5. Coal conversion and oil yields using a model biomass-derived phenolic mixture and phenol.[11]

5.3.7 ATR-FTIR Spectroscopy

Figure 5.6–5.8 shows the ATR-FTIR spectra of the coal, PAAs, and hexane soluble products (oil). ATR-FTIR spectrometry represents a relatively useful means of characterization of coal and coal-derived products in terms of functional groups. Table 5.3 shows a summary of bands of the functional groups observed in Figure 5.6–5.8.

Table 5.3. Characteristic ATR-FTIR bands of functional groups

Wavenumber (cm^{-1})	Assignment	Reference(s)
3600–3100	O–H stretching vibrations of hydrogen-bonded hydroxyl groups	11,36,37
3100–2800	Aromatic C-H stretching mode	11,36,38
3000–2800	Aliphatic C-H stretching mode	11,36,39
2900–2800	Aliphatic C-H stretching mode	11,36,40
1600	Aromatic ring (C=C in plane) stretching symmetric	37,39
1450	Symmetric aliphatic C-H deformation of methylene	11,36,40
1133–1060	Stretching vibration of the ether groups, C-O stretch and OH bending vibrations	39
900–650	Assigned to the C-H out-of-plane vibration of aromatic ring structures	40,41

These results show that the coal and the coal-derived products spectra were nearly similar in functional groups and with minimal apparent structural changes observed after extraction temperatures.[42] The peaks within 700–800 cm^{-1} can also be attributed to mineral matter especially in the case of the coal and THFI residues. However, the peaks around this region were observed to be weak for extraction products (HI and HS fractions) due to the absence of mineral matter.[43] Similar results were observed for bituminous coal and extraction products using phenol as a single solvent system in a previous study.[11] The FTIR results, therefore, indicate a similar extraction process for pure phenol and a model biomass-derived phenolic mixture despite the differences in the extraction yields (see Section 5.3.3). The SEM image of the coal also showed structural changes after solvent extraction at specific temperatures where the coal residues were characterized by porous structures that are due to the release of volatiles during thermal treatment (Appendix C.2).

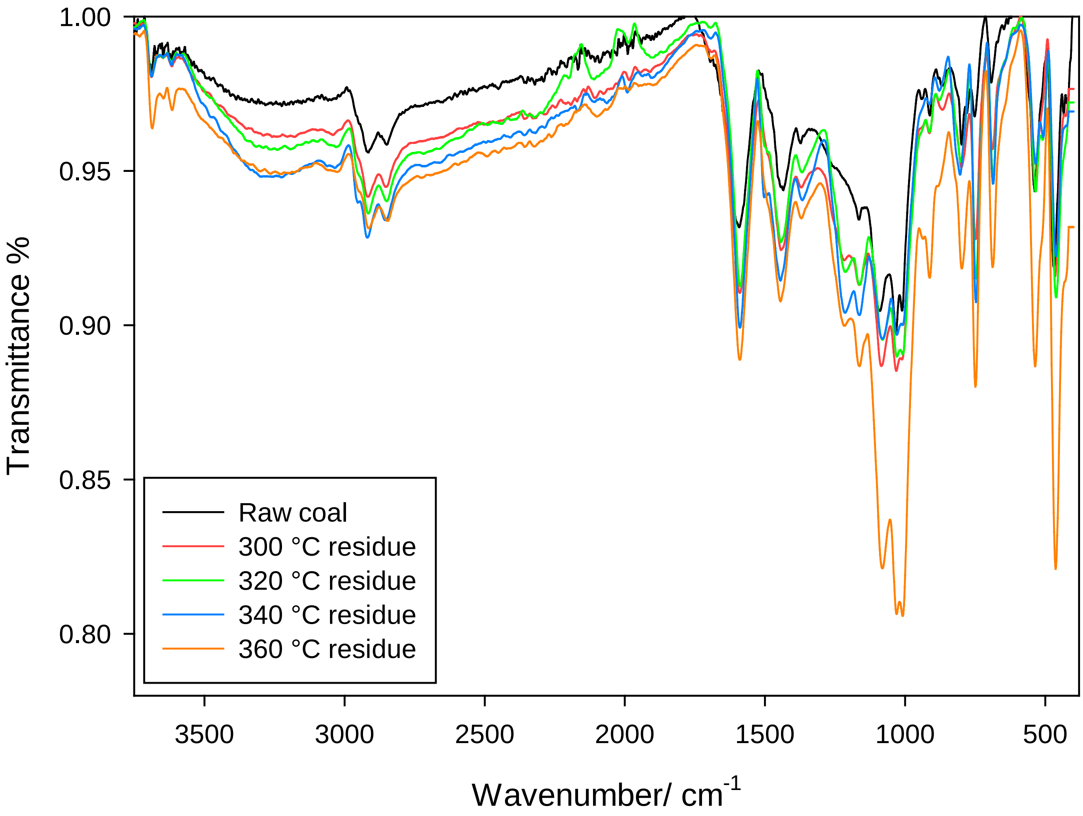


Figure 5.6. The infrared spectrum of the coal sample and unreacted coal residues (THFIs) after the coal solvent extraction at temperatures between 300 °C and 360 °C, using a model biomass-derived phenolic mixture

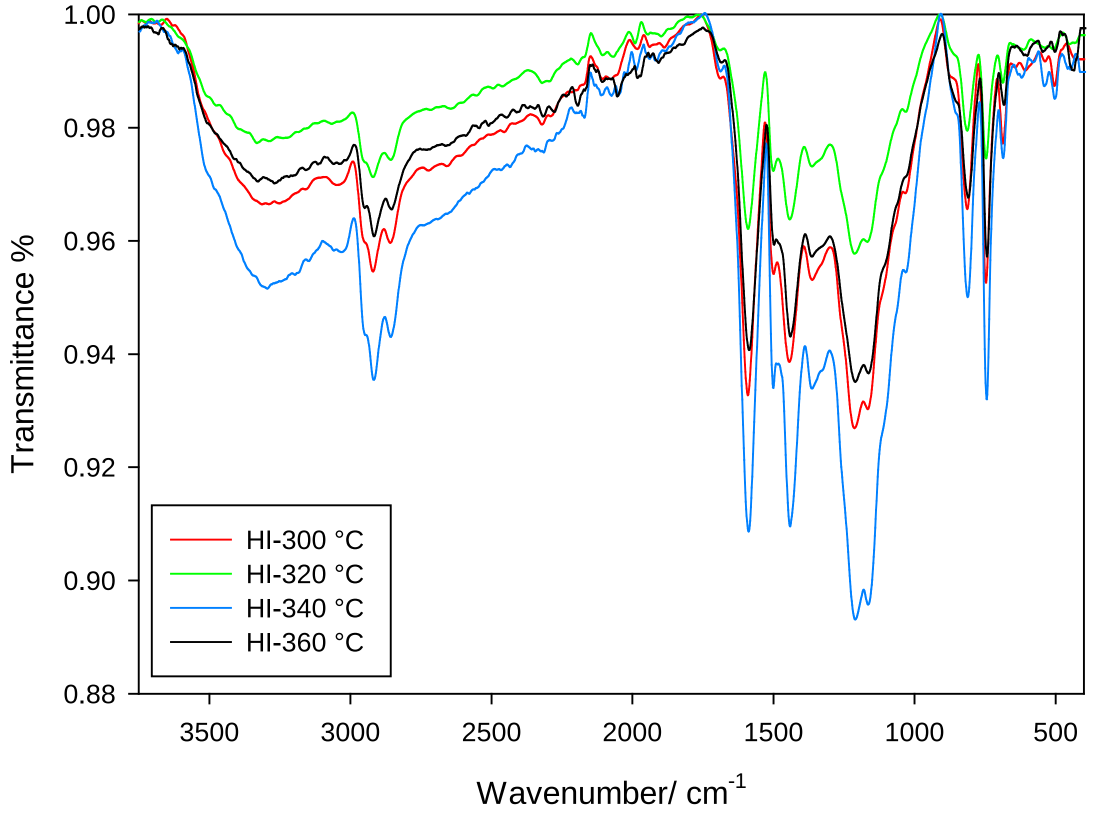


Figure 5.7. The infrared spectrum of hexane-insoluble products (PAAs) after the coal solvent extraction at temperatures between 300 °C and 360 °C, using a model biomass-derived phenolic mixture

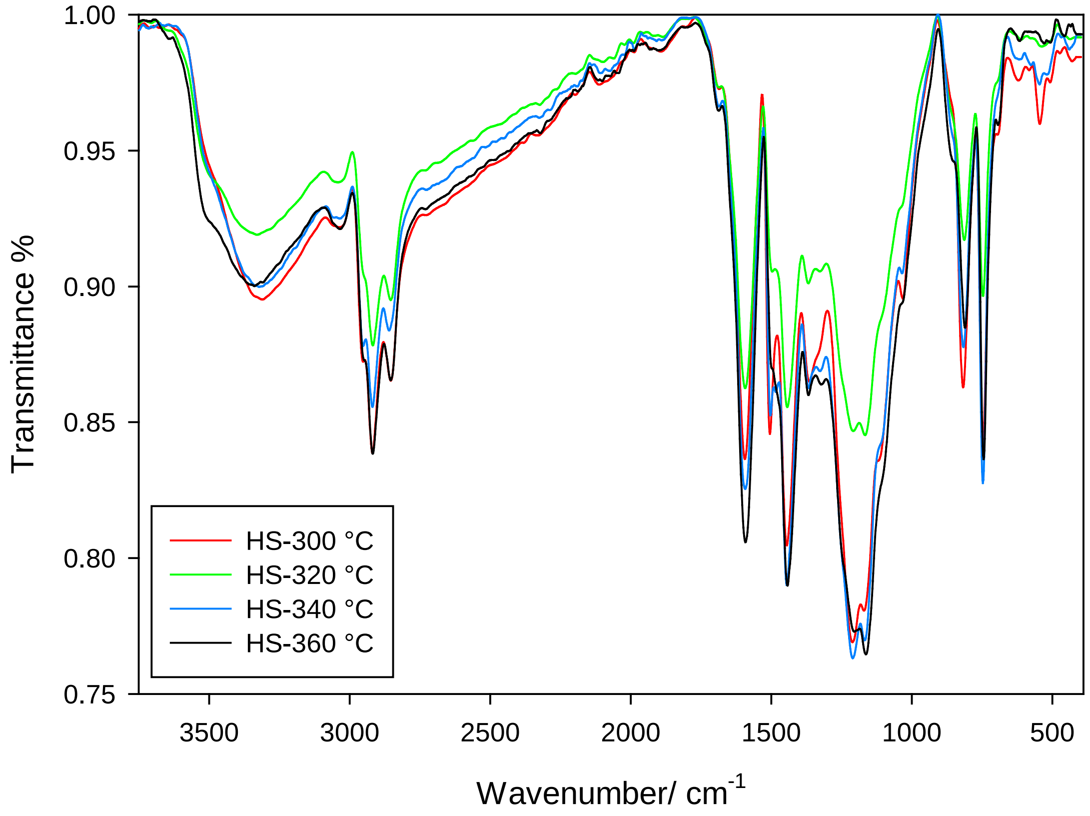


Figure 5.8. The infrared spectrum of the hexane soluble products (oil) after the coal solvent extraction at temperatures between 300 °C and 360 °C, using a model biomass-derived phenolic mixture

5.3.8 SimDis GC analysis

The distillation curves of the coal-derived liquefied HS fractions obtained through coal extraction using a model biomass-derived phenolic mixture at the temperature range of 300–360 °C, are shown in Figure 5.9. The fractionation of coal liquids is based largely on schemes modified and developed for the characterization of petroleum.[44–47] It is important to note that the evaluation of the distillation curves of the HS fractions has been determined on a phenol-free basis due to the hindrance of the phenols peak that masks the low boiling point fraction (79–191 °C) peaks.[11] The HS fractions contain compounds with a wide range of boiling points (208–520 °C) with about 40% of the composition distilling off below ≈360 °C. The HS fractions produced at 360 °C yielded the highest boiling point distribution with regard to constant recovered mass, followed by fractions produced at 340 °C, 320 °C, and 300 °C. For components boiling below 500° C, the variation of boiling point distributions when phenol was used as a solvent was the reverse; the highest boiling point distribution was observed for the extract produced at 300° C, and the lowest for the 360° C extract. The present study shows that the properties of the HS fractions were affected by the type of solvent; considering that the coal and process conditions were kept the same throughout the extractions using pure phenol and using the model phenolic mixture (300–360 °C).

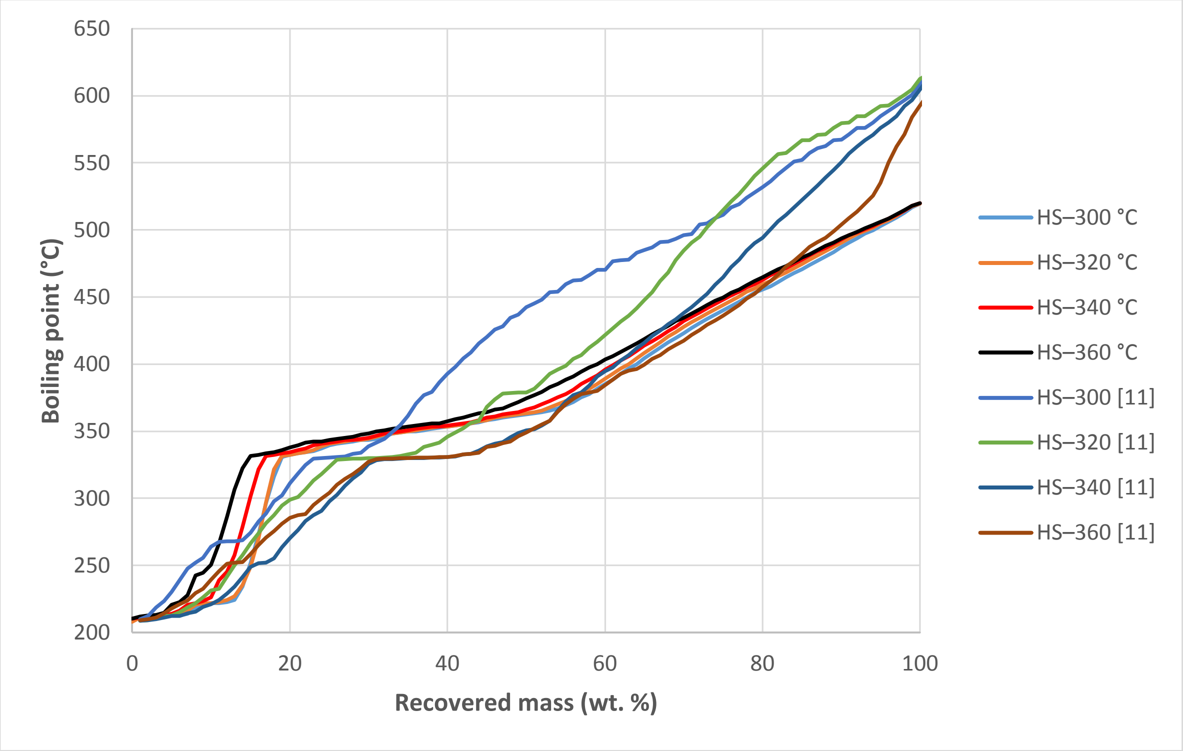


Figure 5.9. Distillation curves of the HS products obtained using a model biomass-derived phenolic mixture and phenol[11] at different extraction temperatures

The boiling point distribution of HS fractions using a model biomass-derived phenolic mixture for coal extraction are summarized in Table 5.4. The quality of the oil obtained depends significantly on its boiling point distribution.[42] The boiling point fraction of kerosene decreases as the extraction temperature increases (16–11 wt. %). The study shows that the extraction temperature has little effect on the number of products in the boiling fractions, with the distillate fuel oil, light vacuum gas oil, heavy vacuum gas oil and heavy vacuum gas oil fractions remaining the same with values of approximately 14 wt. %, 50 wt. %, and 22 wt. % respectively. The largest proportion of the boiling fractions obtained with the model biomass-derived phenolic mixture could be arranged in decreasing order of light vacuum gas oil, heavy vacuum gas oil, distillate fuel oil, and kerosene (300–360 °C). From these results, nearly 70% of the total fractions corresponded to light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGO), with about 50% correlating with LVGO which were obtained at low extraction temperatures. The LVGO fractions through advanced processes (i.e. hydrocracking) can be used as a feedstock preferably to produce C_3–C_4 compounds, light, and middle distillates. According to the GC-MS results (Appendix C.3), these results showed that the main products in model biomass-derived phenolic mixture extraction were mainly bis-phenol alkyl compounds.

The average boiling point of the hydrocarbon constituents of the fractions was calculated as shown in a previous study.[11] It can be observed that the average boiling point (WABP) of HS fractions obtained using a model biomass-derived phenolic mixture increased with extraction temperatures from 368 to 380 °C (Table 5.4). This trend is in contrast with the results obtained by using phenol as the extraction solvent where the WABP of HS fractions decreased with extraction temperatures (425–372 °C).[11] Thus, the decrease in average boiling points may be related to the difference in the average molecular mass of the extracts obtained using these solvents.

Table 5.4. Boiling point distributions for the different HS fractions based on crude oil fractions obtained using a model biomass-derived phenolic mixture and phenol[11] as extraction solvent

Boiling fraction/ definition	**Boiling Range (°C)**	**Unit**	**HS–300 °C**	**HS–300 °C[11]**	**HS–320 °C**	**HS–320 °C[11]**	**HS–340 °C**	**HS–340 °C[11]**	**HS–360 °C**	**HS–360 °C[11]**
Medium naphtha	79–121	wt.%	–	–	–	–	–	–	–	–
Heavy naphtha	121–191	wt.%	–	–	–	–	–	–	–	–
Kerosene	191–277	wt.%	16.0	14.0	16.0	15.0	14.0	20.0	11.0	17.0
Distillate fuel oil	277–343	wt.%	14.0	16.0	13.0	23.0	14.0	26.0	14.0	30.0
Light vacuum gas oil	343–455	wt.%	50.0	23.0	49.0	27.0	49.0	26.0	52.0	31.0
Heavy vacuum gas oil	455–566	wt.%	20.0	34.0	22.0	18.0	23.0	19.0	23.0	18.0
Residual oil	>566	wt.%	–	12.0	–	16.0	–	8.0	–	3.0
Total	**–**	**wt.%**	**100.0**	**99.0**	**100.0**	**99.0**	**100.0**	**99.0**	**100.0**	**99.0**
Initial boiling point	–	°C	208.8	209.8	208.0	208.6	210.2	208.6	210.2	209.2
Average boiling point (WABP)	**100–550**	**°C**	**367.56**	**424.6**	**370.2**	**403.0**	**372.4**	**380.7**	**380.2**	**371.6**
Final boiling point	–	°C	519.4	615.4	519.4	615.6	520.0	612.4	520.0	600.6

5.4. Conclusions

The utilization of a model biomass-derived phenolic mixture for the solvent extraction of a South African bituminous coal under mild conditions was investigated. The choice of a phenolic mixture as a model for the extraction of bituminous coal allowed this study to investigate the feasibility of coal extraction using a biomass-derived solvent. This model biomass-derived phenolic mixture was found to be effective in extracting 14–37 wt. % of coal with increasing temperature (300 °C up to 360 °C). Alkyl-substituted phenols showed less depolymerization ability than compared with phenol may be due to poor hydrogen carrier capability. The extraction yields were influenced by the effect of physical and chemical properties of the solvent used in coal extraction.

The THFIs and PAAs obtained using a model biomass-derived mixture had similar H/C atomic ratios, which are similar to the H/C of the coal. These results confirm that PAAs are the intermediate product coal and oil in coal extraction. The drop of the PAAs yield between 340 °C and 360 °C during coal conversion corresponded with an increase of the oil yields as a function of temperature. The ATR-FTIR spectra of the coal and the extraction products showed nearly the same functional groups with no significant structural changes. These results show that the extraction production of the phenol-based solvents during coal extraction are of similar chemical nature, despite differences in the extraction yields.

SimDis results showed that the increasing extraction temperature influenced the number of products in the boiling fractions. The differences in the boiling point distribution obtained using phenolic based solvents may be related to the difference in average molecular mass of the extracts during coal extraction (300–360 °C). However, more work ought to be carried out using biomass-derived phenolic solvent to examine the nature of the extracts (i.e. carbon distribution and the molecular weight distribution) and all alkyl substituted phenols that may lead to higher extractions at maximum experimental conditions. The utilization of a biomass-derived solvent will assist in the facilitation of the production of useful liquids from South African coals and address environmental challenges associated with the currently favoured approach of producing synthetic liquid fuels, indirect coal liquefaction.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

The authors thank Mr. Kgutso Mokoena (Sasol) for SimDis analysis. The work presented in this paper is based on research financially supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa (Coal Research Chair Grant No. 86880, UID85643, Grant No. TP1208137225). Any opinion, finding, conclusion, or recommendation expressed in this material is that of the authors(s), and the NRF does not accept any liability in this regard.

Chapter References

1. Winkler, H.; Davidson, O.; Kenny, A.; Prasad, G.; Nkomo, J.; Sparks, D.; Howells, M.; Alfstad, T. Energy policies for sustainable development in South Africa. Energy Research Centre, University of Cape Town. April 2006, pp 1-4 & 13-60.
2. Falcon, R.; van der Riet, M. In Effect of milling and coal quality on combustion, International Pittsburgh Coal Conference, Sandton, South Africa, 2007.
3. Department of Minerals and Energy (DME) 2006. Energy Security Master Plan –Liquid Fuels.
4. Fletcher, J.; Sun, Q.; Bajura, R.; Zhang, Y.; Ren, X. Coal to clean fuel-The Shenhua investment in direct coal liquefaction. In: 21st Annual International Pittsburgh Coal Conference, Osaka, Japan, 13–17 September, 2004.
5. Nolan, P.; Shioman, A.; Rui, H. Eur. Manage. J. **2004**, 22, 150–164.
6. Zhao, L., Gallagher, K. Energy Policy **2007**, 35, 6467–6477.
7. Barta, P. South Africa has a way to get more oil; make it from coal. WSJ 2006, *CCXLVIII*, 1.
8. Andrews, A.; Logan, J. Fischer-Tropsch fuels from coal, natural gas and biomass: Background and policy. Congressional Research Service (CRS) Report for Congress. Order Code RL34133. 27 March, 2008, pp 1–26.
9. Aida, T.M.; Sato, T.; Sekiguchi, G.; Adschiri, T.; Arai, K. Fuel **2002**, 81, 1453–1461.
10. Speight, J.G.; Moschopedis, S.E. Fuel Process. Technol. **1986**, 13, 215–232.
11. Sehume, T.Z.; Strydom, C.A.; Bunt, J.R; Schobert, H.H. Energy Fuels **2017**, 31, 13655–13665.
12. Kabe, T.; Ishihara, A.; Qian, E. W.; Sutrisna, I.P.; Kabe, Y. Coal and coal-related compounds: structures, reactivity and catalytic reactions. Studies in surface science and catalysis series, 150. Elsevier, Amsterdam, 2004.
13. Kiebler, M. W. The action of solvents on coal. In Chemistry of Coal Utilization (Lowry, H. H., Ed.), Wiley: New York, 1945, pp 677−760.
14. Illingworth, S. R. Fuel Sci. Pract. **1922**, 1, 213−219.
15. Parr, S.W.; Hadley, H.F. Fuel **1925**, 4, 31, 49.
16. Pott, A.; Broche, H.; Nedelmann, H.; Schmitz, H.; Scheer, W. Glückauf, 69, 903–12 (**1933**); Fuel, 13, 91–5, 125–8, 154–7 (**1934**).
17. Speight, J.G. The Chemistry and Technology of coal, third edition, CRC-Taylor and Francis Group, Boca Raton, FL, 2013, Chapter 11 and 13.
18. Kuznetzov, M.I. Khim. Tverdogo Topliva, 6, **1936**, 515; Fuel, 16, **1937**, 114.
19. Berkowitz, N. An introduction to coal technology. Energy Science and Engineering. Academic Press, 1979, Chapter 7.

20. Orchin, M.; Storch, H.H. Ind. Eng. Chem. **1948**, 40, 1385–1389.
21. Fieldner, A.C.; Ambrose, P.M. U.S. Bureau Mines Information Circ. 7446 (1948).
22. Pande, S.; Sharma, D.K. Energy Fuel **2002**, 16, 194–204.
23. Iino, M., Takanohashi, T., Obara, S., Tsueta, H., Sanokawa, Y. Fuel **1989**, 68, 1588–1593.
24. Miura, K; Mae, T. Proceedings of the Society of Chemical Engineers Japan 63rd Annual Meeting (2000) p. G104.
25. Iino, M.; Matsuda, M. Bull. Chem. Soc. Jpn. **1984**, 57, 3290–3294.
26. Miura, K.; Mae, K.; Yoshimura, T.; Masuda, K.; Hashimoto, K. Energy Fuels **1991**, 5, 803–808.
27. Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Bio-oil production from sweet sorghum bagasse via liquefaction using alkaline solutions and identification of phenolic products. Waste & Biomass Valorization submitted for publication, 2019 (Manuscript number WAVE-D-19-00223).
28. Darlage, L.J.; Bailey, M. Fuel **1976**, 55, 205–210.
29. Pew, J.C.; Withrow, J.R. Fuel **1931**, 10, 44–7.
30. Kiebler, M.W. ibid., 32, **1940**, 1389–94; Gas J., 232, **1940**, 433–6.
31. Larsen, J.W.; Sams, T.L.; Rodgers, B.R. Fuel **1981**, 60, 335–341.
32. For a thorough discussion of the chemistry of phenoxy radicals see: Scott, G. ‘Atmospheric Oxidation and Antioxidents’. Elsevier Publishing Co., New York, 1965.
33. Schobert, H.H. Chemistry of fossil fuels and biofuels. Cambridge University Press, Cambridge, New York, 2013, Chapter 22.
34. Buchanan, D.H. J. Am. Chem. Soc. **1994**, 39, 64–68.
35. Yan, J.; Bai, J.; Li, W.; Bai, J. Fuel **2014**, 136, 280–286.
36. Ouchi, K.; Imuta, K.; Yamashita, Y. Fuel **1965**, 44, 29−38.
37. Painter P.C.; Snyder R.W.; Starsinic M.; Coleman M.M.; Kuehn D.W.; Davis A. Appl. Spectrosc. **1981**, 35, 475-485.
38. Painter P.C.; Starsinic M.; Squires E.; Davis A.A. Fuel **1983**, 62, 742–743.
39. Van Niekerk, D.; Pugmire, R.J.; Solum, M.S.; Painter, P.C.; Mathews, J.P. Int. J. Coal Geol. **2008**, 76, 290–300.
40. Yen T. F.; Wu, W. H.; Chilingar, G. V. Energy Sources **1984**, 7, 203–235.
41. Ibarra, J. V.; Munoz, E.; Moliner, R. Org. Geochem. **1996**, 24, 725–735.
42. Sofianos, A.; Butler, A. Fuel Process. Technol. **1989**, 22, 189–204.
43. Nag, D.; Biswas, P.; Chandaliya, V.K.; Banerjee, P.K. Int. J. Coal Prep. Util. **2011**, 31, 1–8.

44. Ruberto, R.G.; Jewell, D.M.; Jensen, R.K.; Cronauer, D.C. In Shale Oil, Tar Sands, and Related Fuel Sources, T.F. Yen (Ed). Advances in Chemistry Series No. 151. American Chemical Society, Washington, DC, 1976, Chapter 3.
45. Dooley, J.E.; Thompson, C.J.; Scheppele, S.E. In Analytical Methods for Coal and Coal Products, C. Karr, Jr (Ed.). Academic Press, Inc., New York, Vol. I, 1978, Chapter 16.
46. Bartle, K.D. In Spectroscopic Analysis of Coal Liquids, J. Kershaw (Ed.) Elsevier, Amsterdam, the Netherlands, 1989, Chapter 2.
47. Speight, J.G. Synthetic fuels handbook: properties, processes, and performance. New York: McGraw-Hill, 2008.

Chapter 6

Conclusions and Recommendations

This chapter contains a summary of conclusions based on the experimental results obtained from this study, and as well as some recommendations for future studies concerning the utilization of South African coals for solvent extraction.

The research and development of solvent extraction of South African bituminous coal were investigated in this study. The main objectives of this study were outlined in **Chapter 1**. The utilization of a model biomass-derived phenolic mixture as a solvent for coal extraction in comparison to the use of phenol is one of the main objectives that have been reported in this study.[1,3] Direct comparisons of the results can be made since the experiments were conducted at similar process conditions using the same autoclave. Therefore, general conclusions and recommendations pertaining to this study are discussed as follows:

6.1. General Conclusions

Based on the findings observed from this study, the following main conclusions can be summarized as follows:

- The coal extraction yield increased with the rise of the temperature (300–360 °C) for both phenol and a model biomass-derived phenolic solvents, and the yields were in the range of 12.3–50.2 wt. % and 13.9–37.11 wt.%, respectively.[1,3] Highest coal extraction yields were obtained at 360 °C by using phenol and a model biomass-derived phenolic solvent, which were 50.2 wt. % and 37.11 wt. %, respectively.[1,3] These results show that a model biomass-derived phenolic mixture is less effective compared to phenol as a solvent for coal extraction at a higher temperature. The degree of coal extraction is influenced by the properties of the solvent as different solvents can produce different extract yields from the same coal.
- The PAAs yields obtained after coal extraction were in the range of 4–28 wt. % at a temperature of 300–340 °C with phenol as a solvent, whilst the yields were in the range of 5–15 wt. % for a model biomass-derived phenolic mixture.[1,3] The coal conversion presented decreasing functionality in the PAAs as a function of temperature (340–360 °C) as solvents were altered. The transformation of the coal matrix to PAAs can be ascribed to the depolymerization reactions predominated by the abilities/properties of the solvents; ability to shuttle hydrogen within the coal structure.
- The oil yield of 10 wt. % was obtained using a model biomass-derived phenolic mixture which was below that reported for phenol (≥27 wt. %) at 360 °C.[1,3] This could be the result of lower internal redistribution of the available hydrogen in the coal based on the lower coal conversions yields obtained using a model biomass-derived phenolic mixture (39.8 wt. %) at 360 °C.
- The gaseous products as a result of high-temperature heating (300–360 °C) led to gaseous yields in the range of 4.9–6.4 wt. % and 7.2–10.4 wt. % respectively for phenol and model biomass-derived phenolic mixture after coal extraction.[1,3] These low yields

suggests that depolymerization rather than the decomposition of the coal is taking place at temperatures of 300–360 °C in the presence of a solvent. In addition, these results suggest that the solvent extraction of coal using an effective solvent does not favour large amounts of gaseous products.

- The THFIs obtained using a model biomass-derived phenolic mixture had an H/C atomic ratio (calculated from the ultimate results) in the range of 0.83-0.87, which was similar to using phenol as a solvent (0.70–0.77).[1,3] These values are similar to the H/C ratio of 0.82 for the bituminous coal. This observation is consistent with the literature that the extraction products display chemical analytical results which are similar to the coal.
- The ash percentages in the THFIs obtained from the coal extraction process increased with increasing temperatures (300–360 °C), and both phenol (10.2–20.6 wt. %) and model biomass-derived phenolic (10.4–14.2 wt. %) solvents showed a similar trend. However, the ash percentage of the THFI residues obtained at the extraction temperature of 360 °C with a model biomass-derived phenolic mixture was lower compared with phenol. This observation also coincides with a decrease in volatile matter, the high contents of the THFIs may be indicative of higher coal extractability with phenol than with a model biomass-derived phenolic mixture.[1,3] This is as expected as the total volume of THFIs decreased with increase in temperature.
- The oxygen content of the THFIs obtained using phenol dropped from 13.3 to 9.9% between 300 and 360 °C.[1] Similar trends were also observed for THFIs obtained using a model biomass-derived phenolic mixture (14.2 to 9.9 wt. % between 300 and 360 °C).[3] These results suggest that higher coal extractions correspond with chemical interactions above 300 °C in the presence of a solvent. At temperatures ≥330 °C, phenol based solvents could be interacting with the coal and this observation is consistent with the higher conversions observed at 360 °C.[1,3] This interaction can occur through the cleavages of ether linkages by phenol. For example, if the oxygen-bearing fragment of the ether cleavage reaction dissolves into solution in the phenol or reacted, the effect would be a reduction of oxygen content in the insoluble residues. This is exactly what was observed from this study,[1,3] as illustrated by the ultimate results.
- The thermogravimetric analysis was used to study the influence of thermal degradation on the behaviour of the coal without solvent and PAAs during pyrolysis. The bituminous coal showed a single main peak with a maximum mass loss rate at ~430 °C, while the PAAs showed two peaks with a maximum mass loss rate at ~220 °C and 430 °C, respectively.[1,3] These results confirm that PAAs are the intermediate product in solvent

extraction, as PAAs displays similar characteristics as coal at 430 °C. This observation is also corroborated by the ultimate and ATR-FTIR results.

- The comparison of the infrared spectra of coal and extraction products obtained through phenol and a model biomass-derived phenolic mixture illustrates the great similarity between coal and coal-derived products obtained via these extraction processes. Although the yields were somewhat different, the extracts had similar functional groups.[1,3]
- SEM analysis results indicate no significant structural changes to the surface of the THFs obtained using phenol and a model biomass-derived phenolic mixture, apart from changes associated with high-temperature heating that had left residues more porous than the unreacted coal.[1,3]
- GC-MS results of the extract fractions were obtained after coal extraction using phenol and a model biomass-derived phenolic mixture. The results showed that the main products in phenol extraction were alkyl substituted mono-aromatics, polyaromatics, and heterocyclic organic compounds, whilst in model biomass-derived phenolic mixture extraction were mainly bis-phenol alkyl compounds.[1,3] These results suggest that the nature of the extract fractions can be influenced significantly by the chemical and physical properties of the solvents used during coal extraction reactions.
- From the simulated distillation results, the product distribution of HS fractions (300–360 °C) led to about 50 wt. % correlating with light vacuum gas oil (LVGO) using a model biomass-derived phenolic mixture, whilst LVGO was in the range of 23–31 wt. % using pure phenol.[1,3] Thus, the differences in the boiling point distribution may be related to the difference in the average molecular mass of the extracts obtained using these solvents during coal extraction (300–360 °C).

6.2. Contributions to knowledge of coal science

The achievements reached by this study are summarized as follows:

- The research and development of cleaner conversion technology, solvent extraction, for effective utilization of Permian aged South African coals such as Waterberg bituminous coal for the production of value-added chemicals and liquid fuels.[1,3]
- The study may provide valuable insight into the mechanism of coal extraction using phenol or phenol-based solvent where a well-known model presumes sequential reactions (or extractions), i.e., coal → PAAs → oil + gas.[1,3] Taking into consideration that there is an alternative model, in which coal converts (or is extracted) to PAAs and oil simultaneously. Changes observed in the 340–360 °C range indicate that certain

effects shut down the route of coal → PAAs, and/or greatly increases the rate of coal → oils.[1,3] Furthermore, this may provide an explanation into which reaction is more possible to occur during coal extraction using phenol as a solvent, i.e., two parallel reactions (coal → PAAs and coal → oils) or two sequential reactions (coal → PAAs then coal → oils).

- The development of an acid-base neutralization method was reported in chapter 4. It can be used to extract phenolic compounds derived from the liquefaction of sweet sorghum bagasse using alkaline solutions at lower reaction temperatures than 300 ºC.[2]
- This method can be compared with the phenolic extraction that is usually obtained through high-temperature pyrolysis of biomass that is not of industrial benefit. The results show the potential to extract phenolic compounds at lower temperatures.[2]
- A novel approach to the development of solvent extraction of coal using a model biomass-derived solvent to produce a carbon-rich and low nitrogen and sulphur coal - derived residues (THFIs). Thus, using biomass to derive a phenolic compounds mixture for coal extraction will be of industrial benefit.[3]
- This is a promising method to produce coal-derived liquids from coal extraction using a renewable energy source which can also be used to pre-treat coal required for other coal conversion processes (i.e. liquefaction or gasification).

6.3. Recommendations

The results obtained from this study lead to the proposal of the following recommendations to aid in the extension of knowledge related to liquefaction by solvent extraction of South African coals:

- Considerable further research ought to be carried out at a temperature near or below the maximum decomposition rate of bituminous coal (430 °C), as the coal conversion was not near completion at a reaction temperature of 360 °C.
- Improvement of the autoclave for effective heating of the coal/solvent in a short time, with fast heating rates >4 °C/min.
- Experiments of solvent extraction on the different rank of coals, especially for coals which are vitrinite-rich, in order to identify the best South African coal which could yield high extraction values.
- Set up control experiments where the solvent is heated at reaction temperatures selected in this study (300–360 °C) with no coal inside an autoclave, in order to evaluate the influence of the solvent on product distribution.

- Application of catalyst and hydro-treatment of coal and extracts is required for further treatment. This would allow the determination of optimum conditions for higher extraction yields.
- A detailed characterization of the coal and subsequent solid residues (unreacted coal residues, THFIs) using the following techniques; XRD, solid-state ^{13}C NMR (solid state), HRTEM. These analyses complement each other and can also bridge quantitative and qualitative results together.
- Determination of the gasification behaviour of Waterberg bituminous coal and the unreacted coal residues (THFIs) in CO_2 atmosphere in order to compare their reactivities. The unreacted coal residues may have coking coal properties that may be recommended for other thermal applications.
- The chromatographic analysis methods may be evaluated and established, especially using a high-temperature GC. The use of high-temperature GC can allow a better determination of the carbon number distribution of the compounds present in the coal and extracts. In addition, the application of more advanced methods such as flash-pyrolysis GC-MS and GC-GC-MS can corroborate the GC-MS results or provide a more detailed understanding of co-eluting compounds in coal-derived liquids.
- Application of size-exclusion chromatography (SEC) or gel permeation analyses in order to determine the molecular weight distribution of the coal-derived products.
- An investigation into the recovery of the solvent after coal extraction may be examined further.
- Determination of analysis into economic, financial aspects and potential advantages in the solvent extraction process; a comparison between the economics of applying the commercial solvent versus the bagasse-derived solvent. Alternatively, a comparison between the liquid extraction of coal-derived fuels with the indirect method via gasification and then fuel production.

Chapter References

1. Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Energy Fuels **2017**, 31, 13655–13665.
2. Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Bio-oil production from sweet sorghum bagasse via liquefaction using alkaline solutions and identification of phenolic products. Waste and Biomass Valorization, submitted for publication, 2019 (Manuscript number: WAVE-D-19-00223).
3. Sehume, T.Z.; Strydom, C.A.; Bunt, J.R.; Schobert, H.H. Solvent extraction of a South African bituminous coal using a model biomass-derived phenolic mixture. S. Afr. J. Chem., submitted for publication, 2019 (Manuscript number: sajc-001855).

Appendices

Additional Results

This section includes additional experimental results and supplementary information which are not included in the preceding Chapters (**3**, **4** and **5**).

Appendix A

A.1. SEM Analysis: In addition to the results presented in **Chapter 3**, Figure A.1 shows surface morphological changes of the coal after solvent extraction at specific temperatures.

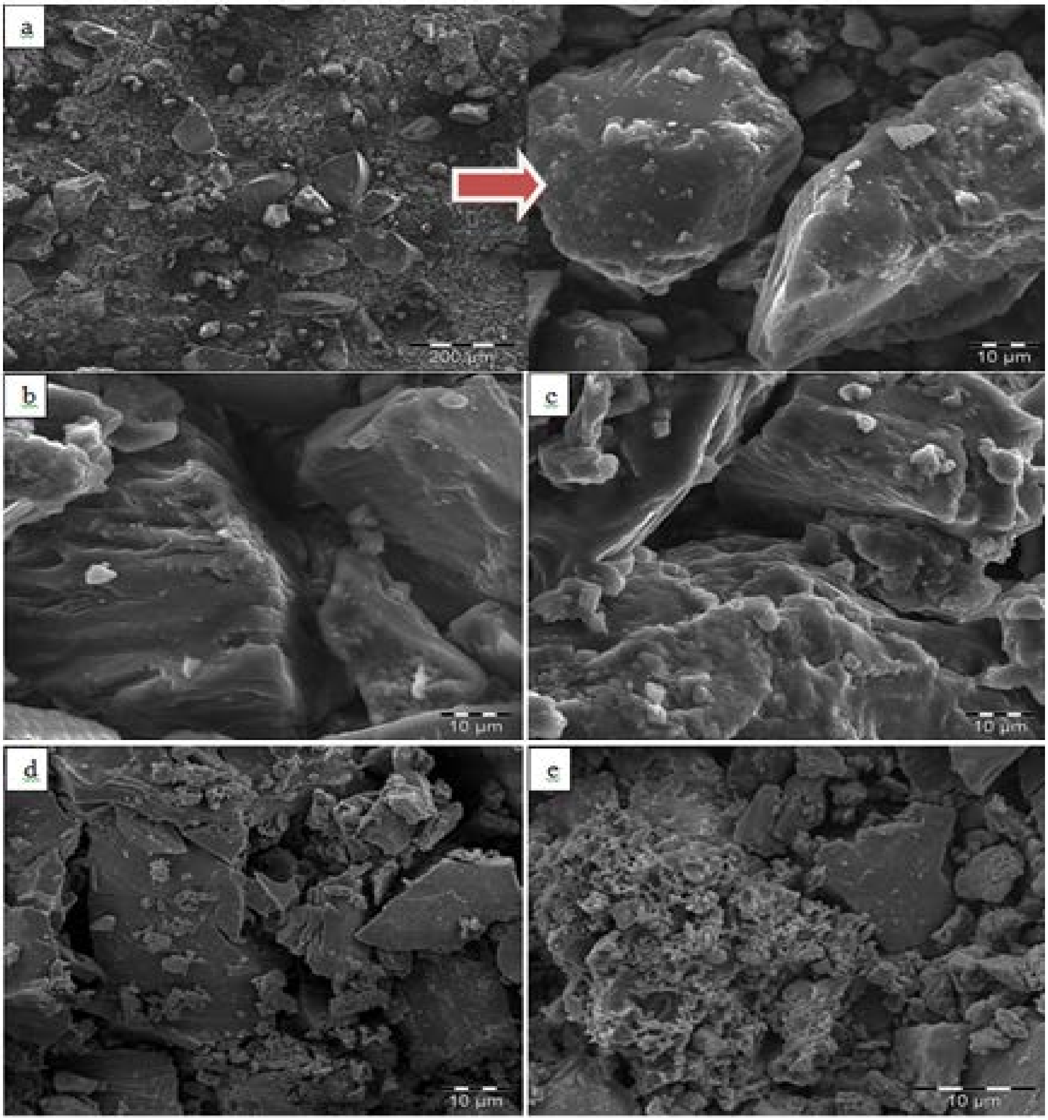


Figure A.1. SEM micrographs of (a) raw coal, (b) THFI-300 °C, (c) THFI-320 °C, (d) THFI-340 °C and (e) THFI-360 °C

A2. GC-MS analysis**:** In addition to the results presented in **Chapter 3**, Table A.1 shows the composition of HS products after solvent extraction.

Table A.1. Peak identification for HS fractions by GC-MS qualification[a]

		Intensity of HS fractions peaks at selected temperatures (°C)			
Peak number	**Compound**	**300**	**320**	**340**	**360**
1	Cyclopropylacetylene	+	+	-	-
2	3-Methylpyridazine	++	++	++	-
3	Furan, 2-(3-imino-3-ethoxyprop-1-enyl)	-	-	+	-
4	Hydroquinone	+	-	-	+
5	**Phenol (Solvent)**	**+++**	**+++**	**+++**	**+++**
6	Phenol, 2-methyl	-	-	-	+
7	Phenol, 2-ethyl	+	+	+	+
8	Phenol, 3-ethyl	-	+	-	-
9	Phenol, 4-ethyl	+	-	-	+
10	Phenol, 2-propyl	+	-	-	+
11	Phenol, 2-butyl	-	-	-	+
12	Phenol, 2-(1-methylethyl)	+	+	-	+
13	Phenol, 4(1-methylethyl)	-	+	-	-
14	Phenol, 2,2'-methylenebis-phenol, 2-[(4-hydroxyphenyl) methyl]	-	+	-	-
15	Phenol, 2-[(4-hydroxyphenyl) methyl]	-	+	+	+
16	Phenol, 2,2'-methylenebis	-	-	+	+
17	Phenol, 4,4'-methylenebis	-	+	+	+
18	4,4'-Ethylidenediphenol	-	-	+	+
19	Phenol, 3,5-dimethyl	+	-	-	-
20	Alkane hydrocarbons	+	+	+	+
21	2-Bromo dodecane	+	-	-	-
22	Naphthalenes	+	-	+	+
23	9H-Xanthene	+	+	+	+
24	Chamazulene	+	-	-	-
25	3,5-Dimethyl-1-dimethylphenylsilyloxybenzene	-	+	-	+
26	Benzoic acid., 2,4-dimethyl-, methyl ester	-	-	-	+
27	Formic acid, 2-isopropylphenyl ester	-	-	+	-
28	n-Heptanoic acid, methyl(tetramethylene)silyl ester	-	-	+	-
29	Pentadecanoic acid, 14-methyl-, methyl ester	-	+	-	-
30	Hexadecanoic acid, methyl ester	-	+	-	-
31	9-Octadecenoic acid, methyl ester	-	+	-	-
32	Dibutyl phthalate	-	+	-	-
33	3-Methylcarbazole	-	-	-	+
34	p-Methylsulfonyloxyacetophenone	-	-	-	+
35	3-Pyridinol, 2-nitro	+	-	-	-

Note: [a] + weak; ++ middle; +++ strong; - absent or traces

Appendix B

B.1. Ultimate analysis: In addition to the results presented in **Chapter 4**, Table B.1 shows the distribution of elemental composition of liquefaction solid residues (SR's).

Table B.1. Elemental analysis of liquefaction SR's obtained at different temperatures and NaOH concentrations

wt. % (dry basis, d.b.)	Carbon	Hydrogen	Nitrogen	Oxygen + Sulphur
Biomass	**43.19**	**5.65**	**0.89**	**50.27**
0.5ML260	38.8	4.77	0.5	55.93
0.5ML280	58.78	5.98	1.18	34.06
0.5ML300	46.42	4.77	0.81	48.00
0.5ML320	**63.21**	**6.15**	**1.2**	**29.44**
1.0ML260	36.49	4.47	0.46	58.58
1.0ML280	47.07	4.89	0.72	47.32
1.0ML300	42.17	4.48	0.68	52.67
1.0ML320	**37.11**	**3.08**	**1.35**	**58.46**
3.0ML260	46.53	4.86	0.85	47.76
3.0ML280	53.25	5.24	1.23	40.28
3.0ML300	31.93	4.2	0.27	63.6
3.0ML320	**38.58**	**5.3**	**0.34**	**55.78**
6.0ML260	38.57	5.22	0.3	55.91
6.0ML280	22.58	1.9	0.16	75.36
6.0ML300	19.88	1.78	0.13	78.21
6.0ML320	**16.25**	**1.47**	**0.11**	**82.17**

B.2. Certificate of analysis: In addition to the results presented in **Chapter 4**, Table B.2 shows certified reference material of standard solution.

Table B.2. Organic standard solution (density=0.7843 g/cm^3 at 21.3 °C)

Compound	Chem. Formula	CAS No.	Certified Value/Uncertainty (µg/mL)	Purity (%)
Phenol	C_6H_5OH	108-95-2	100.25 ± 1.49	99.4
Guaiacol	$C_7H_8O_2$	90-05-1	101.14 ± 1.37	97.6
4-Ethylphenol	$C_8H_{10}O$	123-07-9	100.08 ± 1.59	95.8
2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	93-51-6	100.73 ± 1.13	99.0
Catechol	$C_6H_6O_2$	120-80-9	99.94 ± 1.29	99.7
3-Methoxycatechol	$C_7H_8O_3$	934-00-9	100.92 ± 1 .26	99.8
4-Ethylguaiacol	$C_9H_{12}O_2$	2785-89-9	101.05 ± 1.16	99.1
2,6-Dimethoxyphenol	$(CH_3O)_2C_6H_3OH$	91-10-1	99.72 ± 1.19	99.6
4-Ethylresorcinol	$C_8H_{10}O_2$	2896-60-8	100.30 ± 1.16	100.0
4-Methylphenol	C_7H_8O	106-44-5	100.22 ± 1.52	98.6
4-Isopropylphenol	$C_9H_{12}O$	99-89-8	99.98 ± 1.25	99.9
2-Propylphenol	$C_9H_{12}O$	644-35-9	100.44 ± 1.44	99.9
4-n-Propylphenol	$C_9H_{12}O$	645-56-7	100.03 ± 1.38	99.9
4-Hydroxybenzaldehyde	HOC_6H_4CHO	123-08-0	100.69 ± 1.54	100.0
Phloretic Acid	$C_9H_{10}O_3$	501-97-3	103.35 ± 1.42	99.7

B.3. GC-MS analysis**:** In addition to the results presented in **Chapter 4**, Table B.3–B.6 shows the distribution of chemical composition of bio-oils

Table B.3. GC-MS analysis (semi-quantitative, wt. %) of extracted bio-oil at 0.5 M NaOH concentration

0.5 M NaOH	260 °C	280 °C	300 °C	320 °C
2-Cyclopenten-1-one, 2-methyl	-	1.29	2.77	-
2-Cyclopenten-1-one, 2,3-dimethyl	-	-	1.66	-
2-Cyclopenten-1-one, 3,4-dimethyl	-	-	1.16	-
Ethylbenzene	0.34	-	0.16	0.35
Benzene, 1,3-dimethyl	1.24	2.59	-	11.84
Xylene	3.8	4.99	5.16	2.97
2-Propanoic acid, 2-methyl	-	-	-	2.68
Tiglic acid	1.47	-	-	-
Phenol	13.77	15.45	15.78	18.47
Phenol, 2-methyl	-	-	0.25	0.56
Decane	5.08	1.04	-	8.34
Hexanoic acid	-	-	-	0.6

Benzeneethanol, 4-hydroxy	-	0.53	-	0.61
Phenol, 2-methoxy	1.44	4.45	4.8	0.93
p-Cresol	-	-	5.45	0.96
Phenol, 4-ethyl	-	0.21	0.99	0.39
Benzoic acid	-	-	-	1
Creosol	-	-	0.27	-
Catechol	-	1.52	1.48	1.28
Phenol, 4-ethyl-2-methoxy	-	-	0.63	-
Benzenemethanol, 3-hydroxy	-	-	0.42	0.5
Benzeneethanol, 4-hydroxy	-	-	-	0.97
Phenol, 2,6-dimethoxy	1.62	0.88	1.99	-
Acetophenone, 4'-hydroxy	1.62	1.39	1.2	1.3
Benzenepropanoic acid, 4-hydroxy	-	-	0.93	-
Butylated Hydroxytoluene	-	0.56	-	0.66
Homovanillyl alcohol	-	0.36	-	-
Heptadecane	1.21	0.64	0.25	0.95
Benzeneacetic acid, .alpha.-hydroxy-3-methoxy-, methyl ester	-	0.5	0.6	-
Octadecane	-	0.17	-	-
Ethanone, 1-(4-hydroxy-3,5-dimexyphenyl)	0.94	0.45	-	-
Tridecane, 7-propyl	0.43	-	-	-
Hexadecanoic acid, methyl ester	1.85	0.46	6.17	1.63
11-Octadecenoic acid, methyl ester	0.52	0.32	-	2.71
Methyl stearate	0.62	-	6.87	0.98
Bis(2-ethylhexyl) phthalate	5.19	3.8	1.06	2.8
Benzeneacetic acid	1.12	-	-	-
Ethanone, 1-(2-hydroxyphenyl)-	2.98	-	-	-
Apocynin	0.46	-	-	-
Tetradecanoic acid	0.53	0.99	-	-
cis-9-Hexadecenoic acid	0.3	-	-	1.97
Octadecanoic acid	-	-	-	0.81
n-Hexadecanoic acid	6.02	4.85	1.38	0.59
Hexadecanamide	-	-	-	1.69
9,12-Octadecanoic acid, methyl ester	-	-	10.93	2.2
cis-13-Octadecenoic acid, methyl ester	-	-	-	-
cis-Vaccenic acid	1.78	4.16	8.37	-
trans-13-Octadecanoic acid, methyl ester	-	-	0.4	-
Heptadecanoic acid, methyl ester	-	-	0.24	-
Octadecanoic acid	2.58	1.99	1.16	-
Pentadecane, 8-hexyl-	0.57	-	-	-
Heptacosane	0.76	-	-	0.55
Eicosane	-	-	-	0.39
Dodecane, 2-methyl-6-propyl-	1.12	0.21	-	-
Hexadecane	1.21	0.39	-	-
Tetradecane	0.45	-	-	-

9-Octadecenamide, (z)-	2.54	-	-	5.84
Octadecanamide	-	-	-	1.29
Squalene	8.97	3.23	0.62	-
1-Nonadecene	-	1.09	0.23	-
.beta.-(4-Hydroxy-3-methoxyphenyl) propionic acid	-	0.93	0.36	-
cis-13-Octadecenoic acid	-	1.385	-	-
Tridecane, 7-hexyl	-	0.73	-	-
Pentadecanoic acid, 14-methyl-, methyl ester	-	0.73	0.21	-
Others	27.47	37.715	16.05	21.19

Table B.4. GC-MS analysis (semi-quantitative, wt. %) of extracted bio-oil at 1.0 M NaOH concentration

1.0 M NaOH	260 °C	280 °C	300 °C	320 °C
Ethylbenzene	0.12	0.01	-	0.41
Benzene, 1,3-dimethyl	1.21	1.30	-	0.21
Butanoic acid, 2-methyl	0.29	-	-	-
Xylene	0.33	1.09	2.04	0.06
Butyrolactone	-	1.52	1.34	1.36
Phenol	10.25	19.90	15.94	7.86
Phenol, 2-methyl	-	-	0.65	-
Phenol, 2-methoxy	1.49	6.48	3.63	-
1,4-Hexadiene, 4-methyl	-	0.60	1.17	1.06
p-Cresol	-	0.35	1.73	1.47
Phenol, 4-ethyl	0.70	1.32	2.65	1.08
Benzoic acid	0.52	-	0.26	0.21
Creosol	-	0.66	0.54	-
Catechol	-	-	0.68	-
Phenol, 4-ethyl-2-methoxy	-	0.80	0.48	-
Benzeneacetic acid	0.56	-	-	-
Phenol, 2,6-dimethoxy	-	0.69	-	-
Acetophenone, 4'-hydroxy	2.25	3.87	2.39	3.07
Homovanillyl alcohol	0.14	0.29	-	-
Dodecanoic acid	0.20	-	1.02	-
Octadecane	-	-	-	0.23
Ethanone, 1-(4-hydroxy-3,5-dimexyphenyl)	3.22	1.07	0.23	-
Hexadecanoic acid, methyl ester	1.08	-	0.17	3.66
Hexadecanoic acid, Z-11	2.38	-	-	-
11-Octadecenoic acid, methyl ester	0.49	-	-	0.16
Methyl stearate	0.41	0.53	-	2.05
9-Octadecenoic acid, (E)-	12.56	0.60	2.85	-
9-Octadecenoic acid, methyl ester	-	1.34	-	-
Bis(2-ethylhexyl) phthalate	1.84	2.20	2.50	1.39
Ethanone, 1-(2,4-hydroxyphenyl)-	-	-	1.20	-

Apocynin	1.05	0.67	0.37	0.27
Pentadecane	0.26	0.27	-	0.07
Nonadecane	0.14	-	0.09	-
Homovanillic acid	0.33	-	-	-
Heptadecane	0.98	0.21	-	-
Methyl tetradecanoate	0.25	-	-	-
Tetradecanoic acid	0.30	1.12	0.90	0.91
cis-9-Hexadecenoic acid	2.29	2.31	0.81	-
Octadecanoic acid	2.24	-	-	0.64
n-Hexadecanoic acid	10.52	4.13	4.18	2.24
9,12-Octadecanoic acid (Z, Z)	3.46	-	-	-
9,12-Octadecanoic acid, methyl ester	0.68	-	-	1.29
9,12-Octadecadienoic acid (Z, Z)	4.14	-	-	-
9,12-Octadecadienoic acid, methyl ester	-	1.02	-	-
cis-Vaccenic acid	13.75	2.51	-	0.35
Heptadecanoic acid	0.39	-	-	-
Heptadecanoic acid, methyl ester	2.34	0.73	-	-
Octadecanoic acid	3.26	0.97	1.07	0.31
Pentadecane, 8-hexyl-	-	-	0.15	-
Heptadecane	0.12	0.77	-	0.35
Heptacosane	-	-	-	-
Heneicosane	0.27	-	0.10	-
Eicosane	-	-	0.07	-
Hexadecane	-	0.65	-	0.21
Tetradecane	0.16	0.14	-	-
9-Octadecenamide, (z)-	3.97	6.63	6.48	4.77
Squalene	0.18	3.72	3.24	1.35
1-Nonadecene	-	3.53	1.74	0.67
.beta.-(4-Hydroxy-3-methoxyphenyl) propionic acid	0.22	-	-	-
Octadecane	0.54	0.21	0.05	-
cis-13-Octadecenoic acid	-	-	1.16	1.04
Tridecane, 7-hexyl	-	-	-	0.20
Pentadecanoic acid	0.22	0.61	0.65	0.30
Pentadecanoic acid, 14-methyl-, methyl ester	1.70	-	-	-
Others	6.21	25.21	37.50	60.78

Table B.5. GC-MS analysis (semi-quantitative, wt. %) of extracted bio-oil at 3.0 M NaOH concentration

3.0 M NaOH	260 °C	280 °C	300 °C	320 °C
Ethylbenzene	-	-	-	0.05
Benzene, 1,3-dimethyl	-	-	-	0.12
Butanoic acid, 2-methyl	-	-	-	0.34
Xylene	1.49	1.87	1.10	0.04
Phenol	14.21	17.56	14.40	14.03
Phenol, 2-methyl	0.32	0.22	0.22	1.91
Phenol, 2-methoxy	10.67	7.07	0.38	0.49
Phenol, 2-ethyl	0.30	0.33	0.24	0.80
Phenol, 2,4-dimethyl	0.12	0.17	0.87	0.36
p-Cresol	-	-	2.88	3.44
Phenol, 4-ethyl	13.78	17.35	15.31	15.28
Benzoic acid	0.46	0.89	0.41	0.33
Creosol	1.04	0.15	-	-
Phenol, 4-(1-methylethyl)	0.61	1.00	0.77	1.13
Phenol, 4-ethyl-3-methyl	0.15	0.17	-	-
Phenol, 2-propyl	0.05	0.16	0.32	1.05
Phenol, 4-ethyl-2-methoxy	6.67	1.34	-	0.51
2-Methoxy-4-vinylphenol	0.18	-	-	-
Vanillin	0.74	1.08	-	-
Acetophenone, 4'-hydroxy	2.31	2.61	1.50	1.29
Benzenepropanoic acid, 4-hydroxy	0.23	1.14	1.09	0.36
Homovanillyl alcohol	0.60	-	-	-
Octadecane	0.18	-	0.25	-
Ethanone, 1-(4-hydroxy-3,5-dimexyphenyl)	0.52	-	-	-
Hexadecanoic acid, methyl ester	-	1.55	0.18	0.47
11-Octadecenoic acid, methyl ester	-	-	-	0.18
Methyl stearate	0.26	1.69	-	0.15
9-Octadecenoic acid, (E)-	1.44	1.53	-	-
9-Octadecenoic acid, methyl ester	0.76	-	-	-
Bis(2-ethylhexyl) phthalate	0.45	0.45	0.30	0.42
Apocynin	1.14	0.35	-	-
Pentadecane	-	-	1.62	-
Nonadecane	-	-	1.03	-
Naphthalene, 2,3,6-trimethyl	-	-	0.21	-
Homovanillic acid	0.69	0.20	-	-
Heptadecane	-	-	-	-
Methyl tetradecanoate	0.05	-	-	-
Tetradecanoic acid	0.29	0.20	0.39	0.43
cis-9-Hexadecenoic acid	-	-	-	0.52
Octadecanoic acid	0.53	-	0.55	-
n-Hexadecanoic acid	2.30	2.39	2.26	2.85

Hexadecanamide	-	0.67	-	-
Tetradecanamide	0.60	-	-	-
9,12-Octadecanoic acid (Z, Z)	-	0.20	-	-
9,12-Octadecanoic acid, methyl ester	0.33	1.43	-	-
9,12-Octadecadienoic acid (Z, Z)	0.52	0.34	-	0.13
9,12-Octadecadienoic acid, methyl ester	0.83	-	-	-
cis-Vaccenic acid	2.24	3.15	3.71	3.38
trans-13-Octadecanoic acid, methyl ester	-	-	-	-
Heptadecanoic acid	-	-	-	0.13
Heptadecanoic acid, methyl ester	-	-	0.24	0.22
Octadecanoic acid	0.26	0.64	0.45	0.62
Heptadecane	-	0.14	8.63	-
Hexacosane	-	-	2.14	-
Heptacosane	-	0.24	0.24	-
Heneicosane	-	-	1.56	-
Eicosane	-	-	2.32	-
Hexadecane	-	0.34	1.57	-
Tetradecane	-	-	1.00	-
9-Octadecenamide, (z)-	1.69	1.61	1.27	-
Octadecanamide	-	0.45	-	-
Squalene	0.24	0.47	0.11	0.03
.beta.-(4-Hydroxy-3-methoxyphenyl) propionic acid	0.62	0.20	-	-
Octadecane	0.04	0.24	4.80	-
Pentadecanoic acid	0.16	0.13	-	0.07
Pentadecanoic acid, 14-methyl-, methyl ester	3.30	-	-	0.13
Others	26.64	28.32	25.69	48.75

Table B.6. GC-MS analysis (semi-quantitative, wt. %) of extracted bio-oil at 6.0 M NaOH concentration

6.0 M NaOH	260 °C	280 °C	300 °C	320 °C
Butanoic acid, 2-methyl	-	-	-	0.40
Xylene	2.36	1.83	2.62	5.53
Phenol	13.99	14.04	13.21	14.20
Phenol, 2-methyl	0.34	0.39	0.18	0.25
Phenol, 2-ethyl	0.15	0.24	0.10	0.14
Phenol, 2,4-dimethyl	0.02	-	-	0.09
p-Cresol	9.63	7.22	8.59	8.75
Phenol, 4-ethyl	20.56	22.13	21.11	20.46
Benzoic acid	0.18	0.63	0.72	0.31
Creosol	0.65	-	-	-
Phenol, 4-(1-methylethyl)	1.11	1.31	0.86	0.95
Phenol, 4-ethyl-3-methyl	-	-	-	0.11

Phenol, 2-propyl	0.11	0.20	0.26	1.36
Phenol, 4-ethyl-2-methoxy	2.57	0.10	-	-
Benzeneacetic acid		0.22	0.31	0.23
Acetophenone, 4'-hydroxy	1.98	1.82	0.53	0.43
Benzenepropanoic acid, 4-hydroxy	1.11	1.51	1.61	2.36
Heptadecane	-	2.23	-	-
Tridecane	0.06	-	-	-
Hexadecanoic acid, methyl ester	0.35	-	0.22	0.37
11-Octadecenoic acid, methyl ester	-	-	-	0.18
Methyl stearate	-	-	-	0.09
9-Octadecenoic acid, (E)-	-	0.23	-	-
Bis(2-ethylhexyl) phthalate	0.52	0.37	0.43	0.36
Apocynin	0.51	-	-	-
Homovanillic acid	0.38	-	-	-
Tetradecanoic acid	0.18		0.19	0.21
cis-9-Hexadecenoic acid	0.21			
Octadecanoic acid	0.17	-	0.14	0.13
n-Hexadecanoic acid	0.96	0.46	0.39	0.49
Tetradecanamide	0.69	-	-	-
cis-Vaccenic acid	1.01	0.41	-	-
Octadecanoic acid	0.17	-	-	-
Hexacosane	0.11	0.52	0.10	-
Heptacosane	-	-	0.06	-
Heneicosane	0.12	0.12	0.05	-
Eicosane	-	0.07	0.10	0.05
Hexadecane	-	0.37	-	-
Tetradecane	-	-	-	0.20
9-Octadecenamide, (z)-	2.21		2.01	0.80
Octadecanamide	0.87	-	-	-
Squalene	0.15	0.06	0.06	0.05
.beta.-(4-Hydroxy-3-methoxyphenyl) propionic acid	0.45	-	-	-
Octadecane	-	-	0.09	-
Tridecane, 7-hexyl	0.11	-	-	-
Others	36.05	43.53	46.05	41.51

Appendix C

C.1. In addition to the results presented in Chapter 5, Figure C.1 shows the pyrolysis behaviour of PAAs produced after coal extraction using a model biomass-derived phenolic mixture

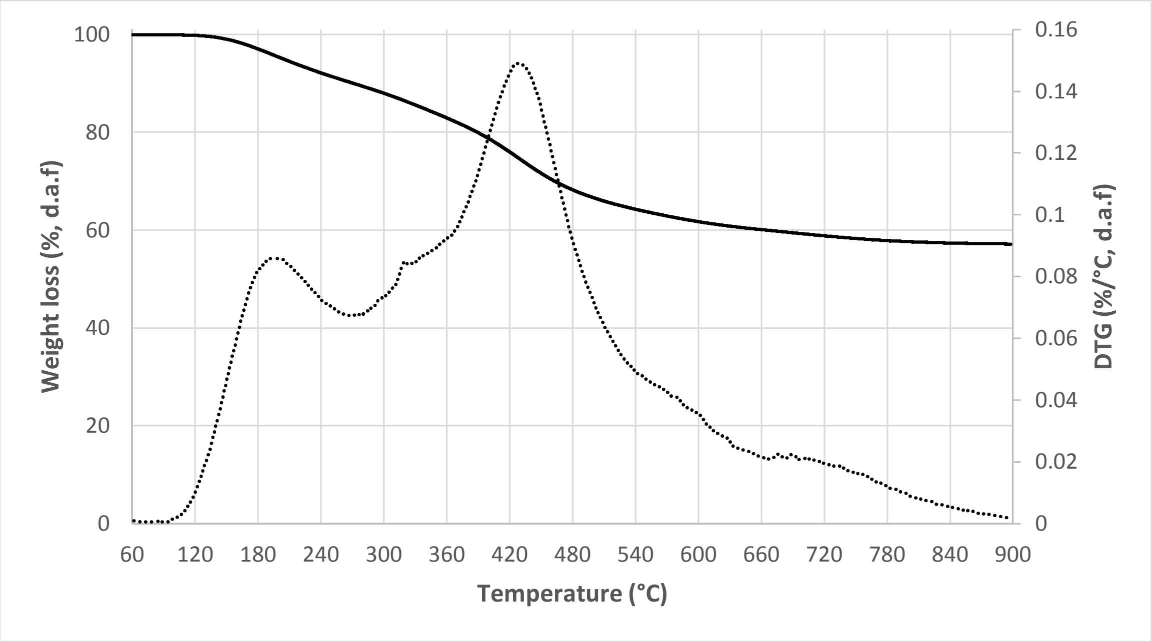


Figure C.1. Weight loss thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves of pyrolysis oft PAAs

C.2. In addition to the results presented in **Chapter 5,** Figure C.2 shows surface morphological changes of the coal after solvent extraction at specific temperatures

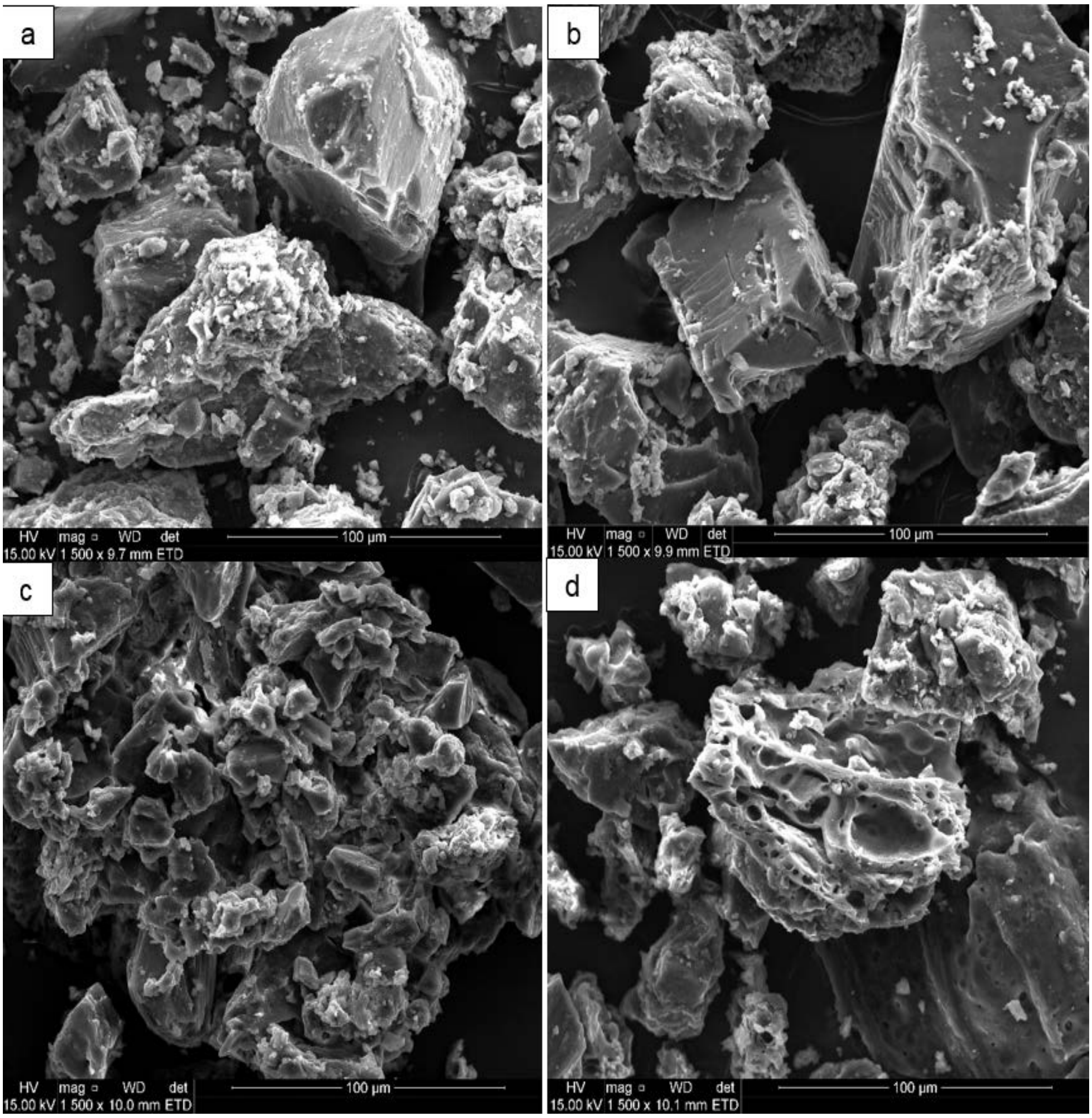


Figure C.2. SEM micrographs of (a) THFI-300 °C, (b) THFI-320 °C, (c) THFI-340 °C and (d) THFI-360 °C

C.3. GC-MS analysis**:** In addition to the results presented in **Chapter 5**, Table C.3 shows the composition of HS products after solvent extraction using a model mixture as a solvent.

Table C.3. Peak identification for HS fractions by GC-MS qualification[a]

		Area % of HS fractions at selected temperatures (°C)			
		300	320	340	360
Peak number	Compound	Area %	Area %	Area %	Area %
1	Phenol	5.14	4.03	5.08	4.10
2	p-Cresol	3.61	3.40	3.26	3.20
3	Phenol, 4-ethyl	4.99	5.12	4.81	3.89
4	Phenol, 2-propyl	1.65	1.66	1.42	1.40
5	Phenol, 4-(methylethyl)	1.93	1.23	1.61	1.70
6	Phenol, 4-ethyl-2-methoxy	2.08	2.49	2.55	3.70
7	4-Ethylcatechol	–	–	2.91	7.13
8	9H-Xanthene	–	–	–	0.36
9	Benzamide, 2-hydroxy-N-(4-pyridinyl)	1.10	0.95	–	0.66
10	Phenol, 2-((4-hydroxyphenyl)methyl))	6.82	5.04	8.30	9.60
11	Phenol, 2,4' -isopropylidenedi	0.91	5.69	0.81	0.94
12	4,4' - Ethylidenediphenol	17.46	18.16	21.11	26.17
13	Tetracyclo [.4.1.0.0(4,9] pentadeca-4,6,8-trien-3-one, 15-acetoxy	3.12	3.98	–	–
14	4,4'-Dihydroxybenzophenone	0.71	–	–	–
15	Phenol, 4,4'-methylenebis	3.74	4.50	7.45	6.84
16	Benzocyclopentene, 4,5,6,7-tetraethyl-1-methyl	7.76	8.81	–	–
17	6-Methyl-4-propyl-2-thixo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester	0.64	–	–	–
18	Phenol, 4,4'-(1-methyethylidene)bis	7.13	7.15	–	2.08
19	Ethanone, 1-(2,3-dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl)	–	–	–	4.00
20	1-Dimethylphenylsilyloxy-4-mehoxy benzene	–	0.62	–	4.45
21	2,8-Disilatricyclo[7.3.0.0(3,7)]dodeca-4,6,10,12-tetraene, 2,2,8,8-tetramethyl	–	3.11	–	–
22	Tetralin, 6-acetyl-8-isopropyl-2,5-dimethyl	3.27	–	–	–
23	Phenol, 2,4-di(2-penten-4-yl)-6-methyl	3.18	–	–	–
24	Bisphenol C	0.38	0.42	0.48	0.68
	Others	26.38	25.64	42.21	21.1