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Application of subcritical and supercritical fluids in coal extraction and analysis

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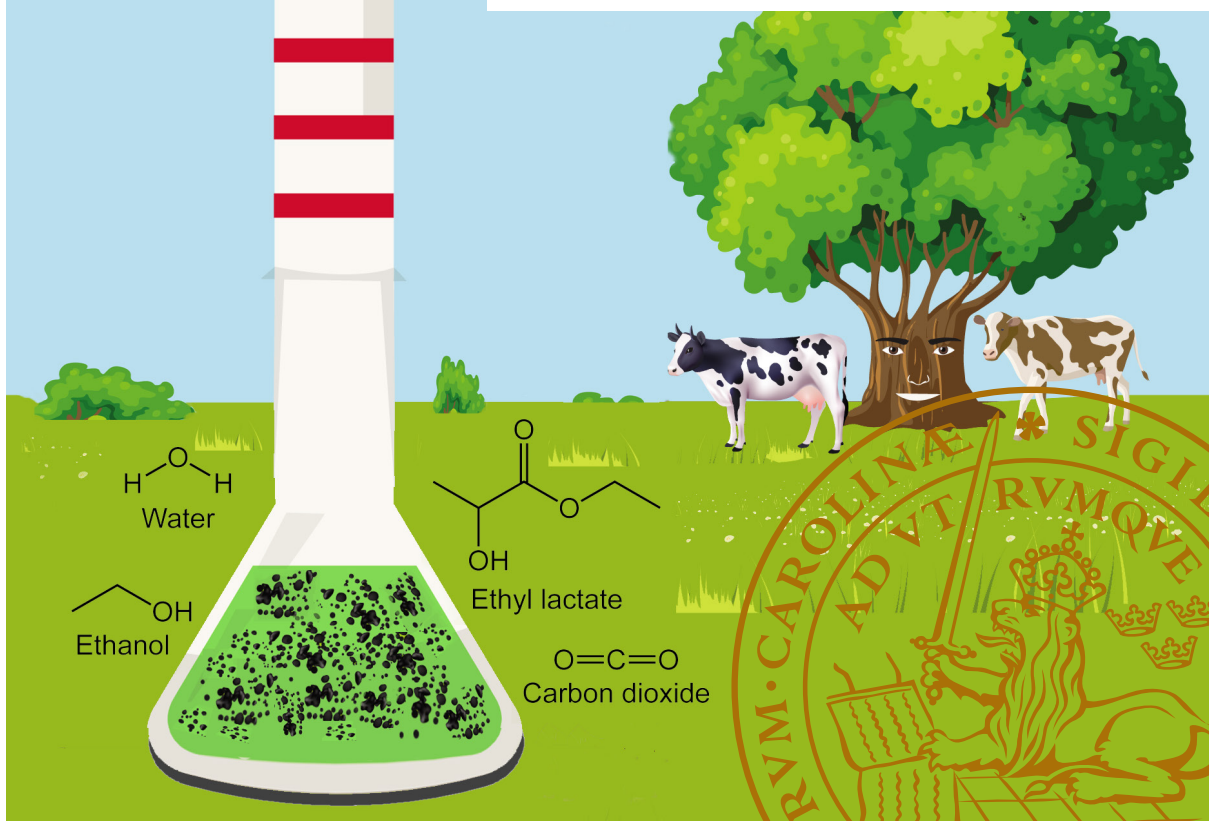
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Application of subcritical and supercritical fluids in coal extraction and analysis

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Application of subcritical and supercritical fluids
in coal extraction and analysis

Application of subcritical and supercritical fluids in coal extraction and analysis

Fiona Maungo Nermark



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DOCTORAL DISSERTATION

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Abstract <p>Coal is used to generate electricity and produce high-value chemicals through coal gasification, liquefaction, and coke. During combustion sulfur is released, which leads to acid rain formation. Mineral matter present in coal is undesirable because it causes technological problems such as corrosion of equipment and reduction of overall rate of combustion of coal. Also, after combustion, the mineral matter which has been transformed to solid waste (ash) is disposed of in landfills. The reported pre-combustion extraction methods for desulfurization and demineralization are time consuming, require the use of large volumes of environmentally toxic reagents at high temperature and they are not selective.</p> <p>The main aim of this thesis was to systematically develop desulfurization and demineralization methods based on non-toxic solvents using pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE). The main emphasis was placed on achieving high selectivity for total sulfur and mineral matter during solvent extraction. Therefore, optimization of extraction methods in terms of solvent composition, extraction temperature and extraction time using Box Benhken design was carried out. The aim was to maximize solubility of target analytes, to improve mass transfer properties of the extraction solvent as well as reducing extraction temperature and time.</p> <p>Water with ethanol as a co-solvent was used during PLE method development. The results showed that increasing ethanol content resulted in higher extracted amount of total sulfur at mild temperature in a short time, corresponding to decrease in viscosity which resulted in fast diffusion of solvent and fast mass transfer. At optimum conditions, total sulfur extraction efficiency of 79 wt.% from the raw coal was achieved. SFE utilized supercritical carbon dioxide (scCO₂) with ethyl lactate (EL) as a co-solvent. Higher temperature and lower ethyl lactate content significantly increased extraction of total sulfur even though increasing temperature reduces the density of scCO₂. Higher solubility of sulfur compounds may be due to their increased vapour pressure in addition to the more polar solvent. At optimum conditions, total sulfur extraction efficiency of 93 wt.% from the raw coal was achieved. Neither of the methods were efficient in extracting mineral matter from the raw coal in comparison to extraction with acids/bases such as nitric acid and sodium hydroxide.</p> <p>Overall, the two methods have similar effects on the raw coal. Additionally, the properties of the raw coal were slightly improved. In addition to the reduction of the sulfur content, the thermal decomposition and burnout temperatures were decreased to a more considerable extent compared to the combustion temperature and the temperature at which maximum conversion of coal occurs. The calorific value, fixed carbon and volatile content have also increased and these parameters are all important in the combustion efficiency of coal. The research presented here serves as a base for the scaling up of extraction methods that utilizes green and environmentally sustainable solvents for reduction of pollution from coal combustion.</p>		
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Fiona Maungo Nermark



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To my mother-in-law

Table of Contents

Abstract	10
Popular Scientific Summary	12
List of papers	14
Contribution to the papers	15
Abbreviations	16
1 Introduction.....	17
1.1 Background	17
1.2 Motivation and scope	18
1.3 Aims and Research questions	19
2 Desulfurization and demineralization methods.....	21
2.1 Sulfur in coal	21
2.2 Mineral matter in coal	21
2.3 Desulfurization and demineralization methods	22
2.4 Supercritical fluids in coal desulfurization and demineralization	23
3 Materials and methods	26
3.1 Sampling site, sampling and sample pre-preparation	26
3.2 Physicochemical properties of Morupule coal	27
3.2.1 Proximate, ultimate and calorific value analyses	28
3.2.2 Thermogravimetric analysis	30
3.3 Desulfurization and demineralization of raw Morupule coal	32
3.3.1 Experimental design.....	32
3.3.2 Sulfur analysis.....	33
3.3.3 Mineral matter analysis	33

4 Results and discussions	34
4.1 Desulfurization of coal.....	34
4.2 Sulfur speciation.....	37
4.3 Demineralization of coal.....	39
4.4 Validity of the models	41
5 Supercritical fluid chromatography and mass spectrometry	43
5.1 Supercritical fluid chromatography (SFC)	43
5.2 Mass spectrometry	51
6 Conclusion and future work	53
6.1 Future work.....	54
7 Acknowledgements	55
8 References	58

Abstract

Coal is used to generate electricity and produce high-value chemicals through coal gasification, liquefaction, and coke. During combustion sulfur is released, which leads to acid rain formation. Mineral matter present in coal is undesirable because it causes technological problems such as corrosion of equipment and reduction of overall rate of combustion of coal. Also, after combustion, the mineral matter which has been transformed to solid waste (ash) is disposed of in landfills. The reported pre-combustion extraction methods for desulfurization and demineralization are time consuming, require the use of large volumes of environmentally toxic reagents at high temperature and they are not selective.

The main aim of this thesis was to systematically develop desulfurization and demineralization methods based on non-toxic solvents using pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE). The main emphasis was placed on achieving high selectivity for total sulfur and mineral matter during solvent extraction. Therefore, optimization of extraction methods in terms of solvent composition, extraction temperature and extraction time using Box Benhken design was carried out. The aim was to maximize solubility of target analytes, to improve mass transfer properties of the extraction solvent as well as reducing extraction temperature and time.

Water with ethanol as a co-solvent was used during PLE method development. The results showed that increasing ethanol content resulted in higher extracted amount of total sulfur at mild temperature in a short time, corresponding to decrease in viscosity which resulted in fast diffusion of solvent and fast mass transfer. At optimum conditions, total sulfur extraction efficiency of 79 wt.% from the raw coal was achieved. SFE utilized supercritical carbon dioxide (scCO₂) with ethyl lactate (EL) as a co-solvent. Higher temperature and lower ethyl lactate content significantly increased extraction of total sulfur even though increasing temperature reduces the density of scCO₂. Higher solubility of sulfur compounds may be due to their increased vapour pressure in addition to the more polar solvent. At optimum conditions, total sulfur extraction efficiency of 93 wt.% from the raw coal was achieved. Neither of the methods were efficient in extracting mineral matter from the raw coal in comparison to extraction with acids/bases such as nitric acid and sodium hydroxide.

Overall, the two methods have similar effects on the raw coal. Additionally, the properties of the raw coal were slightly improved. In addition to the reduction of the sulfur content, the thermal decomposition and burnout temperatures were decreased to a more considerable extent compared to the combustion temperature and the

temperature at which maximum conversion of coal occurs. The calorific value, fixed carbon and volatile content have also increased and these parameters are all important in the combustion efficiency of coal. The research presented here serves as a base for the scaling up of extraction methods that utilizes green and environmentally sustainable solvents for reduction of pollution from coal combustion

Popular Scientific Summary

Botswana is an African country with an estimated 200 billion tons of coal deposits. The coal from Morupule mine is currently used to generate electricity with plans to diversify its use to produce high-value compounds. Unfortunately, coal combustion is accompanied by the emission of toxic gases such as NO_x and SO_x . These gases react with rain water to form what is called acid rain, which affects plant growth. In addition, through chemical tests, it was established that the Morupule coal contains high amounts of mineral matter, some of which remains intact during combustion and forms the solid by-product called ash. The ash is usually taken to landfills, and over time some of the inorganic material starts to dissolve, especially if there is acid rain. The dissolved toxic substances are then washed away into rivers and lakes where they poison aquatic life, a food source in some communities. The reality is that coal will continue to be burned, especially in developing countries such as Botswana. As such, it is important to find ways to remove pollution-causing components in the coal before its combustion. This thesis presents research to find ways to remove sulfur compounds and mineral matter from coal by a technique called extraction. While a large number of extraction methods have been described in the literature, most of them cannot be utilised as the chemicals used are toxic to humans and to the environment.

This thesis presents research carried out to develop extraction methods for the removal of sulfur and minerals from coal using non-toxic chemicals. Various solvents such as water, ethanol, ethyl lactate and supercritical carbon dioxide have been tested in the framework of this thesis. The efficiency of the developed methods for extracting sulfur compounds and mineral matter was evaluated based on their selectivity, i.e., how much of the target compound can be removed from the coal while the rest of the coal properties remain unchanged. In order to try and minimize the chance of changing the properties of the coal, the experiments were performed at temperatures below 200°C . Two methods were developed. In the first method, the extraction of coal with a water-ethanol mixture (10/90 v/v %) at 129°C (105 bar) for 10 minutes resulted in a total sulfur reduction from 1.9 to 0.4 (wt.%) from the coal. In the second method, supercritical CO_2 was used. In order to achieve a supercritical state, CO_2 is raised above its critical pressure and temperature (72 bar, 31°C). The density, and consequently the solvent power of supercritical fluids, is tuneable by varying pressure and temperature. If the pressure is increased, the density of scCO_2 also increases, the liquid penetrates into the coal much easier which increases the extraction rate of the target compounds, in this case sulfur compounds and mineral matter

In the application for coal extraction, scCO₂ is reported to cause the coal to swell. Eventually, some bonds holding the coal molecules together break, and compounds of interest solubilize in the extraction solvent. Ethyl lactate was added to scCO₂ with the idea to make scCO₂ more polar to dissolve polar sulfur compounds better. The best conditions for extracting total sulfur were scCO₂ (95%) mixed with ethyl lactate (5%) at 80 °C and 300 bar for 10 minutes with a total sulfur reduction from 1.9 to 0.4 (wt.%) from the coal.

Both methods showed approximately 10 wt. % reduction in mineral matter. Although the developed methods were not efficient in the extraction of mineral matter, they have shown that total sulfur can be reduced from coal on an analytical scale before combustion. With less acid rain formation due to less release of SO_x, the ash will most likely remain intact until a better method is developed to remove mineral matter from coal. The solvents used are non-toxic, the extraction is done under mild temperature and the extraction time is short. The methods have the potential to be scaled up for application in the industry because of the mild conditions used. The solvents also have low boiling points, another positive quality because the energy required to evaporate the solvent is low and the solvents might be recycled and reused.

List of papers

- I. Desulfurization of Morupule coal by subcritical aqueous ethanol extraction
Fiona M. Nermark, Mmilili M. Mapolelo, James Darkwa, Ola F. Wendt, Charlotta Turner
ChemistryOpen 2022, *in press*. <https://doi.org/10.1002/open.202200046>

- II. Coal desulfurization and demineralization by sub/supercritical fluid extraction using binary mixtures of carbon dioxide and ethyl lactate as solvent
Fiona M. Nermark, Rebecka Lindblad, Rebecca Clulow, Mmilili M. Mapolelo, Ola F. Wendt, Margareta Sandahl, Charlotta Turner
Manuscript to be submitted to Analytical and Bioanalytical Chemistry (2022-09-27)

- III. Effect of desulfurization of coal on physicochemical characteristics and combustion behavior of Morupule coal
Fiona M. Nermark, Mmilili M. Mapolelo, Charlotta Turner, Ola F. Wendt
Manuscript in preparation

Contribution to the papers

- I. I came up with the initial research idea. I designed and planned the experiments with CT. I performed most of the experiments, evaluated all the data, and wrote the manuscript. CT, OFW and MMM revised the manuscript.
- II. I came up with the initial research idea, performed most of the experiments, evaluated most of the data and wrote the manuscript. RL and RC each performed one part of the experimental work. CT, OFW, MMM, RL and RC helped to refine the idea and revise the manuscript.
- III. I came up with the initial research idea, planned the experiment and performed part of the experiments, evaluated all the data and wrote the manuscript. CT, OFW and MMM helped to revise the manuscript.

CT: Charlotta Turner

MMM: Mmilili M. Mapolelo

OFW: Ola F. Wendt

JD: James Darkwa

RL: Rebecka Lindblad

RC: Rebecca Clulow

Abbreviations

2-PIC	2-picoylamine
APCI	Atmospheric pressure chemical ionization
ASTM	American Society for Testing and Materials
CCTs	Clean coal technologies
CXL	CO ₂ expanded liquid
CXLE	CO ₂ expanded liquid extraction
DoE	Design of experiments
DTG	Derivative thermogravimetric analysis
EL	Ethyl lactate
ESI	Electrospray ionization
GC	Gas chromatography
GXL	Gas-expanded liquid
HPLC	High-performance liquid chromatography
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
MCM	Morupule coal mine
MS	Mass spectrometry
NMP	N-Methyl-2-pyrrolidone
PHWE	Pressurized hot water extraction
PLE	Pressurized liquid extraction
QTOF-MS	Quadrupole time-of-flight mass spectrometer
ScCO ₂	Supercritical carbon dioxide
SFC	Supercritical fluid chromatography
SFE	Supercritical fluid extraction
SLE	Solid-liquid extraction
TGA	Thermogravimetric analysis
UHPLC	Ultra-high performance liquid chromatography
UHPSFC	Ultra-high performance supercritical fluid chromatography
VLE	Vapour-liquid equilibrium
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

1 Introduction

This thesis is composed of a summary and three papers. It also includes some results that will not be published due to various challenges that were not resolved within the duration of the study period. The summary presents an overview of my research, discusses it from the perspective of Clean Coal Technology (CCT) research, and summarizes the key findings and conclusions from the development on extraction methods for desulfurization and demineralization before coal combustion. The three papers describe the scientific approaches used, including experimental design approach, extraction experiments and physicochemical characterization of the coal before and after extraction. This chapter presents a background to the research subject, the motivation and scope of the research as well as description of the aims and research questions.

1.1 Background

Coal is a complex structure of inorganic and organic materials [1]. Coal has been a valuable natural resource for the generation of electricity. It is also used as a fuel in the steel industries to extract iron from iron ore and in the production of cement. Coal is also converted to high-value products using different thermal decomposition methods which are gasification, direct liquefaction [2] and indirect liquefaction [3]. Gasification and indirect liquefaction are used industrially to produce fuels and chemical raw materials such as ammonia (NH_3) to produce fertilizers [4].

Regardless of the conversion process (combustion, gasification or liquefaction), large quantities of pollutants are emitted, the type of which is determined by both the properties of the fuel and the process conditions used. Such pollutants occur as (a) carbon dioxide, sulfur and nitrogen oxides and volatile toxic metals which are emitted during combustion [5, 6], (b) waterborne pollutants from mine treatment plants and coal conversion processes such as hydrocarbons, polyaromatic hydrocarbons (PAHs) and trace elements [7, 8] (c) solid waste (ash) and dust from coal mining, and solid waste (ash) generated from coal processing [9, 10].

The potential health hazards of emissions from coal combustion and their effects on aquatic ecosystem (fresh water and marine), as well as on terrestrial ecosystem (forest, grass, mountain and desert), are well documented [11–13].

CCTs are designed to improve the efficiency (complete combustion) and the environmental sustainability of coal mining, processing and use. The CCTs incorporate pollution control devices to reduce sulfur dioxide, nitrous oxides and dust emissions during coal gasification. Coal gasification processes in connection with the combined use of the synthesis gas are much more efficient than conventional processes. Due to the excellent mass transfer and the mixing of volatile substances with solid particles in fluidized beds, the gasification achieves an overall higher conversion of the chemical energy in coal into product gas. Coal gasification utilizes an isothermal temperature environment which facilitates rapid heating that results in fast mass transfer and high chemical reaction rates, which are beneficial from a process control point of view. During coal gasification process, the coal is completely converted into a gas mixture mainly composed of carbon monoxide (CO) and hydrogen (H₂) called synthesis gas (syngas) [14]. Syngas is then catalytically converted into chemical feedstocks such as methanol [4]. Despite of advantages of coal gasification, the process also produces wastewater enriched with aromatics [15], coal tar [16], ash [17], greenhouse gases (carbon dioxide (CO₂) and methane (CH₄)) nitrogen oxides (NO_x) and sulfur dioxide (SO₂) [18] and organic pollutant [19].

The mineral matter present as ash after combustion and the sulfur content of coal significantly limits its utilization. The mineral matter in the coal decreases the calorific value, causes fouling, slagging and clinkering of heaters, furnaces and turbines during combustion, resulting in equipment corrosion, thereby reducing their lifespan [20]. In addition to CO₂, the primary atmospheric pollutant associated with coal combustion is sulfur dioxide, which causes the formation of sulfatic aerosols, resulting in the formation of acid rain [21]. Thus, it is both economically and environmentally important to reduce the amount of ash and sulfur in coal before utilization.

1.2 Motivation and scope

In Southern Africa, South Africa is the largest coal producer, with over 250 million tonnes produced yearly [22]. Botswana is also known for its large coal reserves, which are estimated to be around 200 billion tonnes [23]. The Morupule Coal Mine is the only mine currently mining coal. Now, the consumer of Morupule coal in Botswana is the Botswana Power Corporation (BPC), which uses it to generate electricity [24]. The

project's relevance is based on developing Botswana's natural resources and their use for the country's benefit through production processes and a diversified range of products.

Studies on the stratigraphy and geology of Morupule coal are well described [25]. Tabbiruka et al. (2014) reported an average calorific value for crude Morupule coal to be 27.3 MJkg^{-1} with an ash content of 70.4% [26]. Keboletse et al (2018) investigated the suitability of Morupule coal for gasification technology, and characterized the coal as high ash (23.4 wt. %) and sulfur (0.8 wt.%) with a calorific value of 23 MJkg^{-1} [27]. Their numerical simulation of the coal gasification process concluded that Morupule coal has good properties for coal gasification technology. Bikane et al. (2020) investigated the pyrolysis behavior of Morupule coal at different temperatures and pressures, as well as the kinetics of gasification in atmospheric pressure CO_2 at isothermal temperatures of 900 - 1050 °C [28, 29]. The research on Morupule coal to date has tended to focus on exploring the performance of combustion with no reference on how the pollutants produced such as SO_x and ash will be reduced. Therefore, there is a need to develop and optimize analytical extraction methods for removal of pollutants such as NO_x and mineral matter from coal before thermal conversion and analysis methods to monitor organic pollutants in the extracts produced from extraction process.

Scope

The focus of this project was to develop faster and environmentally sustainable extraction methods targeting sulfur and mineral matter as the main pollutants from coal. The extraction methods are hypothesized to reduce air pollution (reduction of SO_x), land pollution (ash reduction), as well as to improve the combustion performance.

1.3 Aims and Research questions

The overall goal of this project was to demonstrate a strategy for solvent desulfurization and demineralization using non-toxic and environmentally sustainable solvents. The emphases of the thesis were on the systematic optimization of pressurized liquid extraction and supercritical fluid extraction methods to achieve high selectivity in the extraction of sulfur and mineral matter from the coal.

The work was based on addressing the following research questions:

1. What is the efficiency of pressurized liquid extraction, in terms of selectivity and recovery of total sulfur and mineral matter compared to similar methods in literature?
2. What is the efficiency of supercritical fluid extraction (SFE) for desulfurization and demineralization of coal in comparison to pressurized liquid extraction (PLE) in terms of selectivity and recovery of sulfur and mineral matter. Additionally, is it possible to achieve higher recovery at lower temperature by using carbon dioxide expanded liquid extraction (CXLE) compared to PLE and SFE?
3. Is it possible to improve the combustion characteristic of coal such as calorific value, ignition temperature and activation energy?

2 Desulfurization and demineralization methods

The main aim of this thesis was the development of desulfurization and demineralization methods using green solvent. In this chapter, a brief introduction of the sulfur and mineral matter present in coal is given. The desulfurization and demineralization methods are then summarized and finally the introduction of green solvents used in **Paper I-II** presented.

2.1 Sulfur in coal

Sulfur in coal is classified into three types, which are inorganic sulfur, organic sulfur, and elemental sulfur [30]. Elemental sulfur is generally formed by the weathering effect and its percentage in total sulfur is relatively low, thus it is neglected in the most sulfur-related analysis [31]. Pyrite is reported to be the most abundant inorganic mineral in coal, with some other sulfide minerals that exist as marcasite (FeS_2), sphalerite (ZnS), galena (PbS), and chalcopyrite (CuFeS_2) [32]. Sulfate, usually with a lower content in coal, includes gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barite (BaSO_4), anhydrite (CaSO_4), and some iron sulfate minerals which are formed from the weathering of pyrite. Organic sulfur is directly associated with the coal matrix and part of the macromolecular structure of coal. The forms of organic sulfur in coal that have been reported mainly include thiols, sulfides and disulfides and thiophene with its derivatives [32, 33].

2.2 Mineral matter in coal

Coal generally incorporates various amounts of mineral matter as impurities. Mineral matter adversely affects different aspects of coal processing and utilization. Mineral matter is the solid material in coal, and after combustion it forms the residual ash. The

mineral matter is deposited into the peat bed during the coal (syngenetic) formation and can be incorporated contaminants during mining. Mineral matter can be divided into either inherent or extraneous mineral matter [34]. Minerals which are not attached to or included in the organic component are classified as extraneous or excluded. In contrast, minerals that are surrounded by or included in an organic matrix, are classified as inherent or included minerals. Clays, quartz, carbonates and pyrites group of minerals are examples of inherent mineral matter. Extraneous mineral matter occurs as discrete particulates of minerals in the coal seam as or introduced during the mining of the coal bed [35, 36].

2.3 Desulfurization and demineralization methods

Coal desulfurization and demineralization are mainly carried out at the mining sites by physical methods such as froth flotation, dense medium washing and hydrocyclones, which are used to remove mineral matter and part of the inorganic sulfur from coal especially pyrite sulfur, but it cannot remove organic sulfur [37, 38]. On the other hand, biological desulfurization with microbes such as *Acidithiobacillus ferrooxidans* is said to efficiently remove both organic and inorganic sulfur by up to 79 % [39, 40]. Unfortunately, the pH sensitivity of the microbes and the long extraction times are unfavourable for commercialization.

Chemical methods have been investigated to test the efficiency of desulfurization and demineralization. Chemical methods are generally grouped based on the chemicals used during extraction. Acid/base desulfurization and demineralization methods using nitric acid, hydrochloric acid, sodium hydroxide and ammonia have been reported [38]. Treatment of coal by different acids/bases followed by oxidation of sulfur utilizing hydrogen peroxide with ultraviolet (UV) light has also been investigated [41]. The utilization of microwaves in combination with solvents during chemical desulfurization have been demonstrated to remove total sulfur effectively. However, more efficiently for organic compared to inorganic sulfur [42]. Tao et.al., (2016) demonstrated that selective heating of organic sulfur functional groups in coal by microwave frequencies can be achieved which results in carbon-sulfur bond dissociation [43]. Organic solvents such as carbon disulfide (CS₂), 1-methyl-2-pyrrolidine (NMP), tetrahydrofuran (THF), and pyridine [44–46] have also been examined for solubilization of total sulfur and inorganic constituents (mineral matter). Ionic liquids (ILs) such as pyridinium salts have shown higher desulfurization efficiency at room temperature [47], in addition to their high stability and low volatility. The challenge with using ILs is that they are expensive in the sense that they are not produced in high volumes compared to other

organic solvents such as ethanol. Moreover, their toxicity is not fully understood as compared to organic solvents such as NMP [33]. In general, desulfurization with chemical methods is more effective than physical methods [48] and faster than microbial desulfurization [49]. However, there are still challenges, such as using large amounts of harsh and toxic chemical reagents coupled with an increase in temperature to increase desulfurization yields.

Therefore, the aim of this thesis was to investigate the use of non-toxic solvents for desulfurization and demineralization.

2.4 Supercritical fluids in coal desulfurization and demineralization

To define a supercritical fluid a phase diagram is commonly used. A supercritical fluid is essentially a substance in supercritical state above the critical temperature (T_c) and critical pressure (P_c). **Figure 1** shows the phase diagrams of water (a) and CO_2 (b).

Supercritical fluids based on green solvents, particularly ethanol, methanol or acetone-water mixtures, have been described as good media for selective coal desulfurization [50, 51]. Even though the solvents were considered green, the operation temperatures were high, so the extraction methods were actually coal conversion rather than extraction, in the sense that the methods produced tar. From the analytical chemistry perspective, an extraction method is meant to isolate target compounds with no chemical reactions involved. With respect to the coal used in the thesis, the thermal decomposition temperature was determined to be 382 °C by thermogravimetric analysis and is presented in **Chapter 3**.

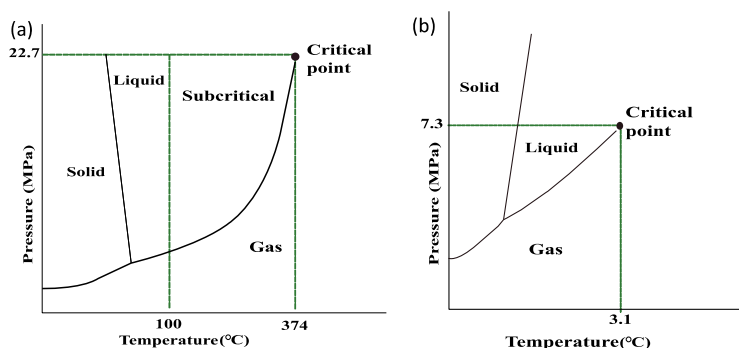


Figure 1. Phase diagrams of water (a) and carbon dioxide (a) with the critical points indicated.

The application of supercritical carbon dioxide for desulfurization and demineralization of coal has also been reported [52, 53]. Particularly, CO₂ with 10 % v/v methanol has been studied for extraction of elemental sulfur [54] and total sulfur [55]. However, as already mentioned for solvent extraction methods, temperatures of above 400 °C were used. In addition, the reported studies did not include a wide range of solvents that have the potential to interact more strongly with inorganic sulfur such as ethanol and water [33].

In this thesis, water with ethanol as the co-solvent was used in **Paper I** and carbon dioxide-ethyl lactate mixtures in **Paper II**. The chosen solvents are considered to be “green” solvents. In general, solvents which have minimal negative environmental impact in their production and utilization are considered to be green and it is based on the 12 principles of green chemistry [56].

Firstly, water is non-toxic and it is abundant in nature. For as long as it keeps raining, water can be considered as a renewable resource. Some drawbacks of using water as an extraction solvent is that at high temperatures (T_c) and pressures it leads to corrosion [57, 58]. In addition, the energy required to evaporate water is high after extraction.

Secondly, Capello et.al., (2007) demonstrated that ethanol is an environmentally preferred solvent using the environment, health, and safety (EHS) assessment [59] and life-cycle assessment (LCA) methods [60].

Thirdly, there are two parts to the choice of ethyl lactate (EL). The first part was that, NMP was found to be effective for desulfurization and demineralization, the problem is its toxicity, EL was found to have similar solvating properties such as the Hildebrand parameter, disperse Hansen parameter and polar Hansen parameter to those of NMP [61, 62]. The second part is that EL is a bio-based solvent which is produced through fermentation of corn feedstock, it is bio-degradability and it is non-corrosive [63].

Lastly, there are two parts for the selection of carbon dioxide. The first part is that it is considered to be a green solvent because it is a non-toxic and it is a by-product from chemical processing. Moreover, the critical temperature and pressure are low (Figure 1) compared to water making it safer to work with. Above its critical point, CO₂ is in a supercritical state in which it has a liquid-like density, gas-like viscosity and diffusion coefficient intermediate to those of a liquid and a gas. Its density can be changed by varying temperature and pressure [64]. This results in a high solvation power for non-polar and medium-polar compounds [65]. The polarity can also be modified by adding polar co-solvents [66]. The second part relates to the behaviour of scCO₂ when it interacts with coal during CO₂ sequestration. It has been shown that, scCO₂ induces changes in the mechanical and physical properties of coal seams such as coal strength due as a result of cracking [67]. In addition, scCO₂ acidifies which results in the

dissolution of mineral [68]. These properties are desirable from an extraction point of view. Therefore, it was hypothesized that addition of a co-solvent to scCO₂ will modify the polarity so that medium polar sulfur compounds can be extracted in addition to minerals.

3 Materials and methods

In this chapter, a brief description of the sampling site and the sampling process is given. The experimental design for extraction used in Paper I-II is briefly introduced. The methods followed for characterization of coal before and after extraction are also given (**Paper III**).

3.1 Sampling site, sampling and sample pre-preparation

The thesis work is based on coal samples collected from Morupule coal mine (MCM). MCM is slope mine i.e., access to the coal bed is through a shaft that slants down instead of drilling shafts straight down. The mine extends to 120 meters below ground level. MCM has four active mining sites that are labelled or designated as S3/9 (South main 3 development panel/ production panel number 9), S4/1 (South main 4 development panel/ production panel number 1), S4/4 (South main 4 development panel/ production panel number 4 and EM1 (East main development panel 1/ production panel number 1). The coal samples from the different sites are blended together before utilization. As such.

The purpose of collecting and preparing coal samples is to provide a test sample which can be analysed, and provide test results that are representative of the sampled lot. The challenge with analysing coal is that it is highly heterogeneous in nature, even within the same seam [29, 69, 70], therefore results are usually presented as a range [71]. In addition, sometimes the coal to be sampled may be a blend of different coal types. Sampling of coal can take place from either stationary lots or from moving streams. For instance, coal samples can be taken from a broad range of locations such as feed and product streams, conveyor belts, trucks, railway wagons, and stockpiles. In this thesis, as a way to investigate if there are any differences in the coal from the different mining sites at the Morupule mine, samples were collected at the actual mining site, as the coal was being mined and loaded in the trucks which transport the raw coal to the conveyor belt. At this point, the only option was to collect the samples manually using a shovel (grab sampling). Approximately 15 kg was collected at each mining site. In total, 60 kg

of coal samples (lumps) were then crushed sieved to 1.4 mm at the MCM coal preparation lab. In the end, approximately 12 kg were collected from each sampling site. The different samples were stored in heavy-duty plastic zip-lock bags and transported to the Coal-To-Liquid lab in Gaborone for further analysis. Representative samples were prepared by cone/and/quarter method as shown in **Figure 2** [35].

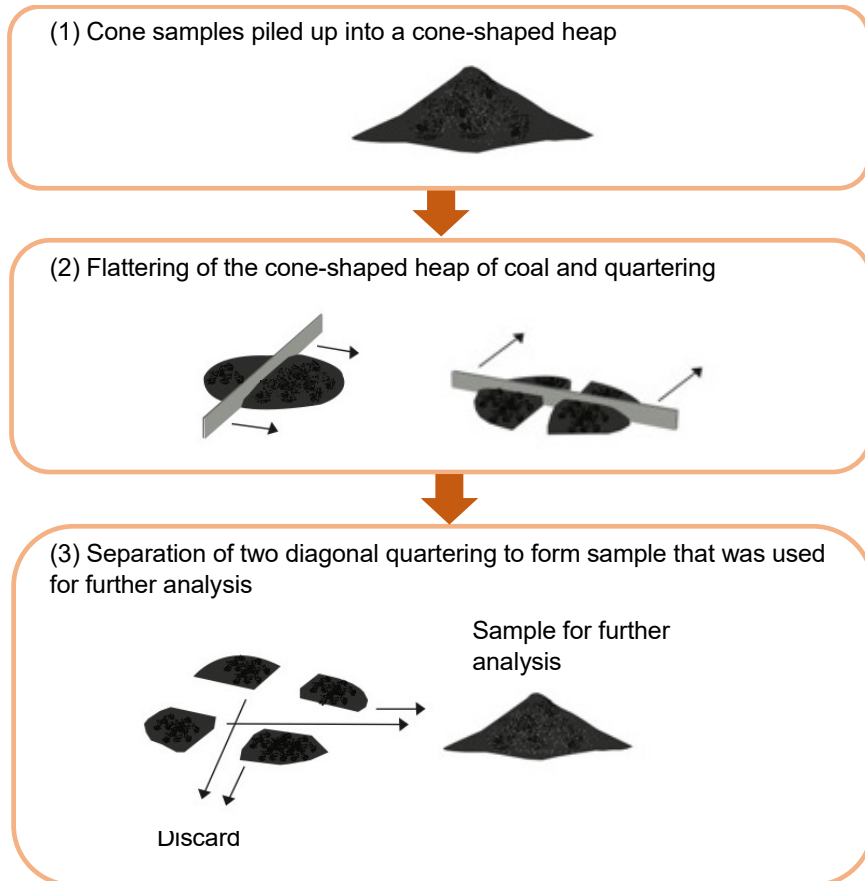


Figure 2. The coning and quartering method was used to reduce the sample.

3.2 Physicochemical properties of Morupule coal

As already mentioned, coal is used in many ways and the different applications of coal requires coal to have certain characteristics. Therefore, analysis of the characteristics of the coal is done to determine whether it meets the needs of a particular application

based on general quality as well as to control mining and cleaning operations. In commercial operations, the price of coal reflects not only the quantity of coal but also the relationship of a desirable property or combination of properties to the coal's performance under operating conditions. For example, metallurgical coal must be able to soften and re-solidify to form coke when heated in the absence of air from 300 to 550°C in a coking oven [72, 73]. Studies of coal quality mainly provide information about ash content, moisture, volatile matter, minerals, elemental composition (i.e. carbon, hydrogen, nitrogen, oxygen and sulphur content), trace elements, ash composition and calorific value [74]. Several analytical techniques such as thermogravimetric analysis (TGA), X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and inductively coupled plasma-mass spectroscopy (ICP-MS) have been extensively used to characterize coal [35, 75–78].

3.2.1 Proximate, ultimate and calorific value analyses

In the same way, conventional analyses were performed on the coal from the different mining sites, mainly to determine if there were any apparent differences. Proximate and Ultimate analysis of the raw coal samples were carried out at SGS laboratories (SGS (Pty) Ltd) in South Africa. The same analyses were later performed on the coal samples after extraction experiments at optimum conditions, which were determined as described in Papers I and II at the RISE Institute in Sweden. Proximate analysis was carried out by the American Society for Testing and Materials (ASTM) methods as shown in Table 1.

It can be observed that there are some differences in the proximate and ultimate analysis among the coal samples from the different mining sites. The coal samples from the different mining sites have total sulfur content of less than 2 wt. % of the whole coal (Table 1). What stands out is the higher total sulfur content in the EM1 coal sample compared to the other 3 samples. Low grade coals have been blended with high grade coal as a way to produce a better grade coal, reduce emission of pollutants and reduce costs [79]. However if the ratios of the different coal that are blended is not optimized, the resulting might perform worse than the individual coals, especially if the ignition temperature and activation energy are very different [80]. Therefore, EM1 sample was chosen for further studies with the aim to reduce the total sulfur content.

Table 1. Comparison of the proximate and ultimate analysis of the raw coal and the solvent extracted coal following ASTM methods for coal and coke

	Raw coal sample				Solvent extracted EM1 coal sample	
	S4/1	S4/4	S3/9	EM1	PLE: aqueous ethanol extracted coal	SFE: scCO ₂ /ethyl lactate extracted coal
Proximate analysis (wt. %)						
Moisture ^[a]	3.8±0.1	3.6±0.2	3.9±0.1	3.6±0.1	1.3±0.3	1.1±0.1
Volatile matter ^[b]	21.8±0.6	23.6±0.3	23.1±0.2	23.8±0.3	26±1.2	26±0.1
Fixed Carbon ^[c]	53.9±0.5	47.1±0.4	53.2±0.2	48.2±0.2	54.6±0.7	48.7±0.3
Ash ^[d]	20.6±0.2	25.7±0.3	19.8±0.2	24.4±0.4	23.9±0.3	22.5±0.4
Ultimate analysis (wt. %)						
Carbon ^[e]	60.9±0.2	55.9±0.3	60.7±0.3	56.4±0.8	61.0±2.0	57.8±0.4
Hydrogen ^[e]	4.7±0.01	4.0±0.06	4.4±0.29	4.6±0.06	2.2±0.2	2.2±0.1
Nitrogen ^[e]	1.4±0.01	1.2±0.01	1.4±0.1	1.3±0.1	1.9±0.0	1.4±0.0
Oxygen (by difference)	7.9±0.2	8.1±0.2	8.9±0.2	8.0±0.6	3.5±0.8	2.9±0.4
Total sulphur ^[f]	0.7±0.2	1.6±0.1	1.0±0.1	1.9±0.2	0.6±0.1	0.2±0.1
Calorific value ^[g] (MJ/Kg)	23.9±0.1	21.5±0.07	23.6±0.1	22.3±0.2	24.2±0.1	23.2±0.1
A _{O/C}	0.13	0.14	0.15	0.14	0.06	0.05

[a]ASTM D3173,[81] [b]ASTM D3175,[82] [c]ASTM D5142,[83] [d]ASTM D3174,[84] [e]ASTMD5373,[85] [f]ASTMD4239,[86] [g]ASTMD5865[87]

Table 1 also shows the results obtained after extraction of the EM1 sample. The parameters used for extraction were optimized for total sulfur reduction. The full optimization process is described in **Paper I** in which water with ethanol as a co-solvent was used (PLE) and **Paper II** supercritical carbon dioxide (scCO₂) with ethyl lactate (EL) as the co-solvent was used. The moisture content of the EM1 coal was significantly decreased after solvent extraction, with scCO₂/EL reducing it the most. The observation is consistent with what is reported in literature where scCO₂ has been used for dewatering coal [88, 89]. The fixed carbon and elemental carbon both increased and subsequently the calorific value and the coal rank also increased. The decrease of the oxygen/carbon atomic ratio ($A_{O/C}$), which is another parameter related to the coal rank, indicated that the coal rank of the solvent extracted coal improved [88]. The total sulfur content of the extracted coal samples decreased, with the largest decrease

observed when scCO₂/EL was used. Most probably, the lower viscosity of scCO₂, which results in higher diffusivity of the solvent, combined with the higher polarity of EL, resulted in higher extraction efficiency when compared to aqueous ethanol solvent.

3.2.2 Thermogravimetric analysis

Many factors affect coal burning characteristics and various parameters have been used to rate coal burning performance [80]. Coal combustion properties refer to the relationship between individual parameters (such as volatile matter, calorific value, combustion efficiency and activation energy) and coal combustibility. These parameters have been studied by observing sample weight loss as a function of temperature and plotting the rate of mass change with respect to temperature or time (TG-DTG plot) [90]. In **Paper III**, the effect of desulfurization on the combustion of coal was investigated and the TG-DTG plots are shown in **Figure 3**. The initial thermal decomposition temperature, (T_{on}) and the temperature at which combustion is complete (T_f) in the raw coal decreases after desulfurization. This simply means that less energy is needed to start the decomposition process.

The ignition temperature (T_i), which shows that the coal has started combusting, was determined by the TG-DTG tangent method [91], as shown in **Figure 3**. Desulfurized coal samples have slightly lower T_i values than the raw coal. Similarly, the T_{max} decreases slightly after desulfurization. These two parameters have been shown to be affected by the volatile content of coal [92]. During combustion or pyrolysis, the volatiles are liberated from the coal. They adsorb on the coal surface, preheat the fixed carbon, and initiate combustion, hence the reduction of T_{max} [91]. Therefore, higher volatile matter results in faster ignition of coal and lower T_{max} [93, 94]. As such, the slight decrease in T_i and T_{max} in the extracted coal might be due to the slight increase in the volatile matter, as shown in **Table 1**.

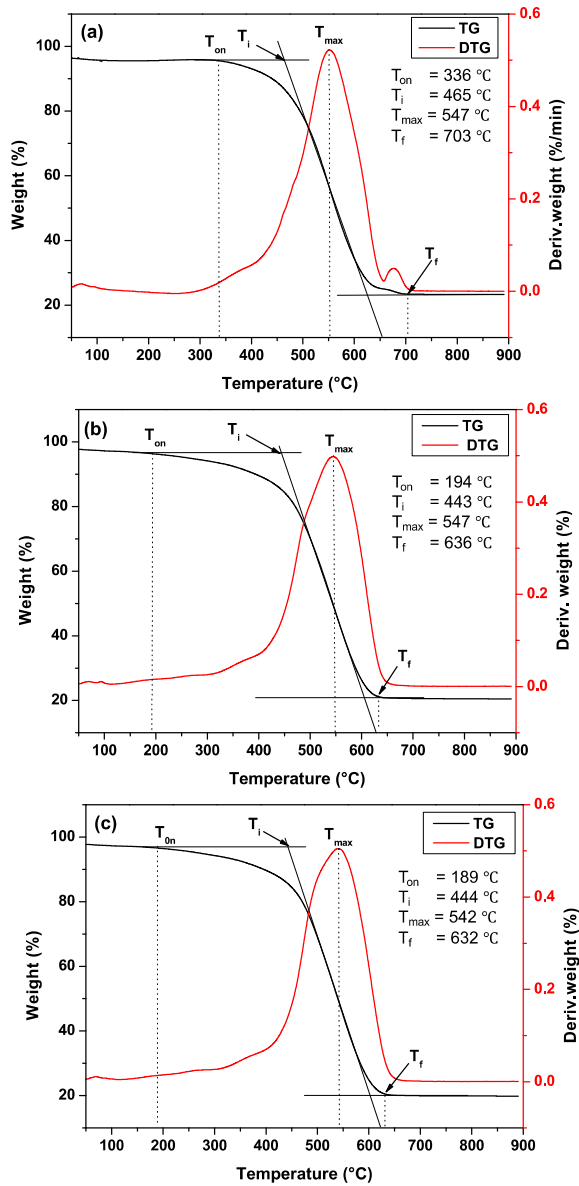


Figure 3. TG-DTG curves of the raw coal (a) and coal after desulfurization with aqueous ethanol (b) and scCO₂/EL (c) solvents at optimum condition. A heating rate of 20 °C/min was used under air atmosphere. (Re-printed with permission).

The finding from **Paper III** shows that physicochemical properties were affected to different degrees by the two extraction methods but there is no significant different between the two methods. In addition, the methods improve the quality of the coal.

3.3 Desulfurization and demineralization of raw Morupule coal

Two approaches were investigated for desulfurization and demineralization of coal in this thesis work. In **Paper I**, pressurized liquid extraction method in which water was used with ethanol as a co-solvent. In **Paper II**, supercritical fluid extraction was performed, whereby scCO₂ was used with EL as a co-solvent.

3.3.1 Experimental design

Every extraction method in analytical chemistry should be optimized before use. The optimization process aims to investigate the influence of factors and their interactions on the response. It also aims to find the conditions where all factors give the optimal response. Many designs can be used to create a design of experiments (DoE) models, such as central composite designs (CCD) [95] and Box Behnken designs (BBD) [96]. The choice of design depends on the study's objective, the type of factors (qualitative and quantitative), the boundary conditions, and the number of factors to be examined. The exact choice of factor and range are sometimes dictated by the physical limitations of the equipment, such as temperature or pressure limits [97]. In this thesis, BBD was used for the optimization of the pressurized liquid extraction (**Paper I**) using the Dionex ASE 150 system (Thermo Scientific, Waltham, MA, USA), and supercritical fluid extraction (**Paper II**) was done using the MV-10 ASFE system (Waters Technologies, Milford, MA, USA), controlled by ChromScope™ software (Waters Technologies, Milford, MA, USA). The preference of the BBD over other approaches was to avoid operating the respective instruments at the condition where all the factors are set at their maximum.

Three variables were investigated for both extraction methods, as shown in **Table 3**. The indicated pressures were constant for all the experimental runs. The amount of total sulfur remaining in the coal after extraction, the amount of mineral matter remaining after extraction (reported as ash content) and the gravimetric yield were taken as the responses. A total of 16 experiments were performed, including four centre points.

Table 3. Range of independent variables used in the design of experiments for subcritical water extraction and supercritical carbon dioxide extraction.

	Subcritical extraction	Supercritical fluid extraction
Temperature range (°C)	60 - 180	60 - 80
Extraction time (minutes)	10 - 30	15 - 45
Co- solvent range (v/v)	Ethanol, 10 - 90	ethyl lactate, 95 - 5
Pressure (bar)	105	300

3.3.2 Sulfur analysis

Analysis of sulfur in coal is not straight forward. As mentioned already, sulfur is present in coal as organic and inorganic compounds. In addition, the distribution of sulfur in the coal matrix is not homogeneous. Therefore, the choice of analysis method is decided by which type of sulfur is of interest. In this thesis, the extraction method is not meant to target a specific type of sulfur. Therefore, total analysis of sulfur is the main target in **Paper I-III**. However, to determine whether there is preferential extraction of sulfur by the developed method, a qualitative analysis of sulfur was also performed.

Microwave-assisted digestion of raw coal and solvent extracted coal was carried out before total sulfur analysis using the Marc 5 CEM microwave digester. The digestion protocol is described in detail in **Paper I-II**. Inductively coupled plasma optical emission spectroscopy (ICP-OES), Optima 8300 from Perkin Elmer was used for quantification of total after acid microwave acid digestion. The acids used for digestion were HNO₃, HCl and HF. Due to the high mineral matter content of the Morupule coal and the fact that no literature reports show how the sulfur is incorporated in coal, an acid mixture which has been shown to completely digest the coal was necessary [98]. In addition, the quantity of HF used was small.

X-ray photoelectron spectroscopy (XPS) was used to qualitatively assess the sulfur forms in the raw coal and coal after solvent extraction using the optimum conditions for desulfurization. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI Quantera II instrument equipped with monochromatic Al-K α radiation ($h\nu = 1487$ eV) as described in **Paper II**. Although XPS could determine some forms of sulfur, it is a technique that could only detect the sulfur on the coal surface.

3.3.3 Mineral matter analysis

The mineral matter in coal includes material that occurs as discrete crystalline mineral particles, poorly crystalline mineraloids as well as a range of non- crystalline inorganic elements. In this thesis, quantification of mineral matter was performed following the ASTM D3174 standard method [84] in **Papers I-III**.

4 Results and discussions

In this chapter, the main results from the desulfurization and demineralization of coal are presented and discussed. In this thesis, two approaches were investigated for desulfurization and demineralization of coal; PLE and SFE as already mentioned. It should be clarified that the goal is to extract total sulfur and total mineral matter from coal. Therefore, an important aspect to bear in mind is that the choice of extracting solvent will have an influence on the solubility of the different sulfur forms and different mineral matter present in coal. The ideal outcome would be to have a method that can simultaneously desulfurize and demineralize coal. In the current work, direct solubility studies of sulfur and mineral matter was not done but instead the solubility was based on the measured amount of total sulfur and mineral matter in the form of ash in the coal after performing extraction. Other parameters such as extraction temperature, extraction time and mode of extraction (static or dynamic) will affect the efficiency of the extraction method.

4.1 Desulfurization of coal

In the first approach, pressurized liquid extraction was investigated in **Paper I**. Water with ethanol as a co-solvent was used. The pressure during extraction was 105 bar. The range of extraction temperature and time were 100-180 °C and 10-30 minutes respectively. Based on the phase diagram of water shown in **Figure 1** (with no co-solvent), the water is in the subcritical state. The highest reduction of total sulfur from coal was from 1.9 wt. % to 0.4 with optimum parameters determined to be water/ethanol (10:90, v/v) at 129 °C and 10 minutes. As indicated in **Paper I**, the effect of extraction time was minimal. Increasing ethanol content in water and increasing temperature enhanced the extractability of total sulfur as seen by the decreasing amount of sulfur remaining in the coal after extraction. The contour plot in **Figure 4** shows these effects on the extraction. The plot shows the amount measured in the coal after extraction, particularly because the coal will be further used, as opposed to measuring the total sulfur content in the extract. These results differ from Azzam and Sunggyu's

1993 which showed a reduction of total sulfur from 7.1 to 6.1 (wt.%), using a temperature of 400 °C at 136 bars for 1 hour, with ethanol/water (16/84 %, v/v) mixture. In addition, they observed the production of tar, a by-product which they suspected was due to the higher content of water in the extraction solvent and the high temperature. They also observed that their methods extracted more inorganic sulfur which they determined by following the ASTM D-2492 testing method [99]. On the contrary, higher reduction of total sulfur was achieved with our method as already indicated using lower temperature and higher content of ethanol. The reason for the higher efficiency of our method is not clear but it might be because of the different forms of sulfur present since the coals are not identical and the extract manner in which the sulfur is incorporated in coal is not known. The results may suggest that the sulfur compounds present in Morupule coal have intermediate polarity because they are extracted with aqueous ethanol and not water. In this thesis, the forms of sulfur were determined by XPS and the results are presented in section 4.2.

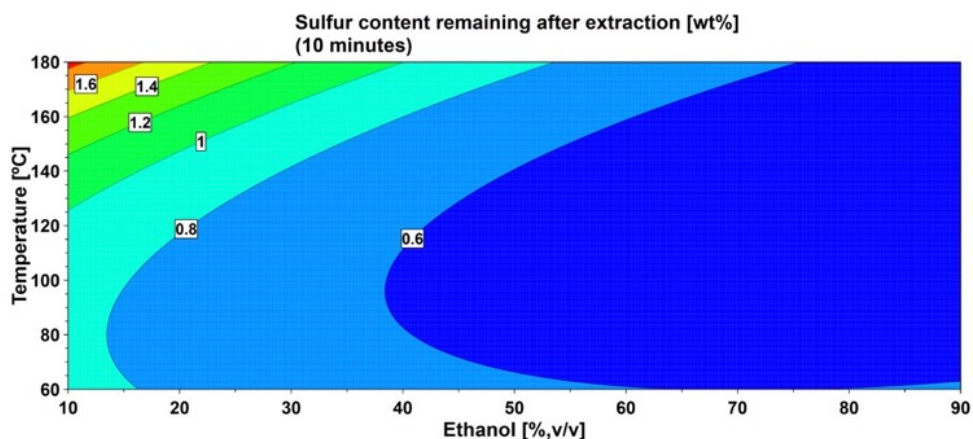


Figure 4. Contour plot from a Box Behnken design (BBD) showing the influence of the ethanol (vol%) water and extraction temperature on the reduction of total sulfur (wt.%) from Morupule coal. The pressure and time were constant at 105 bar and 10 minutes, respectively. (Re-printed with permission).

In the second approach, CO₂ with ethyl lactate as the co-solvent was used for desulfurization of coal. The extraction pressure was set to be constant at 300 bar and the temperature range is above the critical temperature of CO₂, as based on the phase diagram of CO₂ in Figure 1. The main reason for setting the pressure well above the critical pressure was to ensure that the extraction fluid remain as a one phase mixture at all extraction points. A binary phase diagram of CO₂/EL reported by Bermejo et al., (2012) was constructed with a maximum temperature of 49 °C, which is lower than the minimum temperature used in Paper II. They also used a maximum pressure of 81

bar [100]. Therefore, the assumption is that the solvent mixture will remain as one phase in **Paper II**. The maximum total sulfur was reduced from 1.9 to 0.1 wt.% at optimum parameters determined to be CO₂/EL (95:5, v/v) at 80 °C and 15 minutes. It was also observed that increasing temperature increased total sulfur extraction. In addition, extraction efficiency is achieved with lower ethyl lactate content in scCO₂ and lower extraction time of 15 minutes. The effect of extraction temperature and EL content in CO₂ is shown by the contour plot in **Figure 5**. The results may be explained by the fact that higher temperature has been reported to induce relaxation of the coal, whereas sub/supercritical CO₂ results in swelling of the coal [101, 102]. Both these properties could result in increased extractability of sulfur compounds in the coal. It should be added that at each temperature the effect of EL% is rather small. As mentioned in **chapter 2 section 2.4**, at high pressure scCO₂ causes the coal to swell and crack due to the weak bonds. This allows the ethyl lactate to diffuse into the coal and solubilize the sulfur compounds. In comparison to the already published methods that also applied scCO₂ extraction with 10 % methanol as co-solvent, our developed method has higher extraction efficiency [55]. It would appear that the solvating power of scCO₂ was increased by the addition of a small amount of ethyl lactate. In addition, the sulfur compounds that are solubilized are medium polar since the extraction solvent is 95 %, v/v scCO₂. From the aspect of organic solvent usage, the quantity of EL is low, hence the solvent waste generation is low compared to our other developed PLE method with 90 % v/v ethanol consumption.

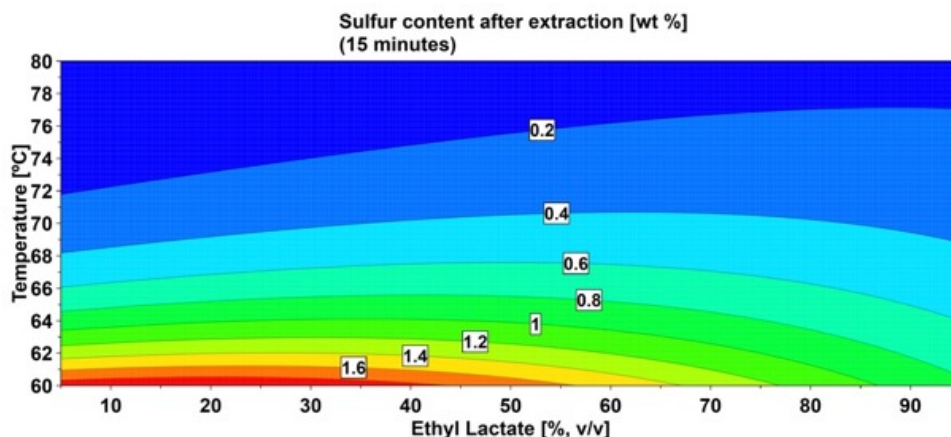


Figure 5. Contour plot from a Box Behnken design (BBD) showing the influence of the ethyl lactate ratio(vol%) in sub/supercritical CO₂ and extraction temperature on the extraction of total sulfur (wt.%). The pressure and time were constant at 300 bar and 15 minutes, respectively. (Re-printed with permission).

4.2 Sulfur speciation

In this thesis, the emphasis is based on total sulfur removal. XPS was used to qualitatively assess the sulfur forms in the raw coal and coal after solvent extraction at optimum conditions. The experimental conditions are well documented in **Paper II**.

Identification of different forms of sulfur is based on the observed core level binding energy. In general, higher binding energy indicates a higher oxidation state of the atom. Metal sulfides are typically found at binding energies between 162-163 eV. Binding energies around 163-165 eV are typical for sulfur bonded to carbon, such as thiophene. From 165 eV up to around 170 eV, sulfur coordinated with an increasing number of oxygen atoms is usually found (sulfoxide, sulfone, sulfonate and sulfate) [103–106]. The S2p core level spectra of raw coal and coal after extraction with scCO₂/EL and aqueous ethanol extracted at optimum conditions are shown in **Figures 6a-c**. The curve fitting in **Figure 6a** shows that the raw coal contains inorganic sulfide/pyrites, organic sulfur, and different sulfur-oxygen species (such as sulfoxides, sulfones and sulfates), similar to what has been observed in the literature [105]. Notable is a very small contribution from organic sulfur species. It is evident that aqueous ethanol and scCO₂/ethyl lactate mixtures solubilize the organic sulfur and highly oxidized sulfur due to the disappearance of their characteristic peaks in **Figure 6b-c**. In addition, aqueous ethanol also completely solubilized all the organic sulfur. In contrast, the scCO₂/EL mixture was not able to completely extract the sulfoxides as observed due to the presence peaks between 165 - 168 eV in Figure 12c. It was observed from the optimization that increasing temperature increased the extraction yield. It might be that for complete extraction of sulfoxides, a temperature outside our design space is required. Nevertheless, the results are consistent with what has been reported by Louie et.al., (1994) [55] where they also observed that scCO₂ with 10 % methanol was less efficient for inorganic sulfur. Nitric acid has been reported to be efficient in the extraction of inorganic sulfur [107, 108]. The overall high efficiency in terms of total sulfur reduction shown by our extraction methods might also be because the overall sulfur content in coal is low and the coal appears to have more organic sulfur than coals that were used in literature. What is also worth noting is that Morupule coal seems to have more organic sulfur based on the relative area of the peaks, compared to inorganic sulfur. To verify these results, the ASTM D-2492 testing method [99] would need to be used.

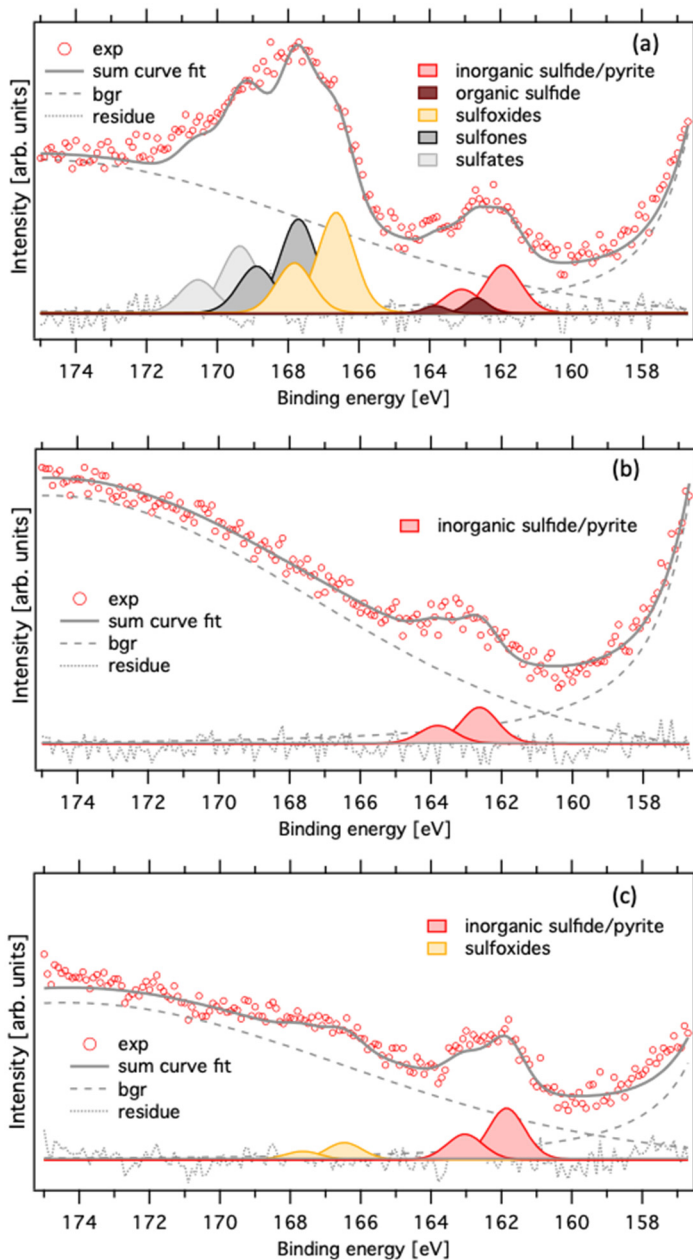


Figure 6. XPS S2p core level spectrum of Morupule coal before desulfurization (a) and after desulfurization with aqueous ethanol (b) and sCCO₂/EL (c) under optimum extraction conditions. The experimental spectrum (open circles) is shown together with a curve fit (solid lines and filled areas). (Re-printed with permission).

4.3 Demineralization of coal

The mineral matter in coal includes material that occurs as discrete crystalline mineral particles (minerals in the traditional sense) and poorly crystalline mineraloids, as well as a range of non-crystalline inorganic elements [34]. Therefore, the determination of the percentage of mineral matter contained within the coal may include identification and quantification of mineral phases or extraction and analysis of total elemental composition of coal [109, 110].

Depending on the goals of the study, this information can then be used to interpret the processes, or combination of processes, that formed the individual components of the mineral in the coal. It could also be used to assess to what extent coal beneficiation processes might alter the nature of the mineral, and how the mineral components react or may interact when the coal is stored or used.

High mineral content coals are unsuitable for efficient carbonization, combustion, gasification and liquefaction. Such coals lead to environmental pollution (high ash production) [111]. The minerals also deposit inside reactors and eventually cause clogging [112]. It has already been determined that Morupule coal is classified as high ash coal. Therefore, in the same way as desulfurization, the applicability of water/ethanol (**Paper I**) and scCO₂/EL (**Paper II**) mixture was investigated following the same BBD approach. Unfortunately, both methods performed poorly in reducing the mineral matter in coal which turns to ash after coal combustion. The ash content was determined following the ASTM D3174 [84] in **Papers I-III**. The contour plots in **Figure 7** shows the effect of temperature and ethanol content (v/v %) in water from **Paper I**. The predicted optimal extraction conditions for maximum reduction of mineral matter were 30 min of extraction with water with 10 % (v/v) ethanol as the co-solvent at 152 °C (105 bars).

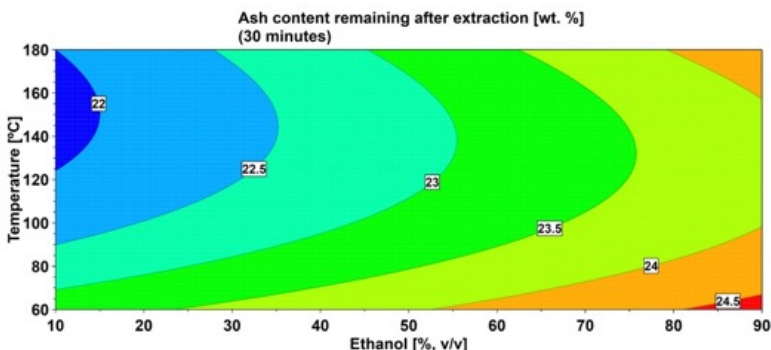


Figure 7. Contour plot from a Box Behnken design (BBD) showing the influence of the ethanol (vol%) water and extraction temperature on the ash content (wt.%) remaining in from Morupule coal after extraction. The pressure and time were constant at 105 bar and 30 minutes, respectively. (Re-printed with permission).

Figure 8 shows the effect of temperature and EL content (v/v %) in sCO_2 from **Paper II** on the extraction of mineral matter from coal. The predicted optimal conditions were found at 60 °C with a CO_2 /ethyl lactate solvent mixture (29/71 %, v/v) for 45 minutes. What can also be observed in the contour plots is that, even though increasing the amount of ethyl lactate increases the extraction of mineral matters, 100 % EL is not the best. A likely explanation can be that the addition of CO_2 is needed to swell the coal which weakens the coal bonding, but also reduces the viscosity of EL. Lower viscosity of EL results in improved diffusivity of the solvent into the coal matrix and improves the extractability of mineral salts such as carbonates and sulfates. As already indicated, some mineral matter may be present in coal as discrete particulates, therefore it is possible that the extracted mineral matter were not chemically bound, hence they could be extracted under mild conditions [34].

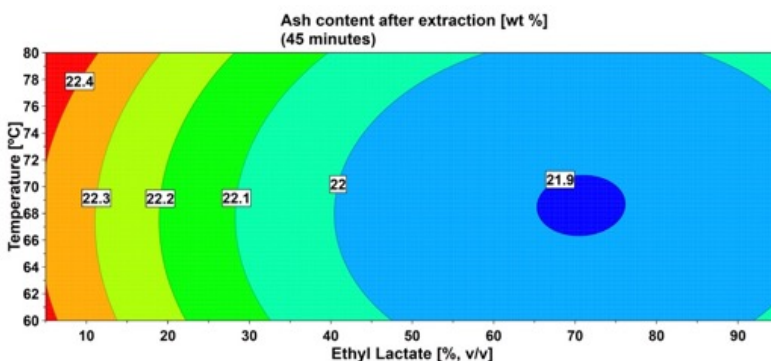


Figure 8. Contour plot from a Box Behnken design (BBD) showing the influence of the ethyl lactate ratio (vol%) in sCO_2 and extraction temperature on the ash content (wt.%) remaining in from Morupule coal after extraction. The pressure and time were constant at 300 bar and 45 minutes, respectively. (Re-printed with permission).

4.4 Validity of the models

The results presented in this chapter are based on models that were predicted after performing only 16 experiments. The question is, can these results be trusted? As already discussed in **Chapter 4 section 4.3**, Box-Behnken design (BBD) was chosen over other approaches to avoid performing extraction experiments at points where all the conditions are set at maximum, since in some cases the instrument cannot sustain such extreme conditions. Based on the extraction of raw coal, an empirical relationship between experimental results obtained and input variables was established by fitting a second-order polynomial equation with interaction terms and applying multiple linear regression. The fitting summary of extraction models for desulfurization and demineralization using aqueous ethanol and sub/supercritical CO₂/ethyl lactate mixture is shown in **Table 4**. The fitted models showed a total explained variance of 97 - 99 % ($R^2 = 0.97 - 0.99$), that indicated an excellent model fit. An estimation of the future prediction and precision is shown by the cross-validated predictability of 53 - 99 % ($Q^2 = 0.53 - 0.99$). A lack-of-fit test was computed to determine whether the regression model accurately fits the experimental data. The calculated p-values of the responses were then compared to the p-value of the significant level (α), which is 0.05. The lack-of-fit p-values are larger than α , showing no evidence that the model does not fit the data. Additional experiments were performed using the predicted optimum conditions. The experimental response was compared to the predicted response. **Tables 5-6** shows the results. The experimental results are not significantly different from the predicted results. This type of validation is particularly important when one of the predicted setting lies at the maximum setting within the experimental domain. For example, the optimum temperature for desulfurization in **Paper II** was predicted to be 80 °C which is why such experiments are necessary. Based on the results in **Table 4**, it shows we can trust the results from the experiments performed.

Table 4. Parameters showing the validity of the models.

	Aqueous ethanol extraction		Sub/Supercritical CO ₂ /ethyl lactate extraction	
	Total sulfur remaining after extraction	Ash content remaining after extraction	Total sulfur remaining after extraction	Ash content remaining after extraction
R ²	0.98	0.97	0.99	0.99
Q ²	0.76	0.53	0.90	0.95
Model Validity	0.26	0.64	0.50	0.97
Reproducibility	0.99	0.95	0.99	0.95
Lack-of-Fit (p-value)	0.55	0.23	0.16	0.31

Table 5. Predicted vs observed values of the total sulfur remaining after extraction (wt. %) and ash content remaining after extraction (wt. %) in Morupule coal at optimum extraction conditions as defined by vol% of ethanol in water, temperature, and extraction time. n=3 at 95% confidence interval.

Extraction method	Optimized method parameters			Response	Initial amount in raw coal (wt. %)	Predicted after extraction (wt. %)	Observed after extraction (wt. %)
	Ethanol (vol %)	Temp. (°C)	Time (mins)				
Desulfurization	90	129	10	Sulfur content remaining in the coal after extraction	1.9 ± 0.2	0.43 ± 0.02	0.4 ± 0.3
Demineralization	10	152	30	Ash content remaining in the coal after extraction	24.4 ± 0.4	21.9 ± 0.3	23.0 ± 0.3

Table 6. Predicted vs observed values of measured total sulfur and ash content after extraction are reported as weight percent of the original amount in coal. Optimum extraction conditions used are defined by vol% of ethyl lactate in CO₂, temperature, and extraction time. (n=3)

Extraction method	Optimized method parameters			Response	Initial amount in raw coal (wt. %)	Predicted after extraction (wt. %)	Observed after extraction (weight %)
	Ethyl lactate (vol%)	Temp. (°C)	Time (mins)				
Desulfurization	5	80	15	Sulfur content remaining in the coal after extraction	1.9	0.04 ± 0.1	0.1 ± 0.0
Demineralization	71	68	45	Ash content remaining in the coal after extraction	24.4	21.9 ± 0.04	22 ± 0.1

5 Supercritical fluid chromatography and mass spectrometry

The goal of this thesis was to reduce air pollution from combustion of coal by developing desulfurization methods. The question intended to be answered in this chapter was whether toxic liquid waste has now been created. A chromatographic separation method of some target analytes was therefore developed. The results presented in this chapter are not ready for publication due to challenges that are yet to be resolved.

A number of methods focusing on desulfurization of coal are available in literature, reporting good extraction efficiency of total sulfur when organic solvents were used. However, limited publications included the analysis of the extract. The few reports indicated the production of tar due to the use of high temperatures. Methods for analysis of coal tar are well established and they are based on gas chromatography/mass spectrometry (GC/MS) and the NIST library is commonly used to identify the compounds present.

In **Paper I-II** of this thesis, the extraction temperatures used were lower than the thermal decomposition and production of coal tar. In addition, there is the aqueous extract from Paper I and the organic extract (EL) from Paper 2. Therefore, the goal was to develop a method for analysis of compounds with a wide range of polarity at the same time.

5.1 Supercritical fluid chromatography (SFC)

A standard mixture containing a mixture mono- and polyaromatic hydrocarbons was used to develop the chromatographic methods. It has been reported that coal combustion results in the production of wastewater containing phenolic and polyaromatic hydrocarbons [113]. Most of the phenolic compounds and PAHs including nitrogen and oxygen containing PAHs generated during coal utilization are

known to have poor biodegradability. In addition, these compounds are toxic to animals and humans [114]. We need to recognize that the coal in that report was thermally converted, thus we might not detect the same compounds in our extracts. Nevertheless, several members of these groups of compounds such as phenol, cresols and naphthalene are soluble in water and they are known to be mutagenic and carcinogenic when ingested, and they are on the EPA list of priority pollutants [115]. Therefore, considerable effort has been spent on analyses of the compounds in wastewater to facilitate the development of treatment techniques [116–118]. Hence, we believe it is important to also determine them in our extracts, which are treated as waste.

It has been shown in **Paper I-II** that the developed methods are efficient for desulfurization. Targeted analysis of well-known pollutants using chromatographic separation and mass spectrometric identification was done on the extracts collected at optimum desulfurization conditions.

The choice of separation techniques depends on the analyte, the extraction method used, for example aqueous or organic solvents and the purpose of the study. For example, high-performance liquid chromatography (HPLC) is the most common technique for analysing phenolic compounds in aqueous extracts, on the other hand, gas chromatography (GC) is more commonly used for the separation of polyaromatic hydrocarbons and paraffinic compounds in organic extracts. A simple, rapid, sensitive, selective, low-cost and reliable separation method is always preferable in chromatography. Supercritical fluid chromatography (SFC) has recently gained popularity because of its high efficiency due to high diffusivity of the mobile phase, shorter analysis times, and the capability to separate non-volatile compounds without any prior derivatization as compared to analysis with GC. Furthermore, SFC uses less organic solvents in comparison to LC but the analysis time can be comparable when ultra-high performance liquid chromatography (UHPLC) is used instead of HPLC [119, 120].

The choice of chromatographic technique, i.e., GC, LC or SFC, can be exclusively determined by the nature of the sample, nature of the analyte(s) and the goals of chromatography in question. A generalized comparison between GC, LC and SFC, illustrated in **Figure 9**, shows that SFC can cover a broader range of classes of organic compounds of a wide range of polarity compared to GC and LC. Packed column SFC allows the addition of high ratios of co-solvents to pressurized CO₂ enabling the change of the eluent strength of the mobile phase and broaden the application to polar compounds [121].

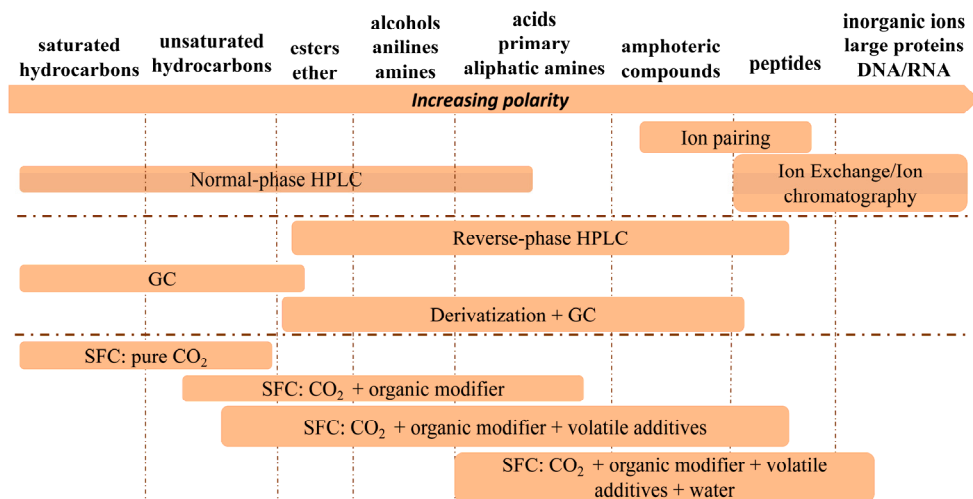


Figure 9. A comparison of various chromatography techniques and their areas of application in terms of the polarity of the analyte. Adapted and modified from Vlckova, H. K [121].

An application of SFC for the simultaneous analysis of polycyclic aromatic hydrocarbons and oxygenated polycyclic aromatic hydrocarbons in unconventional oil was demonstrated by Lubeck et al., (2019) focusing on separation of polyaromatic hydrocarbons (PAHs) and oxygenated polyaromatic hydrocarbons (OPACs) [122]. Aiming to broaden the applicability, the goal in this thesis was to develop a method to include sulfur containing mono- and polyaromatic hydrocarbons and nitrogen containing mono- and polyaromatic hydrocarbons using the abovementioned method as a starting point. **Figure 10** shows a total of 29 analytes that were used for this study.

The goal of the study was to separate target analytes in a single run. A desirable chromatographic method should provide increased selectivity and efficiency. These are achieved by optimizing stationary and mobile phases to obtain rapid separation with narrow peaks. For this, the density of the mobile phase must be fine-tuned via temperature and backpressure to alter the retention of analytes in the column [123] as well as other separating factors such as mobile phase co-solvents, possible additives and injection solvent [124, 125].

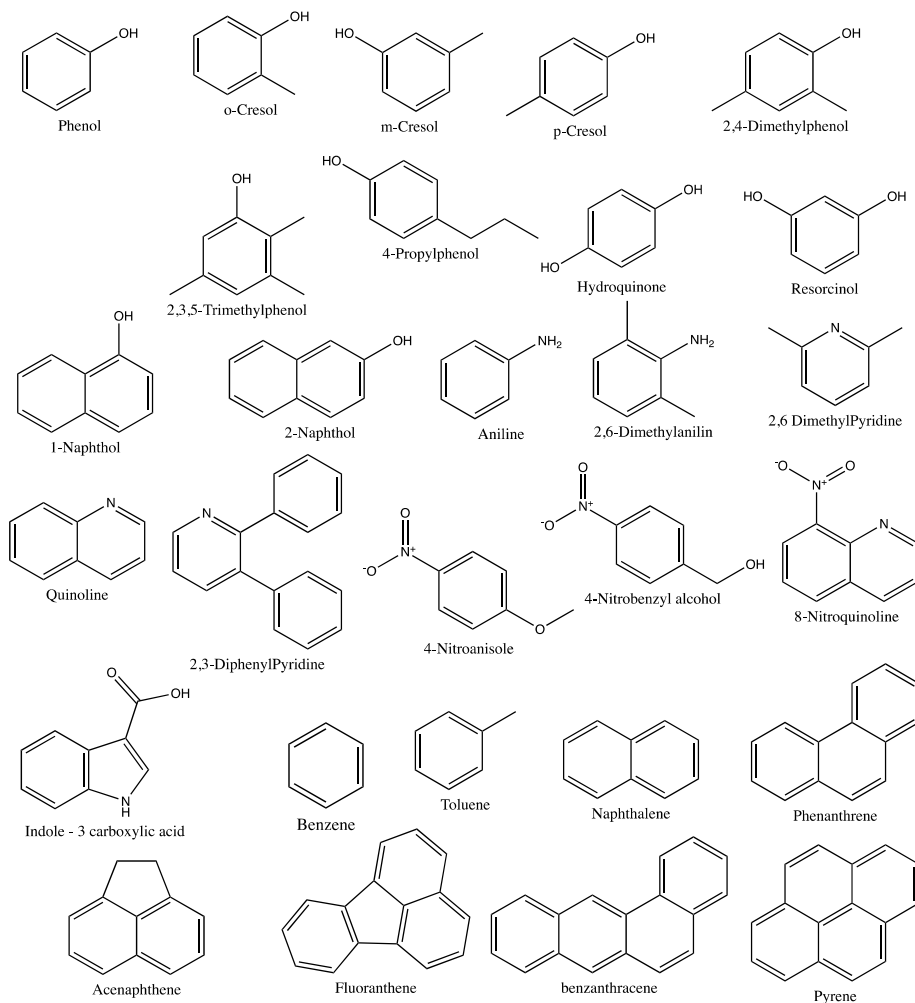


Figure 10. Chemical structures of the nitrogen containing mono- and polyaromatic hydrocarbons in addition to the oxygen containing mono- and polyaromatic hydrocarbons

The separation was performed using a Waters Acquity Ultra Performance Convergence chromatography (UPC²) system (Waters, Milford, MA, USA) coupled to a Waters XEVO-G2 Q-TOF (Quadruple-Time of Flight) mass spectrometer (Waters, Milford, MA, USA). The backpressure is set by the automatic backpressure regulator (ABPR). A pre-BPR split approach (Acquity UPC² splitter) was used to interface the UHPSFC system to the MS, and the approximate split ratio is estimated to be 1:100 [126].

In SFC, the chemistry of the stationary phase has the most significant influence on selectivity and separation efficiency such as resolution between two adjacent peaks.

Solvation parameter model that include single electron pair (E), dipole type (S), hydrogen bond acceptor (A), hydrogen bond donor (B) and dispersion (V) was used by West et al., to characterize columns according to their interactions [127]. Lubeck et al. [122] reported that the best separation of PAHs and OPACs was achieved with the ethylene-bridged silica column, but the highest peak capacities were observed with a 2-picolylamine column [122]. In this thesis, three stationary phases with different chemistries (Figure 11) were evaluated using a modification of the abovementioned method.

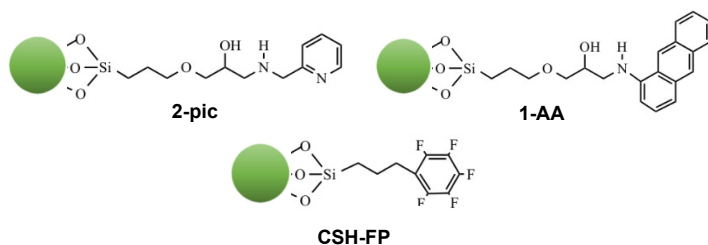


Figure 11: Chemistries of the stationary phases in the columns investigated. 2-picolylamine (2-PIC), charged surface hybrid fluoro-phenyl (CSH-FP) and 1-aminoanthracene (1-AA).

Since the elution strength of pure CO₂ strongly depends on the density of the liquid, pressure gradient have been used with enhanced efficiency and good separation of non-polar compounds [128]. However, compressed pure CO₂ is generally a low polarity solvent. To expand the range of compounds that SFC can analyze, an organic modifier is added to the pure compressed CO₂, which significantly increases the elution strength of the mobile phase and promotes the solubility of analytes [129]. Also, various additives such as salts, acids or bases have been added to the co-solvent to improve peak shapes via blocking secondary interactions between the analyte and the stationary phase [129]. Methanol is often considered a good organic modifier and it has been used in many SFC applications [125, 130]. Ethanol and acetonitrile were also investigated as possible organic co-solvents. The aim of any chromatographic separation always to achieve baseline resolution of at least 1.5 between adjacent peak pairs. A summary of the number of peaks that could be counted when the different organic modifiers were used in combination with the different additives using the screening methods is presented in Figure 12a-b. Two peaks were considered separated if there was a valley between them. At this point in method development, the possibility for analytes to co-elute was anticipated. Of Overall, it was possible to count 18 peaks from the expected 29 peaks on the 2-PIC and 1-AA columns using ethanol and methanol. Acetonitrile as an organic modifier in both columns performed poorly compare to ethanol and methanol. To quantify the separation between peak pairs, resolution bar graphs for the

two columns were constructed and they are also shown in **Figure 12c-d**. Even though in the 1-AA column EtOH/0.1 % FA had 18 peaks, using MeOH/0.1% FA resulted in the highest number of peak pairs separated with a resolution of 1.5 and above (13). Similarly, in the 2-Pic column, MeOH/3% H₂O separated more peaks pairs (14) compare to other organic modifiers with a resolution of 1.5 and above. Therefore, the 2-PIC column was chosen for further method developmental work, because it had one more peak pair separated compare to 1-AA column. The third column, CSH-PFP was also tested, however, it performed considerably worse than the 1-AA or 2-PIC columns

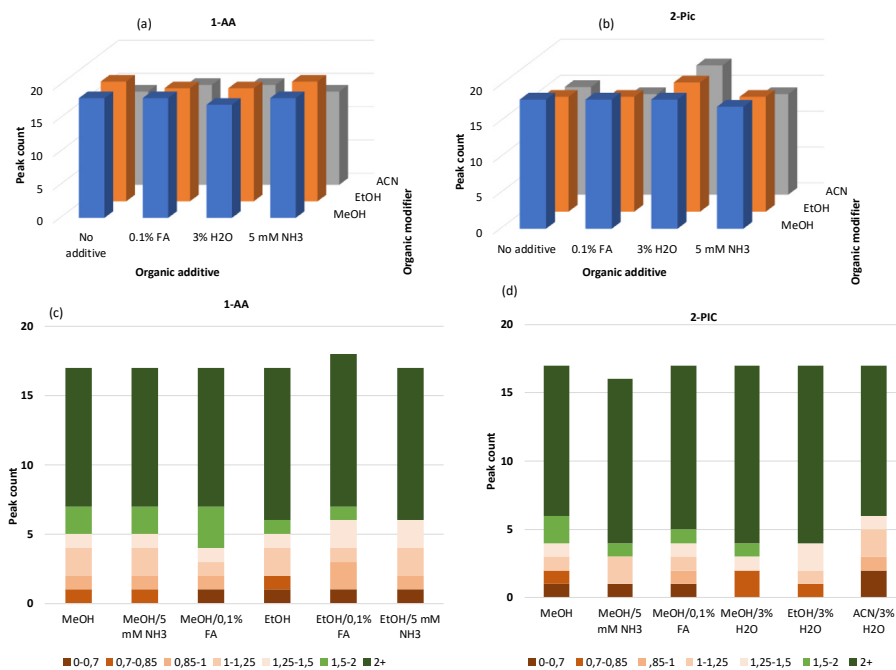


Figure 12. Resolution graph for column screening, organic modifier and additive. The y-axis shows the number of peak pairs separated with a resolution indicated by the colour.

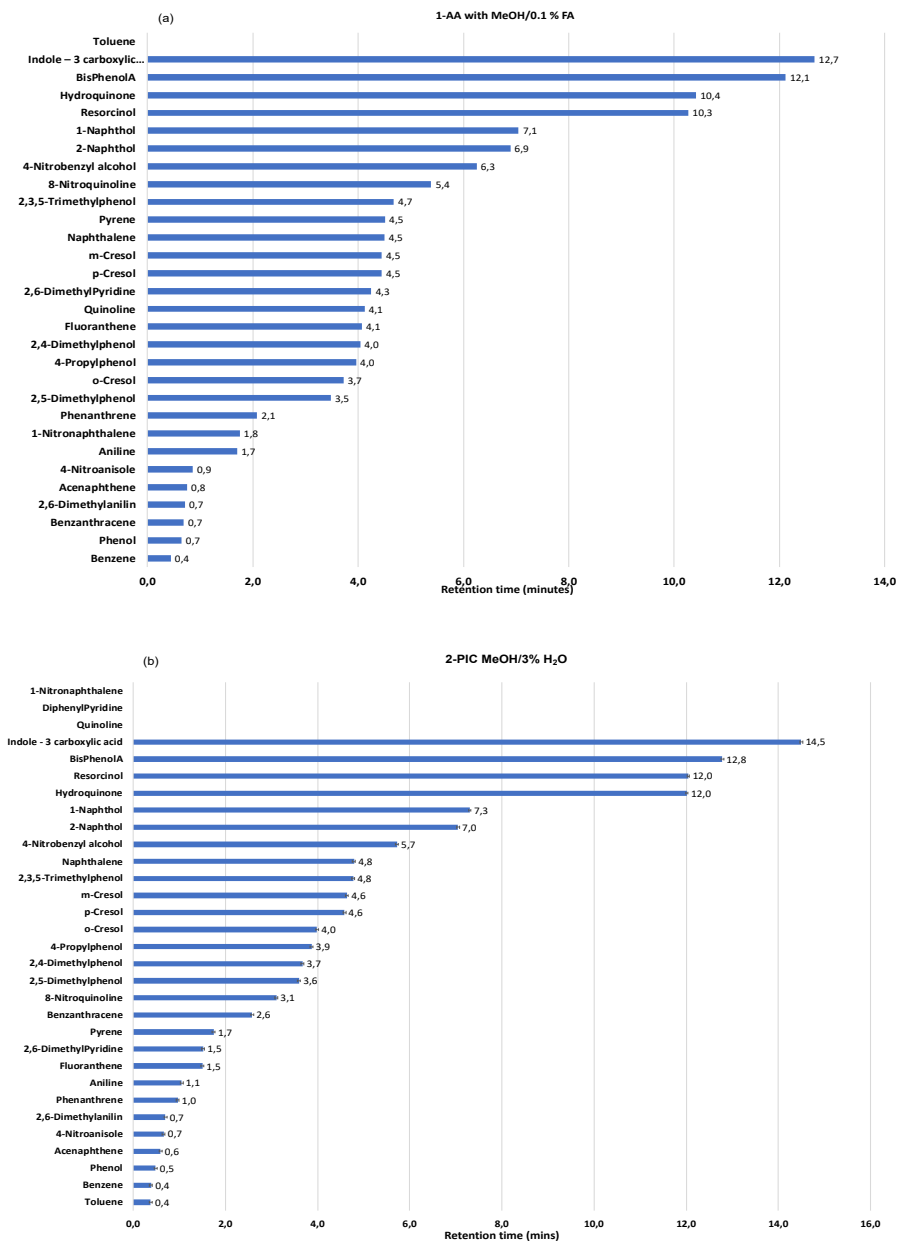


Figure 11. Graph showing the retention times of the individual standard analyzed by acquired using SFC-DAD on the (a) Torus 1-aminoanthracene (1-AA) with MeOH/1 % FA as organic modifier and (b) Torus 2-picolyamine (2-PIC) with MeOH/3 % H₂O as organic modifier. Chromatographic conditions: backpressure of 140 bar, temperature of 30 °C, flow rate at 1.60 mL/min, gradient elution from 0.1 to 15% of modifier in 17 min, injection volume of 2.0 µL, and detection wavelength set at 254 nm.

In order to improve the retention of analytes in the column, the density and initial mobile phase composition had to be optimized. Therefore, Box-Behnken design was used with the aim of optimizing column temperature (15-50 °C), flow rate (1-2 mL/min), starting isocratic time (1-5 minutes), gradient time (5-15 minutes), final organic modifier % (10-20) and backpressure (90-140 bar). It was not possible to model the resolution because of the co-elution observed under many conditions. Even with increasing the column length from 10 cm to 15 cm (Figure 12) did not improve the retention of early eluting peaks or improve the resolution between adjacent peaks. A possible reason for low retention of certain analytes is high injection solvent strength which prevented analytes from interacting with the stationary phase. Hence, changing the density of the mobile phase and initial mobile phase composition was not able to improve the retention of these compounds.

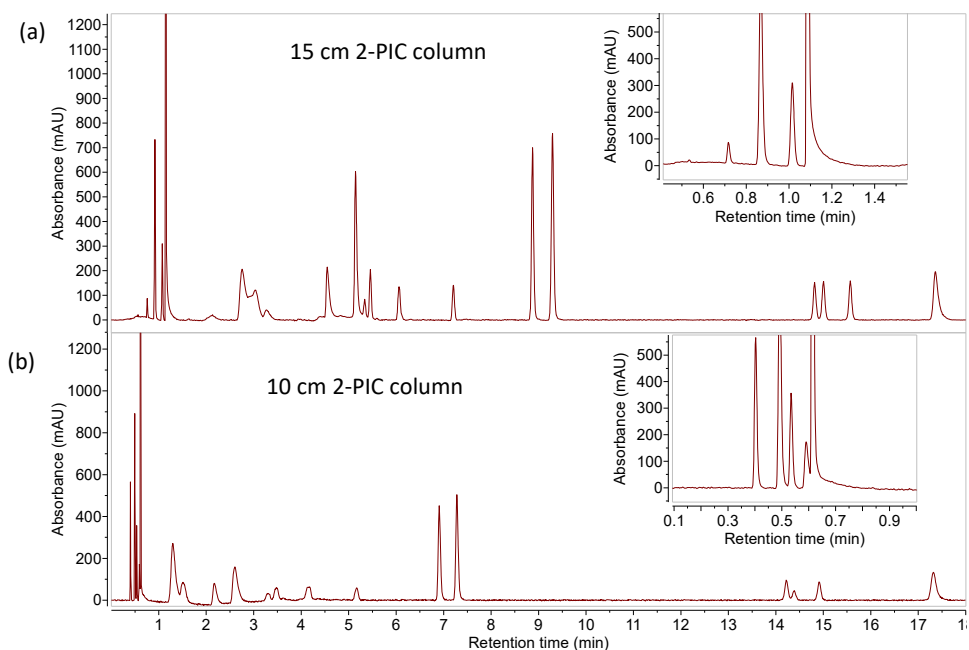


Figure 12. Graph showing the retention times of the individual standard analyzed by acquired using SFC-DAD on the (a) Torus 1-aminoanthracene (1-AA) with MeOH/1 % FA as organic modifier and (b) Torus 2-picolylamine (2-PIC) with MeOH/3 % H₂O as organic modifier. Chromatographic conditions: backpressure: 140 bar, temperature: 30 °C, flow rate: 1.60 mL/min, gradient elution from 0.1 to 15% of modifier in 17 min, injection volume: 2.0 µL, detection wavelength: 254 nm. The red box shows the region with multiple coeluting analytes.

5.2 Mass spectrometry

Mass spectrometry separates ionized compounds based on their mass-to-charge (m/z) ratio. For example, analytes that coelute in a UV detector can be separated by mass spectrometry if they have different mass-to-charge ratios. As already shown in the previous section, separation of the majority of the analytes was not achieved chromatographically, thus mass spectrometry was used to improve the selectivity of the method.

The selection of the ionization source and the m/z analyser must be carefully chosen depending on the analytes to be determined. A commonly used ionization source to ionize polar compounds is the electrospray ionization (ESI) [131], while atmospheric pressure chemical ionization (APCI) is mostly employed for the ionization of analytes with relatively lower molecular weights and semi-polar units. Non-polar to semi polar compounds can be best ionized by APPI [132]. In this thesis, ESI and APCI ion sources were available to use with quadrupole time-of-flight mass analyser (QTOF). At this point, the main focus was to choose the ionization source that will be able to particularly ionize compounds that were co-eluting from the chromatographic column. In addition, the coal extract most probably contains a mixture of polar to non-polar compounds.

Comparison of ESI and APCI in negative and positive mode using direct infusion was carried out. Aiming to enhance ionization, experiments were carried out utilizing MeOH as makeup liquid with FA, AmF and ammonia additives. Mass spectra were recorded at different settings of the ion sources such as flow rate of the makeup liquid, ion source temperature, cone voltage and corona current. The following information was gathered from the experiments:

- ESI in negative mode was able to ionize some monoaromatic phenolic compounds such as resorcinol and monoaromatic nitrogenated compounds with AmF as the additive in MeOH. In total six compounds could be ionized with an intensity above $4.03 \times 10^{+3}$.
- APCI on the other hand was found to be able to ionize PAHs, oxygenated PAHs such as naphthalene and pyrene, mono and polyaromatic phenolic compounds as well as mono aromatic nitrogenated aromatic compounds, also in negative mode. In total thirteen compounds could be ionized with an intensity above $4.03 \times 10^{+03}$

Based on the results, it was still a challenge to have an SFC-DAD-QTOF method that would be able to separate and identify the range of analytes chosen for this study. Our observations regarding the ionization of oxygenated aromatic compounds by ESI corroborate with the findings of Lubeck et al., (2019) [122]. Moreover, our method includes additional nitrogenated aromatics in the analyte list as well, as it was proven to be able to detect PAHs by MS. In short, our method has shown great potential with APCI as ionization source. Furthermore, detection limits could be improved by using triple quadrupole mass spectrometer (QqQ) instead of the QTOF by using multiple reaction monitoring (MRM) to reduce interferences and provide higher selectivity compared to QTOF.

6 Conclusion and future work

The primary objective of this thesis was to develop fast and environmentally sustainable methods for desulfurization and demineralization of coal from the Morupule mine as the case study.

In the study described in **Paper I**, water with ethanol as the co-solvent was investigated under subcritical conditions of water (100-180 °C) and 105 bar for extraction of total sulfur and mineral matter. The results showed that aqueous ethanol significantly reduced the sulfur content in coal. At optimum conditions (temperature = 129 °C, ethanol = 10%, extraction time = 10 minutes), a 79% reduction was achieved. The reduction in mineral matter reported as ash was only 5 % at the optimized parameters (10 % ethanol in pressurized hot water at 152 °C within 30 minutes). The study shows that the optimum conditions for the extraction of sulfur are not optimum for reducing ash. The removal of ash is poor; therefore, the experimental domain needs to be expanded. The increase of temperature may improve the extraction of mineral matter, but it may result in the thermal decomposition of the coal matrix if it is too high.

In **Paper II** supercritical CO₂ with ethyl lactate as a co-solvent was investigated for coal's desulfurization and demineralization (ash reduction) before combustion. Temperature was found to positively influence the extractability of total sulfur. The optimum parameters were determined to be scCO₂ with 5 vol% ethyl lactate at 300 bar and 80 °C for 15 minutes. The total sulfur content was reduced from 1.90 to 0.13 wt%. EL showed higher efficiency for desulfurization as a co-solvent in scCO₂ compared to methanol as a co-solvent [55]. The consumption of organic solvent is also reduced and the extraction time is shorter with less steps involved compared with methods in literature which are reported to be efficient [41, 50, 133, 134]. The efficiency of scCO₂ with EL outperforms the aqueous ethanol method developed in **Paper I**.

The physicochemical studied done in **Paper III** to assess the effect of desulfurization methods in **Paper I-II** shows Overall, the two methods have similar effects on the raw coal. Additionally, the properties of the raw coal were slightly improved. In addition to the reduction of the sulfur content, the thermal decomposition and burnout temperatures were decreased to a more considerable extent compared to the

combustion temperature and the temperature at which maximum conversion of coal occurs. The calorific value, fixed carbon and volatile content have also increased and these parameters are all important in the combustion efficiency of coal.

6.1 Future work

There is still a lot of research work needed on this topic.

1. The design space for the extraction methods needs to be expanded, especially since some optimum conditions were at the maximum setting.
2. There is still a need to find a green solvent for demineralization, and it would certainly be a good idea to explore ionic liquids.
3. A thorough separation and identification method for compounds in the extracts was lacking in this thesis. Exploration of other columns and clean-up method needs to be developed.
4. Finally, further studies need to be performed to determine the energy demand for both desulfurization methods and compare the applicability on a large scale and financial implications.
5. It was observed that the nitrogen content in the extracted coal was higher than in the raw coal. This poses another problem of NO_x emission during combustion. As such, for the future, it would be wise to investigate the extraction of sulfur and nitrogen.

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