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Solvent Extraction of Coal: Influence of solvent chemical structure on extraction yield and product composition

by

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DEDICATION

To my Mom who gave me the push I needed to follow my dreams

To my Dad who supported me

To my Sisters who always encouraged me

To Roberto who was next to me from beginning to end

ABSTRACT

In recent years the need for new carbon sources to supplement crude oil for the production of fuels and chemicals, again focused on coal as suitable candidate. Old and new technologies are being developed to convert coal in valuable products. An old technology such as solvent extraction of coal is again attracting industry attention. Despite being a widely studied technology, several questions remain unanswered. The present work aims to set the basis for further understanding of the solvent role. Physical and chemical properties reported in the literature, each one related to the solvent functional group, were put to the test. At low temperature, chemical structure of the solvent and its polarity are the most important properties for obtaining high extraction yields. At high temperature, solvents with high hydrogen donor ability give the highest extraction yields. Further investigation is needed to establish the influence of the solvent functional group on product composition.

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LIST OF SYMBOLS

AN: Electron acceptor number
Ash: Ash content (%)
CED: cohesive energy density
DN: Electron donor number
EY: Extraction yield (%)
FC: Fixed carbon (%)
M: Mass (g)
Moisture: Moisture content (%)
P: Internal pressure
R: Universal gas constant
SW: sample weight (g)
T: Temperature
V: Volume
VM: Volatile matter content (%)
W: Weight percentage (%)
δ: Solubility parameter ($\text{MPa}^{1/2}$)
ΔE: Internal energy
ΔH: internal enthalpy
ΔH: Total donor-acceptor energy of interaction (Kcal/mol)

Subscripts

ash: Ash
beads: Agitation beads
C: Carbon
coal: Coal
cont: Content
emp: Empty
f: Final
F: Flask
full: Full

m: moisture free coal

m: molar

MR: Micro-reactor

N: Nitrogen

o: Initial

O: Oxygen

raw: Raw

res: Residue

S: Sulphur

solv: Solvent

v: vaporization

1: Species 1

2: species 2

INTRODUCTION

In recent years the rising consumption of energy and chemical feedstocks of the world has greatly increased oil prices. This has renewed the interest in alternative carbon sources, such as coal. This natural resource is widely distributed and its reserves are large, attracting the attention of the industry. The aim is to develop economically feasible processes to convert coal to more valuable products.

Solvent extraction of coal is one option to achieve the proposed objective. The process consists of using an organic solvent to solubilise the coal molecules; yielding hydrocarbons with lower molecular weight. In previous works solvents providing high extraction yields have been proposed. Attempts to explain why these solvents are the most suitable for the process have also been made; however, success has been limited. The most important properties, so far identified, are: polarity and chemical structure, hydrogen donor ability, electron donor number and viscosity.

One would expect to find plenty information regarding the influence of the solvent chemical structure on the extraction of coal process. However, some of the previous correlations are not as accurate as desired, and will be further discussed through the present work. Regarding the quality of the products obtained, information about its composition is very difficult to find. The present work aims to provide information regarding the effect of the solvent functional group on the solvent extraction of coal; specifically about the extraction yield and product composition.

The conditions at which solvent extraction of coal is performed, greatly influences the extraction yield and the products obtained. For this work, extraction was performed in batch reactors, built of stainless steel. Solvent and coal mixtures were heated to the extraction temperature, using a fluidized sand bath. Initially, solvent extraction was performed for coals varying in rank. After analyzing these results one coal was selected to continue the study using different solvents: tetralin, quinoline, 1-naphthol and one industrial solvent. The selected coal was the only to provide favourable results when extraction was performed at low temperatures. All experiments were carried out under inert atmosphere (N_2).

The present work is comprised of 5 chapters. The first chapter contains the problem statement, and it is followed by the bibliographic review presented in chapter

II. Chapter three and four contain the experimental method and the experimental results, respectively. And finally, chapter V presents the discussions, followed by conclusions and recommendations.

Industrial application of solvent extraction of coal is an option that nowadays seems feasible for different companies. However, developing this new technology requires a complete understanding of the solvent extraction of coal process. This work will provide valuable information primarily regarding the selection of solvent and temperature of extraction. It will also aim to prove some theories found in literature, regarding the solvent properties that are most important for the process. In summary, the present work will set the basis for the understanding of the solvent functional groups and the role of its physical chemical properties in the solvent extraction of coal.

CHAPTER I:

PROBLEM STATEMENT

The following section explains the current issues in the process of solvent extraction of coal that require further investigation. A concise and brief description of the problem that leads to this investigation is given, as well as the objectives, justification and limitations of the present work.

1.1 Problem description

Increasing demand of transportation fuels has driven the research efforts towards coal upgrading technologies. Alberta's coal reserves have attracted the attention of the industry, promoting research and development in pursuit of profitable processes to convert coal into more valuable products. Obtaining liquid products form solid coal is the main issue of interest.

The main approaches for direct coal liquefaction are pyrolysis, solvent extraction and catalytic liquefaction. In pyrolysis coal is rapidly heated up to 450 ^{o}C, in presence of hydrogen. The rapid heating, fragments the coal molecules and hydrogen is used to stabilize these fragments. When milder conditions are used, in order to obtain liquid hydrocarbons, the conversion is typically between 30 and 50 %. (1)

Liquefaction techniques involve a catalyzed interaction between molecular hydrogen and coal-oil slurries. This process requires elevated temperatures and pressures. (1)

Solvent extraction of coal has been under study for several years. The extraction aims to recover different components from the coal of diverse molecular weight, generally by means of extraction by an organic solvent in a batch or semi-batch reactor. Some researchers have worked with mixtures of organic solvents, seeking to increase the amount of liquids extracted. The reason for using mixtures is to exploit a combination of different solvent properties. The most important properties, so far identified, are: polarity and chemical structure, hydrogen donor ability and electron donor number and viscosity. The cost and safety risks of using hydrogen to obtain coal liquids can be reduced by making use of solvent extraction with hydrogen donor solvents, under inert atmosphere (N_2).

Extraction of coal may be performed at different conditions, which depend on coal properties and the purpose of the process. Low temperature extraction (< 350 °C) aims to release the low molecular weight structures trapped in the coal matrix, by swelling and solvating the coal; in order to achieve high extraction yields. Aromatics and hydroxylated aromatic solvents may be used for this purpose (1). High temperature extraction (> 350 °C) involves free radical reactions, where new molecules are formed. The free radicals formed during high temperature extraction need to be stabilized before recombining, to avoid products with high molecular weight, which reduce the extraction yield. For this purpose a hydrogen donor solvent or hydrogen atmosphere is useful (1).

A full understanding of the dissolution mechanism is necessary in order to select the appropriate conditions and solvents for each type of coal. Relationships between coal properties, solvent functional groups and reaction conditions have to be established in order to be able to predict the system behaviour.

For many years researchers have attempted to correlate solvent and coal properties in order to predict extraction yield. However, as it may be seen in different works (2) (3), these correlations often show scatter. This scatter indicates that more than one property affects the results. Even those seemingly perfect correlations (4) (5) (6) that are found for specific solvent-coal systems are system specific. As will be further discussed in this work, those correlations will not provide generally useful information, unless the role of the property in the process is well understood.

1.2 Problem formulation

Although many studies in solvent extraction of coal have been made, there still are several questions without answer. Since the knowledge of the fundamentals of the solvent extraction of coal process is incomplete, more information in this regard will improve the application of the process at industrial scale.

1.2.1 Current situation

There is little knowledge of the physical chemical mechanism by which the solvent is able to extract low molecular weight material out of the coal matrix. If the process is completely understood, then more efficient processes may be designed, making them profitable at industrial scale. Chapter II gives a detailed overview of the current situation and improvement opportunities are pointed out.

1.2.2 Desired situation

Improved knowledge of the physical chemical process of solvent extraction of coal will allow the determination of the most appropriate solvent chemical structure. Once it is known how each solvent functional group affects the process, the right solvent or solvent combination may be selected in order to design the most profitable process.

1.3 Objectives

1.3.1 General objective

Understand the role of the solvent functional groups in the physical chemical mechanism of solvent extraction of coal at temperatures of 400 °C and lower.

1.3.2 Specific objectives

- Observe the coal rank influence on the solvent extraction of coal at low temperatures (below 300 ^{o}C), to select the most appropriate coal rank.
- Examine the temperature influence on the solvent extraction of coal, to provide a solubility curve of coal in a given solvent at different temperatures.
- Observe the influence of the functional groups of the solvent on the extraction yield, to gain understanding of their role in the process.
- Determine the influence of the functional groups of the solvent on the extract composition, to gain understanding of their influence on the final product.

1.4 Justification

The present work will set the basis to further understanding of the solvent extraction of coal mechanism, by establishing fundamental knowledge on the effect of the functional groups in the solvent. This will allow the rational selection of the most effective functional groups in the solvent and the systematic evaluation of the combined properties of solvent mixtures.

Once enough knowledge on the fundamentals of the solvent extraction of coal process is gained; an improved design may be proposed.

1.5 Limitations

The main limitation of this research was the experimental set up employed for the reactions. It consists of four batch micro-reactors that are submerged in a fluidised sand bath at the reaction temperature for the reaction time. This setup did not allow the study of short contact time reactions due to the heating time required for the reactors to reach the reaction temperature. However, during the study it became clear that it is necessary to investigate short contact time extraction in order to provide answers to some questions, regarding the mechanism of extraction at low temperatures.

It was impossible to separate the extraction solvent from the coal extracts with the techniques available. The high concentration of the solvent made difficult the detection and identification of the principal components extracted from the coal.

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CHAPTER II:

BIBLIOGRAPHIC REVIEW

This chapter conveys current knowledge regarding coal structure and composition that will influence the present work; gives an introduction of the solvent properties that are reported to play an important role in the solvent extraction of coal. Information from previous investigations, which set the basis for the development of the present work, will also be presented.

2.1 Coal composition

Solvent extraction of coal depends on coal and its properties. Since coal was formed in different places by a wide variety of components, their properties greatly vary from one to another. The main properties used to characterize coals are its physical composition, its chemical composition and its rank classification.

2.1.1 Physical composition

The different petrographic components of the coal are called macerals, which are characterized by their appearance, chemical composition, and optical properties. Macerals may be linked to components of plant debris from which the coal was formed. They are classified in three groups, each one with a variety of sub-classifications or microlithotype groups (1). The main maceral groups are: Vitrinite, Exinite and Inertinite.

A more methodological study was conducted in the late 1930, giving valuable information about the reactivity of the coal macerals for coal hydrogenation. The experiment consisted of keeping the coal, the solvent (1, 2, 3, 4, tetra-hydronaphthalene) and a catalyst (stannous sulphide) in a batch reactor, pressurized with hydrogen to 1,000 psi (7 MPa), at room temperature for three hours. The experiment showed that fusains (macerals belonging to the inertinite maceral grouping) are not entirely inert; but the oil yield obtained from it was very low in comparison to the whole coal or other macerals. Vitrinites were found to be readily liquefied and almost completely converted to pitch. It was reported that the opaque attritus (micrinite, which is a maceral belonging to the inertinite maceral grouping) is more resistant to hydrogenation than inertinite in general. (1)

These findings showed that the petrographic composition may be used to select appropriate coals for the solvent extraction of coal process.

2.1.2 Chemical composition

The chemical composition of the coal is defined by its ultimate and proximate analyses. These analyses do not offer any information about the coal structure, but the data can be correlated with most facets of coal behaviour. (2)

Proximate analysis gives information about the coal moisture, ash and volatile matter contents. Indirectly it gives the amount of fixed carbon. The American Society for Testing and Materials (ASTM) established standards for the proximate analysis of coal, which will be further discussed in chapter III.

The moisture content includes bulk water and physically adsorbed water. The first is contained in large cracks and capillaries, while the later is in the small pores and has a vapour pressure corresponding to its adsorbed state (2).

The volatile matter varies with the rank and petrographic composition of the coal. It consists of a wide spectrum of hydrocarbons, carbon monoxide, carbon dioxide and chemically combined water.

Ultimate analysis gives information about the elemental composition of coal: carbon, hydrogen, nitrogen, sulphur, and oxygen (by difference).

2.1.3 Coal classification

Classification of solid fuels as peat, lignite, subbituminous coal, bituminous coal and anthracite resulted from the obvious differences in their burning characteristics. This classification attempts to organize the fuels by one significant property, in this case petrographers used the degree of metamorphosis of the plant debris. (1)

Since the composition of the coal is so important and variable, table 2.1 shows the ultimate and proximate analyses for the different coals.

2.2 Dissolution process

Dissolution processes may be purely physical or may involve some chemical reactions that affect the solute and solvent properties.

Table 2.1

Ultimate and proximate analysis of different coals

Coal	Rank	Elemental composition (% daf)					Ultimate analysis (%)		
		C	H	N	S	O*	Ash	Moisture	Volatile
Tunçbilek 1 (3)	Lignite	77.7	5.6	3.0	2.1	11.5	_	_	_
Yatağan (3)	Lignite	62.4	5.3	1.6	3.4	27.4	_	_	_
Zao Zuang (4)	_	86.9	5.1	1.5	1.6	4.9	7.4	dry basis	28.6
Neyveli (5)	Lignite	62.0	5.0	2.0	1.4	29.6	2.9	8.2	54.3
Assam (5)	Bituminous	78.1	5.8	1.5	0.9	13.7	2.2	4.0	42.0
Samla (5)	Bituminous	78.7	5.3	2.6	0.6	12.8	14.3	6.6	32.6
Chinakuri (5)	Bituminous	78.5	5.5	2.4	0.5	13.1	13.6	5.1	32.9
Pasang (5)	Bituminous	76.5	5.0	1.5	1.0	16.5	13.3	6.3	31.9
Topa (5)	Bituminous	82.5	5.0	1.6	0.4	10.5	32.7	0.7	26.1
Godavari (5)	Bituminous	85.8	5.0	2.0	1.0	6.2	17.7	5.3	30.8
Kuzu (5)	Bituminous	74.3	4.6	2.0	0.9	18.2	13.6	2.8	27.8
Loiyo (5)	Bituminous	88.9	6.5	3.2	0.4	1.0	19.4	1.0	26.2
North Tisra (5)	Bituminous	90.9	5.3	2.4	0.9	0.5	36.2	1.8	20.7
KPD (5)	Bituminous	72.2	4.9	1.6	1.3	20	40.5	3.0	26.2

*O is calculated by difference

2.2.1 Physical dissolution

In order to obtain a solution a physical dissolution process must take place. This process consists of the isolation of the atoms or molecules composing the solute, by being surrounded with solvent molecules.

There are different ways to classify the solutions. One of them takes into account the relation between the amount of solute and solvent: unsaturated, saturated and supersaturated. This classification shows that a given amount of solvent is able to dissolve only a certain amount of solute at certain temperature and pressure conditions. This value is indicated by the solubility constant.

Depending on the type of dissolution that one is dealing with, there are different conditions that may affect the dissolution rate, those are the following:

- Particle size
- Temperature effect on solubility
- Kinetic energy

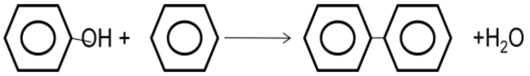
2.2.1.1 Physical dissolution of coal

Coal is a complex substance composed by several hydrocarbons molecules with different physical properties. Dissolution of coal is governed by the extraction of those components, and as every dissolution process, is expected to be affected by the factors mentioned above.

Coal dissolution processes that are entirely physical take place at temperatures where no chemical reaction occurs. It is said that below 350 °C there is no chemical decomposition in bituminous coals (250 °C for lignites), however the process is far more complex and several regimes can be identified. It is important to mention that the temperature for each regime depends on coal rank.

For most coals, below 200 °C little chemical activity is detected. Here, small quantities of chemically bonded water, oxides of carbon and hydrogen sulphides are released. Also some detachment of functional groups (2.1) and condensation reactions (2.2) take place.(2)

(2.1) (2)



(2.2) (2)

When the temperature is kept between 200 and 350 °C, the predominant reactions are benzylic carbons forming methyl phenyl derivates and evolving of traces of alkylbenzenes. There are not many studies in this temperature zone, but it is significant since it alters the original structure of the coal and influences its subsequent thermal behavior. In the case of solvent extraction, pretreatment of coal at 200 °C increases its solubility in organic solvents. This pretreatment also destroys caking properties of coals (2). Chemical reaction in this interval (below 250 °C) was reported for Zao Zhuang coal with deca-hydroantracene and hexa-hydroantracene (4).

The zone of active thermal decomposition is between 350 and 550 °C. (1) In this zone, the coal dissolution is strongly affected by the chemical reactions that take place. This regime will be discussed in section 2.3.2.

Low temperature regimes are often disregarded, and most authors consider only one low temperature regime by avoiding the zone of free radical formation: for bituminous coal below 350 °C (4) (9), while for brown coal below 250 °C (10). This includes errors in the analysis of the behaviour of coal during the extraction, since different regimes may alter the coal composition and properties (porosity, functional groups, among others), affecting the overall extraction results.

The mechanism by which the extraction of coal occurs at low temperatures is uncertain. It is said that solvents have the ability to relax coal molecules, disrupting weak linkages (3) (5) (11) (12). This allows small molecular weight components to go outside of the coal matrix and remain in the solvent, by means of physical interactions. It is expected that the law “like dissolves like” applies in solvent extraction of coal. Depending on the chemical structure of the solvent, some components of the coal will physically interact with it.

It has been mentioned that physical properties of the solvent such as viscosity and diffusivity play an important role. Mixtures of solvents have been reported to enhance the extraction yields by modifying the properties of the solvent mixture. It was found that small amounts of CS_2 in NMP reduce the viscosity of the solvent (13). This allows the solvent to penetrate the coal pores easily, dragging out low molecular weight molecules and increasing the extraction yield. However, these results may be influenced by other properties of the solvent mixture.

For every dissolution process where like dissolves like, polarity should be taken into account. This property seems to play an important role in the solvent-coal interaction for certain authors (11). For example, low rank coals contain several carboxylic and hydroxyl groups, lignites contain acidic and other polar groups. Polar solvents such as NMP interact with the polar sites of the low rank coal (C < 85%), giving good extraction yields (14). Mengen lignite gives a high swelling ratio with pyridine, due to the interaction with polar sites (3). According to the amount of polar sites in the coal, using a non-polar or polar solvent will help to qualitative predict the extraction yield.

2.2.2 Chemical dissolution

Chemical dissolution of coal can take place in a single phase (thermal decomposition), or involve interaction of the solvent with the coal. In the latter case the reaction is heterogeneous, the coal being a "solid" and the solvent a liquid.

Heterogeneous chemical reactions strongly depend on the contact surface area available between the solid and reagents. When the solid contains a high porous area, then the reaction takes place faster. It may also happen that the progressive reaction increases the porosity of the solid, making the reaction faster as times goes by. Conversely, some reactions may reduce the porosity of the solute by blocking the pores or increasing the viscosity, reducing the reaction rate. Usually, grinding the solute to small particle size allows faster reaction rates.

2.2.2.1 Chemical dissolution of coal

Chemical dissolution plays an important role in solvent extraction of coal. Some of the coal molecules are very large and cannot be physically dissolved due to its high molecular weight. However, thermal decomposition reactions produce molecules with lower molecular weight, which may physically interact with the solvent.

At high temperatures (350 - 550 ^{o}C) the active thermal decomposition regime is reached. In this region seventy five percent (75 %) of the volatile matter is released by the coal, including all tar, and lighter condensable hydrocarbons are evolved. It is important to mention that for solvent extraction of coal above 400 ^{o}C retrogressive reactions (free radical addition reactions) in the coal make it progressively less soluble. (1)

Most researchers agree that one of the chemical roles of the solvent is to donate hydrogen to stabilize the free radicals formed during the extraction at high temperatures (above 350 ^{o}C). These free radicals are formed due to the bond breaking of the coal molecules by thermal decomposition. Smaller new molecules are formed. And the larger and more stable molecules that cannot be broken or that are formed by retrogressive reactions remain un-extracted. Physical dissolution takes place in parallel.

Under inert atmosphere, there are two ways in which free radicals may be stabilized. First by hydrogen shuttling: the use of hydrogen from another part of the coal molecule, or another coal molecule to achieve self-stabilization. It may lead to the formation of more refractory coal molecules (If stabilization occurs by free radical recombination, larger coal molecules may be formed.). The second is hydrogen transfer form a hydrogen donor solvent. The last mechanism of stabilization leads to degradation of the solvent. (7)

When the reaction in a hydrogen donor solvent is allowed to continue for long periods, hydrogen is consumed to produce more benzene soluble products. On the other hand, it was proven that conversion decreases with residence time for the non donor solvents (15). The difference lies in the ability to donate hydrogen and stabilize the free radicals, that hydrogen donor solvents have. While non donor solvents, are not able to donate hydrogen, and the free radicals are only stabilized by hydrogen shuttling or recombination.

The chemistry of coal dissolution at high temperature is very complex and further understanding of the process is required to optimize the solvent extraction of coal. The most important advance made in this field is recognizing the role of donor solvents and the possibility of using non donor solvents, when extraction periods are short, despite obtaining lower extraction yields.

2.3 Solvent properties affecting coal extraction

Different approaches have been made to determine the properties of solvents that allow high extraction yields. Several researchers have been trying to correlate properties such as:

- Solubility parameter
- Hydrogen donor ability
- Electron donor number
- Polarity
- Chemical structure

The aim of the proposed correlations was to gain a better understanding of the coal dissolution process, by using the five properties mentioned above. Table 2.2 shows different properties for solvents commonly used in solvent extraction of coal.

The solvent extraction of coal is possible due to the ability of organic solvents to solubilise some of the coal components. Although the general process seems simple, several factors modify the dissolution rate and the process itself. When no reaction is involved, the dissolution takes place via physical interactions among solute and solvents. When reactions are involved, free radical formation and stabilization create new smaller molecules that are extracted from the coal matrix.

Table 2.1

Properties of solvents commonly used in solvent extraction of coal

Solvent	Empirical formula	Specific gravity (20/4)	Dipolar Moment	Dielectric Constant 20 °C	Solubility parameter	Electron donor number
tetrahydrofuran	C_4H_8O	0.89 (6)	1.75 (6)	7.60 (6)	9.10 (6)	20 (7)
pyridine	C_5H_6N	0.98 (6)	2.30 (6)	12.90 (6)	10.70 (6)	-
quinoline	C_9H_7N	1.09	-	8.6 0(6)	10.8 (8)	-
N-metyl-2 pyrrolidone (NMP)	C_5H_9NO	1.03 (6)	4.10 (6)	32.20 (6)	11.00 (6)	27.3 (7)

There are several properties of the solvent that may improve the extraction yield. It is important to identify those properties in order to select an appropriate solvent, according to the coal and the extraction conditions. So far some properties have been investigated, but no conclusive finding has been made.

2.3.1 Solubility parameter

The solubility parameter gives a numerical estimate of the molecular interaction between two non polar molecules. Several researchers have tried to find a correlation between this property and the extraction yield.

The solubility parameter may be calculated from the square root of the cohesive energy density (CED). Cohesive energy density is the energy needed to remove a molecule from its nearest neighbours, divided by the total volume of the moved molecule. This is a direct reflection of the strength of the Van der

Waals forces holding the molecules of the liquid together. The cohesive energy density is defined as (16)

$$CED = \delta^2 = {}^{\Delta E_v}/_{V} = \frac{\Delta H_v - R \cdot T}{V_m} \qquad (2.3)\ ^{(16)}$$

Where ΔEv and ΔHv are the internal energy and enthalpy of vaporization, respectively, and V_m is the molar volume. *R* is the universal gas constant. The cohesive energy density has the units of pressure or stress. (16)

The cohesive energy density and the internal pressure, *P* are interchangeable parameters, similar to the energies or forces at the surface of liquids, which describe the powerful cohesive forces that hold liquid together. Hence, the solubility parameter is the square root of internal pressure (16)

$$\delta = P^{1/2} \qquad (2.4)\ ^{(16)}$$

The solubility parameter may be subdivided into three independent components: dispersion forces ($\delta_{\,o}$), dipole moments (δ_p) and hydrogen bonding (δ_h). This subdivision is based on the notion that the polar interactions may be divided into contributions from the two phases in the same way as for the dispersion forces. This assumption can be criticized on theoretical grounds, but the division has been useful in practice and the parameters are available for several industrial solvents. (16) Table 2.3 shows some of the typical values of solubility for different liquids.

Table 2.2

Solubility parameters for various organic solvents at 1 atm (17)

Substance	T (K)	δ (MPa$^{1/2}$)
n-pentane	293.15	15.1
Toluene	293.15	18.2
Tetrahydrofurane	293.15	19.49

Adapted from Goharshadi, E.; Hesabi, M. 2004.

Some correlations with solubility parameter have been successfully made. Solvents with different chemical structure, but similar solubility parameter may give high extraction yield. For example pyridine (δ=21.9 MPa$^{1/2}$), phenol (δ =22.1 MPa$^{1/2}$) and thionyl chloride (δ =21.1 MPa$^{1/2}$) (7). This shows that solubility parameter may be one of the key properties of solvents to look at when selecting an appropriate solvent for coal extraction.

It is important to mention that solubility parameter cannot predict behaviours of solvents with negative deviations from Raoult's law (adhesive forces greater than cohesive). The later explains the invalidity of the parameter in substances that form hydrogen bonding.

As mentioned above, the correlations made using the solubility parameter prove that despite the different chemical structure of the solvents, solvents with solubility parameter similar to that of coal, may have a high molecular interaction with coal.

2.3.2 Electron donor and acceptor number

Organic media have very low dielectric constants, which cause a drastic reduction in the free ion concentration. In extreme cases, the particle interaction is described as Coulombic repulsion. The magnitude of the electrostatic repulsion depends on the particle charge. Particles may acquire electric charges in non-aqueous media by ion formation from surface group dissociation. This mechanism of particle charging is a consequence of an electron transfer between the particle surface and the liquid organic phase. The donor-acceptor concept approach to molecular interactions can be applied to this latter mechanism. This concept considers essentially Lewis acid-base interactions to be prevailing; as one specie donates electrons another accepts them. (18)

"The electron donor number is an indication of the tendency of a molecule to give away electrons in a reaction between electron donor and electron acceptor molecules. Experimentally, the electron donor number is taken as the enthalpy of interaction between a donor and a standard acceptor (SbCl,) in an inert solvent (1,2-dichloroethane). Donor numbers are in the range 0 - 60 kcal/mol." (18).

The electron acceptor number is an indication of the ability of the molecule for sharing or accepting an electron pair. "It is measured by NMR using the chemical shift of ^{31}P when the acceptor is brought into contact with triethylphosphine oxide ((Et),P=O). The dimensionless acceptor number scale is normalized: 0 for hexane and 100 for the 1:1 adduct formed between SbCl, and (Et),P=O in 1,2-dichloroethane. The acceptor number series contains both protic and aprotic liquids.” (18)

Finally, the total donor-acceptor energy of interaction (ΔH) between two amphoteric molecules would be given by equation 2.4.

$$\Delta \boldsymbol{H}_{\mathbf{1,2}} = \frac{(\boldsymbol{AN}_{\mathbf{1}}\boldsymbol{DN}_{\mathbf{2}})+(\boldsymbol{AN}_{\mathbf{2}}\boldsymbol{DN}_{\mathbf{1}})}{\mathbf{100}} \qquad (2.5)^{(18)}$$

where ΔH is given in kilocalories per mole, AN and DN are de acceptor and donor numbers, for species 1 and 2.

Table 2.4 shows the electron donor number for different organic solvents.

Table 2. 3

Electron donor and acceptor number for different organic solvents (7)

Solvent	Electron donor number	Electron acceptor number
n-hexane	0.0	0.0
benzene	0.1	8.2
tetrahydrofurane	20.0	8.0
pyridine	33.1	14.2
1-mety-2-pyrrolidinone	27.3	13.3

Adapted from Pullen, J. 1981.

“The electron-donor-acceptor (e-d-a) bonds are responsible for binding together the coal macromolecular network and extractable substances. A suggested mechanism for low temperature extraction involves an exchange reaction between a solvent molecule and one of the constituents of e-d-a complexes in coal. Therefore, the solvent exchange capacity depends on its donor and acceptor number. Weak linkages are disrupted and guest components are freed by the action of solvent on these bonds.” (3)

Different studies have shown a relation between the electron donor - acceptor number of the solvent and its ability to swell the coal (3). Expansion of the coal matrix by swelling makes the penetration of the solvent easier and allows the low molecular weight components to escape. Thus, swelling and extraction may be interconnected. The ability of the solvent to donate electrons helps it to interact with some acid sites in the coal matrix. Hence, the electron donor ability may be one of the key solvent properties to look at.

In order to obtain the best electron donor-acceptor interaction between coal and solvent, the energy of interaction must be determined. The limitation is given by the difficulty of determining the electron donor-acceptor number of the solid component (18)

The nature of the interaction also limits the benefit it brings to solvent extraction of coal. Only a certain amount of coal may be extracted trough this interaction, once the weakest bonds are disrupted, there will be no further extraction.

2.3.3 Hydrogen donor ability

Hydrogen donor ability of the solvent becomes important at high temperatures in the active thermal decomposition regime. When the extraction is performed at low temperature, the donor ability of the solvent does not affect the extraction yield (19) (20).

To experimentally determine the hydrogen donor ability of a compound, a hydrogen acceptor compound has to be used. After reaction between the donor and hydrogen acceptors, the amount of hydrogen transferred may be calculated by the concentration of the products. Limitations of this method are that it relies on the acceptor ability of the selected compound and the accuracy of the methods used to determine the concentration of the products.

The chemical reaction is represented by equations 2.6 to 2.8. First the solvent reacts with a free radical from the coal, producing free radical solvent specie.

$$\text{Solvent-H}_2 + \bullet\text{Coal} \rightarrow \bullet\text{Solvent-H} + \text{Coal-H} \qquad (2.6)$$

After, the solvent then stabilizes itself by donating another hydrogen atom to another coal-derived radical and forming a double bond in the solvent.

$$\bullet\text{Solvent-H} + \bullet\text{Coal} \rightarrow \text{Solvent} + \text{Coal-H} \qquad (2.7)$$

where •Solvent-H is the radical species of the solvent.

Hydrogen donor ability is associated with the difference in binding energies of the donor-solvent compound (Solvent-H_2) and its radical (•Solvent-H) formed by hydrogen donation. Thus, compounds with smaller values of binding energy form radicals more easily than those with higher values. This binding energy represents the bond dissociation energy of the hydrogen atom and the solvent. (21)

Researchers are able to determine how much hydrogen may be donated by a solvent, but how much hydrogen is needed by the coal is another issue. The relation between loss of donor-hydrogen from tetralin and the conversion of coal to benzene soluble material was studied by Neavel.(15) After 13 hours, hydrogen equivalent to 2.7 % of the d.a.f. feed coal was transferred from the donor to the coal. This is equivalent to 43 % of the hydrogen that can be donated by the solvent. The amount transferred apparently depends upon the extent of rupture in the coal (15). Sadly the author did not show any proof of the previous statement, which is then only an assumption. However, this could mean that the greater the formation of free radicals, the greater the hydrogen exchange.

The hydrogen donation process can only be sustained if there is enough solvent in relation to the coal, or if the solvent is re-hydrogenated. In order to reuse the solvent, the latter course of action is usually taken.

$$\text{Solvent} + H_2 \rightarrow \text{Solvent-}H_2 \qquad (2.8)$$

2.3.4 Polarity

Dipole moment is the total polarity of a non-charged molecule with polar covalent bonds, and it is related to the distance of the two charges. The net dipole moment of the molecule is related to its geometry and the presence of unbounded electron pairs.

To determine the total dipole moment of the molecule, the electric forces of each bond are added as vectors, considering the geometry of the molecule. Polarity is a key property to achieve a good interaction between molecules. Molecules with similar dipole moment will interact, while molecules with different moments will not.

Coal molecules are very complex and contain polar and non polar sites. This allows them to interact with either polar or non polar solvents; this interaction takes place with different magnitude depending on the coal composition.

A few authors have established differences between working with polar and non polar solvents (14) (22). For example, an increase in the nitrogen content in the solvent is reported to enhance extraction yield. They found that the role of the nitrogen is to promote the interaction with the polar sites of the coal. Denitrification (down to 0.16 %) of crude methylnaphthalene oil (CMNO) decreased the yield of extraction. The composition of the CMNO is: 91.14 % C, 6.66 % H, 1.78 % N, 0.30 % S, 0.12 % O (22). This finding might be an isolated case, since extraction yield did not reach the same value as that with CMNO, despite the similarity in the nitrogen content of solvent-additive mixture. Thus unknown factors may influence the results. They also mention that some polar compounds do not seem to give a significant increase in extraction yield. (22)

2.4 Solvent action

Now that the possible key properties of the solvent have been presented, it is necessary to know how the solvent physically and chemically interacts with the coal molecules.

2.4.1 Electron donor number

As it was mentioned in section 2.4.2, in the suggested mechanism for low temperature extraction, an exchange reaction takes place between the solvent and coal that involves electron donor and acceptor complexes.

Solvents with pairs of electrons available for coordination (O, N) have stronger interaction with coals. Different swelling ratios for the same lignite may be explained by inter- and intra-molecular interactions with the solvents. In a study pyridine gave the highest swelling ratio with all lignites due to the pair of free electrons on the nitrogen. An attempt to show the relationship between the swelling ratio of Tunçilek coal and the electron donor number of different solvents was made. But, the scatter in the data suggests that there are other properties of the solvent affecting the swelling ratio in addition to the electron donor number. (3)

2.4.2 Hydrogen donor ability

When solvent extraction of coal is conducted at high temperature, free radical formation occurs. These free radicals have to be stabilized, usually by means of hydrogen transfer from a hydrogen donor solvent. The hydrogen donation stops the reaction by keeping the free radical molecule at its original size and terminating the free radical. When hydrogen is not present, the free radicals will stabilize themselves, causing the formation of larger molecular weight compounds that are stable at the extraction temperature. Breaking these new molecules will not be possible without increasing the severity of the reaction.

Experiments show the influence of hydrogen donor ability in the solvent extraction of coal, using different solvents. (19) (23) Visually, the influence of the hydrogen donor ability of the coal was observed by the size of the coal particles, after the extraction. Tetralin and creosote oil are good hydrogen donors, producing smaller particles. Paraffin oil is the weakest hydrogen donor solvent, and larger particles may be seen. Decalin is an intermediate hydrogen donor solvent. (23) Most likely more than one factor adds up to obtain the results. The different composition of the solvents as well as their hydrogen donor ability may be involved. When comparing the results between tetralin and decalin, which have similar chemical structure, it is mainly the hydrogen donor ability of the solvent that affects the results.

Hydrogen donor ability is not important when reaction takes place in the low temperature regime for Pittsburg coal. It was proven that the yield of residue, soluble and deposit when reacting with tetralin (hydrogen donor) and 1-methyl-naphthalene (poor hydrogen donor) are very similar in both solvents (19). Since there is very little free radical formation, there is no need to use a hydrogen donor solvent to obtain molecules with low molecular weight.

2.4.3 Polarity

According to the polarity of the solvent, it will interact with the polar sites in coal. When liquefying a low rank coal with a large amount of carboxylic and hydroxyl groups, polar solvents will interact with those groups. When liquefying coals with small amount of polar groups, a non polar solvent will give better extraction yields. The simple principle behind this is “like dissolves like”.

According to the coal properties and composition, extraction yield might be predicted. A study tried to find a correlation between extraction yield of various coals (bituminous and lignites) with NMP (containing a small amount of ethylene-di-amine). This suggests that coals with a high volatile content and low oxygen content might give a higher extraction yield (5). However, the trend obtained is not conclusive and further experiments should be made to prove that statement. This is due to the influence of other coal properties that must be included in the correlation to get an accurate result.

Coals with high content in carboxyl and hydroxyl groups, may give high extraction yield with polar solvents. Usually these are low rank coals (C<85 %) like Banko, Beluah Zap, Wyoming, Tanito Harum, Illinois No 6 (14). As it was mentioned before, this is related to the premise "like dissolves like". Polar groups in the coal will readily interact with the polar group of the solvent; allowing the solvent to pull the molecule out of the coal matrix.

Table 2.5 shows the effect of the addition of a polar compound on the extraction yield using light cycle oil (LCO). Notice that ten parts of quinoline have the same effect as 1 part of 2-metylquinoline. There also seems to be an upper extraction limit. The data shows that not only the nitrogen content of the solvent or the polarity will improve the extraction yield, but also that there are other important properties involved.

Table 2.4

Effect of addition of various polar compounds to LCO on the extraction yield for Illinois #6 coal at 360 °C for 60 min in a flow type reactor (22)

Additive	Addition ratio (wt. %)	Extraction yield (wt. % daf)
Quinoline	1	52.0
	10	55.6
2-Napthol	1	51.3
2-metyl-quinoline	1	55.5

Adapted from Yoshida, T., Li, T. Takanohashi, A. Matsumura, S. Sato, I. Saito. 2004

2.4.4 Chemical structure

From general dissolution theories it is well known that solvents and solutes with similar chemical structures are able to interact, due to similar intermolecular forces. The same theory may be applied to the coal dissolution process. Solvent with functional groups that are in common with the coal matrix and with similar molecular weight will interact with those molecules in the coal.

As an example, Soxhlet extraction of Turkish lignites was performed using linear alkylamines (C_3-C_8). Extraction yield increased as the alkyl chain became larger. A larger carbon chain has a more similar structure to coal molecules, thus increasing the extraction yield (3). However, this statement might only apply to the Turkish lignites evaluated by the authors.

The observation discussed previously leads to the thinking: solvents with long hydrocarbon chains will give higher extraction yield. Since solubility is the inverse process of precipitation, solvent deasphalting shows the validity of the previous statement. When precipitating asphaltenes (defined as benzene soluble-pentane insoluble) the amount of insolubles obtained, varies depending on the carbon chain of the solvent used to precipitate the benzene soluble. When using propane, the amount of insolubles is remarkably higher than the amount obtained when using pentane, which is higher than the obtained when using hexane (28). Thus, the dissolving power of shorter chain paraffins is less than the larger paraffins.

2.5 Solubility

When a solvent reaches the maximum amount of solute that it may dissolve it becomes saturated and further dissolution will not occur. In the case of coal extraction, the appropriate coal to solvent ratio has to take into account the saturation point of the solvent. So far experiments have been carried out trying to prove that the process is suitable for industrial implementation, thus the smallest amount of solvent or the highest one have been studied. (24) (25) The lowest solvent to coal ratio reduces the size of the equipment, reducing the costs of building a plant for the process. The highest solvent to coal ratios were studied aiming to increase the extraction yield. But there is little or no information regarding the maximum solubility of coal in different solvents.

Commonly, solubility is affected by temperature and pressure (in the case of gases). Several researchers have shown that the influence of the N_2 pressure is negligible on the extraction yield, so it does not seem to directly affect the solubility of the coal in the solvent (19) (24).

Further information needs to be produced in order to understand the factors and the limitations of coal solubility in an organic solvent.

2.6 Applications of solvent extraction of coal

Depending on the reaction conditions, different products may be obtained from the solvent extraction of coal. Some of the applications found by different researchers are explained next.

2.6.1 Application of coal extraction without reaction

Researchers are trying to gain valuable information about the coal structure. In order to do this, they try to extract coal components without decomposition. This is achieved by low temperature extraction of coal. This way, they are able to look at the structure of coal components outside the matrix, making the analysis easier, by separating the complex structure in smaller components.

The same extraction conditions are being used to upgrade brown coal. There are large reserves of brown coal, but it cannot be used for other purpose than being burned to produce energy for the mines, due to its high water content. Drying brown coal makes it susceptible to self ignition, so another solution has to be found (26). One successful attempt was the successive thermal extraction of Loy Yang coal using tetralin, 1-methyl-naphthalene and water. The extraction was performed in batch reactors. These extractions were performed successively at different temperatures, taking advantage of the coal behaviour at each temperature regime. Successive temperature extraction is not the main objective of this study, but it illustrates the influence of temperature on the products of the solvent extraction of brown coal.

It was proved that the extraction of molecules with lower molecular weight occurs at the lowest temperatures (26). The average molecular weight of the extract increased as the temperature of extraction was increased. The fractions obtained were characterized to examine the possibility of their utilization, but no detail about the application was given.

2.6.2 Application of coal extraction with reaction

2.6.2.1 Ash free coal

Given the increase in the environmentally friendly awareness, reducing flue gas emissions from coal fired power plants is a must. One effective technology is the Combined Cycle, by firing the ash free coal directly into the gas turbine, where the heat of waste gases is used to produce steam that moves a turbine; increasing the overall efficiency of the power plant.

Ashless coal is needed for this process since ash and other by products of the combustion reaction cause damage to the turbine.

The conversion of coal to ash free coal takes place with a solvent under inert atmosphere, aiming to extract the coal, but leaving most of the sulphur, nitrogen and metal content in the residue. The solubilised coal is then precipitated. The extraction temperature is kept bellow 400 ^{o}C and relatively low N_2 pressure (1 MPa) is used (14) (22).

2.6.2.2 Anode for aluminum production

Manufacture of anodes for use in electrowinning of aluminum is one large scale use of carbon materials. Huge quantities of anode material are required each year, due to the aluminum demand (estimated in 39.25 millions of tons for 2011 (27)).

Ash from the anode carbon may contaminate the aluminum or the electrolyte, thus high purity carbon is required. Impurities such as vanadium and sulfur are harmful for the electrolytic process. Sulfur is also known to affect the reactivity of anodes. Phosphorous can undergo cyclic redox reactions consuming electric current without forming product.

Usually petroleum coke is used for carbon anodes if it can satisfy the low level of impurities required. New sources are under study, and clean coal obtained trough solvent extraction of coal is attracting industry interest.

2.6.2.3 Coal upgrading

Low rank coals are a potentially important energy resource because of their worldwide abundant minable reserves. Due to their high water content those coals are only used to produce energy near the coal mines. When water is removed from these low rank coals self-ignition takes place by re-adsorption of water and auto-oxidation. These disadvantages make it economically unfeasible to transport the coals as they are (high transport cost associated with the water) or in their dried form (danger of self-ignition) (22). This makes pre-treatment necessary to remove the moisture and upgrade the coal to a form that is not susceptible to self-ignition.

Currently there are different technologies being developed to achieve this objective. The preferred ones are those that do not involve high energy consumption. In this case the temperatures are kept below the active thermal decomposition regime, and extraction of water and ashes take place. (22)

2.7 Background remarks

Although many studies in solvent extraction of coal have been made, there still are several questions without satisfactory answers, regarding the mechanism of extraction at low temperature, the role of the solvent functional group at different temperature regimes, and the most influential solvent properties along the extraction process.

The functional group in the solvent will trend to interact with functional groups in the coal, meaning that different solvents will behave differently with the same coal. Understanding the interaction of the coal with the functional groups in the solvents will provide a theoretical basis to properly select one solvent or solvents mixtures for the extraction of coal. This rational selection process will translate into higher extraction yields and more valuable products with reduced trial and error experiments.

Once it is understood how the key properties of the solvents influence the extraction process of coal, qualitative predictive correlations may be generated. This will allow the right selection of coal-solvent pairs that lead to high yields of extraction. From an application point of view, industrial solvents may be selected, for each coal rank, based on their composition and properties in order to increase extraction yields making the process more profitable.

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CHAPTER III:

EXPERIMENTAL METHOD

The following chapter outlines the methodology that was followed in order to achieve the proposed specific objectives. The chapter also includes the materials, instruments and analytical methods used for this purpose.

3.1 Materials

1, 2, 3, 4 tetrahydro-naphthalene (Tetralin)

The solvent was used as provided by Sigma-Aldrich, ReagentPlus® 99 % purity. This light yellow liquid was used as the reference solvent, as it will be explained in section 3.4, due to the wide availability of information in solvent extraction of coal.

Its chemical structure is represented in figure 1.

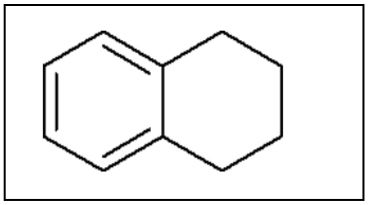

Figure 3.1. Chemical structure of 1, 2, 3, 4 tetrahydro-napthalene

This solvent is well known for its ability to donate hydrogen, ultimately forming naphthalene, according to the following chemical equation.

$$C_{10}H_{12} \longrightarrow C_{10}H_{10} + 2H \qquad (3.1)$$

Its popularity in the solvent extraction of coal is specifically due to its hydrogen donor ability, since hydrogen transfer is necessary to stabilize the free radicals formed by the thermal decomposition of coal.

Quinoline

This light pink liquid solvent was used as provided by Sigma-Aldrich, reagent grade 98 % purity. Its chemical structure is shown in figure 3.2.

This compound was used to study the effect of the aromatic nitrogen functional group and the solvent basicity in the solvent extraction of coal process.

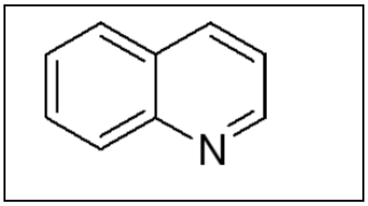

Figure 3.2. Chemical structure of quinoline

1-Naphthol

This colorless solid was used as provided by Sigma-Aldrich, ReagentPlus® 99 % purity. Its chemical structure is shown in figure 3.3.

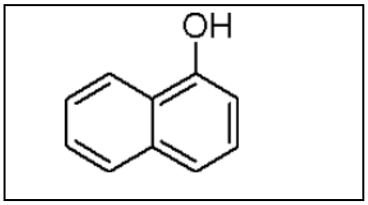

Figure 3.3. Chemical structure of 1-naphthol

This compound was used to study the effect of the hydroxyl group and the solvent acidity in the solvent extraction of coal process.

Toluene

Toluene certified ACS, 99 % purity, was used as provided by Fisher Scientific. This colorless solvent was used for extraction at 100 ^{o}C, as a good example of an aromatic solvent.

Heptane

Heptane certified, 99 % purity was used as provided by Fisher Scientific. This colorless solvent was used for extraction at 100 ^{o}C, as a good example of an aliphatic solvent. It was also used in a known volume, to obtain quantitative results from the GC/MS analysis of samples.

Methylcyclohexane

The solvent was used as provided by Sigma-Aldrich, ReagentPlus® 99 % purity. This colorless solvent was used for extraction of coal at 100 ^{o}C.

Tetrahydrofurane (THF)

This colorless liquid solvent was used to wash the coal residue and the micro-reactors. Fresh solvent as provided by Sigma-Aldrich, ACS reagent > 99 % was used.

HT-1006

This solvent consists of a mixture of hydrocarbons derived from coal, which afterwards was hydrotreated. It is a viscous liquid of dark brown color, as shown in figure 3.4. Little information about this industrial solvent was provided, however using a Varian GC-MS some components were identified. Among the components with the highest concentration were: o-xylene, hexahydroindacene, acenaphthylene, anthracene, 1,4-dimethylanthracene, fluoranthene, 1,2,3,4-tetrahydrochrysene, naphthalene, among several other structures. The solvent was used as provided by Sherritt Technology Inc.

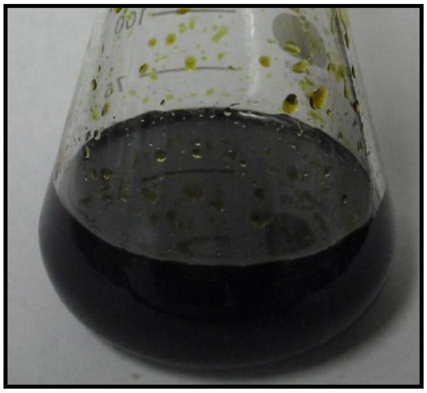

Figure 3.4. HT-1006 appearance

Table 3.1 summarizes some of the solvent properties that, according to chapter II, seem to play an important role in the solvent extraction of coal process.

Table 3.1

Relevant solvent properties

Solvent	Melting Point (°C)*	Boiling Point (°C)*	Dipolar moment	Solubility Parameter (cal/cc)$^{1/2}$
Tetralin	-	207	0	9.5 (1)
Quinoline	-	237	2.29 (2)	10.8 (1)
1-Naphthol	96	280	1.39 (3)	7.9 (1)
Toluene	-	111	0.36 (4)	-
Heptane	-	98	1.96 (5)	-
Metylcyclohexane	-	101	0	-
THF	-	65	1.75 (6)	9.52 (1)

*As indicated by the supplier

Carbon disulfide

Carbon disulfide anhydrous (> 99 %) was used as provided by Sigma Aldrich, to dilute the samples that were analyzed with the GC/MS.

Nitrogen

Nitrogen 4.8 pp (purity 99.998 %) as provided by PRAXAIR was used to remove the remaining air from the micro-reactors and to keep them pressurized to 4 MPa (2 MPa for runs at 100 ^oC) at room temperature. High pressures are required to maintain the solvent in liquid phase.

3.2 Coal Characterization

Four Albertan coals were provided by Sherritt Technology Inc. In crushed form in plastic buckets. Then, they were ground using a ball mill and stored in plastic bags that were refrigerated to avoid oxidation. Afterwards, the coals were sieved to obtain fractions with different particle size ranges. The samples for the micro-reactors were obtained from the 355-1000 µm fraction, using an aleatory sampler, in order to ensure that the samples were representative of the whole coal fraction.

3.2.1 Ultimate analysis

An Elementar Vario MICRO Cube was used to carry out the elemental analysis of the coal, performing the test fivefold with samples between 2 and 4 mg. The coal used for this analysis was previously dried using the ASTM D3173 - 11 standard (7), as explained in section 3.2.2.

Information regarding the oxygen content is determined using equation 3.2.

$$W_O = 100 - W_C - W_S - W_N \tag{3.2}$$

Where each term is oxygen, carbon, sulphur and nitrogen weight percent (daf), respectively.

3.2.2 Proximate analysis

Ash

Ash content of the samples was determined using the ASTM D3174 – 11 standard (8). An electric Barnstead Thermolyne 6000 muffle furnace with airflow of 20 slpm, was set to reach 450 and 700 ^oC following the time periods indicated by the standard.

The ash content of each sample was determined using the following equation:

$$\mathrm{Ash} = \frac{\mathrm{M_{ash}}}{\mathrm{SW_m}} \cdot 100 \qquad (3.3)$$

Where, SW_m is the initial weight of the moisture free sample used and M_{ash}.is the mass of the ash obtained.

Moisture

Moisture of the coal was determined using as a reference the ASTM D3173 - 11 standard (7). The oven used for this purpose was a Lindberg/Blue mechanical oven pre heated to 105 °C. Limitations in this test arise due to the unavailability of an oven with the inlet for the dry air source.

Moisture was determined using the following equation:

$$\mathrm{Moisture} = \frac{\mathrm{SW_o} - \mathrm{SW_f}}{\mathrm{SW_o}} \cdot 100 \qquad (3.4)$$

Where, SW_o and SW_f are the initial and final weight of the sample used, respectively.

Volatile matter

The ASTM D3175 - 11 standard (9) was used to determine the volatile matter content in the coal. However, instead of a vertical electric tube furnace, a muffle furnace had to be used for this purpose. The crucibles used were Fisherbrand nickel chromium.

The volatile matter content in the sample was determined using the following equation:

$$\mathrm{VM} = \frac{\mathrm{SW_o} - \mathrm{SW_f}}{\mathrm{SW_o}} \cdot 100 - \mathrm{Moisture} \qquad (3.5)$$

Where, VM is the percentage of volatile matter in the coal sample.

Fixed Carbon

Fixed carbon was determined using the following equation according to the ASTM D3172 – 07a Standard Practice for Proximate Analysis of Coal and Coke. (10)

$$\mathrm{FC} = 100 - (\mathrm{Moisture} + \mathrm{Ash} + \mathrm{VM}) \qquad (3.6)$$

Where, FC is the fixed carbon in the coal sample.

3.2.3 Petrographic analysis

The petrographic analysis of the coal samples was performed by Pearsons Coal Petrography, Ltd; using a sample obtained with a random sampler and with particle size between 250 and 355 µm.

A summary of the petrographic properties and composition of the Albertan coals is shown in table 3.2.

Table 3.2

Petrographic properties and composition of the Albertan coals

Description	Poplar (lignite)	Valley (subbituminous)	Genesse (subbituminous)	Teck (bituminous)
Ultimate analysis (wt % daf)				
carbon	44.60	72.40	63.29	79.4
hydrogen	3.47	5.10	3.97	4.48
nitrogen	0.69	1.10	1.07	1.46
sulfur	0.50	0.40	0.54	0.61
oxygen	50.46	21.0	31.13	3.83
Proximate analysis (wt %)				
moisture	28.70	5.47	8.92	1.90
ash	21.60	12.40	30.60	10.49
volatile matter	31.15	31.38	31.30	24.58
fixed carbon	18.35	50.75	29.18	63.03
Petrographic Analysis (wt %)				
vitrinite	57.20	67.8	65.20	52.0
liptinite	4.20	7.50	2.10	0.80
reactive semi fusinite	7.20	5.20	8.20	5.4
inertinite	31.40	19.50	24.50	41.80

3.3 Equipment

Reaction setup

The reaction setup consists of four micro-reactors, made with 1” nominal diameter of 316 L stainless steel seamless pipe and Swagelock fittings. The micro-reactors are attached via 1/8” nominal diameter stainless steel tubing to a holder with 1/8” needle valves, as shown in figure 3.5. One of the four sections was modified to introduce a type K thermocouple trough a ¼” 316 L stainless steel tubing. The thermocouple was installed in such a way that its bottom was aligned with the center of the micro-reactor.

The center of the holder adjusts to a rod that is connected to an eccentric motor, as shown in figure 3.5. The motor provides vertical agitation at a rate of 173 rpm. The micro-reactors are submerged in a Techne Fluidised Bath (SBS-4) with aluminum oxide. Temperature is controlled with a Techne TC-8D temperature controller.

Vacuum filtration

Vacuum filtration was used to separate the liquid from the solid phases after the reaction. Whatman fibre glass filter media with 1.0 µm pore diameter and a Welch Dryfast vacuum pump were used.

Vacuum oven

After filtration, solid samples were dried over night in a Stable Temp Cole-Parmer vacuum oven, to remove the remaining solvent. Temperature was kept at 80 ^{o}C, and vacuum at -14 inHg (-47.4 kPa).

Roto-evaporator

A Büchi Roto-vapor R210 was used to separate the washing solvent (THF) from the reaction solvent and the coal liquids. The oil bath was set to 55 ^{o}C and the vacuum to 260 mbar. The separation took place over a period of about 2 hours.

3.4 Procedures

The experimental process was composed by two different sections and more than one experimental method was tested.

3.4.1 Coal preparation

After milling the coals were sieved to obtain fractions with different particle sizes. For this study the fraction ranging from 355 µm to 1 mm was used. Samples of approximately 10 g were obtained using an aleatory sampler, in order to ensure that the sample was representative of the whole coal. The bituminous and subbituminous coals were dried over night in a vacuum oven at 80 ^{o}C and -14 inHg, before its utilization. Lignite was not dried, since removing the water may increase the cross-link strength reducing the extraction yield (11).

Figure 3.5. Left: Holder and micro-reactors. Right: Sand bath, motor and rod.

3.4.2 Method A

Sand bath was preheated to the reaction temperature.

2.7 g of coal (equivalent to approximately 2 g of dried coal) with a particle size ranging from 355 µm to 1mm, and 5 stainless steel beads (3/16” diameter and known weight) were introduced in each micro-reactor. Then 6 g of tetralin was added. The micro-reactor was closed and pressurized to 2 MPa or 4 MPa for runs at 100 or 300 ^{o}C, respectively, using as received nitrogen. A leak check was performed using Snoop from Swagelok. After fixing all the leaks, the gas in the reactor was released and refilled two additional times. Finally, the reactor was pressurized with nitrogen.

The holder and the reactors were later placed and their positions adjusted on the eccentric motor rod, in such a way that the upper section of the reactor was always submerged in the sand. The reaction was allowed to continue for the established period of time.

When reaction temperature was above 100 ^{o}C, reactors were cooled with air, down to approximately 100 ^{o}C. Afterwards, the nitrogen and reaction gases were released inside the fumehood by opening the needle valve attached to the holder. Then, the reactor cap was removed, and a blank end was used to keep the micro-reactor closed.

The solvent and coal mixture was then taken out of the micro-reactor and placed on the filter media, separating liquid from solid using vacuum. The reactor walls and the solid phase were washed with fresh tetralin until the liquid leaving the funnel was clear.

Un-extracted coal or residue, filter media and stainless steel beads were transferred to an alumina pan of known weight, and dried over night in a vacuum oven at 80 ^{o}C and -14 inHg. Liquid samples or extracts were stored in amber vials and were refrigerated.

Extraction yield was gravimetrically determined using equation 3.7.

$$\mathrm{EY}\ (\%) = \frac{\left(\mathrm{M_{Co_{Raw}}} - \mathrm{M_{Co_{Raw}}} \cdot \mathrm{Moisture} - \mathrm{M_{Co_{Raw}}} \cdot \mathrm{Ash}\right) - \left(\mathrm{M_{Co_{Res}}} - \mathrm{M_{Co_{Res}}} \cdot \mathrm{Ash_{Res}}\right)}{\left(\mathrm{M_{Co_{Raw}}} - \mathrm{M_{Co_{Raw}}} \cdot \mathrm{Moisture} - \mathrm{M_{Co_{Raw}}} \cdot \mathrm{Ash}\right)} \cdot 100 \qquad (3.7)$$

Were EY is the extraction yield in percentage of moisture and ash free coal, $\mathrm{M_{Co_{Raw}}}$ is the initial mass of coal, $\mathrm{M_{Co_{Res}}}$ is the mass of the coal residue and $\mathrm{Ash_{Res}}$ is the ash content in the residue.

3.4.3 Method B

Three modifications were made to the previous experimental method:

First: The sand bath was preheated from 10 to 20 ^{o}C above the reaction temperature, and the set-point was re-set to the desired reaction temperature only after the micro-reactors were submerged in the sand bath. Reaction temperatures for this study were: 25, 100, 200, 300, 350, 400 and 450 ^{o}C. (There was no preheating for the run at room temperature)

Second: Instead of washing the solid phase and the micro-reactor walls with fresh solvent, fresh THF was used.

Third: After filtration, a roto-vap was used to separate the washing solvent (THF) from the reaction solvent and the coal extracts. The oil bath was set to 55 ^{o}C and the vacuum to 260 mbar. The separation took place over a period of about 2 hours.

This method was used for all the solvents in study: tetralin, quinoline, 1-naphthol, toluene, heptane, metycyclohexane and the industrial hydrotreated solvent (HT-1006).

3.5 Analytical testing

3.5.1 Element analysis

An elementar Vario MICRO Cube was used to perform the elemental analysis of the residue, the test was performed by threefold or fivefold with samples between 2 and4 mg.

3.5.2 Pore size distribution

A Quantachrome PoreMaster® mercury porosimetry analyzer was used to measure the porosity and pore size distribution for coal samples of particles size between 355 and 1000 µm. All samples -but the lignite- were dried in a vacuum oven over night at 80 °C. The maximum mercury pressure was 30,000 psia (2.068 kbar), and the minimum was ambient pressure. Measurements were done in duplicate for intrusion (volume of mercury injected) and extrusion (volume of mercury released), using the autospeed mode. Results were analysed with Quantachrome Instrument Poremaster for Windows software.

3.5.3 FTIR

An ABB MB3000 Fourier Transformed Infra red was used to obtain the spectra of raw coal and as received solvents, as well as for residue and extracts. All samples were analysed using the MIRacleTM ATR diamond accessory, with a resolution of 2 cm^{-1} and 200 scans were performed. Results were processed using the Horizon MBTM FT-IR software.

3.5.4 Proton NMR

A Varian Inova-400 NMR spectrometer operating at 399.794 MHz, was used to determine the spectra for the liquids samples. Samples were diluted in chloroform 99.8 atomic % D, as provided by Sigma-Aldrich. The proton spectra were recorded by performing 16 scans and were referenced to the residual chloroform ($CHCl_3$) peak resonance at 7.26 ppm. Due to the interference of the washing solvent, samples were further roto-evaporated using a Büchi Roto-vapour R210, the oil bath was set to 60 °C and the vacuum to 200 mbar, for about 4 hours.

Experiments run in by Oxford Instruments were performed on a makeshift spectrometer (a 400 MHz supercon magnet ramped down to 60 MHz with lashed together hardware) and restricted to 1D proton spectra. These tests were performed in collaboration with Oxford Instruments as part of the development of a low-cost 60 MHz NMR for general laboratory use.

3.5.4 Gas chromatograph/ Mass Spectra

A Varian CD-3800 GC and a Varian Saturn 2200 GC/MS/MS were used to analyze the samples. The column used was a Varian FactorFour Capillary column, VF-5ms 30MxO.25MM ID DF=0.25. The temperature method began at 50 ^{o}C, holding the temperature for 10 min, then temperature was increased up to 320 ^{o}C, 10 ^{o}C every minute, and was held at the maximum temperature for additional 10 minutes. Injection temperature was 320 ^{o}C. The FID detector was used for quantification and the MS detector was used for identification.

3.5.5 X ray fluorescence

This analysis was conducted by the department of chemical and materials engineering at the University of Albert. An EDAX Energy dispersive XRF microprobe system was used to analyze the elemental composition of the ashes obtained from the residues. The X-Ray source was rhodium, and the instrument works with a power of 40 kV/500microamps.

3.5.6 X ray photoelectron spectrometry

The XPS analysis was performed by the Alberta Center for Surface Engineering and Science (ACSES), at the University of Alberta. An X-ray Imaging Photoelectron Spectrometer Axis Ultra (Kratos Analytical) was used to determine the relative amount of sulphates and sulphides in residues and ashes from residues.

3.5.7 Microscope

A Zeiss Discovery.V20 microscope was used to observe the ashes obtained from the residues. A 1X planApo S objective with a magnification of 42 X was used to obtain the images.

3.6 Significant figures

The reported experimental results and calculations do not match the reported error. Each measurement is related to a given experimental, which is calculated and reported. However significant figures were not used due to the high variability of the errors.

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CHAPTER IV:

EXPERIMENTAL RESULTS

This chapter conveys the selected experimental data gathered during the development of the present work.

4.1 Coal rank influence on extraction yield

Coal composition and rank directly affects the extraction yield. In order to observe this influence on extraction at low temperature, one lignite, two subbituminous and one bituminous coals were extracted with tetralin.

Table 4.1 shows the experimental results obtained for the four coals employed in this study. Extraction was performed at 300 ^{o}C and 4 MPa for three hours. Extraction yield was calculated using equation 3.7, and the properties shown in table 3.2. Table 4.2 shows the result for the same experiment performed at 100 ^{o}C and 2 MPa.

Table 4.1

Extraction yield for the four Albertan coals after extraction with tetralin at 300 ^{o}C, for three hours, with 4 MPa of nitrogen

Coal	Coal mass (g)	Filter media mass (g)	Petri dish mass (g)	Beads mass (g)	Coal residue mass (g)	Extraction yield (%maf)
Poplar	1.3762	0.9002	5.7575	7.1580	0.7930	27.11
	1.3794	0.9068	5.5372	7.1580	0.7629	29.43
	1.3713	0.9103	5.5425	7.1580	0.7662	29.11
Gene-sse	2.0103	0.8847	5.5575	2.2570	2.0636	1.51
	2.0378	0.8875	5.7970	2.2757	2.0379	1.35
	2.0411	0.8880	5.6095	2.2557	2.0732	0.78
	2.0071	0.8930	5.5578	2.2548	2.0623	-1.25
Valley	2.0005	0.8891	5.5971	2.2531	1.9618	3.70
	2.0080	0.8851	5.7042	2.2590	1.9453	4.54
	2.0017	0.8853	5.7006	2.2573	1.9695	2.88
	2.0041	0.8863	5.7183	2.2569	2.0035	1.97

Table 4.1 (Continued)

Extraction yield for the four Albertan coals after extraction with tetralin at 300 ^{o}C, for three hours, with 4 MPa of nitrogen

Coal	Coal mass (g)	Filter media mass (g)	Petri dish mass (g)	Beads mass (g)	Coal residue mass (g)	Extraction yield (%maf)
Teck	2.0061	0.8908	5.7105	2.2545	1.9623	3.76
	2.0009	0.8951	5.5674	2.2470	1.9524	3.65
	2.0038	0.8821	5.6497	2.2539	2.0010	1.34
	2.0026	0.8829	5.6219	2.2550	2.0035	2.00

Table 4.2

Extraction yield for the four Albertan coals after extraction with tetralin at 100 ^{o}C, for three hours, with 2 MPa of nitrogen

Coal	Coal mass (g)	Coal residue mass (g)	Extraction yield (%maf)
Poplar	2.7182	1.8571	11.44
	2.7121	1.8951	10.15
	2.7088	1.7965	12.52
	2.7106	1.8949	11.43
	2.7010	1.8415	8.74
	2.7012	1.8673	8.00
	2.7001	1.8453	8.82
	2.6997	1.8554	8.39
	2.7050	1.8066	11.43
	2.7051	1.7996	11.01
	2.7062	1.7913	11.60
	2.7056	1.8274	9.02
Genesse	2.0052	2.4557	-11.66
	2.0058	2.0269	-0.79
	2.0037	2.1250	-4.30
	2.0027	2.0818	-2.35
Valley	2.0045	1.9884	1.99
	2.0027	2.0085	1.64
	2.0089	2.0152	1.07
	2.0053	2.0105	0.91

Table 4.2 (Continued)

Extraction yield for the four Albertan coals after extraction with tetralin at 100 °C, for three hours, with 2 MPa of nitrogen

Coal	Coal mass (g)	Coal residue mass (g)	Extraction yield (%maf)
Teck	2.0062	2.0245	1.45
	2.0005	2.0146	0.49
	2.0001	2.0139	0.12
	2.0050	2.0174	-0.28

4.2 Influence of solvent to coal ratio on the extraction yield

Dissolution processes are limited by solubility. Experiments were performed in order to determine if the solvent coal ratio limits the dissolution of Poplar at low temperature.

Table 4.3 shows the experimental results when extraction was performed using different solvent to coal ratios (S/C). It is important to take into account that the mass of coal is for humid coal, while the solvent to coal ratio is calculated for moisture free coal.

Table 4.3

Influence of solvent to coal ratio on the extraction yield for Poplar using tetralin at 100 °C, for one hour, with 2 MPa of nitrogen

S/C	Coal mass (g)	Solvent Mass (g)	Ash content (%)	Residue mass (g)	Extraction yield (%maf)
8.17	1.0030	5.90	25.1	0.6559	13.91
8.15	1.0049	5.90	24.9	0.6615	13.04
8.18	1.0015	5.90	25.3	0.6506	14.67
8.13	1.0081	5.90	25.0	0.6470	15.42
2.08	2.0058	3.00	25.4	1.1913	22.15
2.07	2.0084	3.00	26.3	1.3180	14.98
2.08	2.0042	3.00	27.2	1.3485	13.87
2.08	2.0018	3.00	26.2	1.3120	14.99
3.03	2.7036	5.90	25.35	1.7757	13.80
3.01	2.7188	5.90	25.61	1.8193	12.49
2.98	2.7462	5.90	25.38	1.8212	13.00
3.02	2.7147	5.90	25.74	1.8894	9.13

4.3 Influence of extraction time on the extraction yield

Physical extraction may be limited by mass transfer. Hence, experiments were performed to determine if the extraction time used was enough to overcome mass transfer limitations.

Table 4.4 shows the influence of extraction time over the extraction yield, when extraction of Poplar is performed with tetralin at 100 °C and 3/1 solvent to coal ratio.

Table 4.4

Influence of extraction time on the extraction yield for Poplar using tetralin at 100 °C, with 2 MPa of nitrogen

Extraction time (min)	Coal mass (g)	Solvent Mass (g)	Ash content (%)	Residue mass (g)	Extraction yield (%maf)
15	2.7182	5.90	25.68	1.7970	12.92
	2.7077	5.90	25.31	1.7659	13.68
	2.7011	5.90	25.52	1.7815	12.94
	2.7030	5.90	25.61	1.8147	11.49
60	2.7036	5.90	24.00	1.7757	13.80
	2.7188	5.90	25.61	1.8193	12.49
	2.7462	5.90	25.38	1.8212	13.00
	2.7147	5.90	25.74	1.8894	9.13
180	2.7182	5.90	30.19	1.8571	11.44
	2.7121	5.90	26.85	1.8951	10.15
	2.7088	5.90	27.45	1.7965	12.52
	2.7106	5.90	25.57	1.8949	11.43
	2.7010	5.90	28.51	1.8415	8.74
	2.7012	5.90	24.47	1.8673	8.00
	2.7001	5.90	24.90	1.8453	8.82
	2.6997	5.90	24.72	1.8554	8.39
	2.7050	5.90	24.79	1.8066	11.43
	2.7051	5.90	25.17	1.7996	11.01
	2.7062	5.90	24.52	1.7913	11.60
	2.7056	5.90	24.64	1.8274	9.02

4.4 Influence of temperature on the extraction yield

Coal behaves different according to the temperature regime. Dependence of the extraction yield according to the temperature of extraction was observed for Poplar and tetralin.

Table 4.5 shows the experimental results obtained when extraction of Poplar was performed using tetralin at different temperatures for one hour, under nitrogen atmosphere.

Table 4.5

Influence of temperature over the extraction yield of Poplar using tetralin for one hour, with 2 MPa of nitrogen

Extraction temp. (°C)	Coal mass (g)	Solvent mass (g)	Ash content (%)	Residue mass (g)	Ext.yield (%maf)
25	2.7316	6.10	26.29%	1.8079	14.23
	2.7004	6.00	26.87%	1.7988	14.36
	2.7042	6.10	25.45%	1.8166	11.96
100	2.7036	5.90	25.35%	1.7757	13.80
	2.7188	5.90	25.61%	1.8193	12.49
	2.7462	5.90	25.38%	1.8212	13.00
	2.7147	5.90	25.74%	1.8894	9.13
200	2.7018	5.90	28.75%	1.7597	18.41
	2.7551	5.90	26.84%	1.7624	17.72
	2.6961	5.90	27.14%	1.7472	16.99
	2.7307	5.90	26.46%	1.7403	17.60
300	2.7336	5.90	30.57%	1.6032	28.41
	2.7175	5.90	30.17%	1.6018	27.64
	2.7090	5.90	30.14%	1.6138	26.83
	2.7164	5.90	29.94%	1.5935	27.74
350	2.7401	5.90	34.07%	1.4183	40.00
	2.7120	5.90	34.52%	1.3312	43.49
	2.7042	5.90	34.76%	1.3908	41.01
	2.7069	5.90	34.80%	1.3583	42.48
400	2.7062	5.90	46.63%	0.9756	66.18
	2.7024	5.90	46.46%	1.0025	65.08
	2.6997	5.90	45.87%	1.0413	63.29
	2.7005	5.90	47.86%	0.9925	66.31
450	2.7013	5.90	56.86%	0.7997	77.54
	2.7391	5.90	56.61%	0.8377	76.67
	2.7031	5.90	58.11%	0.7621	78.40
	2.7051	5.90	56.43%	0.8438	76.11
	2.7092	5.90	56.43%	0.8318	76.48

4.5 Influence of solvent functional group on extraction yield

The influence of the solvent functional group was studied, in order to observe the benefits of using a given type of solvent when performing extraction of Poplar

4.5.1 Extraction at low temperature

First influence at low temperature was studied. Table 4.6 shows the experimental results obtained when extraction of Poplar is performed with different solvents at 100 ^{o}C, under nitrogen atmosphere, for one hour.

Table 4.6

Extraction yield of Poplar using different solvents at 100 ^{o}C for one hour, under nitrogen atmosphere

Solvent	Coal mass (g)	Solvent mass (g)	Ash content (%)	Residue mass (g)	Extraction yield (%maf)
Tetralin	2.7036	5.90	25.35%	1.7757	13.80
	2.7188	5.90	25.61%	1.8193	12.49
	2.7462	5.90	25.38%	1.8212	13.00
	2.7147	5.90	25.74%	1.8894	9.13
Toluene	2.7132	6.00	26.24%	1.8002	13.96
	2.7195	6.10	26.60%	1.8122	14.00
	2.7171	6.10	26.35%	1.8253	13.02
Metylcyclohexane	2.7135	6.10	26.34%	1.8261	12.85
	2.7112	6.00	26.20%	1.8293	12.46
	2.7212	6.10	26.12%	1.8032	13.93
Quinoline	2.7128	6.09	25.51%	1.826	11.85
	2.7082	6.04	23.89%	1.8516	8.51
	2.7003	6.03	22.63%	2.1751	-9.56
	2.7084	6.03	22.44%	1.8118	8.78
1-Naphthol	1.312	3.03	22.77%	0.9406	2.65
	1.303	3.01	20.23%	1.2628	-35.91
	1.3051	3.05	20.99%	1.0668	-13.55
	1.3091	3.19	21.33%	1.0976	-15.97
HT-1006	2.7004	6.10	23.79%	1.9974	0.90
	2.71	6.10	24.65%	1.8662	8.78
	2.7076	6.00	23.60%	1.9276	4.38
	2.7129	6.10	23.73%	1.9515	3.54
Heptane	2.7056	6.10	26.62%	1.7683	15.68
	2.7107	6.00	26.13%	1.8007	13.73
	2.7171	6.00	26.35%	1.809	13.79

4.5.2 Extraction with quinoline

Extraction with a nitrogen containing compound was studied. Table 4.7 shows the experimental results obtained when extraction of Poplar is performed with quinoline at different temperatures, under nitrogen atmosphere, for one hour.

Table 4.7

Extraction yield of Poplar using quinoline at different temperatures for one hour, under nitrogen atmosphere

Extraction temperature (^{o}C)	Coal mass (g)	Solvent mass (g)	Ash content (%)	Residue mass (g)	Extraction yield (%maf)
220	2.6992	5.9795	25.18%	2.0558	-0.18
	2.7018	5.9943	24.56%	2.0927	-2.73
	2.7040	6.0256	24.40%	1.8123	10.92
	2.7033	6.0536	24.98%	2.1760	-6.17
320	2.7003	6.0669	29.95%	1.5173	30.80
	2.7041	6.0574	30.75%	1.4904	32.89
	2.7031	6.0137	30.19%	1.5169	31.13
	2.7039	5.7930	28.72%	1.3802	36.03
350	2.7173	6.0344	33.69%	1.3760	40.96
	2.7072	6.0173	33.89%	1.4068	39.60
	2.7215	6.0401	33.97%	1.3943	40.52
	2.7065	6.0369	33.31%	1.4014	39.29
400	2.7297	6.1075	35.05%	1.2663	47.03
	2.7304	6.0198	36.35%	1.3312	45.44
	2.7236	6.0826	36.22%	1.2728	47.60
	2.7039	6.0474	36.36%	1.3227	45.27

4.5.3 Extraction with 1-naphthol

Extraction with an OH containing compound was studied. Table 4.8 shows the experimental results obtained when extraction of Poplar is performed with 1-napthol at different temperatures, under nitrogen atmosphere, for one hour.

4.5.4 Extraction with an industrial solvent (HT-1006)

Extraction with an industrial solvent was also studied. Table 4.9 shows the experimental results obtained when extraction of Poplar is performed with HT-1006 at different temperatures, under nitrogen atmosphere, for one hour.

Table 4.8

Extraction yield of Poplar using 1-naphthol at different temperatures for one hour, under nitrogen atmosphere

Extraction temperature (°C)	Coal mass (g)	Solvent mass (g)	Ash content (%)	Residue mass (g)	Extraction yield (%maf)
200	1.3022	3.0781	22.37%	0.7372	22.73
	1.3029	2.2082	23.88%	0.5391	44.63
	1.3121	3.0097	22.18%	1.0665	-11.21
	1.3027	3.1573	21.04%	1.0764	-14.71
300	1.3018	3.1490	32.18%	0.6686	38.77
	1.2300	3.0332	30.92%	0.7167	29.23
	1.3038	3.1914	31.55%	0.6629	38.81
	1.3571	3.0271	36.93%	0.6078	50.34
350	1.3635	3.0157	36.74%	0.5559	54.66
	1.3534	3.0291	37.09%	0.6547	46.50
	1.3533	3.0222	36.20%	0.5918	50.95
	2.7107	2.9941	18.18%	1.2939	31.34
400	1.3456	3.0100	21.82%	0.4845	50.51
	1.3455	3.0058	19.64%	0.5199	45.41
	1.3480	3.0260	34.14%	0.4583	60.63

Table 4.9

Extraction yield of Poplar using HT-1006 at different temperatures for one hour, under nitrogen atmosphere

Extraction temperature (°C)	Coal mass (g)	Solvent mass (g)	Ash content (%)	Residue mass (g)	Extraction yield (%maf)
200	2.7071	6.10	25.27%	1.8461	10.41
	2.7213	6.10	24.69%	1.8318	10.87
	2.7196	6.10	24.60%	1.8768	8.52
	2.7175	6.00	24.90%	1.879	8.70
300	2.7030	6.00	29.98%	1.5392	29.90
	2.7084	6.00	29.67%	1.5305	30.13
	2.7046	6.10	29.24%	1.5722	27.68
	2.7111	6.10	30.19%	1.5178	31.28
350	2.7037	6.10	37.79%	1.1374	53.99
	2.7018	6.40	37.82%	1.1292	54.31
	2.7036	6.30	39.01%	1.1962	52.56
	2.7081	6.00	51.25%	0.9101	71.20
400	2.7196	6.00	46.87%	1.0281	64.69
	2.7082	6.00	49.57%	0.8716	71.47
	2.6961	6.20	50.53%	0.9386	69.72

CHAPTER V:

DISCUSSIONS

This chapter deals with the results analysis and explanations for the experimental observations, based on the current knowledge of the solvent extraction of coal process.

5.1 Coal rank influence on extraction yield

Different Albertan coals were used for this study, ranging from bituminous to lignites. The possibility to upgrade low rank coal via solvent extraction is of great interest for industry, since these coals are widely available and are inexpensive.

Solvent extraction of the four different coals was performed using the method B, explained in chapter III (for 100 and 300 °C). Figure 5.1 shows the extraction yield obtained for each coal. It was not possible to obtain favourable extraction yields with the bituminous and subbituminous coals while the lignite gave promising results.

Extraction yields were determined using equation 3.7. Method B had to be used since washing with THF is necessary in order to remove the extraction solvent from the solid residue, and gravimetrically determine the extraction yield. As will be further explained in section 5.2, THF washing does not greatly affect the results.

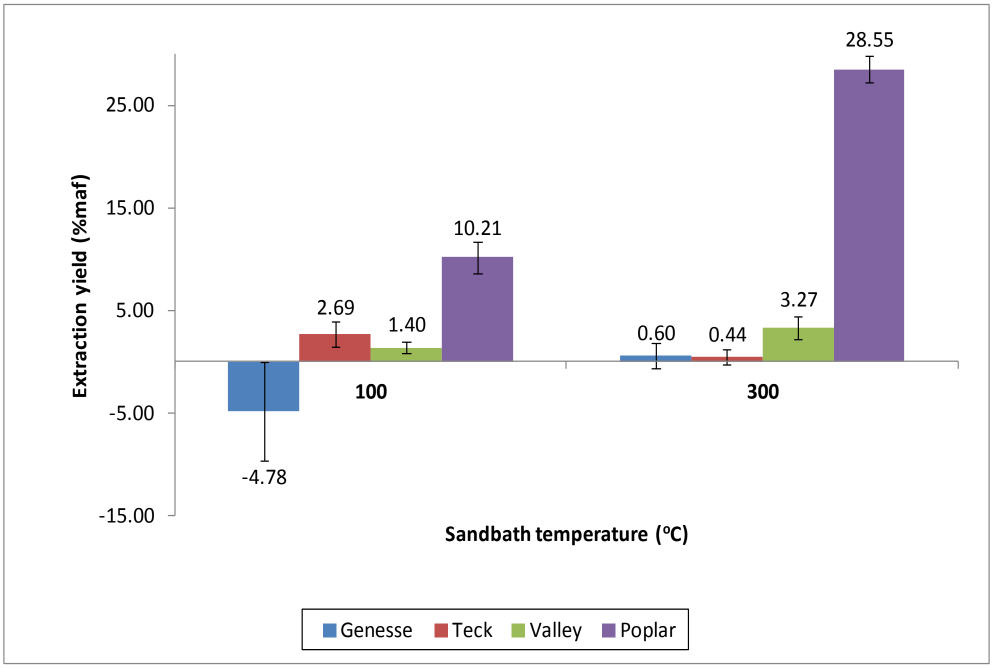


Figure 5.1. Average extraction yield for the Albertan coals, at 100 and 300 °C, for 1hour, under nitrogen atmosphere

From the petrographic composition of the coals -shown in table 3.2- high extraction yields were expected from Genesse and Valley coals, due to their vitrinite content (1)..

Low rank coals are expected to have a large contact surface: the larger the contact surface area, the easier for the solvent to reach the coal matrix and drag the low molecular weight components out of it. By looking at the pore size distribution of the coals in this study, it was found that Poplar has the second highest porosity amongst the four coals, as expected (1). Figure 5.2 shows the pore size distribution for Poplar. The pore size distribution curves for the other coals can be found in the appendix, figure A.1 to A.3. Table 5.1 summarizes the values of the pore sizes and the surface area of the four Albertan coals. Even though Poplar does not have the highest pore volume and surface area, it has a higher amount of liptinite than Genesse. Since liptinite is rich in hydrogen it is very desirable for the extraction process. Thus, a large pore volume and surface area together with a relatively high content of liptinite, favours the extraction of Poplar at 100 and 300 °C.

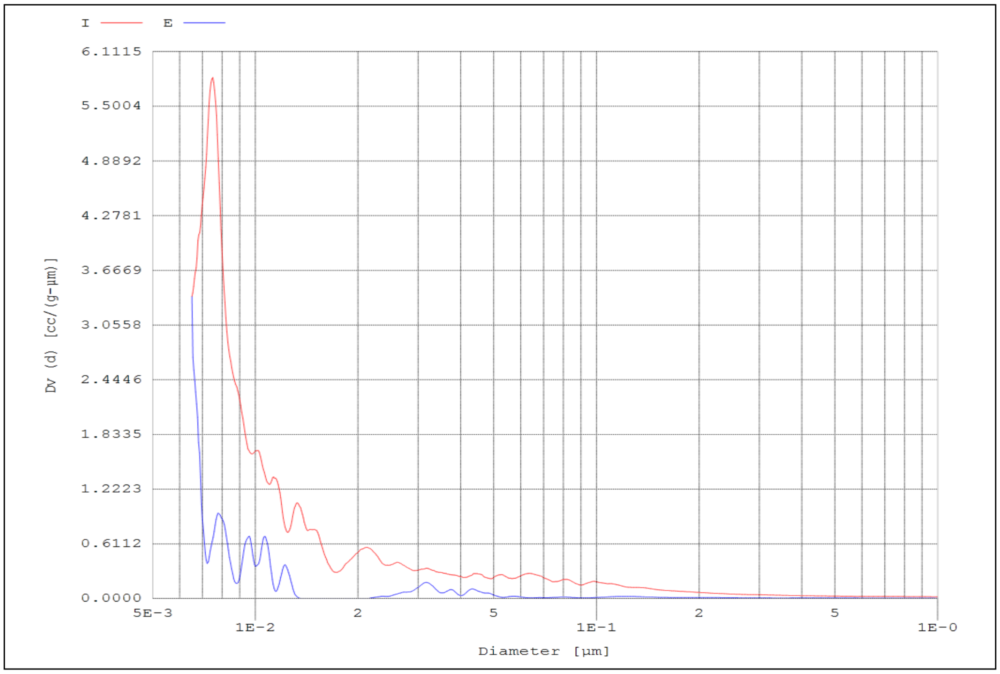


Figure 5.2. Pore size distribution for Poplar coal using a mercury porosimeter. Red: intrusion. Blue: extrusion

Given the scope of the work, which included gaining understanding of the solvent extraction of coal process at low temperatures, only poplar was used for the experiments to follow.

Table 5. 1

Total pore volume and surface area of the four Albertan coals

Coal	Total intruded volume (cc/g)	Surface area (m^2/g)
Teck	0.6712	6.7249
Genesse	0.5856	11.2412
Valley	0.2835	6.3952
Poplar	0.5194	10.7142

5.2 Temperature influence on extraction yield

It has been stated in chapter II, that the temperature regime has an important role in the solvent extraction of coal. For practical purposes, the temperature regimes for the lignite were divided in:

- Low temperature regime (25 to 200 °C)
- Transition regime (300 to 350 °C)
- High temperature regime (300 to 450 °C)

At the low temperature regime no important change in the extraction yield was observed when the extraction time was increased. This observation led to conclude that no chemical reaction occurred up to 200 °C. (2)

The transition regime was defined as a stage in which there is evidence of slow chemical reaction, but physical interactions dominate the process.

When performing extraction for different periods of time at 300 °C, a slow increase in extraction yield can be seen. This increase indicates slow chemical reactions (2). Another characteristic of this regime is the important role that physical properties of solvents play, and will be further discussed in section 5.3.

High temperature regime was studied up to 450 °C, since the temperature range between 400 and 450 °C is of great interest for the industry. It is of industrial interest due to the high extraction yields obtained, as can be seen in figure 5.3. Further increase in temperature leads to an increase in retrogressive reactions, reducing the extraction yields (1).

As mentioned in the experimental methods, coal to solvent ratio was set to be 1:3. This ratio seems to be the most popular among different researchers; nevertheless preliminary studies were made to verify the influence of this parameter. Figure 5.4

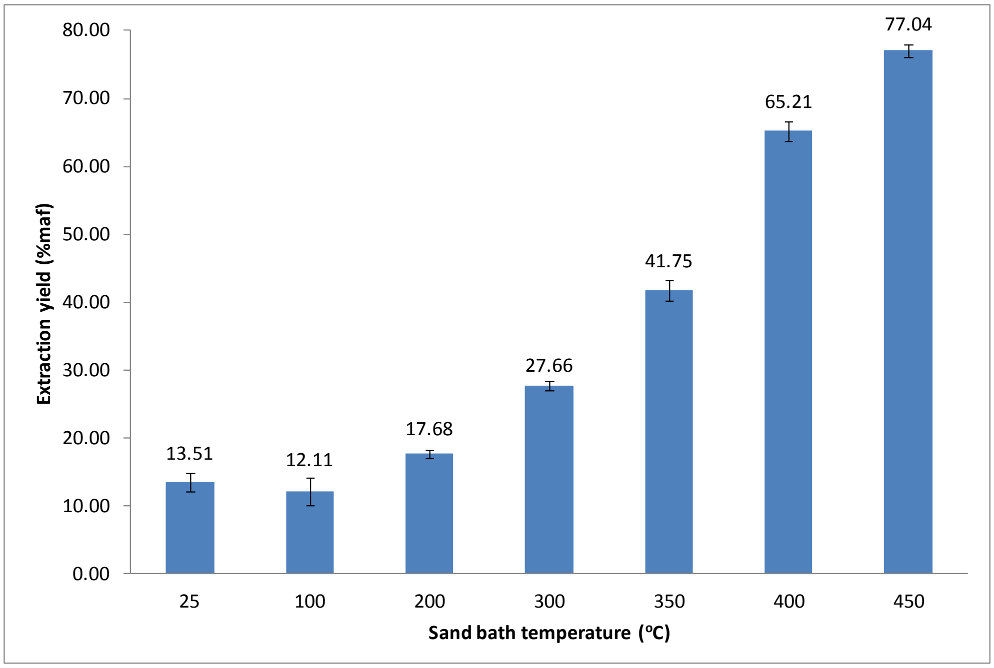


Figure 5.3. Extraction yield for Poplar, using tetralin at different temperatures, 1 hour extraction under nitrogen atmosphere

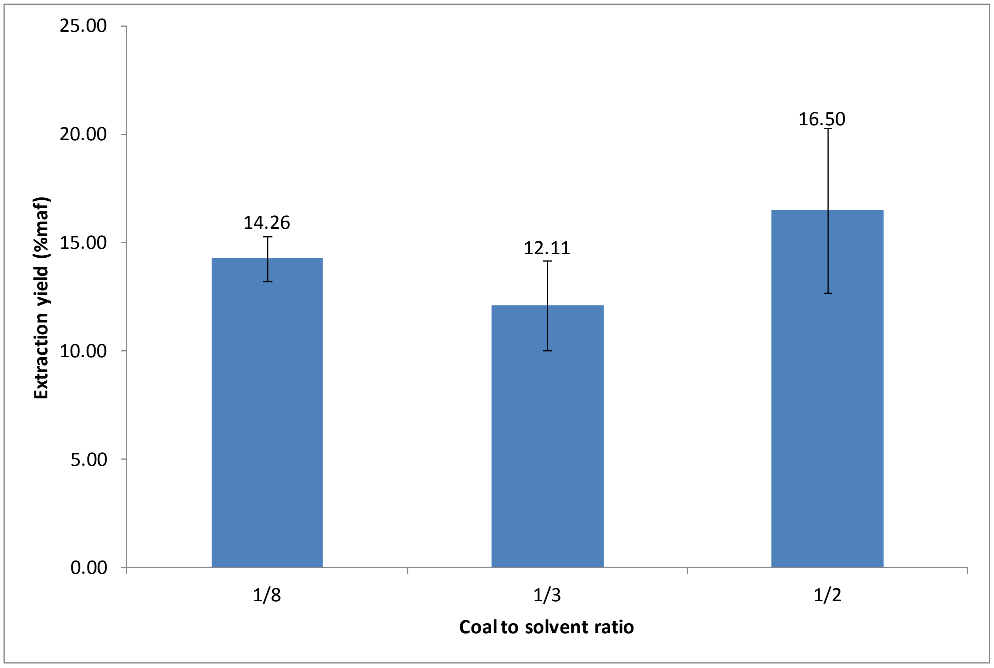


Figure 5.4. Influence of coal to solvent ratio over the extraction yield, for Poplar, one hour extraction at 100 ^{o}C, under nitrogen atmosphere

shows the results from the preliminary work. It can be noticed that this study did not show any conclusive trend as to how this ratio affects the extraction yield. It is important to mention that since the lignite was not dried the coal to solvent ratio was calculated for a moisture free coal.

Another important parameter for these experiments was the extraction time. All experiments were performed for an extraction time of 1 hour. The advantage is that this reduces the influence of the mixture's heating time (See appendix: figure A.4) and the mass transfer limitations.

The experimental methods described in chapter III, mention that different nitrogen pressures were used for low and high temperature extraction. This did not affect the results, since it has been proven that pressure does not influence the extraction yield (3) (4). The objective of using different nitrogen pressures was to keep the solvent in liquid phase at the reaction temperature. Additional to this, nitrogen was used to remove air from the micro-reactor in order to avoid oxidation of the coal and its products.

As it was mentioned in section 5.1, Method B (described in chapter III) was used in order to apply equation 3.7. The question that arises from this method is: will using an additional solvent affect the extraction results? This question is based on the physical interaction that this new solvent will have with the coal matrix. Some components that would not be dissolved by the original solvent may now be extracted. A quick experiment to verify this interaction was performed: washing raw coal with THF and gravimetrically determine the extraction yield, using equation 3.7. To further corroborate the results, the extraction yield was also gravimetrically measured by determining how much extract is left after completely rotoevaporating the THF. The rotoevaporation was performed as described in chapter III, for THF removal. Independent of the method used, the extraction yield was determined to be near 2 % (experimental data can be seen in appendix table A.1).

In view of the previous result it was considered that washing with THF does not have a remarkable influence in the overall extraction yield and will at most increase the observed extraction yield by 2%. Instead, it brings the benefit of removing the remaining solvent from the coal residue, allowing the gravimetrical determination of the extraction yield based on the residue.

To further support this assumption and to confirm that lighter material was indeed extracted when THF was not used, a sample was prepared using method A (extracted and washed with tetralin instead of THF) as described in chapter III. The extraction was performed at 100 °C and the product was analyzed using a GC/MS. Results show that different components were extracted from Poplar. This experiment will be further discussed in section 5.5.

The influence of temperature on the solvent extraction of coal will be analyzed next. Figure 5.3 shows the extraction yield of Poplar coal using tetralin as solvent, for a period of 1 hour, using method B, for several temperatures. This graph provides evidence of the difference between the established temperature regimes, which will be discussed next.

5.2.1 Low temperature regime

From figure 5.3, it can be noticed that at 200 °C, the extraction yield is slightly above the extraction yield for 25 and 100 °C. It has also been proved that below 300 °C there are no chemical reactions, as was mentioned before (2). These results indicate that only a certain amount of Poplar coal can be dissolved at low temperature in tetralin. Hence the physical extraction is limited by coal properties, as will be further explained in section 5.3.

From an industrial point of view, this shows that if low temperature extraction is desired it may be performed at room temperature and the results will not greatly vary from extraction at 200 °C, where the energy consumption is increased.

In view of these results, one would ask: if temperature does not play an important role in this regime, what about time? Extraction at 100 °C for different periods of time, demonstrate that the yield remains within the experimental error, as shown in figure 5.5. There is an apparent reduction of the extraction yield when extraction is carried out for 180 minutes; however when further increasing extraction time, the extraction yield remains unaltered (2).

This result shows that physical dissolution of the coal takes place in a period less than 15 minutes. This finding proves very valuable for industry, since short contact times (less than 15 minutes) are required to completely physically extract the lignite at low temperature.

Further studies need to be done in order to determine the minimum time required to complete the physical extraction. The best way to proceed would be with a short contact time reactor (semi-batch reactor). This setup would allow analyzing the extracts and determining the extraction yield for very short times. Increasing the reaction time progressively will help find the exact time in which the maximum extraction is achieved.

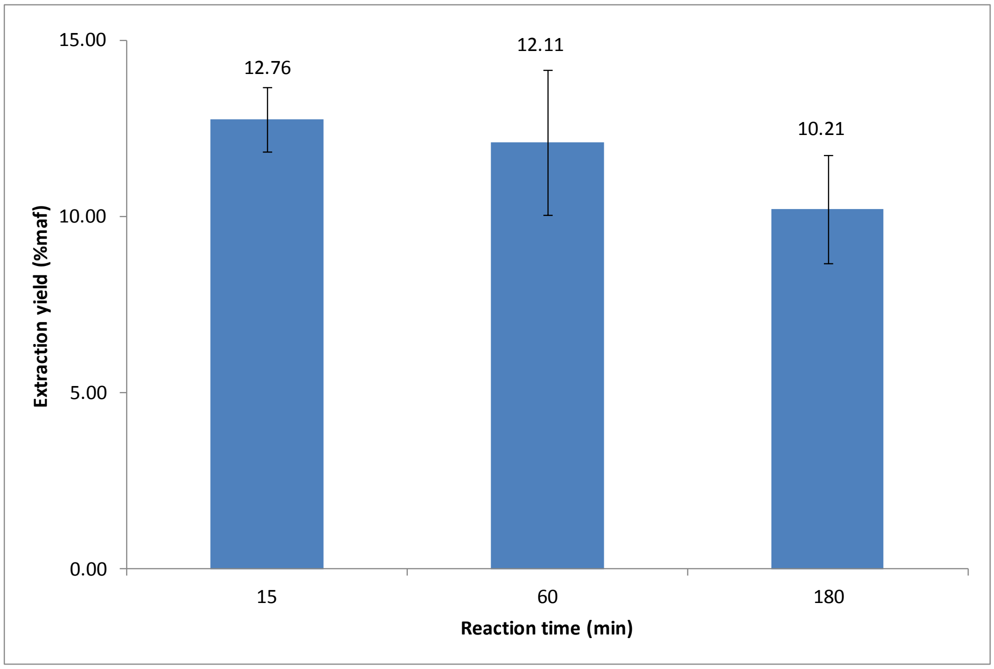


Figure 5.5. Extraction yield for Poplar using tetralin, different extraction times at 100 °C, under nitrogen atmosphere

5.2.2 Transition regime

For the lignite used in this study, the transition regime was said to begin at 300 °C. At this stage, chemical reaction begins to take place, but occurs slowly, and physical properties of the solvent still play an important role, as will be discussed in section 5.3. Extraction yields in this regime will rapidly increase with reaction temperature, as shown in figure 5.3.

Once again, industry could use these data to justify a two step extraction, where the first extraction may be performed in the transition regime. The second step would be at high temperature, which is a more energy demanding process. The benefit is, of course, the use of less severe conditions on the highest volume of material.

5.2.3 High temperature regime

Above 400 °C, thermal decomposition of coal takes place rapidly and free radicals have to be stabilized quickly to avoid retrogressive reactions. As mentioned in section 2.4, a solvent with a good hydrogen donor ability is required in order to obtain high extraction yields and light components. Tetralin is known to be a very good hydrogen donor solvent. It is able to quickly stabilize the free radicals and keep the new molecules small, and soluble.

For one hour extraction of this coal-solvent system, there is a meaningful increase in extraction yield between the transition regime and the high temperature one, as seen in figure 5.3. This clearly shows how the free radical reactions are promoted by the increase in temperature, and explains the strong interest of industry in the zone between 400 and 450 °C. But an increase in the extraction yield does not necessarily leads to products with higher value. The latest statement will be further discussed in section 5.4.

These results show a very marked difference in the three established temperature regimes; and support the need to deal with every one of them as an independent process. The next section will provide more evidence that supports this statement.

5.3 Solvent influence on extraction yield

It has been proven that the temperature directly affects the extraction yield, and several authors claim that solvent properties may be used to predict coal-solvent system behaviour. This section will provide additional information to clarify some of the theories and statements proposed in literature.

All the experiments were performed with an extraction time of 1 hour. For the different solvents (Quinoline, 1-naphthol and the industrial solvent), the highest temperature of extraction was 400 °C. The established time period allows maximum conversion at 400 °C, by analogy with the visbreaking process (5).

For all the solvents in study, there is a clear difference between the low, transition and the high temperature regime. Hence, they will be discussed separately.

5.3.1 Low temperature regime

When solvent extraction of coal is performed at low temperature, physical interaction between solvent and coal drives the extraction process. Therefore, it was expected that solvents with different chemical structures would give a wide range of extraction yields. However, this study proved different as can be seen from 1 hour extraction at 100 °C (Figure 5.6). From all the solvents in this study, only 1-naphthol and quinoline gave lower extraction yields and even so, the observed difference is not statistically significant.

Quinoline may be giving lower extraction yield due to some acid base reactions, forming stable compounds at low temperature. This will be further discussed in section 5.4.1. While 1-napthol's melting point is very close to 100 ^{o}C. Thus, the solvent coal interaction is not occurring properly. Also, during the experiments it was noticed that some solvent crystals remained in the residue, affecting the gravimetrical determination of the extraction yield. This can be seen from the large variation in extraction results (large error bar) associated with the 1-napthol extraction.

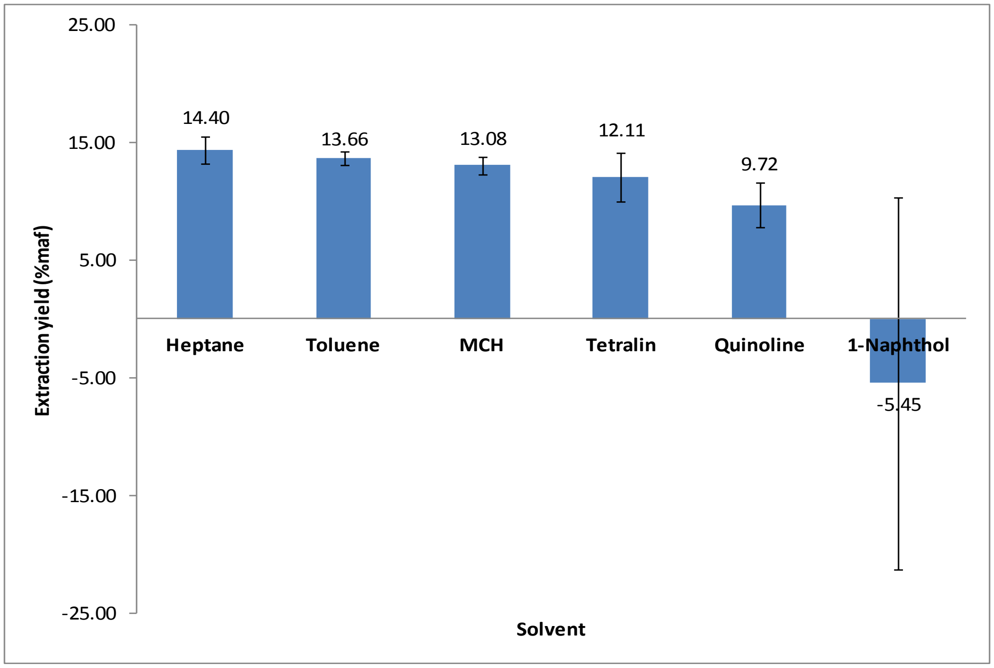


Figure 5.6. Extraction yield of Poplar with different solvents at 100 ^{o}C, for 1 hour, under nitrogen atmosphere

The other solvents in study are capable of extracting the same amount of coal, despite their chemical structure (even though it has not been possible to chemically characterize the extract, it is expected that different molecules have been extracted, depending on the solvent chemical structure). This shows that the coal properties play a more important role than the solvent ones at 100 °C. Hence, if solvent extraction of coal is to be performed at very low temperatures, the cheaper solvent may be used, because it can provide as good result as a more expensive one.

Further information about the effect of low temperature extraction on the subsequent extraction of coal, at higher temperatures, should be generated. It is well known that previous extraction may have a positive or negative impact on further extraction. This depends on the effect that the first extraction has on the coal structure – increase in porosity or increase in cross-linking strength-.(6)

Increasing temperature from 100 to 200 °C provides an increase in extraction yield of approximately 5% for tetralin. In the case of HT-1006, the increase in extraction yield is within the experimental error. For quinoline and 1-napthol, there is no increase in extraction yield, as shown in figure 5.7.

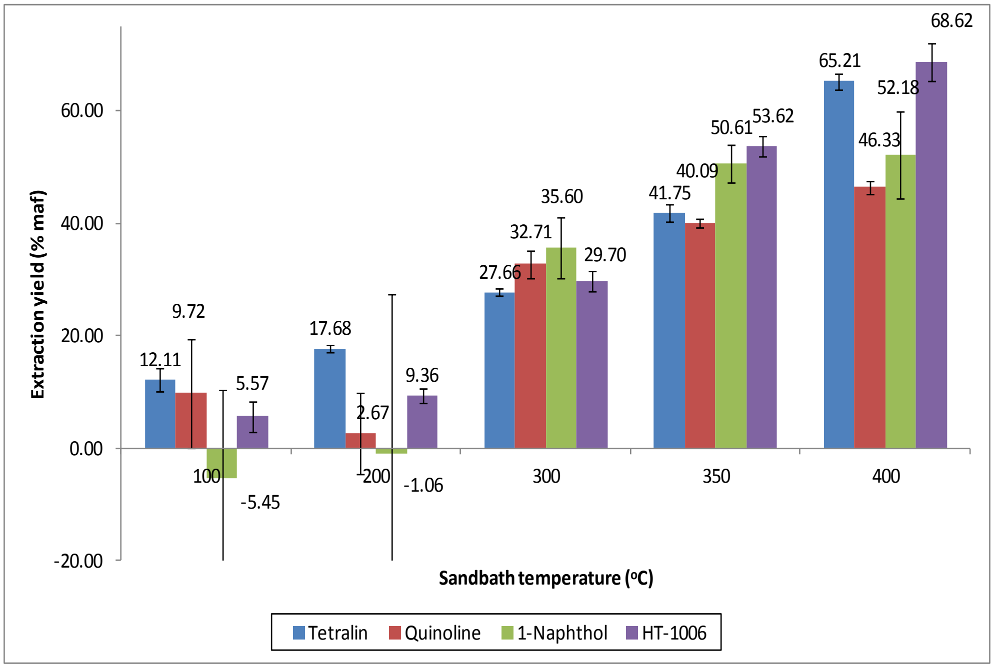


Figure 5.7. Extraction yield of the lignite using different solvents for 1 hour at low and high temperature regime, under nitrogen atmosphere

Once again, these results show that at low temperature, the extraction yield is seemingly determined by the coal properties, rather than the solvent itself. However, it would be very interesting to know what the influence of the different solvents on the product composition is. This will be addressed in section 5.4.

5.3.2 Transition regime

As it was previously mentioned, 300 to 350 °C is the transition regime, where physical properties of the solvent play a very important role, despite the occurrence of chemical reaction.

Figure 5.7 shows that at 300 °C the highest extraction yield is given by 1-naphthol, followed by quinoline. Hence, polar solvents are the best for Poplar coal at this extraction temperature. This might be due to the abundance of polar sites contained in lignites, which will strongly interact with the polar solvents. This is supported by the high content of oxygen, as shown in table 3.2.

Literature mentions the importance of the electron-donor acceptor complexes (section 2.4). Thus, the acid base interaction between the solvent and the acid-base sites in the coal, or the electron donor-acceptor complexes must be taken into account. Quinoline is a basic solvent, while 1-napthol is slightly acidic. Therefore there might be some benefit in using acidic solvents at these extraction conditions.

Tetralin and the HT-1006 are not able to physically interact with those polar sites in the coal, thus their extraction power is diminished, despite their high hydrogen donor ability. Nevertheless, the similarity between the HT-1006 chemical structures with that of coal, gives it a slight advantage over tetralin.

By looking at the solubility parameter of the solvents (table 3.1), no trend can be established. It seems that this property does not significantly affect the extraction yield for the solvents and coal in study at 300 °C.

As the temperature is increased to 350 °C, chemical reactions become faster, as indicated by the increase in the extraction yield. But, physical properties of the solvent seem to still play an important role, even at this high temperature.

HT-1006 provides the second highest extraction yield at 350 °C, as shown in figure 5.7. But this is not due to its hydrogen donor ability, since tetralin shows the worst performance. This is due to its chemical structure. HT-1006 was obtained from coal liquids, meaning that it contains some molecules that are commonly found in the coal. The increase in temperature allows the mobility of the heavy aromatic compounds in the coal and solvent, giving it the best coal-solvent interaction.

Being polar solvents, 1-naphthol and quinoline are expected to keep performing well. However, this is not the observed behaviour for quinoline. One reason might be that at temperatures above 325 ^{o}C, quinoline reacts with itself in the presence of Nickel (10-14% content in SS 316L$^{(7)}$) to produce biquinolyl $^{(8)}$. This compound is very stable and has a melting point of 196 ^{o}C $^{(9)}$. After cooling down this compound might precipitate and remain in the residue diminishing the gravimetrically determined extraction yield. This hypothesis will be further discussed in section 5.4.1.

It is not surprising that 1-naphthol gives the highest extraction yields at 300 and 350 ^{o}C. It was reported that below 350 ^{o}C solvent potency is determined by "the ability of the solvent to swell, peptize and depolymerise and the coal"; the most effective solvents for this purpose are the aromatics such as: α and β-naphthol, phenyl phenols, anthracene, among others. $^{(1)}$ Thus, the good performance of 1-napthol is due to the physical interaction it has with the coal molecules.

The solubility parameter seems to correlate with the extraction yield for each solvent at this temperature. The lower the parameter is, the better the extraction yield. It is important to remember that the solubility parameter does not accurately describe the behaviour of polar molecules, as proven with these results, where the behaviour is the opposite from what literature proposes.

5.3.3 High temperature regime

When looking at the extraction yield at 400 ^{o}C, in figure 5.7, it becomes evident that the hydrogen donor ability of the solvent becomes the most important property; explaining the high performance of tetralin and HT-1006. As expected, the HT-1006 gives a higher extraction yield due to its similarity with the coal chemical structure. This behaviour is in agreement with the literature, as presented in section 2.4.

Even at 400 ^{o}C, 1-naphthol shows a better performance than quinoline, due to the chemical reactions that the latter undergo, as explained previously.

From the experimental results it is obvious that some of the solvent properties reported in literature do not affect the extraction yield, such as the solubility parameter. As mentioned in chapter II, “for mixtures that contain very large molecules (polymers) or for those that contain strongly polar or hydrogen-bonding molecules, the theory of regular solutions is inadequate” (12).

On the other hand, acid-base interactions and chemical structure seem to play an important role in the transition regime. And, as expected, hydrogen donor ability proved its value at the high temperature regime.

5.4 Product composition

It has been mentioned and proven throughout the work, that depending on the solvent physical properties it will interact with Poplar coal in a certain way. Increase and decrease of the extraction yield has been mentioned, but nothing had been said about the quality of the product.

The highest extraction yield could mean nothing if valuable products are not obtained. Hence, not only the extraction yield is important for industrial and research purposes, but the product composition also play an important part.

In the following subsections three sub-products from the extraction will be analyzed in order to determine the influence of the solvent chemical structure on the products: residue, extracts and ashes from the residue. All the analyses were performed for extraction in the low temperature regime (200 °C) and in the high temperature regime (400 °C). At 200 °C, the physical effects are the most important, even though it seems that the solvent does not play an important role. At 400 °C, the active thermal decomposition stage of the coal is reached, and the chemical reactions play the main role in the process.

5.4.1 Influence on residue composition

An elemental analysis was performed for the residue samples after reaction at 200 and 400 °C. This analysis gives information about the content of carbon, hydrogen, nitrogen, sulphur and oxygen; oxygen was calculated by difference. When comparing with the values of the raw coal and the residues obtained from reaction with different solvents, valuable information is gained.

Figure 5.8 shows the hydrogen to carbon ratio for the residues and the raw coal. It can be noticed that at low temperature there is no important change in the ratio. However, at closer inspection, it would seem that the two non hydrogen donor solvents, even at this very low temperature, produce a residue with slightly less hydrogen than the donor solvents; this difference is more evident at high temperature.

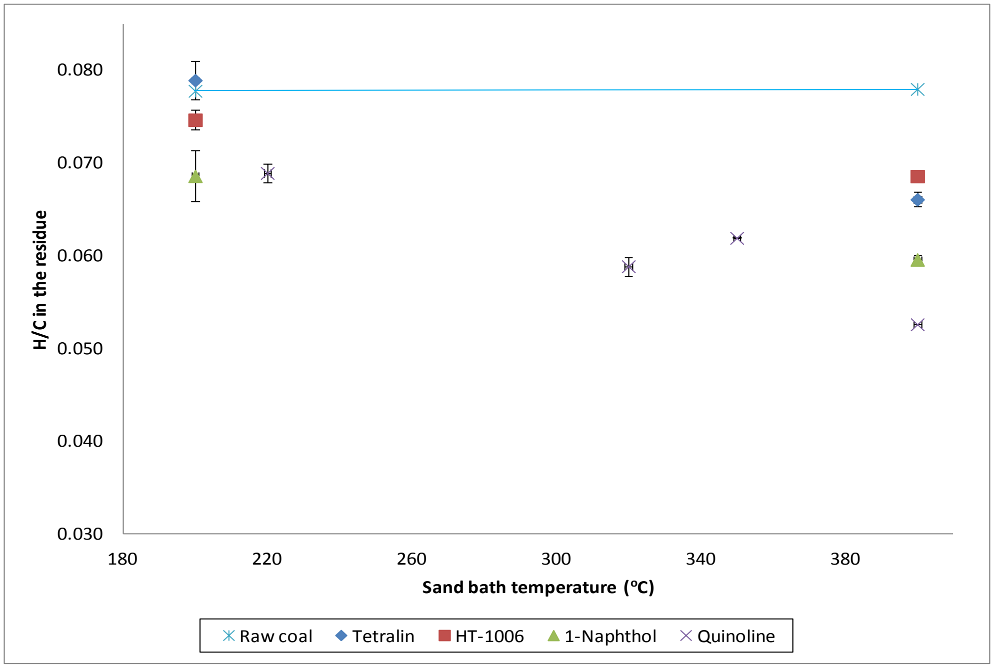


Figure 5.8. Hydrogen to carbon ratio for the lignite residue after 1 hour extraction under nitrogen atmosphere

As it was mentioned, in the low temperature regime only a small part of the coal is extracted and the solvent does not influence the results, so it is no surprise that the H/C ratio did not show remarkable differences.

When looking at the H/C for the highest temperature, two important things can be noticed. First, the H/C ratio is below that of raw coal for the four solvents in study. This means that the hydrogen rich components are being extracted and hydrogen shuttling is occurring. The second is that for the hydrogen donor solvents the ratio is above the one for non hydrogen donor solvents, indicating the occurrence of hydrogen shuttling. Since the solvent is able to donate hydrogen, more of this element is left in the residue. While for non hydrogen donor solvent, hydrogen from another section in the coal is being used to stabilize the free radicals and obtain low molecular weight compounds.

Thus it can be said that using non hydrogen donor solvents consumes more of the hydrogen available in the coal to enrich the liquid extract. While the donor solvents, by donating their own hydrogen, are leaving some of this valuable element in the coal residue.

Finally, from the two extra points for quinoline, it can be noticed that the trend is as expected, the higher the temperature, the less the hydrogen left in the residue. Thus, hydrogen shuttling is promoted by the formation of the free radicals.

The sulphur to carbon ratio is shown in figure 5.9. When looking at the ratio at low temperature it can be noticed that, independent of the solvent, the ratio is very similar to that of raw coal, and within the experimental error for all solvents. However, at the highest temperature a different behaviour is observed.

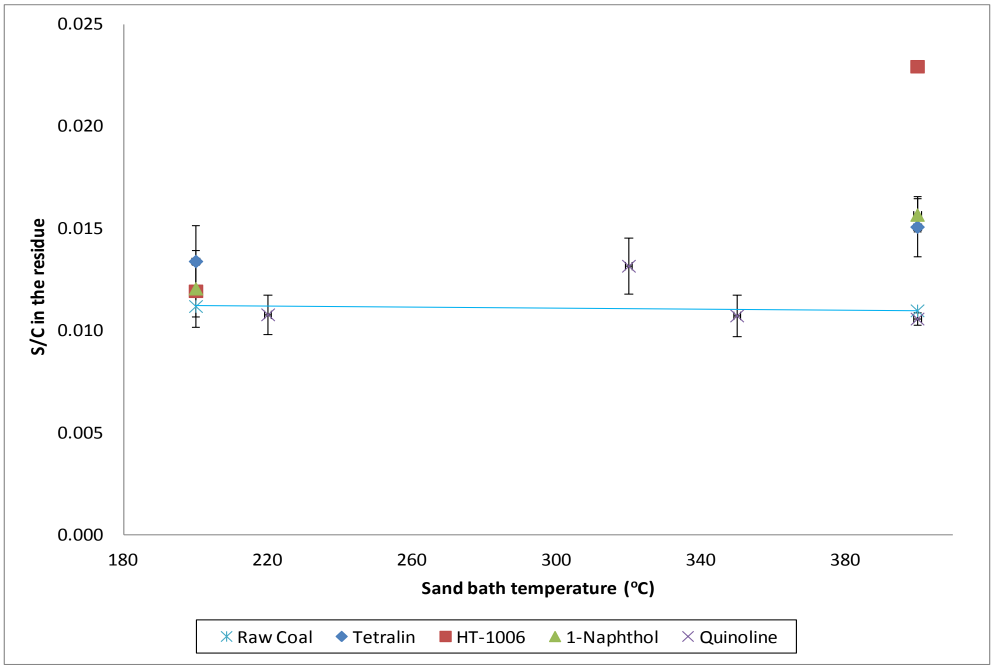


Figure 5.9. Sulphur to carbon ratio for the lignite residue after 1 hour extraction under nitrogen atmosphere

Quinoline gives the lowest S/C ratio, remaining very close to that of raw coal. Thus, this solvent does not show any selectivity towards sulphur containing compounds. Tetralin and 1-napthol show similar behaviour to each other, leaving more sulphur containing compounds in the residue than quinoline, but their selectivity is not as good. The hydrotreated solvent on the other hand shows good selectivity for extraction non-sulphur containing compounds, leaving a larger amount of sulphur in the residue.

It is important to remember that even though it seems to be a big difference in the behaviour of the solvents, the ratio only changes by 0.015. Then, there is some selectivity but it is not a very remarkable one. It is believed that the selectivity of each solvent towards the sulphur containing compounds in coal must be directly related to their solubility, but further investigation needs to be done to confirm this hypothesis.

Once the hypothesis is confirmed, the results show that coals with high sulphur content may be upgraded by selecting a proper solvent in which sulphuric compounds have low solubility, such as the HT-1006 industrial coal derived solvent. This would contribute to the development of industrial desulphurization technology for coals.

By looking at the trend that quinoline shows, it can be noticed that the solvent does not have selectivity toward sulphur compounds at any of the temperatures in study.

Nevertheless, it is of great importance to keep in mind that the previous analysis might be subject to error, since total sulphur is being determined. In order to obtain more accurate results, X-ray photoelectron spectroscopy was performed to ascertain the nature of the sulphur in the residue, but concentration of sulphur is so low that it was not detected with this technique. Other techniques with higher sensitivity should be attempted in order to determine the types of sulphur in the residue. Once the relative amounts of the different sulphur compounds are established, this analysis might lead to different observations and hypotheses.

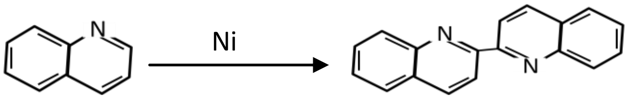
Figure 5.10 shows the nitrogen to carbon ratio in the residue. At low temperature it can be noticed that N/C ratio in the residue after extraction with tetralin, 1-naphthol and HT-1006 are within the experimental error, and slightly above the raw coal. This shows that there is no selectivity in the extraction of nitrogen compounds. The same behaviour can be observed at high temperature for the three solvents. Thus, an increase in extraction temperature does not seem to affect selectivity of nitrogen compounds when the extraction solvent is tetralin, 1-naphthol or HT-1006.

On the other hand, Quinoline produces high nitrogen content in the residue, about three times that of the raw coal. Even though no satisfactory information has been found in literature, it has been noticed that quinoline is able to react with other organic compounds containing strong electrofilic elements, at low temperatures to produce heavier molecular weight compounds with decomposition points above 200 °C.

The solubility of those compounds seems to be limited at the extraction conditions, remaining in the residue. As the temperature is increased these heavier nitrogen-rich compounds are decomposed, becoming soluble, and the nitrogen content in the residue decreases at 320 °C.

As mentioned before, above 330 °C, quinoline undergoes another reaction in the presence of nickel, to form biquinolyl, as show in equation 5.1. The melting point of this product is around 196 °C (9), precipitating when the reactor is cooled down. Hence, the nitrogen content in the coal residue increases again for temperatures above 350 °C.

Attempts to isolate the biquinolyl were made, but due to its high molecular weight it could not be identified using the available GC, and due to its low concentration FTIR was not suitable for detecting it. No information about its normal boiling point was found.



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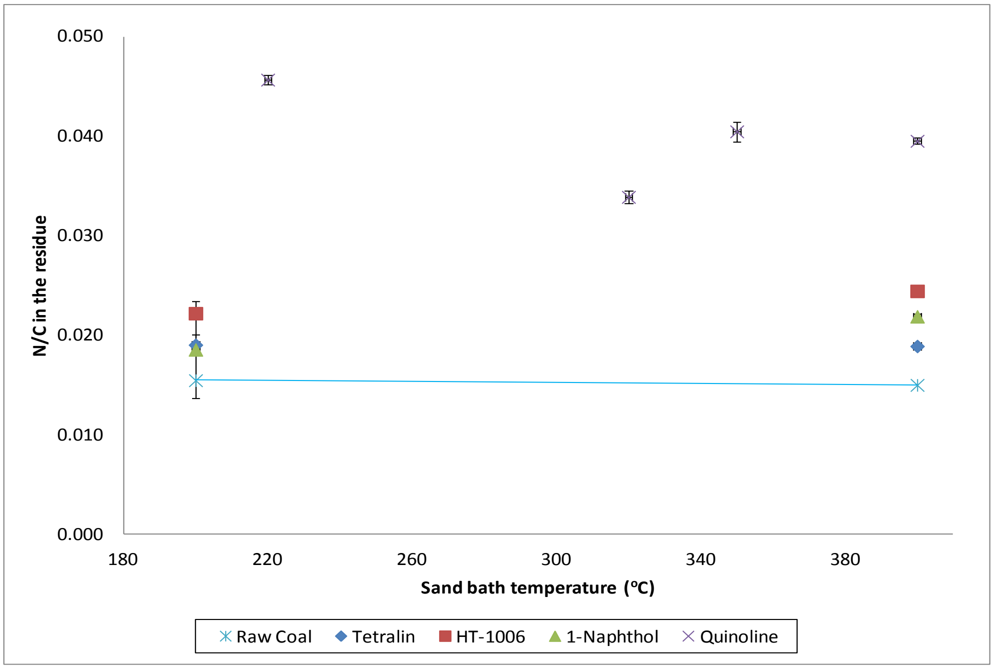

Figure 5.10. Nitrogen to carbon ratio for the lignite residue after 1 hour extraction under nitrogen atmosphere

Figure 5.11 shows the oxygen to carbon ratio for the residues. These values might be influenced by larger experimental errors, since they are obtained by difference, using equation 3.2.

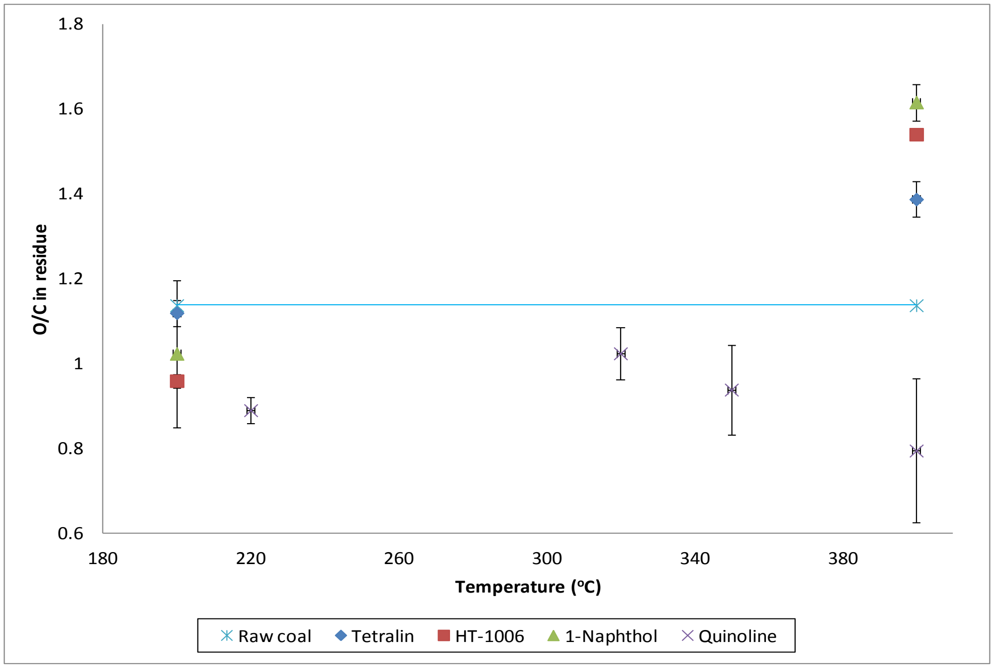

Figure 5.11. Oxygen to carbon ratio for the lignite residue after 1 hour extraction under nitrogen atmosphere

From the figure it can be noticed that at low temperature there is not a big difference between the oxygen content in the raw coal and in the residue treated after extraction with the four solvents in this study.

When extraction is performed at 400 °C, all the solvents, except quinoline, selectively remove components with low oxygen content. Quinoline consistently results in a lower O/C ratio in the residue and no temperature dependence was observed.

Further analysis regarding the oxygen content in the residue requires a more accurate measurement.

Residues were also analyzed using an FTIR. Some differences between the residues after extraction at low and high temperature were observed, as can be seen in figure 5.12. Some of the most notorious changes are described next.

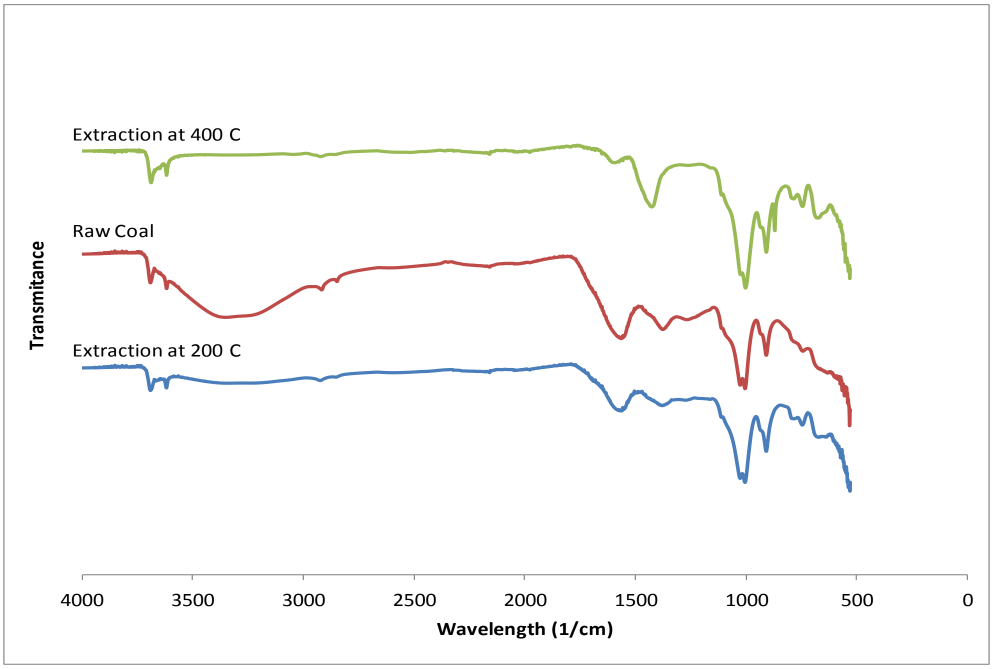

Figure 5.12. FTIR spectra of the raw coal and the residues after extraction at 200 and 400 °C, with tetralin for one hour, under nitrogen atmosphere

When increasing extraction temperature a product with increasing strong absorption around 700 cm^{-1} (typical of aromatic C-H out-of-plane bending) is produced. Increasing absorption may also be noticed around 1425 cm^{-1} (C-C stretching within the aromatic ring). The loss of aliphatic absorptions around

2900 cm^{-1} and the loss of bonded OH (broad around 3500 cm^{-1}) can also be observed.

The main difference between the raw coal and the residues is the broad absorption band around 3500 cm^{-1}, which is due to intermolecular hydrogen bonded O-H. This is gradually replaced by the free O-H stretch at 3700 cm-1; showing that water and phenol content varies.

Using a hierarchic cluster analysis, show in figure 5.14, no difference can be established between the residues, despite the solvent or the extraction temperature (samples: 5, 29, 8, 18, 24, 13, 21, 32)

5.4.2 Influence on extract composition

Due to the complexity of the extracted mixture and the impossibility to remove the extraction solvent, which is present in very large amounts, characterizing the extracts proved to be an elusive task.

First attempts were made using the FTIR. Figure 5.13 shows the spectra for tetralin and extracts after reaction at 200 and 400 °C. From the figure it can be noticed that there is not an evident difference between the tetralin containing extract and the as received tetralin.

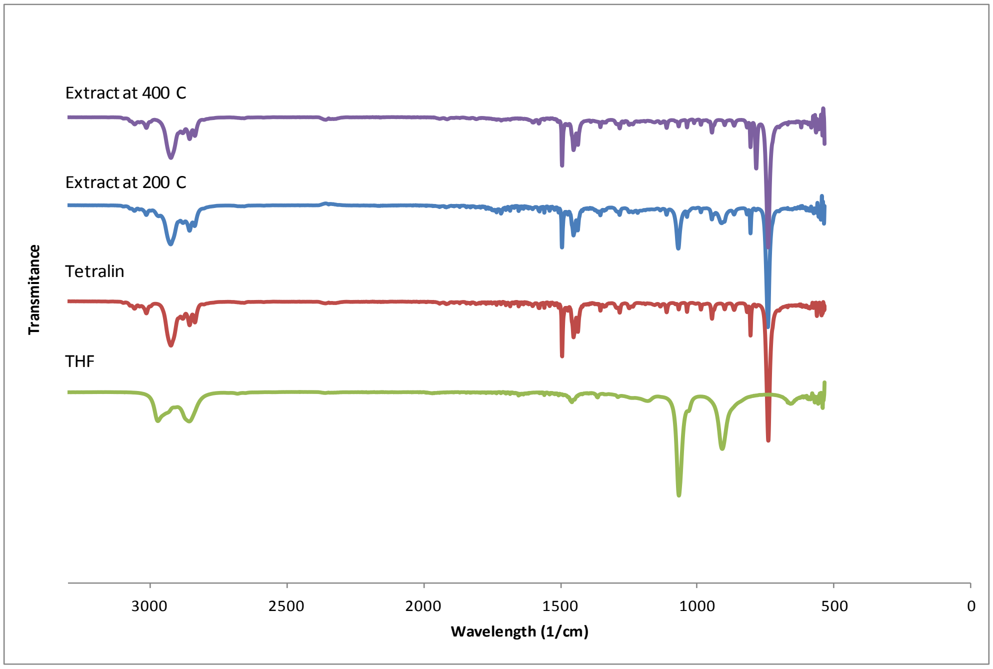

Figure 5.13. FTIR spectra of the raw and washing solvents, and the extracts after extraction at 200 and 400 °C, with tetralin for one hour, under nitrogen atmosphere

Some THF can be seen in the extract obtained after reaction at 400 °C, in an overlapping peak around 800 and 1100 cm $^{-1}$.

Due to the difficulty in establishing the difference and similarities between the extracts and the extraction solvent, hierarchical clustering was used. Figure 5.14 shows the results obtained, using a normalized set of data for the complete FTIR range.

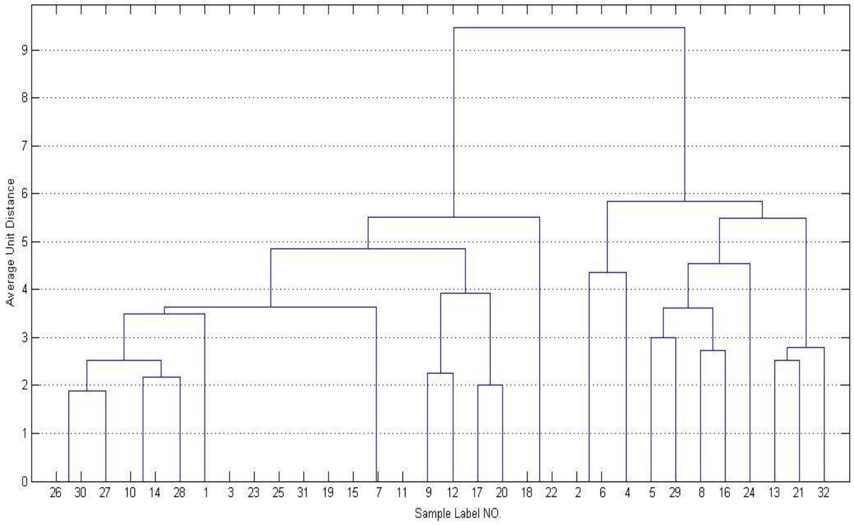

Figure 5.14. Hierarchic clustering of the FTIR data for extracts and residues, using normalized data

From the clustering it can be noticed that there are three major clusters for the liquid samples. The first cluster comprises the pure THF, tetralin and HT-1006, as well as the extracts of HT-1006 at 200 and 400 °C, and with 1-naphthol at 200 °C. As expected there is little difference between the raw solvent and the extracts of HT-1006. However, the extract obtained with 1-naphthol at 200 °C, is more similar to the complex mixture of hydrocarbons that is in the HT-1006 solvent than to its pure solvent; showing that some coal molecules are contained in the sample.

The second cluster is comprised by pure quinoline, as well as the quinoline and tetralin extracts at 200 and 400 °C. This cluster shows that it is not possible to detect any remarkable difference between the extracts at 200 and 400 °C, for both solvents. It is even hard to detect differences between the pure quinoline and the extracts obtained with it.

The third cluster is comprised by pure 1-naphthol and its extract at 400 °C. Showing once again how hard it is to detect any difference between pure solvent and extracts, using this technique.

Since the FTIR did not yield any optimistic result, an attempt to obtain further information about the composition of the extract was made using 1H NMR. Once again the high concentration of the extraction solvent made very difficult the identification of the extracted components. Figure 5.15 shows the spectra for the extract obtained using tetralin at 400 °C. A few peaks additional to the ones from tetralin can be seen. Due to the very low concentration, no attempts were made to identify the components observed.

Sadly the employed techniques were not able to detect the extracted components when quinoline and 1-napthol were used as extraction solvents.

The main reason for the extremely low concentration of extract in the samples used for these analyses may be due to the necessity of roto-evaporating the THF completely. Figure 5.16 shows the 1H NMR of the THF recovered during roto-evaporation. Some small peaks can be seen; those indicate that some of the volatile material that was extracted is being dragged out of the sample during its preparation process.

Table 5.2 shows a summary of the 1H NMR result obtained for the HT-1006 and its extracts at 200 and 400 °C.

By looking at the aromatic protons percentage it can be noticed that there is no change between the raw coal and extraction at 200 °C. But when extraction is performed at 400 °C, an important increase in these types of protons is observed. Coal molecules are highly aromatic and their dissolution in the solvent after the extraction increases the aromatic proton percentage.

Table 5. 2

Summary of the 1H NMR analysis for HT-1006 and its extracts at 200 and 400 °C

Type of proton (%)	**Aromatic**	**Olefinic**	**Aliphatic**	**Total (%)**
Range (ppm)	**(6.3-9.5)**		**(0.5-4.5)**	
HT-1006	58.26	12.06	29.69	100.01
Extract at 200 °C	57.83	0.00	42.18	100.01
Extract at 400 °C	63.83	0.00	36.17	100.00

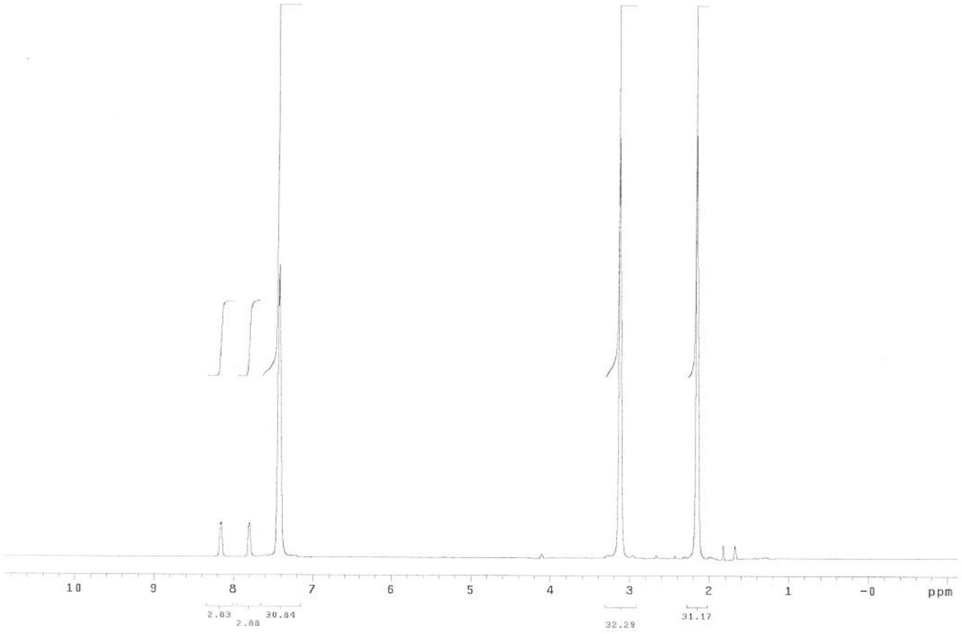

Figure 5.15. 1H NMR spectra of the tetralin extract obtained at 400 ^{o}C for one hour, under nitrogen atmosphere

As for the olefinic protons, it is no surprise to find that after reaction it is not possible to detect this type of protons. Double bond reactivity makes them an easy target for any electrofilic component in the mixture. Bromide titration would provide a more accurate value for the amount of olefinic found in the hydrotreated solvent.

And finally, by looking at the aliphatic protons an increase can be noticed between the raw solvent and the extract at 200 ^{o}C. At low temperature mainly small hydrogen rich aliphatic molecules are dragged out of the coal matrix, increasing the aliphatic content. It is possible that these few aliphatic molecules are the only ones to be extracted by physically interacting with the solvent. Sadly this could not be corroborated due to the impossibility to detect aliphatic protons at low temperatures when using tetralin, quinoline and 1-napthol as extraction solvents.

After extraction at 400 ^{o}C, an increase in the aliphatic proton respect to that of the raw solvent is observed, but it decreases when comparing to the extract at 200 ^{o}C. This is most likely due to the free radical mechanism that takes place at this temperature. Aliphatic chains are broken and new compounds are being formed, thus reducing the aliphatic content in comparison with extract obtained at 200 °C.

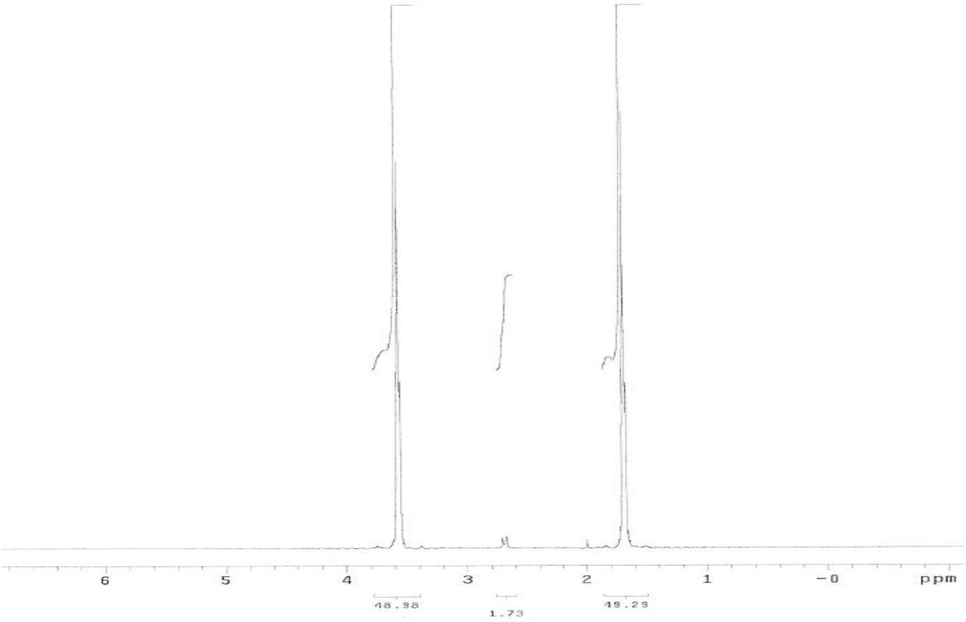

Figure 5.16. 1H NMR spectra of the THF recovered after roto-evaporation of the extracts

This data puts in evidence the difference between products obtained at low temperature and at high temperature.

Further information regarding the percentage of the different protons in the extracts has to be generated to compare the quality of the products according to the solvent used.

Additional analyses were conducted by Oxford instruments in the United Kingdom. The most relevant result obtained was the possibility to quantify the amount of extracted material and residual THF in the samples. Samples obtained from 1-naphthol could not be analyzed since they were solidified.

Table 5.3 clearly shows how the extract content increases as the temperature increases. The THF content in the sample is usually constant, after 4 hour roto-evaporation. The Extract/Tetralin ratio is determined by fitting the region of the spectrum from 6.5 ppm to 8 ppm to model of overlapping Lorentzian peaks, then manually separating them into peaks contribution to the extracts and those contributing to the tetralin. (Williamson, D. Personal communication. Nov.23).

Table 5.3

1H NMR Summary for tetralin samples

Temperature (°C)	THF/Tetralin	Extract/Tetralin
200	0.38 ± 0.03	0.05 ± 0.02
350	0.35 ± 0.05	0.16 ± 0.01
400	0.1 ± 0.08	0.29 ± 0.02

Table 5.4 shows how the extract content increases as the temperature increases. The THF content in the sample is usually removed, even with only two hours of roto-evaporation. When the aliphatic region is partially masked by the THF peak at ~1.8 ppm in the spectrum of sample an estimate for the THF content in the aliphatic region can be made from the peak at ~3.7 ppm. The extract content can be estimated by integrating the aliphatic region and subtracting the integral of the THF peaks at 3.7 ppm. However, when THF is completely removed, the aliphatic region can be integrated to provide an estimate of the extract content and a ratio of extract to quinoline calculated with the assumption that the aromatic to aliphatic ratio is 0.622. (Williamson, D. Personal communication. Nov.23)

Table 5. 4

1H NMR summary for quinoline samples

Temperature (°C)	THF/Quinoline	Extract/Quinoline
400	0.077 ± 0.010	0.115 ± 0.019
400*	Not detected	0.103 ± 0.010
200	Not detected	0.039 ± 0.002
200*	Not detected	0.086 ± 0.007

*After additional roto-evaporation of THF

A GC/MS analysis was performed for an extract sample diluted in CS_2 (2.7 % wt/wt), containing 0.03457 % wt/wt of heptane. The extract was obtained after reaction with tetralin at 100 °C for 15 minutes, and was prepared using method A, described in chapter III. Figure 5.17 shows the obtained spectra.

When looking at the mass spectra for the major peaks, products from the dehydrogenation of tetralin can be identified, such as naphthalene and dihydronaphthalene. The first peak of the GC spectra is decalin, and figure 5.18 shows the spectra for the peak number 6 in the GC spectra, which is identified as naphthalene. This provides evidence that even at very low temperatures and short extraction times, there may be hydrogen donation, which may be responsible for the absence of the olefinic protons detected using the 1H NMR (table 5.1). Hence, it can be seen that even a very low temperatures, product upgrading occurs; providing the possibility for solvent extraction at low temperature as a previous step to a process at more severe conditions.

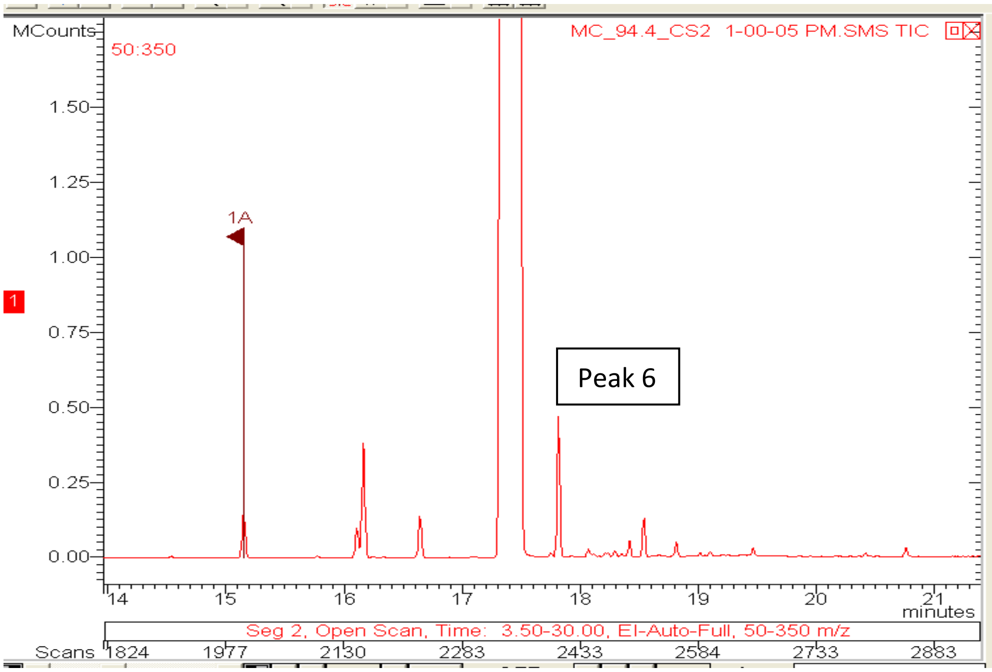

Figure 5.17. GC/FID spectra of the extract obtained with tetralin at 100 ^{o}C, after 15 minute extraction under nitrogen atmosphere

Characterizing and establishing differences in the products obtained from extraction with solvents containing different functional groups was not possible, despite all the efforts. Thus, further analyses should be performed in order to establish which solvent functional group is able to yield the most commercially valuable products. One valuable tool to achieve this is SimDist. This will provide a boiling point distribution of the products, which is used in industry to separate the refined products. Another valuable tool is high performance liquid chromatography (HPLC) that may be able to separate the compound classes in the extract.

It was noticed that selectively extracting the coal seems feasible. Gaining further knowledge in this regard will provide valuable information for the design and implementation of the solvent extraction of coal process at industrial scale. The key to achieve this selective extraction may lie in the selection of the proper industrial solvent, pure solvent or mixture of solvents. Further analysis with a wider range of solvents and additional identification techniques, such as an improved separation technique, HPLC, UV-Vis and CHNS analysis could be used to gain further knowledge in this area.

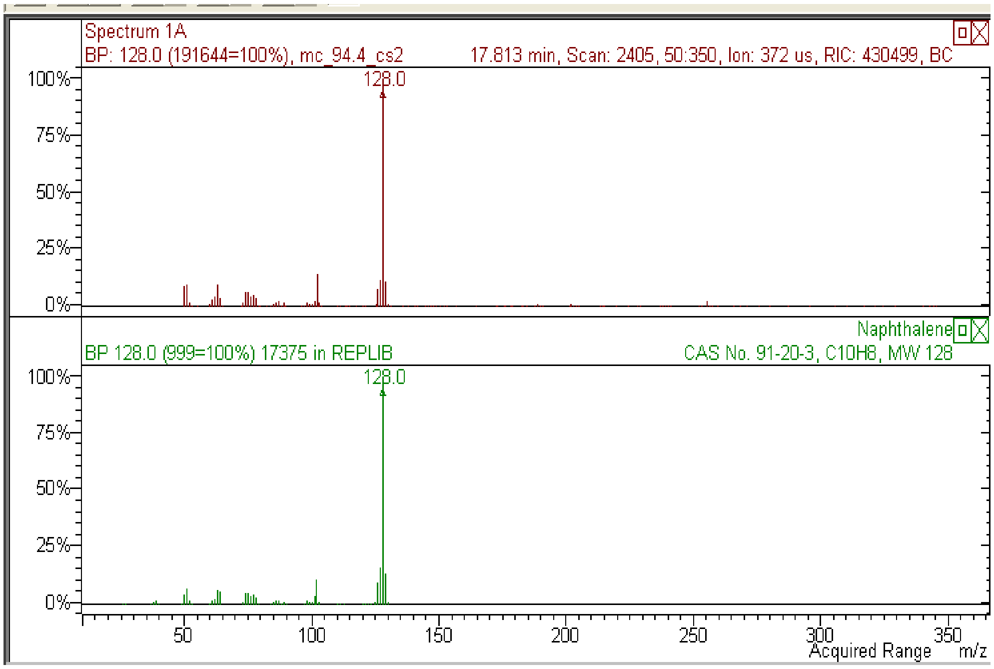

Figure 5. 18. Top: mass spectra for the sixth GC peak of the extract obtained with tetralin at 100 °C, after 15 minute extraction under nitrogen atmosphere. Bottom: Mass spectra from the software library

5.4.3 Influence on ash composition

For an efficient solvent extraction of coal process, it is desired that the inorganic matter remains unaltered. Experimentally it was observed a slight difference in coloration between the ashes when treated with various solvents at the temperatures investigated in this study. Figure 5.19 shows an example of the ashes obtained from the residue when extraction is performed with tetralin at 200 and 400 °C. From the picture it can be noticed that ashes from residue treated at 200 °C show a lighter color and larger.

The difference in appearance could be evidence of dissimilarity in chemical composition. Therefore, an X-Ray fluorescence analysis was performed on the ashes of lignite residues treated at low temperature (200 °C) and high temperature (400 °C).

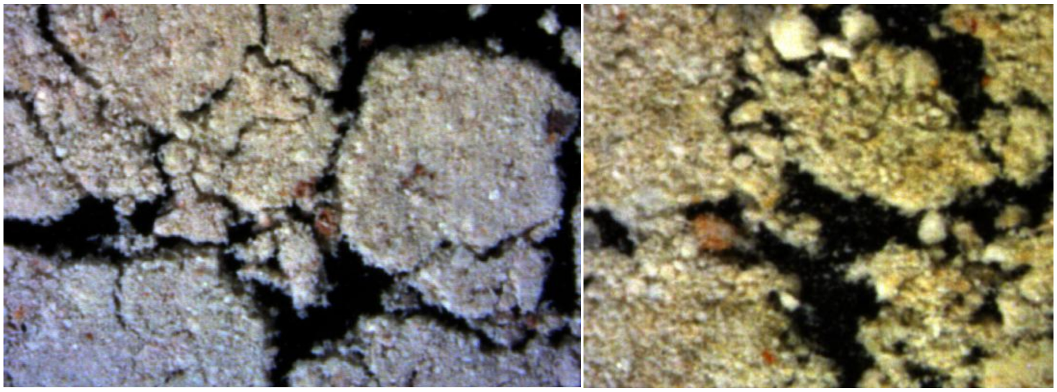

Figure 5.19. Left: Ash from residue obtained after extraction with tetralin at 400 °C. Right: Ash from residue obtained after extraction with tetralin at 200 °C

The main components of the ash remain unaffected when changing solvent and temperature. However inorganic sulphur is an exception. Figure 5.20 shows how sulphur content decreases as the reaction temperature increases. This variation also shows some dependence upon the solvent used.

The highest difference in sulphur content is obtained when 1-napthol is used as extraction solvent, tetralin and HT-1006 extract about the same amount of sulphur, while quinoline extract the lowest.

One study was found that mentions that some polar solvents may extract ashes, depending on coal, solvent and extraction conditions; yet no further information was given (9). It is possible that the authors referred to some components in the ashes, such as the inorganic sulphur.

This shows that at high temperature, depending on the solvent that is being used, sulphur from ashes consumes hydrogen to produce H_2S. Unfortunately, the tools to analyze the gases from the reactions were not available, never the less, from experimental observation it is know that H_2S is being released after the reaction at high temperature (350 and 400 °C). A more accurate study to detect this should be conducted. Gases may be analyzed in line using a GC/MS in order to obtain information about their composition.

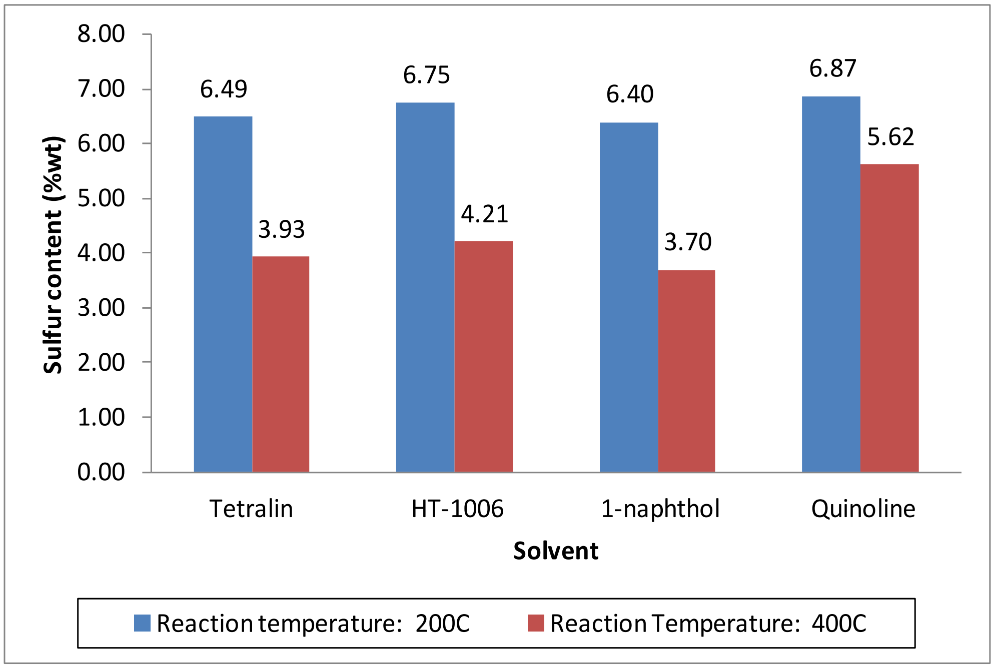

Figure 5.20. Sulphur content in ashes of the lignite residue, after extraction with different solvents at 200 and 400 ^oC, for 1 hour, in nitrogen atmosphere.

X-ray photoelectron technique, showed that in the ashes sulphur is found only as sulphate. The technique also confirms the trend observed in the elemental analysis of the residues. The lower the temperature, the highest the sulphur content, related to the carbon content. The results are shown in table 5.5.

Table 5. 5

Sulphate to Carbon ration in ashes, determined with XPS

Solvent	Temperature of extraction (^oC)	Sulphate/carbon
Tetralin	200	0.23
	400	0.16
Quinoline	200	0.16
	400	0.11
1-Napthol	200	0.15
	400	0.12
HT-1006	200	0.11
	400	0.15

Only HT-1006 does not follow the trend observed with XRF elemental analysis technique. This may be due to the small amount of sample available for the elemental analysis. Thus this value might have a large experimental error.

The analyses made to the different sub-products of the solvent extraction of coal process show many development opportunities that will lead to a better understanding of the role of the solvent in the solvent extraction of coal.

5.5 References

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CONCLUSIONS

1. When extraction is performed at 100 and 300 °C for three hours, Poplar (the lowest coal rank investigated) gives the highest extraction yield among the four Albertan coals in this study.
2. From the four Albertan coals in study, the second one with highest liptinite content gave the highest extraction yield at low temperature. High porosity, surface area and liptinite content, are the characteristics that defined which coal yielded better results for low temperature extraction.
3. Washing with tetrahydrofurane is a standard industrial procedure that helps removing the solvent used for extraction from the coal residue. It was demonstrated that it does not remarkably affect the extraction yield, at the experimental conditions.
4. Increasing temperature within the low temperature regime (25 – 200 °C), when performing extraction of Poplar with tetralin for one hour, increases the extraction yield only by around three percent.
5. Increasing the coal to solvent ratio from 1:2 to 1:8 does not provide benefits regarding the extraction yield, for extraction of Poplar with tetralin at 100 °C.
6. Increasing extraction time from 15 to 180 minutes, does not affect the extraction yield, for Poplar with tetralin at 100 °C. Physical dissolution of the physically extractable compounds occurs in less than 15 minutes.
7. Increasing extraction temperature within the transition (300 – 350 °C) and high temperature regimes (>350 °C) rapidly increases the extraction yield obtained with Poplar and tetralin for one hour extraction, under nitrogen atmosphere. Promotion of chemical reactions with temperature is responsible for this.
8. When extraction of coal is performed at 100 °C, properties of Poplar limit the extraction yield to around 14 %, seemingly irrespective of the properties of the solvent used.
9. When any of the four solvents in this study is used for extraction, increasing extraction temperature in the low temperature regime yields little improvement in the extraction yield for Poplar.
10. In the transition regime of Poplar, physical properties of the solvents determine the yield from extraction process, despite evidence of chemical reactions occurring.

11. The polarity of the solvent is its most important property, when extraction of Poplar is performed in the transition regime, for one hour.
12. The extraction yield of Poplar could not be correlated to the solubility parameter of the solvents in study, in agreement with reported literature, regarding the non validity of the dissolution theory for large-size molecules.
13. The similarity of the chemical structure of the HT-1006 to that of coal, gives it an advantage over tetralin when extraction of Poplar is performed in the transition regime.
14. Hydrogen donor ability of the solvent becomes the most important property affecting the extraction yield, when extraction of Poplar is carried out at the high temperature regime.
15. Non hydrogen-donor solvents more effectively use the hydrogen contained in the coal residue. While hydrogen donor solvents use less hydrogen from the coal itself, leaving a higher amount of this element in the residue.
16. For Poplar coal, increasing extraction temperature promotes hydrogen shuttling, decreasing the content of the element in the coal residue.
17. When solvents undergo acid-base reactions with the coal molecules, like quinoline, its efficiency as a solvent for extraction of Poplar is reduced at low temperatures and the nitrogen content in the residue increases.
18. No selectivity towards nitrogen compounds was observed when extraction of Poplar is performed with tetralin, 1-naphthol and HT-1006.
19. 1H NMR results obtained when extraction of poplar is performed with HT-1006 support the free radical mechanism at high temperature and indicates hydrogen transfer at low temperatures.
20. Products of dehydrogenation of tetralin were detected using a GC/MS, when extraction of Poplar is carried out at temperatures as low as 100 ^{o}C for 15 minutes.
21. Sulphur content in ash was identified as sulphates, using XPS technique.

RECOMENDATIONS

1. Lignite was not dried for any of the extractions performed. However, for industrial application handling the large amounts of water vapour is not feasible. Thus, further studies on how drying the coals affect the extraction yield and its products would provide valuable information.
2. Physical extraction of coal was said to occur in less than 15 minutes. Using a short contact time reactor one should be able to determine the exact time that is required for the process to be completed. This information may also be used to determine retention times for industrial processes. The proposed setup may be used to provide information regarding the extract composition as the process advances.
3. A more detailed study in the transition regime would give valuable information to appropriately design a two step extraction process, where the optimum point for less energy consumption and highest extraction yield can be found.
4. Quinoline behaves differently from other solvents, especially when nitrogen content of the residue is considered. The results suggest that acid-base reactions with coal molecules occur at low temperature. The possibility that biquinolyl formation occurs at higher temperature would explain the temperature dependent change encountered during the development of this work.
5. Oxygen content in residue might provide valuable information about the amount of this element that is extracted. However, different tools need to be used in order to accurately measure the amount of this element in the residue.
6. A different approach need to be taken in order to analyze the composition of the extracted liquids. Separation by boiling point ranges, isolating as much extraction solvent as possible, might improve the use of techniques such as FTIR and 1H NMR. Thus, each fraction would be analyzed and compared to the same fraction obtained with different solvents.
7. Industry often uses distillation as separation technique. Analyzing the extract using SimDist may provide information regarding the commercial value of the extracts obtained with different solvents.
8. In line gas analysis using a GC/MS can provide information about the composition of lighter components produced during the solvent extraction of coal.

APPENDIX

ADDITIONAL EXPERIMENTAL RESULTS

Pore size distribution

Figure A.1 to A.3 show the pore size distribution for the different Albertan coals, obtained with the mercury porosimeter.

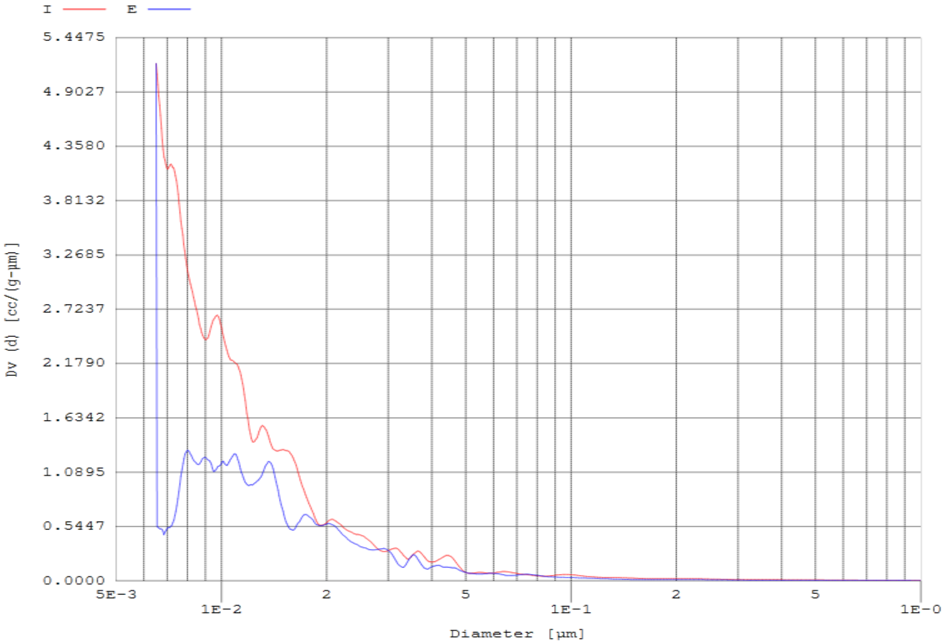

Figure A.1. Mercury pore size distribution for Genesse coal. Red: intrusion. Blue: extrusion

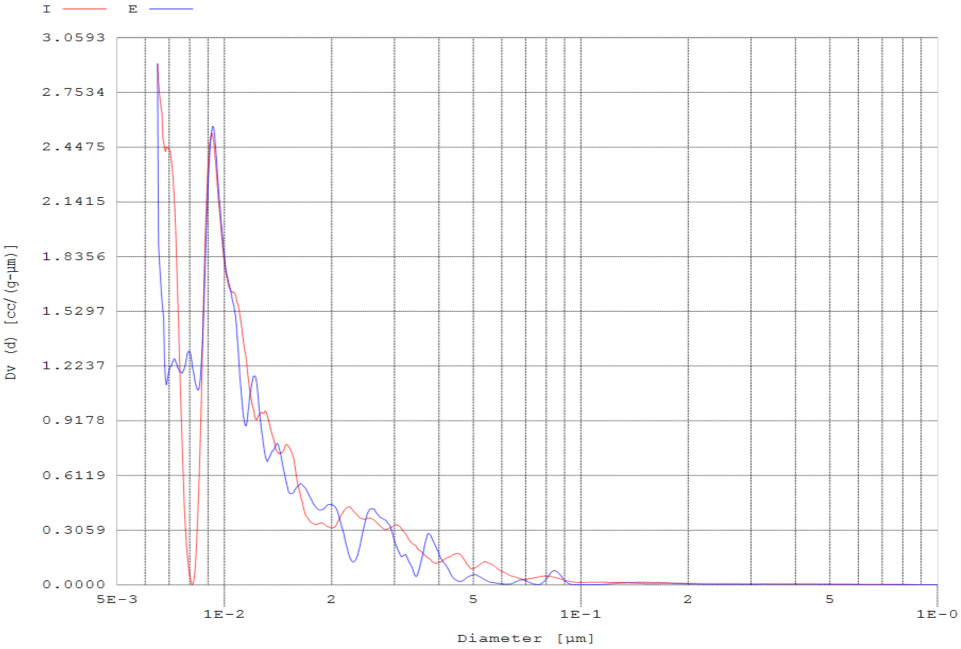

Figure A.2. Mercury pore size distribution for coal Valley. Red: intrusion. Blue: extrusion

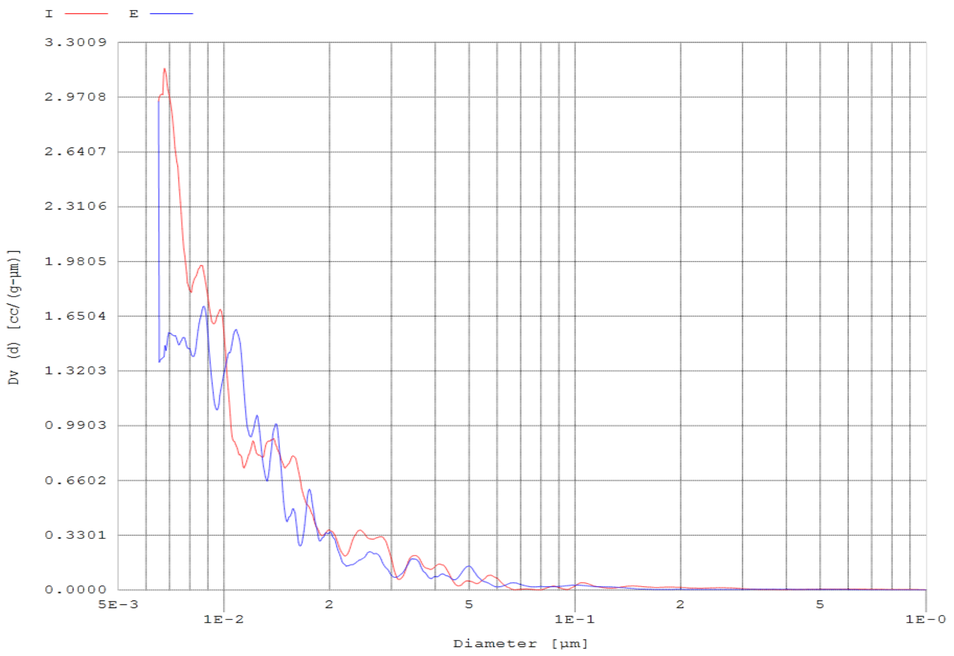

Figure A.3. Mercury pore size distribution for Teck coal. Red: intrusion. Blue: extrusion

Temperature profile

Figure A.4 shows the temperature measured every minute, with a type K thermocouple placed in the center of the reactor. Notice that the isothermal stage is reached within 10 minutes.

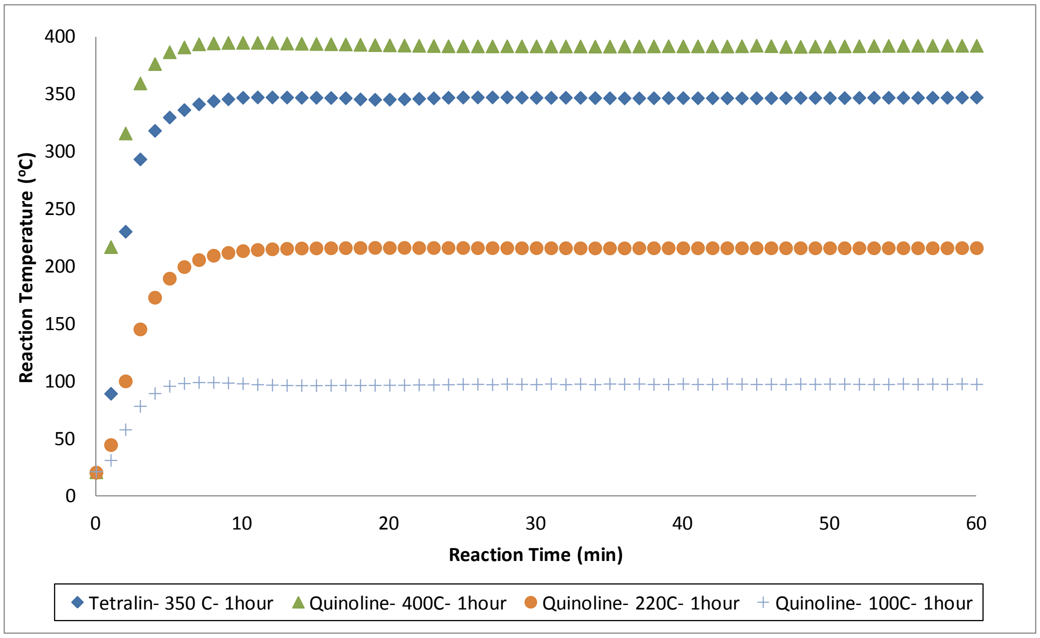

Figure A.4. Sample of the temperature profile of the reaction

THF influence in the extraction yield

Raw poplar lignite (2.7 grams) was place on a filter media. Using vacuum filtration, the coal was washed with fresh THF, until the liquid was clear. Coal residue was then dried over night in a vacuum oven, as indicated in chapter III, conversion 1 was calculated using the equation 3.7. Liquids were transferred to a round bottom flask, of known weight, and THF was completely roto-evaporated as indicated in chapter III. The weight of the residue left in the flask was then determined. Table A.1 shows the experimental results. Conversion 2 was calculated using equation A.1.

$$EY = \frac{(M_{F_{full}} - M_{F_{emp}})}{\mathrm{M}_{\mathrm{Co}_{\mathrm{Raw}}} \cdot (1 - Moisture) \cdot (1 - Ash)} \cdot 100 \tag{A.1}$$

Table A.1

Extraction yield obtained when washing with THF

Run	Coal mass (g)	Conversion 1 (%maf)	Empty Flask (g)	Full Flask (g)	Conversion 2 (% maf)
1	2.7456	2.17	109.8850	109.9174	2.07
2	2.9288	3.41	108.8394	108.8508	0.68

FTIR Spectra

Figure A.5 to A.7 show the spectra obtained for the coal residues, after treatment with the different solvents at 200 and 400 ^{o}C.

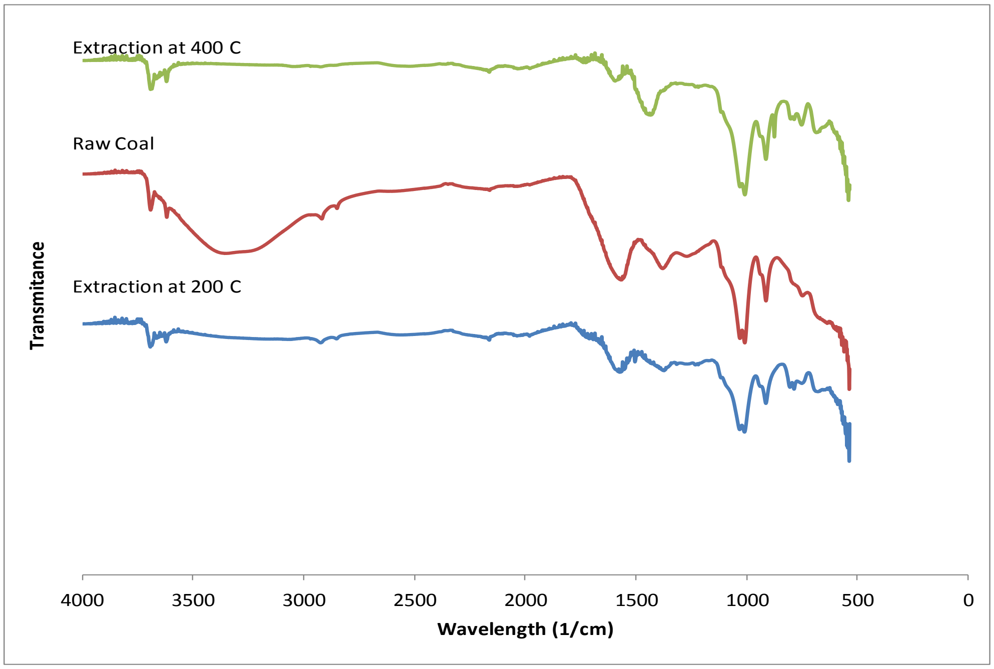

Figure A.5. FTIR spectra of the raw coal and the residues after extraction at 200 and 400 ^{o}C, with Quinoline for one hour, under nitrogen atmosphere

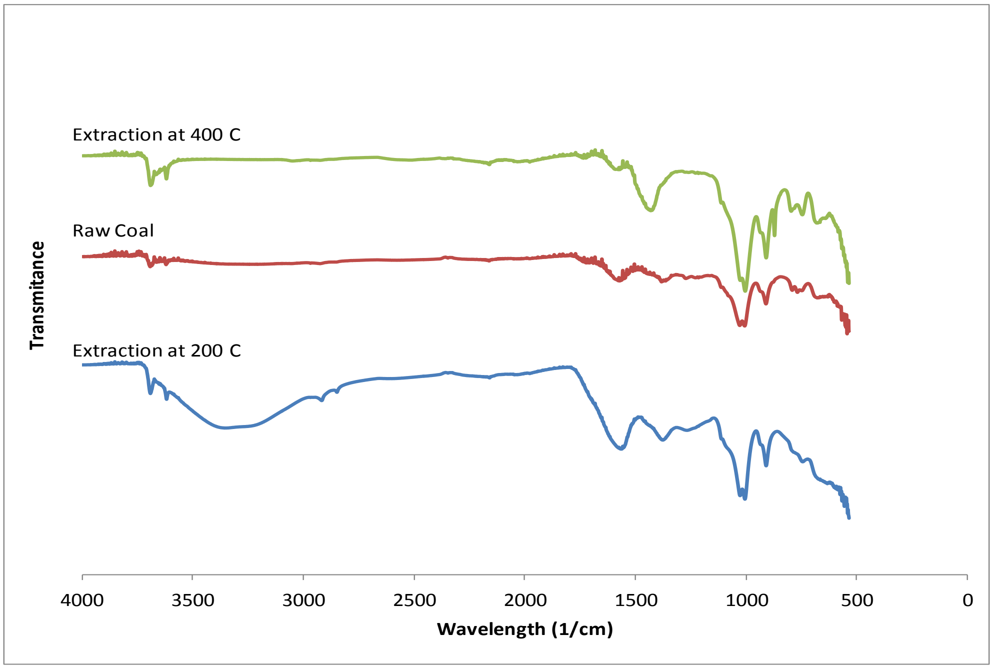

Figure A.6. FTIR spectra of the raw coal and the residues after extraction at 200 and 400 °C, with 1-naphthol for one hour, under nitrogen atmosphere

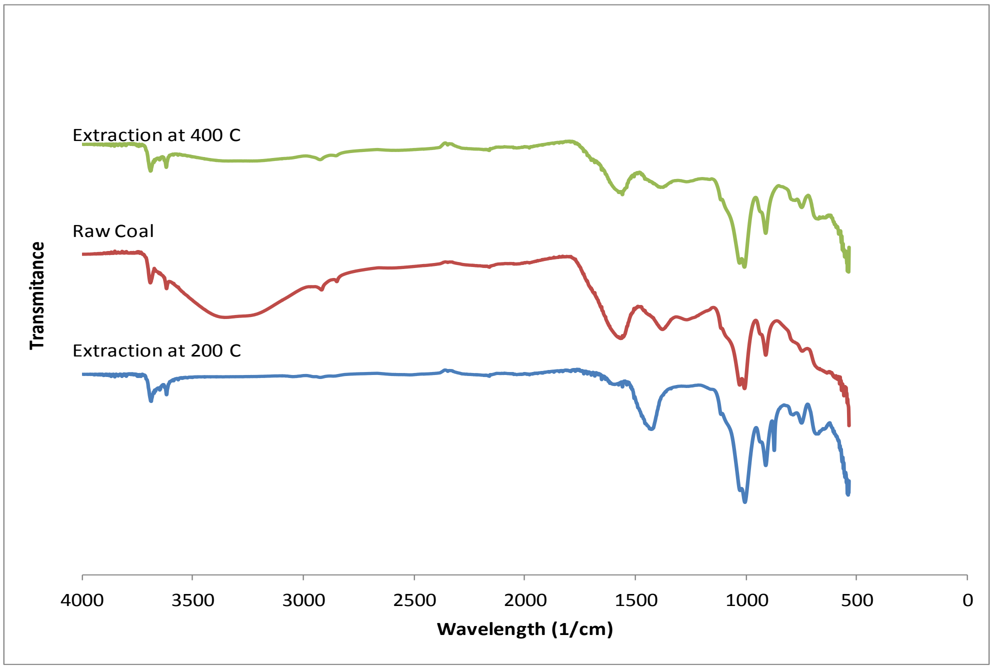

Figure A.7. FTIR spectra of the raw coal and the residues after extraction at 200 and 400 °C, with HT-1006 for one hour, under nitrogen atmosphere

The same observation repeats for all three solvents: increasing strong absorption around 700 cm^{-1} (typical of aromatic C-H out-of-plane bending) and around 1425 cm^{-1}

(C-C stretching within the aromatic ring) when increasing temperature; loss of aliphatic absorptions around 2900 cm^{-1} and the loss of bonded OH (broad around 3500 cm^{-1}).

Figure A.8 to A.10 show the spectra obtained for all the extracts, after treatment with the different solvents at 200 and 400 ^{o}C; as well as the spectra for the raw solvent and the washing solvent.

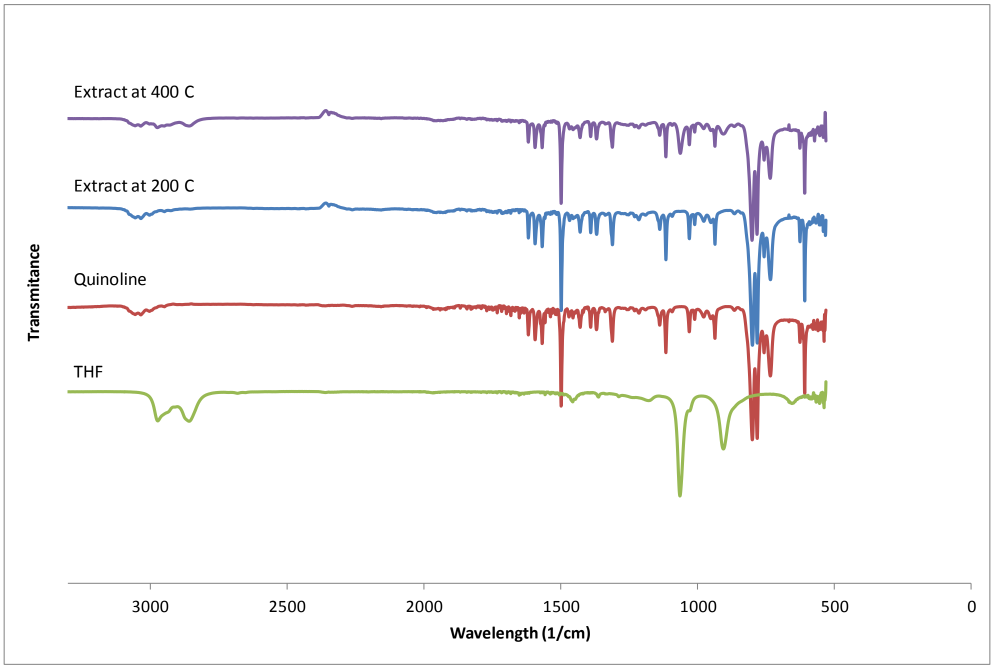

Figure A.8. FTIR spectra of the raw and washing solvents, and the extracts after extraction at 200 and 400 ^{o}C, with quinoline for one hour, under nitrogen atmosphere

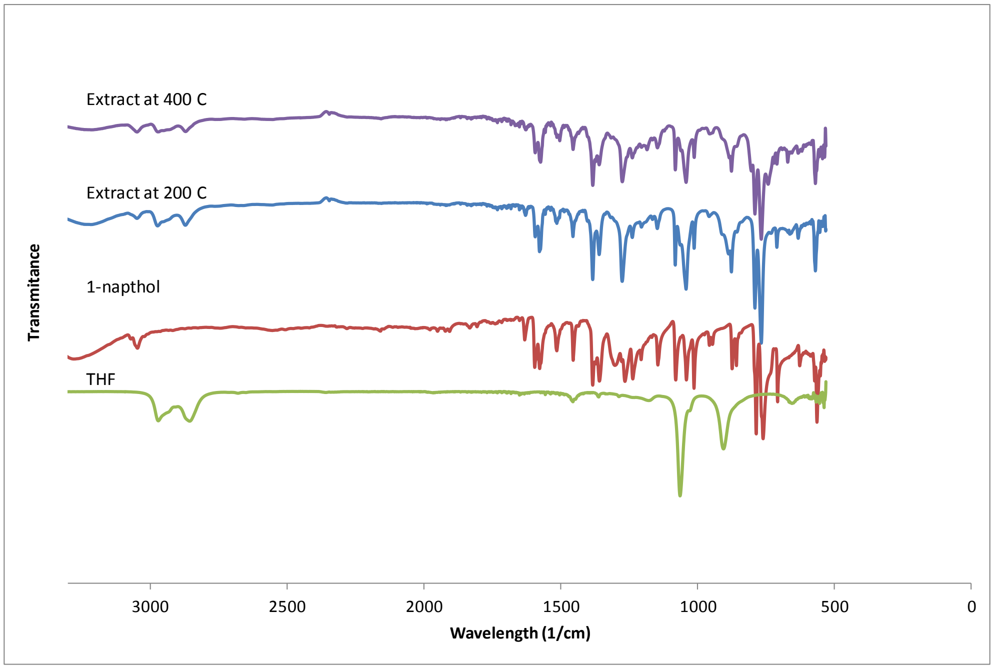

Figure A.9. FTIR spectra of the raw and washing solvents, and the extracts after extraction at 200 and 400 °C, with 1-napthol for one hour, under nitrogen atmosphere

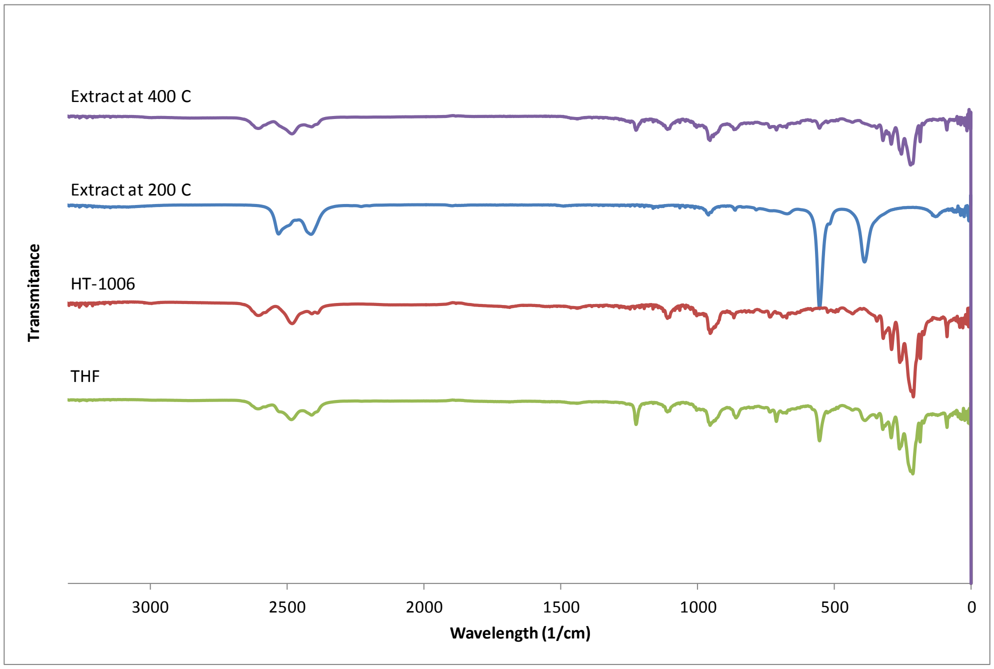

Figure A.10. FTIR spectra of the raw and washing solvents, and the extracts after extraction at 200 and 400 °C, with HT-1006 for one hour, under nitrogen atmosphere

XRF spectra

Figure A.11 and A.12 show the results obtained from the XRF spectra for all the ashes, after treatment with the different solvents at 200 and 400 °C.

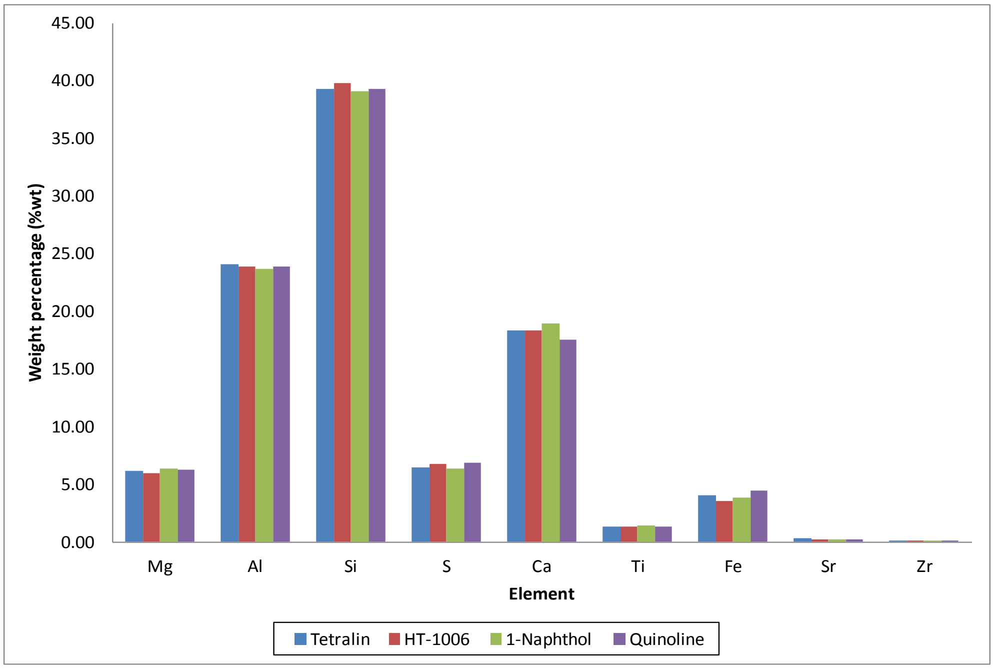

Figure A.11. XRF spectra for the ashes obtained from the residues after treatment with the different solvent at 200 °C, for one hour, under nitrogen atmosphere.

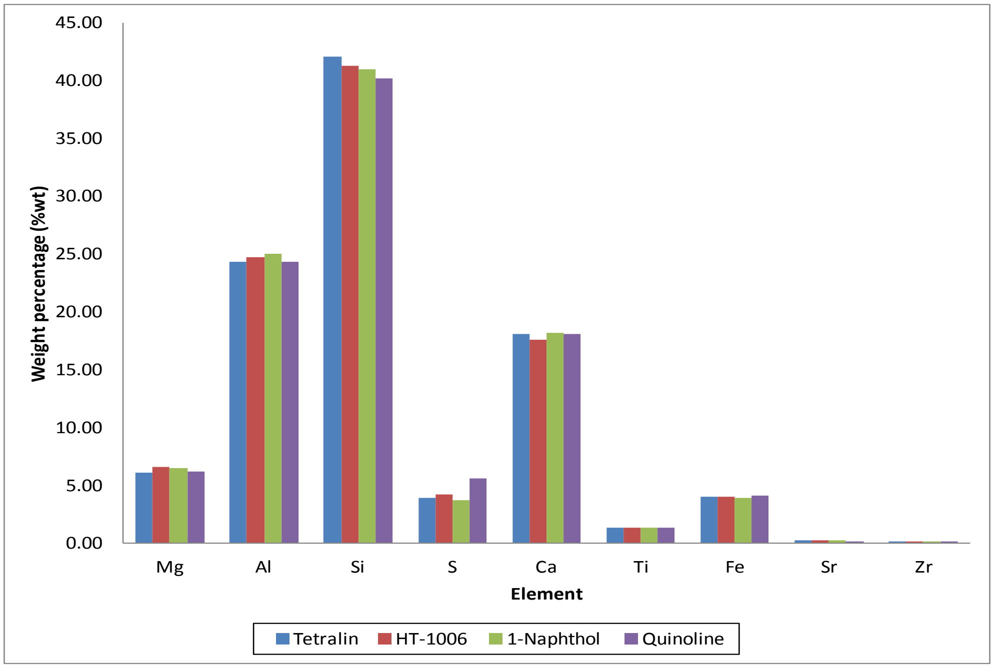

Figure A.12. XRF spectra for the ashes obtained from the residues after treatment with the different solvent at 400 °C, for one hour, under nitrogen atmosphere.

Mass Balance

Table A.2 shows the results from the mass balance. It can be noticed that after reaction there is little or no mass loss. When some mass is lost, it may be due to the formation of gases. Mass gain is due to residues of sand attached to the micro-reactor.

Table A.2

Mass balance for selected experiments

Solvent	Reaction temp. (°C)	Empty reactor mass (g)	Full reactor mass (g)	Final reactor mass (g)	Mass loss (g)	Coal +solv loss (g)
Tetralin	25	229.7	240.7	240.7	0.0	0.0
		228.3	239.1	239.2	0.1	0.1
		227.9	238.9	239.1	0.2	0.2
	350	229.3	240.4	240.2	-0.2	-0.2
		229.9	241.0	240.5	-0.5	-0.2
		229.3	240.3	240.0	-0.3	-0.1
		228.7	239.7	239.2	-0.5	-0.1
Quinoline	220	229.1	239.7	239.6	-0.1	0.3
		229.0	239.9	240.1	0.2	0.1
		229.4	240.1	240.6	0.5	0.3
		229.8	240.6	240.4	-0.2	0.2
	320	229.3	240.2	240.0	-0.2	0.1
		229.2	240.2	239.8	-0.4	0.0
		230.0	240.9	240.5	-0.4	0.1
		228.8	239.4	239.4	0.0	0.2
	350	229.2	240.1	239.8	-0.3	0.1
		228.8	239.8	239.3	-0.5	0.0
		229.2	240.0	240.0	0.0	0.2
		229.6	240.5	240.3	-0.2	0.1
	400	230.3	240.5	239.5	-1	0.9
		229.6	239.8	239.1	-0.7	0.8
		228.6	239.5	239.0	-0.5	0.2
		229.6	240.5	240.1	-0.4	0.1
1-naphthol	100	229.4	235.9	235.5	-0.4	0.1
		230.9	237.4	237.5	0.1	0.1
		229.7	236.3	236.3	0.0	0.0
		229.3	236.0	236.1	0.1	0.1
	200	230.3	236.9	236.8	-0.1	0.0
		230.4	236.9	236.8	-0.1	-0.7
		229.5	235.1	235.3	0.2	1.0
		228.7	236.1	235.7	-0.4	-0.7
	300	229.2	235.9	235.6	-0.3	0.0
		229.1	235.7	235.5	-0.2	-0.1
		229.6	236.3	235.9	-0.4	0.0
		229.3	235.8	235.5	-0.3	0.1
	350	230.3	236.8	236.4	-0.4	0.1
		229.0	235.5	235.3	-0.2	0.1
		229.0	235.5	235.7	0.2	0.1
		230.0	236.5	236.0	-0.5	0.1

Table A.2 (Continued)

Mass balance for selected experiments

Solvent	Reaction temp. (°C)	Empty reactor mass (g)	Full reactor mass (g)	Final reactor mass (g)	Mass loss (g)	Coal +solv loss (g)
1-naphthol	400	228.8	236.6	234.9	-1.7	0.2
		229.3	235.8	235.6	-0.2	0.1
		229.1	235.6	235.3	-0.3	0.1
		229.7	236.0	235.7	-0.3	0.3
HT-1006	100	230.1	241.2	241.3	0.1	0.0
		229.8	241.0	240.9	-0.1	-0.1
		229.4	240.4	240.2	-0.2	0.0
		229.2	240.3	240.4	0.1	0.0
	200	228.6	239.7	238.9	-0.8	0.0
		229.7	240.7	240.4	-0.3	0.1
		229.6	241.0	240.5	-0.5	-0.3
		229.3	240.2	240.5	0.3	0.1
	300	229.3	240.3	240.8	0.5	0.0
		229.4	240.3	240.4	0.1	0.1
		230.0	241.1	241.0	-0.1	0.0
		229.5	240.6	240.4	-0.2	0.0
	350	229.8	241.0	240.4	-0.6	-0.1
		229.3	240.6	24.00	-0.6	0.1
		229.0	239.8	239.3	-0.5	0.1
		228.8	239.8	239.2	-0.6	0.3
	400	229.7	240.5	239.8	-0.7	0.2
		229.5	240.3	239.1	-1.2	0.2
		229.1	240.4	239.9	-0.5	-0.2
Metyl-cyclohexane	100	228.3	239.1	239.0	-0.1	-0.1
		227.8	238.5	238.4	-0.1	-0.1
		228.0	238.8	238.8	0.0	0.0
Heptane	100	228.3	239.2	239.2	0.0	0.0
		227.8	238.6	238.0	-0.6	-0.6
		228.0	238.9	238.0	-0.9	-0.9
Toluene	100	227.5	238.3	238.3	0.0	0.0
		230.1	241.0	240.9	-0.1	-0.1
		228.5	239.4	239.4	0.0	0.0

Coal + Solvent loss is the amount of material lost during handling, before reaction. It was determined using the following equation:

$$M_{MR_{full}} = M_{MR_{emp}} + M_{Solv} + M_{coal} + M_{Beads} \tag{A.2}$$

Where $M_{MR_{full}}$ is the mass of the micro-reactor full, $M_{MR_{emp}}$is the mass of the micro-reactor empty and M_{Solv}, M_{coal}, $M_{Beads}$are the mass of solvent, coal and beads, respectively.

It can be noticed that little to no material is lost during handling. Hence, the experimental error originated from this issue is kept to the minimum possible.