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Investigation of solvent extraction of coal at low temperatures

by

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Dedicated to my late father

For all his love, kindness and support

Abstract

Solvent extraction of coal is a method to produce low molecular weight products from coal. It also can be used as a pretreatment for Direct Coal Liquefaction to enhance its efficiency.

Yield, rate and nature of coal dissolution at low temperatures (25-150°C) and short contact time have been studied, using a flow micro-reactor. The results show it can be done in less than 15 minutes and the yield is about 7-9%, depending on the temperature. Also it has been observed the solvent to coal ratio has no significant effect on yield as it increases. Extraction of Poplar coal with tetralin at 150°C enhances the porosity of the coal. This knowledge about low temperature extraction was applied to liquefaction at 350°C by performing preheating in different ways. The yield increased as the mean temperature of the temperature profile during preheating was increased.

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Contents

1 INTRODUCTION 1

1.1 Background 1

1.1.1 Direct Coal Liquefaction 4

1.2 Objective 6

1.3 Scope of work 6

1.4 References 8

2 COAL OVERVIEW 10

2.1 Literature review 10

2.2 Coal Composition 10

2.2.1 Physical composition 11

2.2.2 Chemical Composition 12

2.3 Structure 14

2.4 Classification of coal 16

2.5 Coal dissolution 16

2.5.1 Physical dissolution 17

2.5.2 Chemical dissolution 19

2.6 Solvent extraction 20

2.7 Coal Conversion 25

2.7.1 Pyrolysis 25

2.7.2 Gasification 25

2.7.3 Liquefaction 25

2.8 Applications of coal and coal extraction 27

2.8.1 Pitch 27

2.8.2 Coke 28

2.8.3 Carbon fibers 28

2.9 References 29

3 PHYSICAL COAL DISSOLUTION AT LOW TEMPERATURE AND SHORT CONTACT TIME 32

3.1 Introduction 32
3.1.1 Problem 33

3.1.2 Approach 33

3.2 Experimental 34
3.2.1 Material 34

3.2.2 Coal characterization 36

3.2.3 Equipment 38

3.2.4 Procedure 40

3.2.5 Analyses 41

3.2.6 Calculations 41

3.3 Results 44
3.3.1 Extraction yield 44

3.3.2 Extraction rate 47

3.4 Discussion 49
3.4.1 Extraction yield 49

3.4.2 Extraction rate 51

3.4.3 Precipitate analysis 52

3.5 Conclusion 54

3.6 References 55

4 EFFECT OF SOLVENT TO COAL RATIO ON PHYSICAL COAL DISSOLUTION AT LOW TEMPERATURE AND SHORT CONTACT TIME 56

4.1 Introduction 56
4.1.1 Problem 57
4.1.2 Approach 58

4.2 Experimental 59
4.2.1 Material 59
4.2.2 Equipment and procedure 59
4.2.3 Analyses 61
4.2.4 Calculations 61

4.3 Results 62
4.3.1 Solvent extraction using flow micro-reactor 62
4.3.2 Solvent extraction using beakers and magnetic stirrers 63

4.4 Discussion 66
4.4.1 Solvent extraction using flow micro-reactor 66
4.4.2 Solvent extraction using beakers and magnetic stirrers 68
4.4.3 UV-Vis results 70

4.5 Conclusion 70

5 EFFECT OF SOLVENT EXTRACTION ON COAL POROSITY AT LOW TEMPERATURES 71

5.1 Introduction 71
5.1.1 Background Literature 72
5.1.2 Problem 76
5.1.3 Approach 76

5.2 Experimental 76

5.2.1 Material ... 76
5.2.2 Coal characterization ... 77
5.2.3 Equipment and procedure ... 77
5.2.4 Procedure ... 78
5.2.5 Analyses ... 78
5.2.6 Calculations ... 79

5.3 Results ... 79
5.3.1 Extraction yields ... 79
5.3.2 Total intruded volume and surface area ... 79
5.3.3 Changes in pore diameter after extraction ... 81

5.4 Discussion ... 82
5.4.1 Total surface area and total volume ... 82
5.4.2 Changes in pore diameter after extraction ... 84

5.5 Conclusion ... 86

5.6 References ... 87

6 INVESTIGATION OF THE EFFECT OF HEATING RATE ON COAL EXTRACTION ... 88

6.1 Introduction ... 88
6.1.1 Background Literature ... 89
6.1.2 Problem ... 92
6.1.3 Approach ... 92

6.2 Experimental ... 93
6.2.1 Materials ... 93
6.2.2 Coal characterization ... 94
6.2.3 Equipment ... 94

6.3 Procedures 96

6.4 Results 97
6.4.1 Extraction with isothermal step 98
6.4.2 Extraction without isothermal step 100

6.5 Discussion 102
6.5.1 Extraction with isothermal step 102
6.5.2 Extraction without isothermal step 104
6.5.3 Comparing extraction yields for with and without isothermal step 105

6.6 Conclusion 107

6.7 References 108

7 CONCLUSION 109

List of tables

TABLE 1-1 ESTIMATED PRODUCTION COST FOR NATURAL AND SYNTHETIC CRUDE OILS PRODUCED FROM VARIOUS SOURCES 3

TABLE 2-1ULTIMATE ANALYSIS OF COAL SAMPLES, DIFFERENT RANKS, WT % (DRY ASH FREE BASIS)..13

TABLE 3-1 ULTIMATE AND PROXIMATE ANALYSES OF COAL. (ASH FREE BASES)...................35

TABLE 3-2 ASH MEASUREMENT RESULTS FOR RESIDUES AT 25 °C EXPERIMENTS 42

TABLE 3-3 ASH MEASUREMENT RESULTS FOR RESIDUES AT 100 °C EXPERIMENTS 42

TABLE 3-4 ASH MEASUREMENT RESULTS FOR RESIDUES AT 150 °C EXPERIMENTS 43

TABLE 3-5 EXTRACTION YIELDS, ASH AND MOISTURE FREE AT 25 °C AND DIFFERENT TIMES 44

TABLE 3-6 EXTRACTION YIELDS, ASH AND MOISTURE FREE AT 100 °C AND DIFFERENT TIMES 45

TABLE 3-7 EXTRACTION YIELDS, ASH AND MOISTURE FREE AT 150 °C AND DIFFERENT TIMES 46

TABLE 3-8 ANALYSES OF DIFFERENT EXTRACT-TETRALIN DILUTED SOLUTIONS, FOR SAMPLES AT DIFFERENT TIMES AND TEMPERATURES. 48

TABLE 4-1 EXTRACTION YIELDS, ASH AND MOISTURE FREE AT DIFFERENT SOLVENT TO COAL RATIOS, IN FLOW MICRO-REACTOR,100 °C AND 8 MINUTES...................................62

TABLE 4-2 UV-VIS ABSORPTION UNITS FOR THE CLEAR LIQUID EXTRACT FROM POPLAR LIGNITE WITH TETRALIN IN FLOW MICRO-REACTOR, 100 °C AND 8 MINUTES................63

TABLE 4-3 EXTRACTION YIELDS, ASH AND MOISTURE FREE AT DIFFERENT SOLVENT TO COAL RATIOS, IN BEAKERS, 100 °C AND 8 MINUTES 63

TABLE 4-4 UV-VIS ABSORPTION OF THE CLEAR LIQUID EXTRACT FROM POPLAR LIGNITE WITH TETRALIN IN BEAKERS...64

TABLE 4-5 STUDENT T-TEST RESULTS FOR EXTRACTION YIELD RESULTS PERFORMED IN FLOW MICRO-REACTOR AND DIFFERENT SOLVENT: COAL RATIOS 67

TABLE 4-6 STUDENT T-TEST RESULTS FOR EXTRACTION YIELD RESULTS PERFORMED IN BEAKERS AND DIFFERENT SOLVENT: COAL RATIOS...69

TABLE 5-1 EXTRACTION YIELDS FOR SOLVENT EXTRACTION OF COAL AT 150 °C, ASH AND MOISTURE FREE BASES%...79

TABLE 5-2 TOTAL SURFACE AREA (M^2/G) FOR RAW AND EXTRACTED COAL............................80

TABLE 5-3 TOTAL INTRUDED VOLUME (CM^3/G), RAW AND EXTRACTED COAL........................80

TABLE 5-4 INTRUDED VOLUME FOR PORES WITH DIFFERENT DIAMETER RANGES.................81

TABLE 6-1 ULTIMATE AND PROXIMATE ANALYSES OF COAL. (ASH FREE BASIS)...................93

TABLE 6-2 LOWER MEAN HEATING RATE (SEE FIGURE 6.3), WITH ISOTHERMAL STEP, AT 350 °C FOR 90 MIN....99
TABLE 6-3 CONSTANT HEATING RATE (SEE FIGURE 6.3), WITH ISOTHERMAL STEP, AT 350 °C FOR 90 MIN....99
TABLE 6-4 HIGHER MEAN HEATING RATE (SEE FIGURE 6.3), WITH ISOTHERMAL STEP, AT 350 °C FOR 90 MIN....100
TABLE 6-5 LOWER MEAN HEATING RATE (SEE FIGURE 6.4), NO ISOTHERMAL STEP, AT 350 °C FOR 70 MIN....101
TABLE 6-6 CONSTANT HEATING RATE (SEE FIGURE 6.4), NO ISOTHERMAL STEP, AT 350 °C FOR 70 MIN....101
TABLE 6-7 HIGHER MEAN HEATING RATE (SEE FIGURE 6.4), NO ISOTHERMAL STEP, AT 350 °C FOR 70 MIN....101
TABLE 6-8 THE STUDENT T-TEST RESULTS FOR LOWER MEAN HEATING RATE (L), CONSTANT HEATING RATE (C) AND HIGHER HEATING RATE (H) DATA POINTS WITH ISOTHERMAL STEP....102
TABLE 6-9 THE STUDENT T-TEST RESULTS FOR LOWER MEAN HEATING RATE (L), CONSTANT HEATING RATE (C) AND HIGHER HEATING RATE (H) DATA POINTS WITHOUT ISOTHERMAL STEP....104
TABLE 6-10 ABSOLUTE DIFFERENCE BETWEEN LIQUID YIELD RESULTS FOR EXPERIMENTS WITH SAME HEATING RATE BUT WITH AND WITHOUT ISOTHERMAL STEP.....106

List of Figures

FIGURE 2-1 PROPOSED STRUCTURE FOR BITUMINOUS COAL. (KIRK-OTHMER, 1993) 15

FIGURE 2-2 EXTRACTION YIELD USING DIFFERENT SOLVENTS AS THE FUNCTION OF THE RANK OF COAL (VAN KREVELEN, 1993)..23

FIGURE 2-3 SOLUBILITY PARAMETER OF COAL AS A FUNCTION OF RANK AND AROMATICITY (VAN KREVELEN, 1993)..24

FIGURE 3-1 CHEMICAL STRUCTURE OF 1,2,3,4-TETRAHYDRONAPTHALENE 35

FIGURE 3-2 A SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SETUP. 39

FIGURE 3-3 UV-VIS SPECTRA OF DILUTED TETRALIN EXTRACTS OBTAINED FROM POPLAR AT 25, 100 AND 150 °C RESPECTIVELY...47

FIGURE 3-4 EXTRACTION YIELD (WT %) ON ASH AND MOISTURE-FREE BASIS OF POPLAR LIGNITE WITH TETRALIN OVER TIME AT 25 °C, 100 °C AND 150 °C. 49

FIGURE 3-5 . UV-VIS ABSORBTION OF THE CLEAR LIQUID EXTRACT FROM POPLAR LIGNITE WITH TETRALIN OVER TIME AT 25, 100 AND 150 °C...52

FIGURE 3-6 COAL EXTRACT IN TETRALIN UNDER DSC MICROSCOPE AT 40 °C (LEFT) AND 110 °C (RIGHT), SHOWING PRECIPITATE LIQUEFYING/DISSOLVING..53

FIGURE 4-1 AVERAGE EXTRACTION YIELDS%, ASH AND MOISTURE FREE, FOR DIFFERENT SOLVENT: COAL RATIOS, USING FLOW MICRO-REACTOR, 100 °C AND 8 MINUTES 66

FIGURE 4-2 AVERAGE EXTRACTION YIELDS%, ASH AND MOISTURE FREE, FOR DIFFERENT SOLVENT: COAL RATIOS, USING BEAKERS AND MAGNETIC STIRRERS, 100 °C AND 8 MINUTES 68

FIGURE 5-1 REACTION SET UP...77

FIGURE 5-2 AVERAGE TOTAL SURFACE AREA (M^2/G) MEASURED BY MERCURY POROSIMETRY FOR THREE SAMPLES OF RAW AND EXTRACTED COAL (TABLE 5.2).....83

FIGURE 5-3 AVERAGE TOTAL INTRUDED VOLUME (CM3/G) MEASURED BY MERCURY POROSIMETRY FOR THREE SAMPLES OF RAW AND EXTRACTED COAL (TABLE 5.3).....83

FIGURE 5-4 85

FIGURE 6-1 THE REACTION SETUP, MICRO-REACTORS AND THE HOLDER 94

FIGURE 6-2 THE SAND BATH, AGITATOR AND THE CONTROLLER..95

FIGURE 6-3 TIME TEMPERATURE PROFILE FOR EXPERIMENTS WITH ISOTHERMAL STEP 98

FIGURE 6-4 TIME TEMPERATURE PROFILE FOR EXPERIMENTS WITH NO ISOTHERMAL STEP. 100

FIGURE 6-5 AVERAGE LIQUID YIELDS, FOR EXPERIMENTS WITH ISOTHERMAL STEP AND DIFFERENT TIME-TEMPERATURE PROFILE...102

FIGURE 6-6 AVERAGE LIQUID YIELDS, FOR EXPERIMENTS WITHOUT ISOTHERMAL STEP. .105

FIGURE 6-7 EXTRACTION YIELDS FOR EXPERIMENTS WITH AND WITHOUT ISOTHERMAL STEP. 105

1 Introduction

1.1 Background

The share of the element carbon in the total bulk structure of the earth is as little as 0.04 percent, and only a small part of this, which is called “dynamic” carbon, can react with oxygen and be useful. Despite its small amount, it can be considered as one of the most important elements and also an important source of energy. It mainly occurs naturally in fossil fuels, inorganic carbonates and carbon dioxide. Fossil fuels include peat, lignite, coal, crude oil and natural gas.

About 100 years ago coal was the dominant source of energy, and 61.3 % of the energy consumption was supplied by it (Van Krevelen, 1981). As the time passed other energy sources gained importance and in the case of transportation fuels and chemicals, coal was replaced by crude oil as primary resource. The important factors for this displacement were oil abundance, availability, ease of refining and low price, and at present the primary feed stock for fuel and chemical products is petroleum. But the need for energy is increasing every day and conventional crude oil is a finite natural resource, in near future it will not be able to meet the global energy demand for transportation fuel and petrochemicals. There is a concept known as “peak oil” which means the point of maximum crude oil production. In 1970 the Hubbert-model predicted peak oil production in the United States, ever since peak oil production has been passed in about half of the crude oil producing countries.

All above facts, the uncertainty about the actual amount of recoverable oil remaining in the reservoirs and a sharp price increase in petroleum products during the past decade make it obvious that refining technologies for the conversion of alternative carbon sources should be developed to reduce the potential future effects of conventional crude oil shortfall (King and de Klerk, 2011) .

In industrialized countries the demand for energy which is mostly supplied by petroleum and natural gas is increasing, and the world petroleum supplies are expected to become limiting in the near future. Also its local distribution caused some crises and supply interruptions. The information about the cost of oil production is rarely revealed, but here is in table 1.1 the estimation of the total costs for producing natural and synthetic crude oil from different sources that has been given in the International Energy Agency (IEA). This information is from different parts of the world and was published in November 2008 to provide a world energy outlook (IEA, 2008).

Around the world you can find the coal as a valuable and abundant fossil fuel resource and Canada has the fifth largest inventory of the coal in the world (Bustin and Smith, 1993). The coal resources are widely spread and have different attributes. Coal is also an important factor for the development of the economy in the world. At present using coal as the main source of transportation fuel and chemical products is not economical. In future the utilization of it can be affected by the changing in the price of the other energy sources, but it is and will remain an important alternative for conventional crude oil (King and de Klerk, 2011). The use of coal is expected to increase to compensate for the anticipated shortage of petroleum and natural gas in some regions of the world.

One of the technologies that can convert carbon based materials to synthetic crude oil is the coal-to-liquid process. As we can see from the energy outlook (Table 1-1), the production cost of this method is not low. Due to the diversity in the nation's coal resources, Canada is in a strong position to support coal development opportunities on national and international scale (Volger, 2006). So, coal-to-liquid processes are getting special attention these days, because high-quality, cost-effective fuels can in principle be made by them, and the technologies can meet environmental regulations.

Table 1-1 Estimated production cost for natural and synthetic crude oils produced from various sources

Oilfields/source	Estimated Production Costs($/barrel 2008)
Middle east/ North Africa oilfields	6 – 28
Other conventional oilfields	6 – 39
Deep/ultra-deep-water oilfields	32 – 65
Arctic oilfields	32 – 100
CO_2 enhanced oil recovery	30 – 80
Enhanced oil recovery	32 – 82
Heavy oil/bitumen	32 – 68
Oil shales	52 – 113
Gas-to-liquids	38 – 113
Coal-to-liquids	60 – 113

The purpose of a coal-to-liquid process is to convert coal to more useful material which can be in the gas or liquid phase. These phases are both easier to handle than solid material, but liquid has much higher density than gas. *Direct liquefaction* is one of the coal-to-liquid technologies which convert the solid feed material to more useful products. In *direct liquefaction* the characteristics of the product can be partially similar to the characteristics of the feed, some of the small molecules can be extracted without change, but the purpose of the direct liquefaction process is to break down larger molecules and to liquefy the feed with some physical or chemical changes (King and de Klerk, 2011). From a chemical view point, the main differences between coal and petroleum are because of the much lower H/C ratio of coal(□ 0.7 as against >1.2 for petroleum); so coal can be converted to liquid hydrocarbons by addition of hydrogen which is called *direct coal liquefaction* (DCL)(Berkowitz, 1979).

1.1.1 Direct Coal Liquefaction

Direct coal liquefaction consists of addition of hydrogen to coal at high temperature and pressure in a solvent slurry. The solvent is a suitable transportation medium where heat and mass transfer can happen during chemical reaction. In many processes the solvent has the ability to donate hydrogen to the coal and is called a donor solvent. At high temperature the carbon-carbon linkages rupture thermally and coal molecules crack and the rate of reaction increases. High pressure helps to keep the solvent and products in the liquid phase, prevents coke build-up on the reactor walls and catalyst surface (in the case of catalytic DCL), and also helps hydrogenation by keeping a high partial pressure of hydrogen (Robinson, 2009).

Direct coal liquefaction can be done at 450-500 °C, usually under 15-30 MPa H_2 in an appropriate solvent with suitable catalysts (Robinson, 2009)(Comolli et al., 1999; Hirano, 2000; Kouzu et al., 2000; Whitehurst, 1980)(Liu et al., 2010). The use of catalysts helps to increase the rate of the reactions such as the cracking, hydrogenation, and heteroatom (O, N and S) removal reactions. Although DCL processes can produce a large number of useful products, there are some issues that increase the capital and maintenance cost of this method. Some of these issues can be a result of the coarse nature of coal slurry which can harm the reactors, and the separation of the solid part of the products from the liquid part. Implementing liquefaction conditions, severe temperature and pressure, also the reactors that can operate in these conditions, and the need for expensive hydrogen-donor solvent, may increase the price of synfuels produced with this method, so they cannot compete with oil products when the crude oil price is less than $70-80/barrel (2009 dollars), but for prices higher than that, direct coal liquefaction can be profitable (Robinson, 2009). A good way to increase DCL profitability is to find ways to increase its efficiency. One of the aspects that were highlighted for further study is the preheating of coal before liquefaction (Shah et al., 1981).

To improve the efficiency of DCL, low temperature extraction can be done on the feed material, and by swelling the structure of coal and dissolving it, molecules with low molecular weight which are trapped in the coal matrix can be released(Berkowitz, 1979). This extraction can decrease the volume of the remaining feed which should be introduced to the high temperature and pressure reactors, so it will reduce the reactor size needed. Coal dissolution starts during preheating of coal and physical coal dissolution is a fast process, although it has limited liquid yield. It can take place in less than 15 minutes at temperature in the range 25-300 °C.(Figueroa Murcia et al., 2011) So this can be an interesting and field of study for commercializing new DCL technology and increasing its efficiency.

1.2 Objective

As we see in the introduction section, solvent extraction of coal can help to increase the DCL efficiency. So, having a good knowledge about the nature of solvent extraction of coal at low temperatures is necessary.

The objective of this work is to study different aspects of coal dissolution at low temperatures such as effect of time temperature and solvent to coal ratio, especially for short contact times, also the changes of pore structure caused by solvent extraction. Then perform extractions at higher temperatures with different preheating, to see the effect of preheating on the solvent extraction of coal.

1.3 Scope of work

Solvent extraction of coal has been studied before at high temperatures using batch reactors. With this kind of setup, it was not possible to investigate dissolution at less than 15 minutes, because of the heating time needed for the reactors to reach the certain temperature of the reaction. In this work the rate and nature of coal dissolution at low temperatures and short contact time have been investigated.

Another factor that can affect the coal dissolution is solvent to coal ratio. Knowing the effect of solvent to coal ratio would help to prevent usage of extra solvent and also designing reactors with proper size. So this factor has been studied to clarify the effect of solvent to coal ratio at low temperatures.

An additional important factor in solvent extraction of coal is the pore structure of coal, and the changes of it during extraction can affect the suitability of coal for further processes. Studying this factor at low temperatures, using tetralin as solvent is important to see if the changes in pore structure are favorable or not.

After investigating the factors mentioned above, on low temperature solvent extraction, liquefaction with different preheating steps have been studied.

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2 Coal overview

2.1 Literature review

Coal is considered as an extremely complex material and can show vastly different physical and chemical properties, these different properties can affect the results of different processes. So to advance technologies for coal upgrading, there should be good knowledge about the classification and the structure of coal. This chapter provides a literature review about coal structure and composition to give an overview of the common knowledge about this field and the properties that will influence this study.

2.2 Coal Composition

Coal properties can influence the solvent extraction of coal to a great extent. Coal has been formed in variety of places in the world and also originated from different kinds of components; these factors caused different compositions in coals and coal reactions show unique problems, because the key reactant is relatively undefined in its organic structure and reaction chemistry. So many research studies have been done on the origin and chemical structure of coal, but there are no ultimate fundamental descriptions of coal structure. The main properties that can be used to characterize coals are physical and chemical composition and its rank classification.

Here is a quick look at coals series based on the increase in their carbon contents.

Peat → lignite → subbituminous coal → bituminous coal → anthracite

2.2.1 Physical composition

Bituminous coal is made up of four banded components that can be clearly identified with the naked eye; vitrain, clarain, durain and fusain. In contemporary literature they are called lithotypes. In immature coals, i.e, in lignites and subbituminous coals, banding are less expressed, so these coals are more homogeneous, not banded and layered like bituminous coal. The ultimate microscopic constituents of coal, are classified into three maceral groups; Vitrinite, Exinite, Inertinite. These different groups are characterized by their chemical composition, appearance and optical properties (Berkowitz, 1979).

Some studies on the coal petrographic composition in the late 1940's gave better understanding of different coal macerals' reactivity in coal hydrogenation process. To study this factor, coal, the solvent (here tetralin, because of its hydrogen-donor ability) and a catalyst (stannous sulphide) were kept in a batch reactor under 7 MPa of hydrogen pressure (Wen and Lee, 1979). The whole experiment was at room temperature for three hours. The results showed fusains are not completely inert, but they yield much less oil than the other coal macerals. Vitrinites have a very high yield in producing pitch and not all the macerals in the inertinite group are resistant to hydrogenation equally (Wen and Lee, 1979). So for choosing an appropriate coal for solvent extraction, one should consider its petrographic composition.

2.2.2 Chemical Composition

The chemical composition of coal can be expressed in terms of its proximate analysis and ultimate or elemental composition. There is no information about coal structure in these two analyses, but both of them result in producing data that can be correlated with many aspects of coal behavior. The parameters of proximate analysis are: moisture content (m), volatile matter content (vm), ash content (a), and fixed carbon (fc) which is different from elemental carbon. American Society for Testing Materials (ASTM) has established methods and standards for the proximate analysis of coal, the ASTM D3172 standard test method (ASTM, 2007, DOI:10.1520/D3172-07A, www.astm.org).

Different kinds of moisture that occur in coal can be; bulk or superficial moisture and physically adsorbed moisture. In addition, low rank coal may contain chemisorbed moisture or they may begin to generate water by thermal decomposition at temperatures as low as 160-170°C.

Volatile matter is composed of a wide spectrum of hydrocarbons, carbon oxides, and chemically bound water and all these materials form by thermal decomposition. Volatile matter can be determined with the weight loss of dried coal during heating. The conditions of heating are, 7 min at 950±20 °C.

Ash content can be determined from the residue of heated coal when the sample is totally incinerated in air at 725±25 °C or slightly higher temperatures.

Elemental analysis (ultimate analysis) shows the amount of carbon, hydrogen, nitrogen, sulfur and oxygen, and usually is performed with classic oxidation, decomposition or reduction methods, as described in the ASTM D3176 standard test method (ASTM,2011,DOI: 10.1520/D3176, www.astm.org).

There are elemental analyses of selected different coal samples with different ranks in table 2.1. (Wen and Lee, 1979) Main elements in coal are carbon and hydrogen. There are also heteroatoms like nitrogen, oxygen, sulfur and different metals in the form of mineral matter. As the rank of coal increases, the carbon content also increases and the oxygen content decreases. But there can be overlaps for the carbon and oxygen contents of coals that are near in rank.

Table 2-1 Ultimate Analysis of Coal samples, Different Ranks, wt % (dry ash free basis)

Coal rank	**C**	**H**	**O**	**N**	**S**
Lignite	70.6	4.7	23.4	0.7	0.6
Subbituminous A	70.6	4.8	23.3	0.7	0.6
Subbituminous B	72.3	4.7	21.0	1.7	0.3
Subbituminous C	78.5	5.3	13.9	1.5	0.8
High Volatile bituminous A	77.3	4.9	14.3	1.2	2.3
High Volatile bituminous B	81.9	5.1	10.5	1.9	0.6
High Volatile bituminous C	84.9	5.6	6.9	1.6	1.0
Medium volatile bituminous	89.1	5.0	3.6	1.7	0.6
Low volatile bituminous	90.8	4.6	3.3	0.7	0.6
Semianthracite	90.5	3.9	3.4	1.5	0.7
Anthracite	92.8	2.7	2.9	1.0	0.6
Anthracite*	95.9	0.89	1.8	0.3	1.8
Meta-anthracite*	97.9	0.21	1.8	0.2	-

Organic oxygen can occur in different functional forms such as, phenolic, hydroxyl, carboxylic acid, carbonyl, ether linkages and heterocyclic oxygen.

Nitrogen usually is present mainly in cyclic structures. Oxygen and nitrogen also occur in the mineral matter. The (organic) sulfur content of coal can change in the range of 0.2-5 % by weight, but mostly is in the range 0.2 to 1.5 %.

Mineral matter is a common part of different types of coal. Minerals in coal are generally clays, quartz, carbonates, sulfide minerals, etc. Clays consist of hydrated aluminosilicates which are generally formulated as $Al_2O_3.4SiO_2.nH_2O$. Clays can be associated with different metals in the coal. Carbonate minerals consist of metal carbonates such as $CaCO_3$, $FeCO_3$, $MgCO_3$, etc. Metal pyrites such as FeS_2 are the sulfide minerals and it is the main source of inorganic sulfur in coal (Speight, 1994).

2.3 Structure

To use coal in different coal conversion processes such as combustion, pyrolysis, liquefaction and gasification, it is important to have an understanding of the coal structure. Despite all studies the coal structure is still not known completely. The reason for this is its highly heterogeneous nature. Coal is usually considered to have a high-molecular weight, polymeric structure. In Figure 2.1 a representative structure of coal is shown, and it is more likely to represent bituminous coal (Kirk-Othmer, 1993). These kinds of structure basically illustrate an average structure and there is a good agreement between this formula and the ultimate analysis. Also it provides an indication of the aromaticity and the nature and quantity of functional groups in a coal sample (Schobert, 1987). In some literature it is said, coal is a network of clusters bonded together covalently

(Larsen et al., 1985). The clusters are constituted of joined aromatic rings with different functional groups attached to them. Hydrogen bonding, ether linkages, aliphatic side chains and etc., are some of the ways that keep these clusters together. Although lots of research has been done to get a better view about the coal structure, there is still much uncertainty and still much effort is needed in this area (Van Heek, 2000). Though among all coal structure models, the three-dimensional macromolecular network of coal is the most accepted these days.

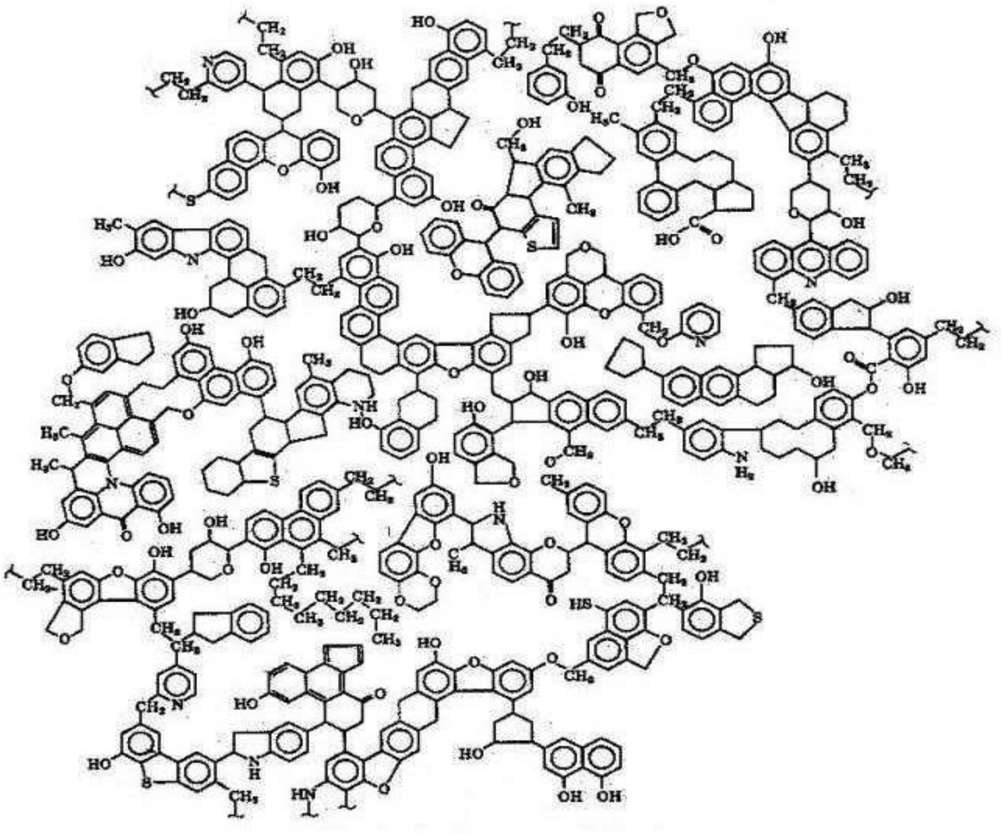

Figure 2-1 Proposed structure for bituminous coal. (Kirk-Othmer, 1993)

2.4 Classification of coal

Coal properties can differ to a great extent, so does its suitability for different applications. A thorough characterization of coal can take a lot of time and is expensive. So, much effort has been put into establishing a simple system for classification of coals. Different classification systems have been developed. One way to classify coal is based on their geological age in which they are assumed to have originated. The fact that the structure of lots of coals is laminated and includes layers that may be noticeably different in thickness, luster and texture is the base of classification by its banded structure. In classification by rank, volatile matter content and heating value of the coal is considered.

As said before, coal rank is usually connected to carbon content and rank increases from low-carbon coal to high-carbon coal (Van Krevelen, 1981). But carbon content can vary with the other parameters in coal in either way, so for choosing a system to classify coal by rank, the purpose of it should be considered.

"For scientific classifications based on a dry, ash-free or dry, mineral-matter-free basis, normally the main parameters are percentage carbon versus percentage hydrogen, or, in certain cases, atomic O/C versus H/C ratios; or percentage volatile matter (vm) of fixed carbon content (FC) versus calorific value (Q) (Berkowitz, 1979)".

2.5 Coal dissolution

The process of dissolution can occur either physically or there might be some chemical reactions involved, in which the solute and solvent properties might change. Dryden (1963a) proposed that dissolution happens when units of colloidal size are removed directly from the coal. He stated that the coal made of a matrix of larger, strongly linked micelles (a molecular aggregate that constitutes a colloidal particle) and they are connected with smaller, not as strongly bonded micelles. The dissolution occurs when these units are removed and smaller parts are dissolved while the larger parts cannot be liberated at the temperature of the physical dissolution process (Guin et al., 1976).

2.5.1 Physical dissolution

To have a solution, a physical solution must happen, in which the solvent molecules surround and separate the solute molecules. One of the classifications of solutions is based on the relation between the quantity of solvent and solute. Based on this classification there are three kinds of solution: unsaturated, saturated, and supersaturated. These categories show if the solvent has the capacity to dissolve more solute, or if the dissolved amount is equal to the capacity of solvent or for the last one, if the solute is more than the amount the solvent can dissolve. The dissolving capacity of the solvent can change with temperature and pressure. The value of this capacity can be shown with solubility constant.

Pure physical coal dissolutions occur in temperature ranges which no chemical reactions happen. For lignite it is below 250 °C and below 350 °C for bituminous coal (Rivolta, 2012). But due to the complexity of the coal composition, these temperatures are only guidelines and not rigorous thresholds.

For different coals different temperature regimes can be identified and it is known these regimes depend on coal rank.

In the temperature range 100-180 °C the decomposition rate is slow and processes that can be seen are: loss of capillary-condensed moisture, loss of “chemically bonded” water and release of gases such as methane, oxides of carbon and hydrogen sulfide.

There is not much information about the low temperature processes but it has been shown (Brenner, 1984; Harris Jr and Petersen, 1979; Klotzkin, 1985; Medeiros and Petersen, 1979; Shibaoka, 1985; Shibaoka, 1985), they can change the original structure of coal and its following thermal behavior would change as a result. So, pretreatment of coal at ~200 °C is likely to increase its solubility in organic solvents and also can wash out its caking properties (Berkowitz, 1979).

Low temperature regime of coal extraction is often neglected in studies dealing with direct coal liquefaction. Most authors consider just one low temperature regime: below 350 °C for bituminous coal and below 250 °C for brown coal (Miura et al., 2001; Shen et al., 1992) (Morimoto et al., 2009). Doing so can cause some deficiencies in the interpretation of results and analysis of the coal behavior in the extraction process.

Researchers are not sure about the mechanism of coal dissolution at low temperatures. It is mentioned in the literature that solvents can relax the coal structure and disrupt weak linkages between molecules (Takanohashi et al., 1996; Önal and Ceylan, 1997). This makes it possible for small molecular weight constituents exit the coal matrix and enter the solvent by physical interactions alone. The rule “like dissolves like” is likely to apply in coal solvent extraction.

The physical interaction of coal components depends on the chemical structure of the solvent. Some physical properties of the solvent such as viscosity and diffusivity can be important factors and changing them can affect the extraction. Using mixtures of solvents can improve the extraction yield by adjusting the solvent properties, for example, it was reported that a small amount of CS_2 in NMP decreases the viscosity of the solvent, and as a result the solvent can penetrate coal pores more easily and facilitate dissolution of small molecules (Shui, 2005).

Polarity of the solvent can be an important factor in dissolution when the coal has polar parts. Carboxylic and hydroxyl groups are present in low rank coals. Considering the rule of thumb “like dissolves like”, with a polar solvent such as NMP, there would be interaction between polar sites of low rank coals and the solvent, so there would be a good extraction yield (Li et al., 2000). So knowing the polar sites of the coal helps having a qualitative expectancy about the extraction yield with polar or non-polar solvents.

2.5.2 Chemical dissolution

Chemical dissolution happens when there are chemical interactions and molecules change chemically. This can happen in one phase, thermal decomposition, or it can be heterogeneous, including interactions of coal and solvent molecules, in solid and liquid phase respectively.

In the coal matrix, there are some large macromolecules with high molecular weight, that cannot be solubilized physically, but at elevated temperatures, when the temperature is high enough, they can be cleaved by thermal decomposition and produce molecules with lower molecular weights (Rivolta, 2012).

The temperature range 350-550°C is the regime where active thermal decomposition takes place. Once free radicals are formed, retrogressive reactions may happen, and if the molecules are not stabilized appropriately, this results in less soluble products (Wen and Lee, 1979). A hydrogen donor solvent can stabilize free radicals produced during thermal decomposition by donating hydrogen.

2.6 Solvent extraction

The first studies of coal were based on a fact that coal is constituted of a mixture of organic material, such as “coking principle”, which was the reason for the good coking properties of certain coals. Solvent extraction of coal was studied to see if it is possible to upgrade coals with poor coking properties by addition of the coking principle by this method. It is also useful for investigating the structure of coal. Due to the complexity of coal and solvent interactions, lots of effort has been put into the investigation of the relationship between the extraction efficiency and the nature of the coal and solvent, and also the extraction conditions.

Based on their effect on coal, there are different types of solvents (Pullen, 1981; Wise, 1971) :

(1) **Non-specific solvents**: They are able to extract about ~10% at temperatures up to 100 °C. The examples are methanol, ethanol, benzene, acetone and ether and all of these solvents are low boiling liquids. The extracts can be from the resins and waxes in the coal matrix.

(2) **Specific solvents**: They are able to extract 20-40% at temperatures below 200 °C. These solvents can be considered non- selective, and the nature of extracts is similar to the original coal. They have a lone of pair electron so they are nucleophilic. The examples can be pyridine, N methylypyrrolidone, dimethylformamide and dimethylacetamide.

(3) **Degrading solvents:** They are able to extract up to 90% of the coal at temperatures up to 400 °C. The mechanism in this kind of extraction is thermal degradation, and high molecular weight components decompose to smaller fragments. Afterwards the solvent can be recovered without change. Examples can be phenanthrene, diphenyl, phenanthridine and tar oil fractions.

(4) **Reactive solvents:** They are able to interact with coal chemically. Reactive solvents are commonly able to donate hydrogen and extraction with them is called “extractive chemical disintegration”. The smaller coal fragments and free radicals formed during disintegration are stabilized by the donated hydrogen by the solvent. In this kind of extraction both coal and solvent change significantly. Hydroaromatic compounds can be good hydrogen donors and they transform to their corresponding aromatic counterparts during the process. A good example is tetralin (1,2,3,4-

tetrahydronaphthalene) that convert to naphthalene after donating four hydrogens.

The results of Dryden experiments on British coals at room temperature and near the boiling point temperatures (Soxhlet extraction), are as follow:

(1) Good solvents for extraction contain a nitrogen or oxygen atom, having a lone-pair or pairs of electrons. Nitrogen compounds happen to be better solvents than oxygen compounds. Alkyl groups can reduce solvent power, it causes steric hindrance to interactions of solvents with coals.

(2) Temperature has a great effect on the extraction yield, so specific solvents with higher boiling points generally result in higher extraction yields.

For a certain solvent, the increase in temperature increases the extraction yield (Renganathan and Zondlo, 1993). The time duration of extraction can be another important factor in extraction. When using a “specific solvent” at its boiling point, as time passes the extent of extraction increases and after a certain time, no more extraction is found. In some studies it is said particle size can be important, for example, for the extraction of Bakerstown coal, with N-methylpyrrolidone, for sizes less than 250 µm, the extraction yield was independent of the particle size. This result can be of great importance for industrial use, because particles of size 250 µm can be prepared by common crushing equipment, but producing coal smaller than 250 µm requires more expensive grinding operations (Renganathan, 1987).

Extraction yield depends on the carbon content of the coal, and for a carbon content equal to or greater than 92%, the coal is no longer soluble in solvents. Figure 2.2.

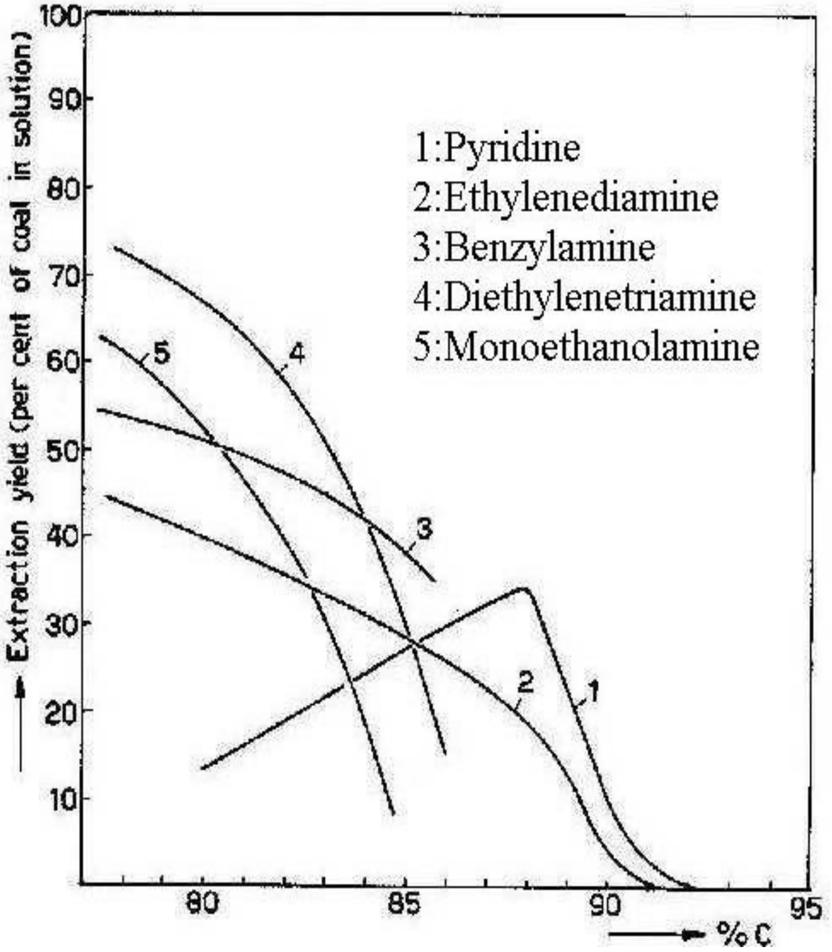

Figure 2-2 Extraction yield using different solvents as the function of the rank of coal (Van Krevelen, 1993).

Coalification is considered as a "progressive polycondensation reaction with cross-linking", which leads to coal with a higher C-content. Poor coal dissolution of coals with high C-content can be explained in terms of its solubility parameter (Van Krevelen, 1965). The solubility parameter is (δ) is related to the cohesive energy density (e) through Equation 2.1.

$$\boldsymbol{\delta} = \sqrt{\boldsymbol{e}} \qquad \text{Equation 2-1}$$

$$\boldsymbol{e} = \frac{\textbf{Molar cohesion energy}}{\textbf{Molar volume}} = \frac{\Delta U_{Vap}}{V_m} \qquad \text{Equation 2-2}$$

The cohesive energy density can be calculated from ΔU_{vap}, which is the molar latent heat of vaporization of the solvent (J/mole) and V_m, which is the molar volume of the solvent (cm^3/mole) as shown in Equation 2.2. For coal to dissolve in a solvent, $\delta_{coal}-\delta_{solvent} = \Delta\delta << 5\ (J/cm^3)^{1/2}$. The solubility parameter of solvent can obtained experimentally and the solubility parameter for coal is a function of carbon content and aromaticity (f_a) of the coal Figure 2.3.

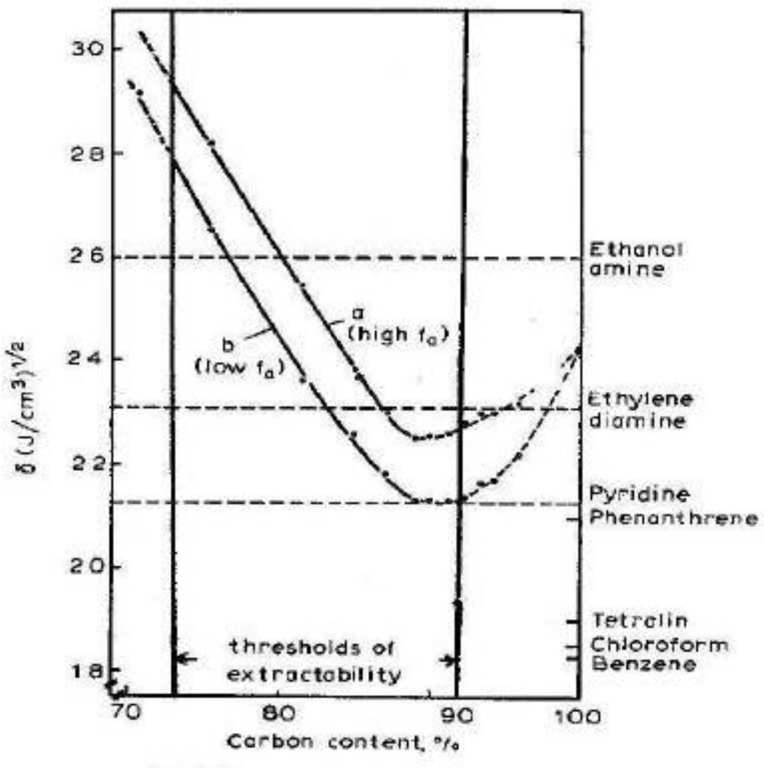

Figure 2-3 Solubility parameter of coal as a function of rank and aromaticity (Van Krevelen, 1993)

2.7 Coal Conversion

The processes which can convert coal into liquid and gaseous products are pyrolysis, gasification and liquefaction with or without catalysts (Wen and Lee, 1979).

2.7.1 Pyrolysis

Pyrolysis or carbonization is a process of heating up the coal without oxygen. In this process to increase the H/C ratio, carbon is rejected from coal as coke. The main products of carbonization are coke or char, coal tar, gases and aqueous liquor. Based on the temperature of operation, it can be categorized into; low temperature carbonization and high temperature carbonization (Speight, 1994), which the former produce gas and smokeless solid fuel and the latter mainly produce metallurgical coke and tar.

2.7.2 Gasification

Coal gasification is the conversion of coal into synthesis gas ($CO + H_2$). In this process the structure of coal break down completely, so it is done in under severe conditions. Steam and oxygen are used as gasification agents.

2.7.3 Liquefaction

This method has been discussed briefly in section 1.1.1.

The parameters that can affect the liquefaction process are (Shui and Cai, 2010) :

(1) Temperature: There are two steps involved in DCL, first the macromolecular structure of coal breaks into radical fragments at high

temperature and then production of lower molecular weights by stabilization and hydrogenation of radical fragments. High temperature can cause thermal rupture of carbon-carbon linkages and improve the rate of reaction. Temperature is one of the most important factors, if it is too low the reactions cannot take place and if it is too high, unwanted coking reactions would occur.

(2) Solvent: In DCL processes, the solvent action is to stabilize free-radicals by hydrogen donation, help rupture of macromolecules by free radical propagation, diluting the intermediates and prevent the coking. Besides, mass and heat transfer happen in the medium of the solvent, it also can carry the hydrogen from gas phase to the coal. Different types of solvents have been discussed in section 2.5.

(3) Pressure and Atmosphere: High pressure maintains the solvent and products in the liquid phase, helps hydrogenation by preserving a high partial pressure of hydrogen, quenching the retrogressive reactions, which results in suppression of coke formation on the reactor walls and catalyst surface. By using a good hydrogen-donor solvent, DCL can take place at lower pressures, but to a certain point, increasing pressure can increase the conversion and after that it is not as effective.

(4) Coal pretreatments: One of the pretreatments of coal is swelling the coal in a solvent before high temperature liquefaction. Swelling the coal results in a higher oil yield with lower use of hydrogen. Usually it is done with a mixture of a non-donor and a donor solvent. The non-donor solvent causes

swelling in the coal structure and the donor solvent can penetrate more easily into the coal.

Shui (2006) reported a significant increase in the extraction yield on low rank coals pretreated with CS_2/N-methyl-2-pyrrolidinine (NMP) at 150-240 °C. During this process oxygen functional groups such as hydroxyl were removed and hydrogen bonds in the macromolecular matrix of coal could be disrupted, as a result the solubility of coal increases.

2.8 Applications of coal and coal extraction

Based on the process and reaction conditions, the products of coal can be different. Coal is mostly used for combustion and producing steam and generating electricity. There are also other uses for coal, other than fuel uses, which are becoming important (Song and Schobert, 1996). Coal can be used as a feedstock to produce electrodes, carbon fibers, artificial graphite, carbon foam, carbon blacks and activated carbon, etc.

2.8.1 Pitch

Pitch is made of a complex combination of polycyclic aromatic hydrocarbons. Two- to four-ring aromatic chemicals can be made from it. Pitch is usually obtained from the production of metallurgical coke in a recovery coke oven. It also can be obtained from solvent extraction of coal under mild conditions.

2.8.2 Coke

Cokes can be used in production of graphite electrodes and some carbon-carbon composites. They are categorized as isotropic or anisotropic, and have different uses. The anisotropic cokes are consist of large crystallite domains, but in isotropic coke the structure is fined-grained. Another usage of cokes can be in production of anodes in aluminum industry, and the anisotropy level of coke is an important factor to determine the suitability of it for this usage.

Isotropic coke can be produced by coking the extracts obtained from solvent extraction of raw coal. Isotropic coke can be used to produce isotropic graphite which is essential for core material in building high-temperature gas-cooled nuclear reactors.

2.8.3 Carbon fibers

Composite materials can be fabricated by means of carbon fibers. Carbon fibers have a high strength-to-weight ratio, high-temperature strength and low coefficient of thermal expansion, so they are good for aerospace applications. There are also activated microporous carbon fibers, which can be used for gas adsorption, liquid purification and for gas storage. Pitch is one of the constituents of carbon fibers and pitch properties can determine the carbon fibers properties (Marsh et al., 1997).

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3 Physical Coal Dissolution at Low Temperature and Short Contact Time

3.1 Introduction

Coal is at present not the preferred feed material for fuel and chemical production. Yet, strategically it is and will remain an important alternative to conventional crude oil (King and de Klerk, 2011). After the 1973 Oil Crisis, the United States embarked on an energy security program, which focused on direct coal liquefaction (DCL). The program failed to commercialize a DCL technology, but it advanced the field (Crow et al., 1988). One of the aspects that were highlighted for further study is the preheating of coal before liquefaction (Shah et al., 1981).

The efficiency of DCL technology can be improved if low temperature dissolution of coal can be exploited to reduce the reactor size needed for high temperature and pressure liquefaction. Coal dissolution starts during preheating of coal and it is a fast process. Shah and co-workers (1981) reported that conversion of coal to tetrahydrofuran (THF) soluble liquids on preheating to 400-450°Cwere essentially complete within 3-4 minutes, even though conversion to benzene soluble liquids was slower. A rapid rate of coal dissolution was also observed at lower temperatures (25-300 °C) in our laboratories (Rivolta, 2012). Physical dissolution was complete within less than 15 minutes.

The aim of this investigation is to determine the yield, rate and nature of coal dissolution in the temperature range 25-150 °C, at short contact times (2-16 minutes). All work was performed with tetralin as solvent, due to its importance as hydrogen donor-solvent for high temperature liquefaction. Physical dissolution of coal was reviewed in Chapter 2.

3.1.1 Problem

Studies on the solvent extraction of coal are usually performed in a batch or semi-batch reactor. Batch and semi-batch reactors cannot be used to collect rate data for extraction times below 15 minutes, due to their slow heat-up rate. Yet, physical extraction of coal was said to occur in less than 15 minutes (Figueroa Murcia et al., 2011).

So, for having information in this time range, the conventional batch and semi-batch reactors cannot be used, and the yield and extraction rate are unknown. In order to overcome this deficiency a different set up should be devised to help us investigate short contact time extraction. The information obtained can clarify how much time is required for physical extraction to finish, and it can ultimately help to determine the retention times required for low temperature extraction as pre-liquefaction step for industrial processes.

3.1.2 Approach

To investigate the solvent extraction of coal with extraction time less than 15 minutes, a flow micro-reactor was designed and built, which enabled us to preheat the solvent and coal separately, as well as contact and separate the solvent from coal in times as short as 2 minutes. So, the whole range from beginning of the extraction process up to 15 minutes contact time could be investigated and samples could be obtained at certain times and be analyzed afterwards to get the extraction yield and rate at low temperatures and short contact times.

3.2 Experimental

In the following section, the experimental method to carry out the solvent extraction, the separation of liquid and solid phases of the samples and further processing and analysis of residue and extract are discussed. After completion of the extraction at different temperatures, the liquid extract and solid residue were separated and the solid residue was dried in a vacuum oven. Measuring the ash content of the samples was carried out in a temperature-programmed furnace. The concentration of coal liquid in the extract was determined using a UV-Vis spectrometer (section 3.2.5). The optical texture of the solid extracts was investigated using a hot stage DSC microscope.

3.2.1 Material

Poplar, a lignite coal (Table 3.1), was used for all of the solvent extraction experiments. The solvent was 99% pure tetralin (1,2,3,4-tetrahydronaphthalene) provided by Sigma Aldrich and it was used without further purification. The chemical structure of tetralin is shown in Figure 3.1

Table 3-1 Ultimate and Proximate Analyses of Coal. (Ash free bases)

Description	Poplar (lignite)
Ultimate analysis (wt %)	
carbon	43.5
hydrogen	4.72
nitrogen	0.8
sulfur	0.93
oxygen	50.05
Proximate analysis (wt % daf)	
Moisture (wt %)	28.5
ash	15.15
volatile matter	46.45
fixed carbon	38.4

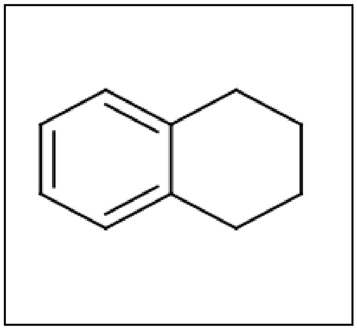

Figure 3-1 Chemical structure of 1,2,3,4-tetrahydronapthalene

This solvent is a good hydrogen donor and due to the importance of hydrogen transfer during the liquefaction, tetralin is a popular solvent in extraction of coal especially at high temperature, but it is not a particularly good solvent at low temperatures (Dryden, 1963) . Tetralin transforms to naphthalene after donating hydrogen (Equation 3.1)

$$C_{10}H_{12} \rightarrow C_{10}H_8 + 2H_2 \qquad \text{Equation 3-1}$$

3.2.2 Coal characterization

Poplar (lignite) was provided by Sherritt Technology Inc. The coal was crushed and kept in plastic buckets. To prepare the fine coal a ball mill was used to ground the coal and then the fine coal was stored in plastic bags in the refrigerator to avoid oxidation. Next, for getting an appropriate particle size distribution, the ground coal was sieved. Samples were taken from the 250-1000 µm fraction.

3.2.2.1 Ultimate analysis

To do the elemental analysis, an Elementer Vario MICRO Cube was used, with sample sizes between 2 and 4 mg. The hydrogen, carbon, sulfur and nitrogen content is determined experimentally.

Oxygen content of the coal can be determined by Equation 3.2.

$$WO = 100 - WH - WC - WS - WN \qquad \text{Equation 3-2}$$

The terms in the equation refer to oxygen, hydrogen, carbon, sulphur and nitrogen weight percent (daf), respectively.

3.2.2.2 Proximate analysis

Ash

Ash content of the samples was determined using the ASTM D3174 – 11 method, "Ash content is determined by weighing the inorganic residue remaining after burning the coal or coke in air under rigidly controlled conditions of sample weight, temperature, time, atmosphere and equipment specification".(ASTM 2011, DOI: 10.1520/D3174-11, www.astm.org)

The equipment used is programmable muffle furnace (Model: F6020C-33-60) with airflow of 20 standard liter per minute (slpm). Typically, in the first hour the temperature of the furnace was raised from room temperature to 450 °C, in the next hour it was raised to 750 °C and then kept isothermally for 2 hours, finally the sample cooled to room temperature over the period of 3 to 4 hours. The ash content of the sample can be measured by the following equation:

$$\boldsymbol{Ash = \frac{M_{Ash}}{SW_m} \times 100} \qquad \text{Equation 3-3}$$

Where, SW_m is the initial weight of the dried sample and M_{Ash} is the mass of ash.

Moisture

The moisture content of the samples can be measured using ASTM D3173 – 11 standard (ASTM,2011,DOI: 10.1520/D3173-11, www.astm.org). A programmable muffle furnace (Model: F6020C-33-60) was used for moisture content of the coal, the temperature of the oven was set at 105 °C and the samples were heated at this temperature in crucibles for 1 hour, the loss of sample weight represents the moisture content of the coal and was calculated using the following equation:

$$\boldsymbol{Moisture = \frac{SW_o - SW_f}{SW_o} \times 100} \qquad \text{Equation 3-4}$$

Where, SW_o and SW_f stand for initial and final weight of the sample respectively.

Volatile matter

The same programmable muffle furnace which used for ash determination (Model: F6020C-33-60) was used the samples were heated at 950 °C for 7 minutes, as is stated in the ASTM D3175 – 11(ASTM , 2011, DOI: 10.1520/D3175-11, www.astm.org). This is the equation for calculating the volatile matter content of the sample:

$$\boldsymbol{VM = \frac{SW_o - SW_f}{SW_o} \times 100 - Moisture} \qquad \text{Equation 3-5}$$

The VM here is the percentage of the volatile matter in the sample.

Fixed carbon

Fixed carbon can be calculated using ASTM D3172 – 7a (ASTM , 2007, DOI:10.1520/D3172-07A, www.astm.org.).

$$\boldsymbol{FC = 100 - (Moisture + Ash + VM)} \qquad \text{Equation 3-6}$$

Here, FC is the fixed carbon content in the coal sample.

3.2.3 Equipment

3.2.3.1 Reaction setup

Solvent extraction of coal was carried out in a stainless steel micro-reactor with 18 mm outside diameter, 1.5 mm wall thickness and 75 mm in length. The set up includes a solvent container and a micro-reactor, a 1/4” needle valve and 1/4” tubing to connect the parts. The tubing is bent 90 degrees at the bottom of the valve and the length of the straight part is 5 cm, which is connected to top of the micro-reactor. The solvent container and the reactor are the same in size and shape. The micro-reactors, stainless steel seamless tubing and fittings are provided by Swagelok. A stainless steel filter with 2 µm opening is placed before the outlet 1/8” needle valve to retain the coal particles. The whole setup is temperature controlled. To control the temperature, heating tapes were used with insulation wrapped around them, to prevent the heat loss. A 1/16” thermocouple was installed in such a way that its bottom was aligned with the center of the micro-reactor and a digital controller was used to set the temperature. A schematic diagram is shown in figure 3.2.

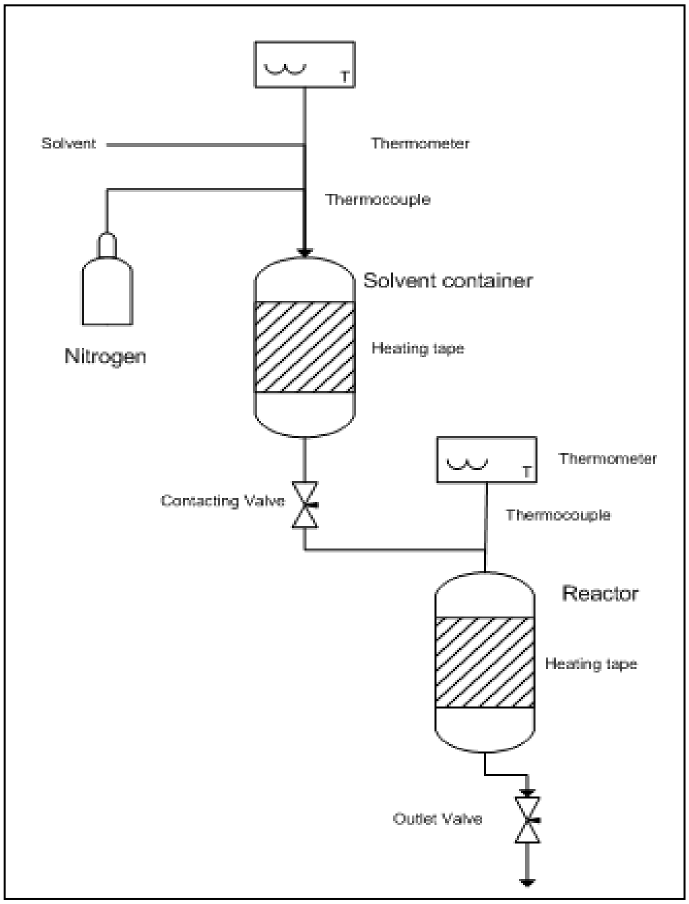

Figure 3-2 A schematic diagram of the experimental setup.

3.2.3.2 Vacuum oven

After the experiment is finished and the liquid extract is discharged, a Stable Cole-Parmer vacuum oven was used to dry the solid sample and remove the remaining solvent. This procedure was done overnight, at 110 °C and vacuum.

3.2.4 Procedure

Coal particles in the size range 250-1000 μm were vacuum dried overnight at 80 °C before solvent extraction. A Metler Toledo XS105 dual range balance was used to weight the coal to the nearest 0.1 mg. For each experiment the reactor was charged with 3 grams of coal, with a bed height of 23 mm, and closed. The solvent container was charged with 10 ml tetralin and then pressurized with nitrogen. Once the desired temperature was reached (25, 100 or 150 °C) the valve between the solvent container and reactor was opened. The contact time between solvent and coal was measured from this time. After the required time for solvent extraction elapsed (2, 4, 8, 12 or 16 min), the outlet valve was opened and the solvent was discharged from the reactor. Then the liquid samples were kept in glass vials and the coal residue that remained in the reactor was removed and vacuum dried overnight at 110 °C. The residue mass and ash content of the residue were determined to calculate the extraction yield. On cooling some precipitate formed in the liquid extract.

The clear liquid extract was analyzed by UV-Vis spectrometry and the precipitate was studied with calorimetry and microscopy.

3.2.5 Analyses

Ash

Ash content was determined using the same method explained in section 3.2.2.2, which involves heating the sample slowly to 750 °C in a ventilated furnace.

Concentration of the liquid extract

The concentration of coal liquid in the extract was determined with a Shimadzu UV-2700 UV-Vis spectrometer, using quartz cuvets with 1 cm path length. Tetralin was the reference. Different extract-tetralin dilutions were prepared and analyzed in order to calculate the concentration of the undiluted extract.

Precipitate analysis

The nature of the precipitate was investigated with a Mettler FP84HT hot stage DSC and Olympus microscope.

3.2.6 Calculations

Extraction yield

After proper drying of coal residue, it was weighed and using the equation below the extraction yield was calculated.

$$\boldsymbol{EY}\,(\%) = \frac{\boldsymbol{Weight\ of\ coal - Weight\ of\ residue}}{\boldsymbol{Weight\ of\ coal}\,(\boldsymbol{1 - Ash\ content\ of\ coal})} \times \mathbf{100} \qquad \text{Equation 3-7}$$

In this equation the Extraction Yield (EY) is in percentage, on ash and moisture free bases.

For calculating the yield on ash and moisture free bases, the ash content of residue samples were measured, the absolute difference between the average ash content of the raw coal and the average ash content of residues, was 0.13 %, 0.05 % and 0.1 % for 25 °C, 100 °C and 150 °C respectively. And as the ash content for the residue scatter around the ash content of the raw coal, not always higher not always lower, we can assume in this temperature range, the ash content of the raw coal and residues are the same and use the Equation 3.7.

Table 3-2 Ash measurement results for residues at 25 °C experiments

Temperature-time(min)	Average Ash%	Total average for 25 °C	Standard deviation
25 °C-2	14.91	15.02	0.23
25 °C -4	14.95		
25 °C -8	15.43		
25 °C -12	14.95		
25 °C -16	14.88		

Table 3-3 Ash measurement results for residues at 100 °C experiments

Temperature-time(min)	Average Ash%	Total Average for 100 °C	Standard deviation
100 °C -2	15.39	15.1	0.28
100 °C -4	14.81		
100 °C -8	15.38		
100 °C -12	14.82		
100 °C -16	15.1		

Table 3-4 Ash measurement results for residues at 150 °C experiments

Temperature-time(min)	**Average Ash%**	**Total Average for 100 °C**	**Standard deviation**
150 °C -2	15.2	15.05	0.41
150 °C -4	14.77		
150 °C -8	15.15		
150 °C -12	14.53		
150 °C -16	15.59		

3.3 Results

Solvent extraction was carried out using tetralin and Poplar coal to investigate the influence of time and temperature on extraction yield and rate. The experiments were done at low temperatures and short contact time.

3.3.1 Extraction yield

The extraction yield results for Poplar lignite coal with tetralin is shown in tables 3-5 to 3-7.

Table 3-5 Extraction yields, ash and moisture free at 25 °C and different times

Temperature-Minute	*Raw coal mass (g)*	*Mass of residue*	*Yield ash – moisture free%*	*Average Yield %*	*Standard Deviation*
25 □C-2	3.1845	2.9801	7.56	7.14	0.53
	3.1862	2.9884	7.31		
	3.1523	2.9775	6.53		
25 □C-4	3.1448	2.9421	7.60	7.56	0.19
	3.1697	2.9614	7.73		
	3.1932	2.9941	7.35		
25 □C- 8	3.1677	2.958	7.79	7.35	0.64
	3.1365	2.9529	6.89		
25 □C-12	3.1745	2.9991	6.5	7.14	0.89
	3.1698	2.9608	7.77		

25 □C-16	3.1534	2.9523	7.52	6.96	0.56
	3.1556	2.9844	6.39		
	3.1435	2.9576	6.97		

Table 3-6 Extraction yields, ash and moisture free at 100 °C and different times

Temperature-Minute	***Raw coal mass (g)***	***Mass of residue***	***Yield ash – moisture free%***	***Average yield%***	***Standard deviation***
100 □C-2	3.1201	2.8926	8.59	8.21	0.36
	3.1543	2.9436	7.86		
	3.1798	2.9596	8.16		
100 □C-4	3.168	2.9439	8.34	8.04	0.25
	3.1367	2.9274	7.85		
	3.1569	2.9444	7.93		
100 □C-8	3.1397	2.9138	8.48	8.61	0.23
	3.1513	2.9251	8.45		
	3.1936	2.9529	8.88		
100 □C-12	3.1498	2.9057	9.13	8.24	1.02
	3.1636	2.9725	7.11		
	3.1698	2.9419	8.47		
100 □C-16	3.205	2.9646	8.84	8.56	0.28
	3.1618	2.9323	8.55		
	3.1435	2.9226	8.28		

Table 3-7 Extraction yields, ash and moisture free at 150 °C and different times

Temperature-Minute	***Raw coal mass (g)***	***Mass of residue***	***Yield ash – moisture free%***	***Average yield%***	***Standard deviation***
150 □C-2	3.1792	2.9403	8.86	8.86	0.10
	3.1385	2.8994	8.97		
	3.1778	2.9415	8.76		
150 □C-4	3.1995	2.9734	8.33	8.9	0.72
	3.1632	2.9023	9.71		
	3.1365	2.9063	8.65		
150 □C-8	3.1246	2.8778	9.31	8.77	0.46
	3.1721	2.9407	8.58		
	3.1435	2.9186	8.43		
150 □C-12	3.1391	2.9183	8.29	8.83	0.52
	3.1415	2.9056	8.84		
	3.1569	2.9064	9.35		
150 □C-16	3.2395	3.01157	8.29	9.03	0.64
	3.1595	2.9092	9.33		
	3.1865	2.9304	9.47		

3.3.2 Extraction rate

The solvent extraction was done with Poplar (lignite) and tetralin as a solvent. The liquid sample was separated from solid residue. The liquid sample was analyzed with UV-2700 UV-Vis spectrometer. To measure the concentration of the undiluted sample, four different extract-tetralin dilutions were prepared, with 10, 30, 50 and 80 percent of extract and were analyzed. The concentration of the coal liquid in the extract should in principle reflect extraction rate. Two absorption maxima were observed in the 310-325 nm wavelength region and were present in all of the extracts. The more intense of these was employed to quantify the concentration of the coal liquids in the tetralin extract.

An example of the graphs is shown in Figure 3.3, for a certain time and certain dilution but different temperatures.

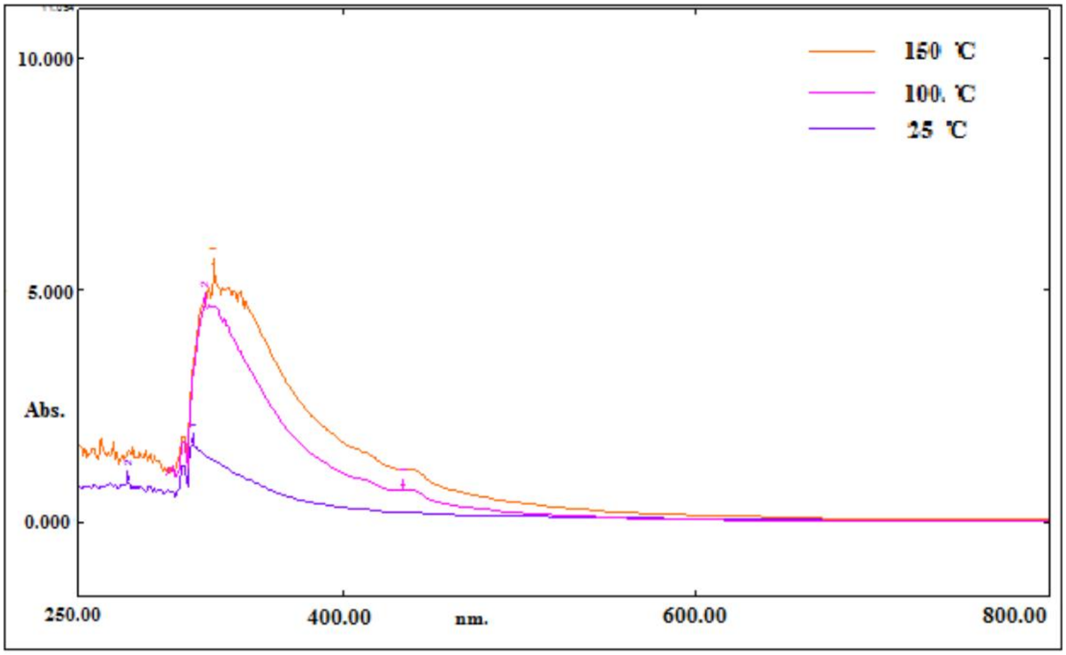

Figure 3-3 UV-Vis spectra of diluted tetralin extracts obtained from Poplar at 25, 100 and 150 °C respectively.

The concentrations of undiluted samples were extrapolated then. The results are shown in table 3.8.

Table 3-8 Analyses of different extract-tetralin diluted solutions, for samples at different times and temperatures.

Temperature-Time	*Concentration of extract%*	*10*	*30*	*50*	*80*	*100*
25 °C -2		0.2	0.489	0.824	1.221	1.5282
25 °C - 4		0.233	0.513	0.867	1.306	1.6205
25 °C -8		0.256	0.572	0.918	1.451	1.7811
25 °C -12		0.279	0.587	1.092	1.539	1.9278
25 °C -16		0.211	0.597	1.017	1.662	2.0679
100 °C -2		0.504	1.275	2.171	3.32	4.1442
100 °C -4		1.108	2.269	3.259	4.608	5.67
100 °C -8		0.995	2.573	3.878	5.261	6.6549
100 °C -12		0.826	2.153	3.288	4.866	6.0764
100 °C -16		0.849	2.129	3.69	4.695	6.055
150 °C -2		1.22	2.892	4.57	5.494	7.0804
150 °C -4		1.422	3.384	4.785	5.851	7.4406
150 °C -8		1.168	3.163	4.448	5.808	7.3776
150 °C -12		1.38	2.993	4.721	5.92	7.5208
150 °C -16		1.352	3.169	4.822	5.452	7.073

3.4 Discussion

In this section, the results are discussed for the extraction yield, rate and also the precipitate.

3.4.1 Extraction yield

The extraction yield results of Poplar lignite coal with tetralin is shown in Figure 3.4. The extraction yield was affected by temperature.

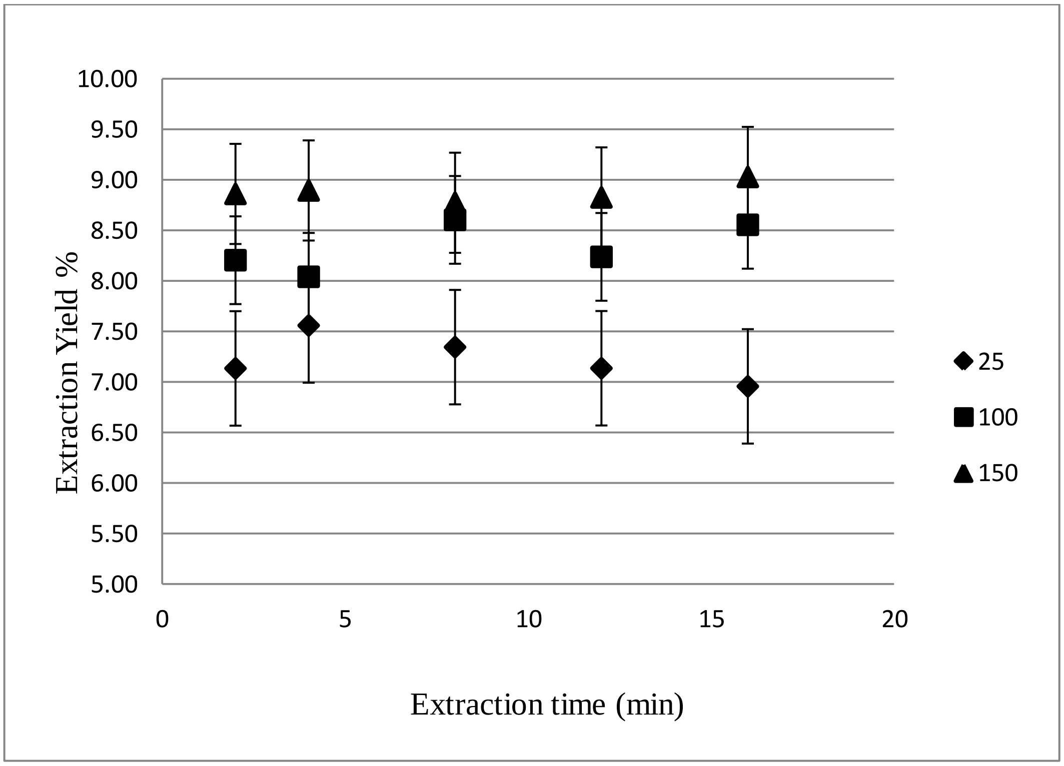

Figure 3-4 Extraction yield (wt %) on ash and moisture-free basis of Poplar lignite with tetralin over time at 25 °C, 100 °C and 150 °C.

As we can see in figure 3.4 temperature has an obvious effect on coal extraction at low temperature, the extraction yield at 25 °C was consistently lower than that at 100 °C and 150 °C. Also the extraction yield at 100 °C is mostly less than that at 150 °C but the results are really close and there is not much difference in the extraction yield. To make sure about the significance of the effect of temperature statistical analyses (Student t-Test) has been done on the extraction yields for different temperatures. The p value related with a Student t-Test with a two tailed distribution is calculated for the extraction yield results for temperatures (25 °C,100 °C) and (100 °C, 150 °C), the results are 7.85E-05 and 0.0015 respectively. The p value is the probability that the null hypothesis is true. The null hypothesis here is, there is no significant difference between the results of the experiments at different temperatures, and the predetermined significant level is $p=0.05$. As the results of the t-test are less than 0.05, the null hypothesis can be rejected and based on the scale of the numbers, it can be stated that the effect of temperature on the extraction yield between 25 °C and 100 °C is very highly significant. And the effect of temperature between 100 °C and 150 °C is highly significant.

The yield obtained at 100 °C (8-9 %) was within the range (8-13 %) previously reported for extraction times from 1 to 30 hours (Figueroa Murcia et al., 2011).

If we want to examine the effect of coal extraction prior to liquefaction, and from an industrial point of view, it can be seen consuming more energy and elevation the temperature from 25 °C to 100 °C or 150 °C is not that effective and the extraction yield is increased just 1-2 %. Considering no energy consumption during extraction at room temperature, this method can be considered as a good option.

3.4.2 Extraction rate

The dependence of extraction as function of time remained elusive. Extraction was seemingly complete within 2 min (Figure3.4). Despite careful experimentation, the data displayed some scatter. Potential sources of error are:

1) The loss of material during the handling at various steps.
2) The loss some light materials from residue during thermal drying.
3) Incomplete solvent removal during drying (boiling point of tetralin is 206-208 °C and it is hard to get the solvent out of coal without disrupting the structure of the residue)

Instead of looking at the residue, one can also analyze the extract. The absorption of the undiluted extract was too high and the samples had to be diluted for analysis. A series of four different dilutions were prepared for each sample. The effective absorption of the undiluted extract was calculated from the calibration curve of each.

The results are shown in figure 3.5. Each point represents the absorption unit for a sample at a certain time and temperature. The changes of the yield with temperature are clear here and there is a good distinction between the lines correlated with 25, 100 and 150 °C. This figure also gives a qualitative indication of the dependence of the extraction on time. At 150 °C the extraction is finished within two minutes, and after that no more dissolution happened during the experiment.

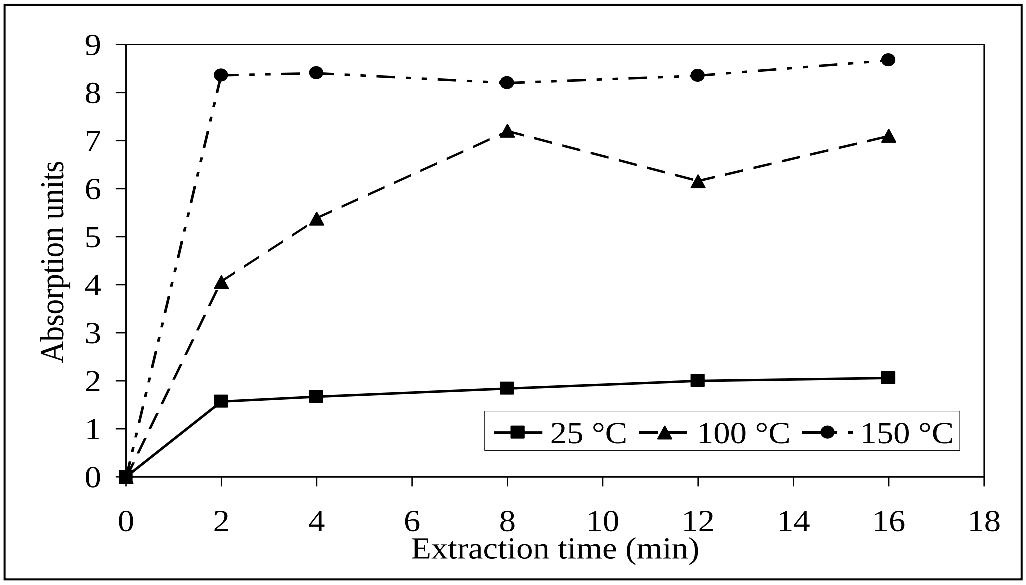

Figure 3-5 . UV-Vis absorbtion of the clear liquid extract from Poplar lignite with tetralin over time at 25, 100 and 150 °C.

Physical extraction takes place quickly and 75 % of the coal liquid extracted at 25 °C is extracted within the first 2 min (Figure 3.5). The effect of time on extraction is clearer for the data at 100 °C, but this data can unfortunately not be used to calculate a reliable extraction rate.

When the extract cooled down, a precipitate was observed in the liquid. The concentration of coal liquid in the clear liquid extract is therefore not the same at the concentration obtained at elevated temperature. The UV-Vis absorption data after extraction at elevated temperature is therefore not representative of the real coal liquid concentration.

3.4.3 Precipitate analysis

During the extraction experiments, after collecting the liquid samples from the micro-reactors, some precipitation was observed in the liquid containing vials. The liquid samples were clear right after the experiment, but after a few minutes and cooling down to the room temperature, some fine black precipitates started to form in the vial. The nature of the precipitants was investigated with differential scanning calorimetry (DSC) microscopy. It can clarify if the black solids formed are coal liquids or just fine coal particles which passed through the stainless steel filter.

The extracts were shaken to suspend the particulates before samples were collected for differential scanning calorimetry (DSC) microscopy. As the temperature was increased the precipitate liquefied/dissolved in the tetralin (Figure 3.6).

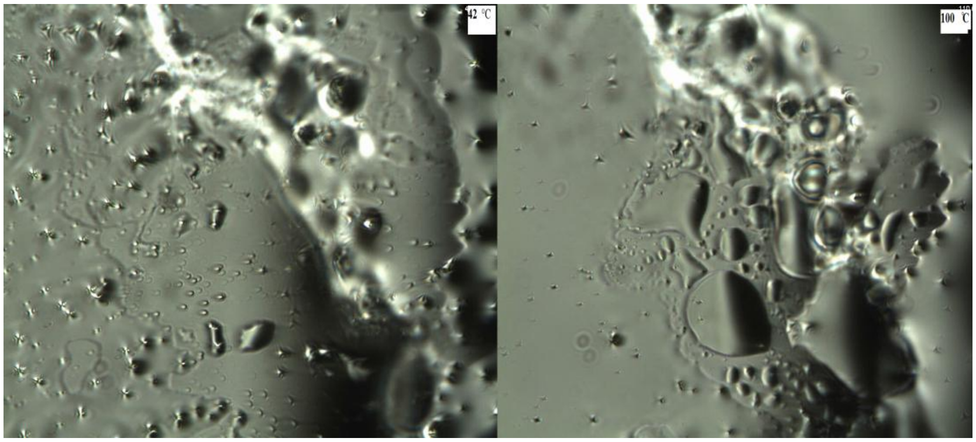

Figure 3-6 Coal extract in tetralin under DSC microscope at 40 °C (left) and 110 °C (right), showing precipitate liquefying/dissolving.

3.5 Conclusion

Tetralin extraction of Poplar was investigated at 25, 100 and 150 °C and 2-16 min contact time. In this temperature range physical dissolution dominates coal extraction. The influence of time and temperature on physical dissolution was investigated. The main results were (Haghighat, 2012):

a) Extraction yield increases with temperature, with a clear increase observed from 25 to 100 °C.

b) The extraction yield in the 25-150 °C range is determined mainly by extraction temperature.

c) Maximum extraction yield is in < 16 min. Even at 25 °C, 75 % of the total extraction yield is obtained within 2 min.

d) On cooling the coal extract precipitates are formed. These precipitates can be reversibly dissolved/liquefied with an increase in temperature.

3.6 References

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4 Effect of solvent to coal ratio on Physical Coal Dissolution at Low Temperature and Short Contact Time

4.1 Introduction

In the process of coal extraction, the solubility of coal in the solvent can affect the results. When a solution is saturated with the solute, more dissolution is not going to happen. So, investigations on the solvent to coal ratio, can illustrate appropriate range of solvent that should be used in the process. Using the lowest effective solvent to coal ratio results in the reduction of the size of the operating equipment, so as the cost of building and maintaining it, and also prevents the use of excessive solvent (Ishak et al., 2005; Rodriguez et al., 1998) . In the case of coal liquefaction, some experiments have been done to investigate different solvent to coal ratios, to find appropriate condition for industrial uses.

In a study done by Rivotla (2012) the effect of solvent to coal ratio at 100 °C and 2MPa for 1 hour was investigated using Poplar coal and tetralin. The experiments were performed in batch micro-reactors and different solvent: coal ratios were 8, 3 and 2. In this work no specific trend was observed as the solvent: coal ratio increased.

Most of the information about the effect of solvent to coal ratio, has been gained at high temperatures which retrogressive reactions can occur, at low temperatures there are no chemical reactions and the dissolution would take place physically. In this study, the effect of solvent to coal ratio on physical coal dissolution at low temperature will be discussed.

4.1.1 Problem

In the third chapter, the yield, rate and nature of coal dissolution at low temperatures and short contact time were discussed. During the investigation of the nature of the precipitates, it was observed that they tend to melt as the temperature of the solution was increased again, but even with the aid of the microscope, it was not clear to what extent the change into the liquid state was dissolution into the tetralin and to what extent a separate liquid phase was formed. This led us to consider solubility as governing factor in low temperature dissolution.

Two possibilities were considered with respect to the solubility of the coal liquids in the solvent:

a) Physical extraction is governed by the solubility of the coal molecules in the solvent. The increase in extraction yield with temperature and the subsequent precipitation of the dissolved coal liquids is a consequence of solubility.

b) The physical extraction is aided by the solvent, but not governed by solubility. The solvent dissolves some material that enables trapped liquids to escape. Trapped liquids escape as liquids and their escape is not dependent on their solubility in the solvent.

Of the two, it is comparatively easy to determine whether the extraction yield is limited by the solubility of the coal liquids in the solvent. So to determine the effect of solubility on the physical coal extraction, experiments with 5, 10 and

15 ml tetralin and 3 g coal at 100 °C for 8 min in the flow micro-reactors, were done.

Doing the above experiments, there was a probability that lack of agitation in the micro-reactor can affect the results of the experiments, because there might not be a good contact between the solvent and the coal. So experiments were carried out both in micro-reactor and beakers with magnetic stirrer.

4.1.2 Approach

To investigate the effect of solubility on the physical dissolution of coal, solvent extractions with 5, 10 and 15 ml tetralin and 3 g coal at 100 °C for 8 min in the flow micro-reactor, were done. Comparing the results can help to clarify whether the solubility is the governing factor, and if changing the solvent to coal ratio has any effect on the physical dissolution of coal.

The height of the bed of coal in the flow micro-reactor was 23 mm and the length of the micro-reactor was 75 mm (Figure 3.2). As there is no agitation in the micro-reactor to mix the solvent and coal, an additional set of experiments were done, to be sure we have considered potential mass transfer effects in our investigation. In these series of experiments, the materials and conditions were kept the same, but the setup was different. The extraction was performed in beakers, and magnetic stirrers were used to assure good mixing between solvent and the coal particles.

4.2 Experimental

In the following section, the experimental method to carry out the solvent extraction, the separation of liquid and solid phase of the samples and further processing and analysis of residue and extract is discussed. For investigating the effect of solvent to coal ratio, two methods were used in this chapter. The first method is the same as the method explained in section 3.2 but at one specific time and temperature, 8 minutes and 100 °C. In the second method, the materials used are the same but the equipment and procedure are different.

4.2.1 Material

Poplar, a lignite coal, was used for all of the solvent extraction experiments (table 3.1). The solvent was 99% pure tetralin (1,2,3,4-tetrahydronaphthalene) provided by Sigma Aldrich and it was used without further purification.

4.2.2 Equipment and procedure

4.2.2.1 Solvent extraction using flow micro-reactor

The reaction set up is discussed in section 3.2.3.1. Coal particles in the size range 250-1000 μm were vacuum dried overnight at 80 °C before solvent extraction. For each experiment the reactor was charged with 3 g coal and closed. Because here the effect of different solvent to coal ratios is the objective of investigation, the other factors which can affect the results should be constant. So, all the experiments were done at 100 °C, and 8 minutes, using 5, 10 and 15 ml solvent. After 8 minutes of contact time between solvent and coal elapsed, the outlet valve is opened and the solvent is discharged from the reactor. Then the liquid samples were kept in glass vials and the coal residue that remained in the reactor was removed and vacuum dried overnight at 110 °C. The residue mass and ash content of the residue were determined to calculate the extraction yield.

The clear liquid extract was analyzed by UV-Vis spectrometry.

4.2.2.2 Solvent extraction using beakers and magnetic stirrer

Solvent extraction of coal was carried out in 50 ml beakers, and using little magnetic stirrers to have agitation in the solution. A heating plate with a controller was used to heat the solution to the required temperature, the controller was adjusted to 100 °C, and the temperature in the solution was measured using a 1/16" thermocouple and a Fluke 54 IIB thermometer during the experiment. A certain amount of solvent (5, 10, 15ml) was charged into the beaker. The magnetic stirrer then was added and the stirring rate was adjusted on 200 rpm. When the solvent temperature reached 100 °C, 3 grams of Poplar coal was added. After 8 minutes, the beakers were removed from the heating plate. Then beakers were placed under the hood and covered. After 4 hours that all the coal particles were settled, the clear liquid sample was removed with pipette.

Then, the liquid samples were kept in glass vials and the coal residue that remained in the beaker was removed and vacuum dried overnight at 110 °C. The analyses after the experiments are the same for both methods.

4.2.3 Analyses

Ash

Ash content was determined using the same method explained in section 1.2.2.2, which involves heating the sample slowly to 750 °C in a ventilated furnace. Ash is not essentially the same, in composition and weight, to the inorganic substances existing in the original coal.

Concentration of the liquid extract

The concentration of coal liquid in the extract was determined with a Shimadzu UV-2700 UV-Vis spectrometer, using quartz cuvets with 1 cm path length. Tetralin was the reference. Different extract-tetralin dilutions were prepared and analyzed in order to calculate the concentration of the undiluted extract.

4.2.4 Calculations

Extraction yield

This part has been discussed in section 3.2.6.

4.3 Results

4.3.1 Solvent extraction using flow micro-reactor

The yield results for the solvent extraction conducted in flow micro-reactor are shown in table 4.1. These results are reported by percent and on ash and moisture free bases. The ash content of the coal was measured 27.3 %.

Table 4-1 Extraction yields, ash and moisture free at different solvent to coal ratios, in flow micro-reactor,100 °C and 8 minutes

Solvent: coal mass ratio-run number	*Raw coal mass (g)*	*Mass of residue*	*Yield ash – moisture free%*	*Average yield%*	*Standard deviation*
1.6-1	3.2001	2.8416	8.13	8.1	0.14
1.6-2	3.2243	2.877	8.23		
1.6-3	3.1819	2.8338	7.95		
3.3-1	3.1686	2.7882	8.72	8.71	0.26
3.3-2	3.1816	2.7889	8.97		
3.3-3	3.1841	2.8141	8.44		
4.9-1	3.1768	2.7994	8.63	8.38	0.25
4.9-2	3.1636	2.8096	8.13		
4.9-3	3.2226	2.8509	8.38		

Table 4-2 UV-Vis absorption units for the clear liquid extract from Poplar lignite with tetralin in flow micro-reactor, 100 °C and 8 minutes

Solvent: coal mass ratio-run number	*Absorption units*	*Average Absorption units*	*Standard deviation*
1.6-1	3.4605	2.9663	0.45
1.6-2	2.8685		
1.6-3	2.57		
3.3-1	2.0898	2.0557	0.02
3.3-2	2.0338		
3.3-3	2.0437		
4.9-1	1.9793	2.0117	0.06
4.9-2	1.9728		
4.9-3	2.0829		

4.3.2 Solvent extraction using beakers and magnetic stirrers

The yield results for the solvent extraction conducted in beakers are shown in table 4.3.

Table 4-3 Extraction yields, ash and moisture free at different solvent to coal ratios, in beakers, 100 °C and 8 minutes

Solvent: coal mass ratio-run number	*Raw coal mass (g)*	*Mass of residue*	*Yield ash – moisture free%*	*Average Yield%*	*Standard deviation*
1.6-1	3.0324	2.8287	4.64	5.61	0.85
1.6-2	3.0163	2.7692	5.95		

1.6-3	3.0493	2.7869	6.25		
3.3-1	3.0294	2.7274	7.31	6.6	0.61
3.3-2	3.0377	2.7783	6.2		
3.3-3	3.0243	2.7625	6.29		
4.9-1	3.0261	2.7412	6.84	6.65	0.48
4.9-2	3.0339	2.7744	6.21		
4.9-3	3.0369	2.7862	6		
4.9-4	3.0159	2.7145	7.26		
4.9-5	3.0502	2.7544	7.05		
4.9-6	3.0461	2.7725	6.52		

Table 4-4 UV-Vis absorption of the clear liquid extract from Poplar lignite with tetralin in beakers

Solvent: coal mass ratio-run number	***Absorption units***	***Average Absorption units***	***Standard deviation***
1.6-1	2.5812	2.6073	0.38
1.6-2	2.2339		
1.6-3	3.007		
3.3-1	2.0317	2.0163	0.04
3.3-2	1.9689		
3.3-3	2.0484		
4.9-1	1.91475	1.8854	0.05

4.9-2	1.9249
4.9-3	1.8314
4.9-4	1.8496
4.9-5	1.8987
4.9-6	1.8935

4.4 Discussion

In this section the results, analyses and the explanation for observations is discussed.

4.4.1 Solvent extraction using flow micro-reactor

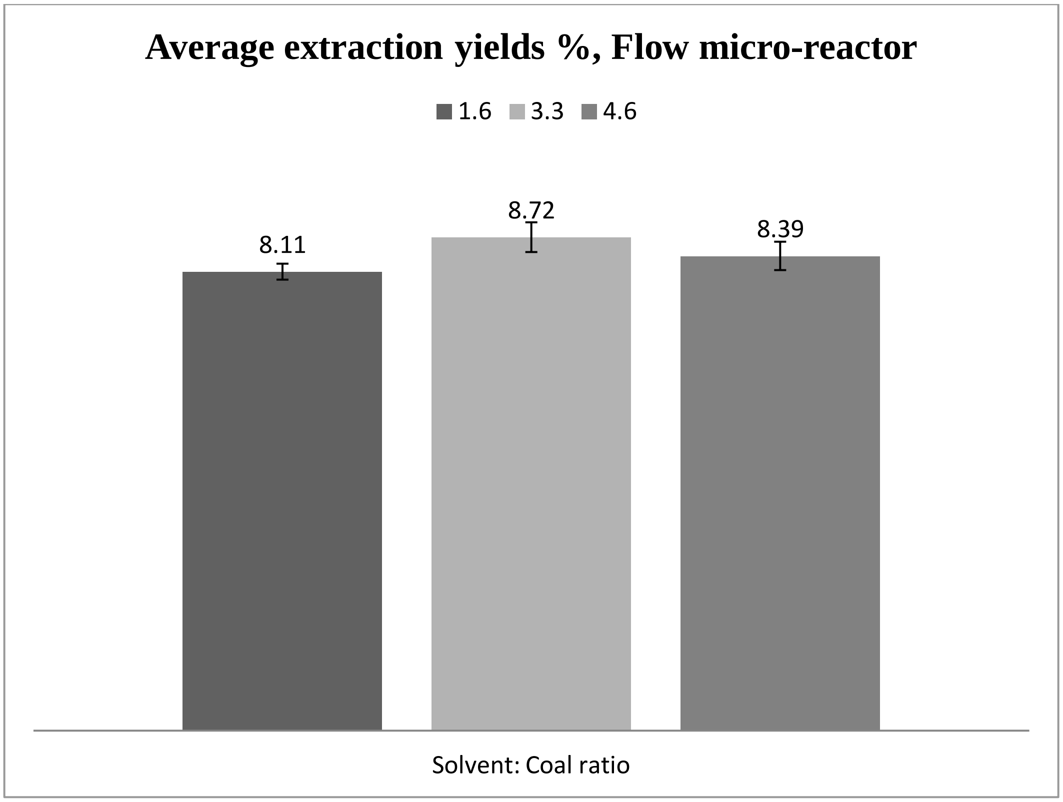

Figure 4-1 Average extraction yields%, ash and moisture free, for different solvent: Coal ratios, using flow micro-reactor, 100 °C and 8 minutes

The average extraction yields, conducted in flow micro-reactor, using Poplar coal and tetralin are shown in Figure 4.1. As we can see the yields don't follow any specific trend. It can be observed that the yield for the lowest solvent to coal ratio is a little less than the others. But for 3.3 and 4.6 solvent: coal ratio, increasing the solvent didn't increase the yield. As the results are so close, it cannot be a conclusive interpretation that for lower solvent: coal ratio, we have less extraction yield. A Student t-Test can help to check if the results differ significantly. So the probability associated with Student t-test two-tailed distribution (student t-test is explained in section 3.4.1) is calculated for three sets of data points (Table 4.5), the null hypothesis is, the data for experiments with various solvent :coal ratio is not different . Based on the results, as the p value for 3.3 and 4.6 data points is greater than 0.05, it can be stated that increasing the solvent: coal ratio from 3.3 to 4.6 does not have a significant effect on the yields. But the p results between 1.6 and 3.3 solvent: coal ratios are less than 0.05, and it might be possible that there are minor effects at low solvent: coal ratios but as it is not less than 0.01 there is still 1 in 20 chance of being wrong. To justify, the data points for 1.6 and 4.6 solvent: coal ratio were compared and the result is 0.16 which indicate that there not a significant difference between them.

The difference between the data for 1.6 and 3.3 can be caused by errors during the experiments.

Table 4-5 Student t-Test results for extraction yield results performed in flow micro-reactor and different solvent: coal ratios

Compared solvent: coal ratios	**1.6 and 3.3**	**3.3 and 4.6**	**1.6 and 4.6**
p value	0.024	0.19	0.16

4.4.2 Solvent extraction using beakers and magnetic stirrers

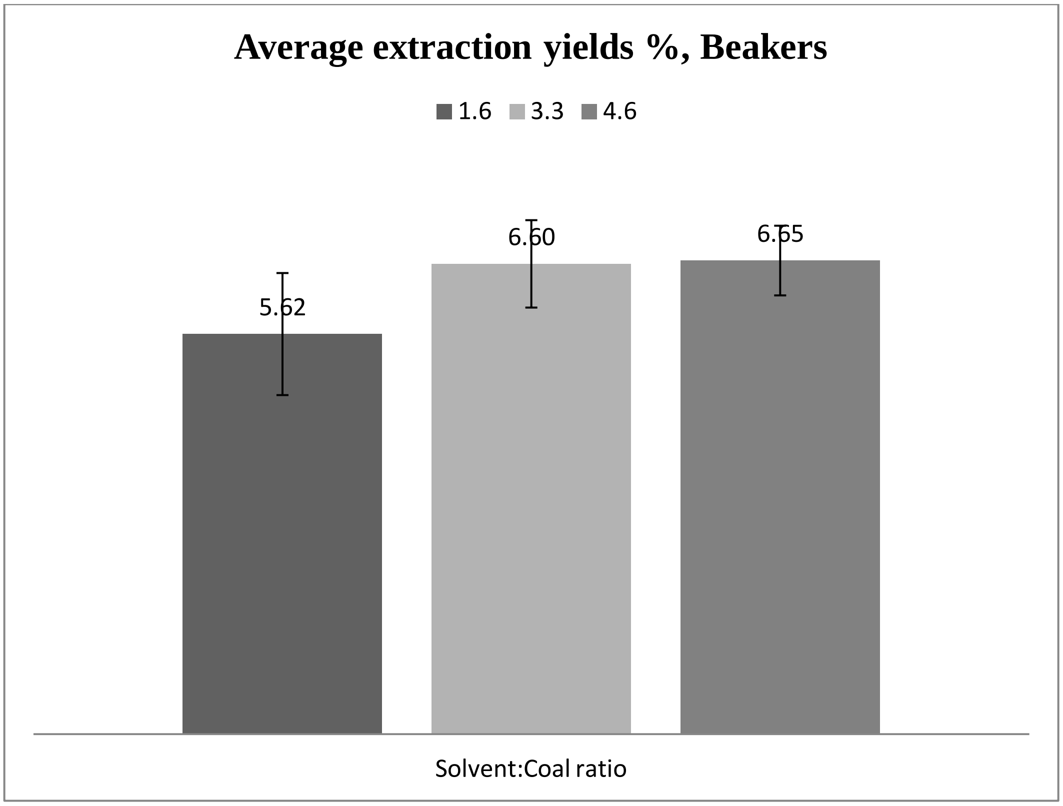

Figure 4-2 Average extraction yields%, ash and moisture free, for different solvent: Coal ratios, using beakers and magnetic stirrers, 100 °C and 8 minutes

In this section to investigate the effect of the solvent: coal ratio, especially to check if not having mixing in the micro-reactor can affect the results, a new set up including magnetic stirrers was used, so proper mixing of solvent and coal is assured. The results of the experiments are shown in figure 4.2. In figure 4.2 it can be observed that the average yield for the extractions with solvent: coal ratio 1.6 is less than the extraction yields with solvent: coal ratio 3.3 and 4.6, and there is no increase in the yield as the solvent: coal ratio increased from 3.3 to 4.6.

Table 4-6 Student t-Test results for extraction yield results performed in beakers and different solvent: coal ratios

Compared solvent: coal ratios	1.6 and 3.3	3.3 and 4.6	1.6 and 4.6
p value	0.18	0.91	0.15

A two-tailed Student t-Test was done on the extraction yield results that were performed in beakers, and the p associated with each t-Test is shown in table 4.6. As all the p values are greater than 0.05, with probability of 95%, the extraction yield results for 1.6, 3.3 and 4.6 solvent: coal ratios are the same, despite the lower average extraction yield for solvent: coal ratio 1.6.

Based on the extraction yield results and the statistical analyses that were performed on them, it can be concluded that solvent; coal ratio does not have a significant effect on coal extraction at 100 °C and the dissolution is not limited by the solubility. Dryden (1963b) stated that the yield of the soluble material at low temperatures is limited, and this limit seems to depend only on the solvent, the type of coal and the temperature in which the extraction is performed. He suggested making sure of achieving this limit, it is necessary to perform the extraction with more than one consecutive portion of solvent. This might be the reason of the lower extraction yield with the lowest solvent: coal ratio 1.6, the extraction with 5ml solvent is not limited by the solubility, but the small amount of solvent can result in experimental errors. This factor was not observed in the experiments using 10 and 15ml of solvent.

4.4.3 UV-Vis results

The UV-Vis results were analyzed but no meaningful relation between the data could be achieved for justification of the discussions in section 4.4.1 and 4.4.2.

4.5 Conclusion

Tetralin extraction of Poplar was investigated at 100 °C and 8 minutes, using solvent to coal ratios 1.6, 3.3 and 4.6 to study the effect of different solvent to coal ratios at low temperatures or in other words, physical dissolution. The experiments were done using two different set ups; flow micro-reactor and beakers and magnetic stirrers. The main results were:

a) Physical extraction is not governed by the solubility of the coal molecules in the solvent.

b) In the experiments performed in flow micro-reactors we can be reasonably confident that solvent: ratio does not affect the extraction yield.

c) In the experiments performed in beakers we can be reasonably confident that solvent: ratio does not affect the extraction yield.

5 Effect of solvent extraction on coal porosity at low temperatures

5.1 Introduction

Coal as a fuel can be used in different ways, generally based on gasification, extraction, or hydrogenation (Berkowitz, 1979). For these processes to happen, reagents or vapors should penetrate the porous structure of coal (Harris Jr and Petersen, 1979). All these processes are rate processes and the extent of the rates is proportional directly to the internal surface area of the coal (Medeiros and Petersen, 1979). Rates of mass transfer can be affected if the openings in the coal structure have very small sizes (Harris Jr and Petersen, 1979). The reactants should go in and be in contact with the solid coal, and products should come out through these pores. So, if the volume and surface area is measured as the process is going forward, it can be seen how the pore system is being used (Harris Jr and Petersen, 1979). For having high rates of reactions and extractions, the internal surface area of coal should be preserved during the process (Medeiros and Petersen, 1979).

In the third chapter the physical dissolution of coal was studied. Due to the importance of the pore structure of coal in different physical processes, we found it an interesting topic to investigate. Understanding the nature of the changes in the pore structure of coal at temperatures low enough that no thermal bond breaking happen, can be useful to understand the coal extraction and its relation to the coal structure better. For example treatments which are able to increase the surface area of coal, can enhance the reaction rate of coal with different reagents under appropriate reaction conditions (Klotzkin, 1985).

5.1.1 Background Literature

The structure of coal naturally contains very small size pores, and this small size can limit the size of molecules which can penetrate the coal. Having this property, coal can be considered as a natural molecular sieve. This determines the possible total surface area coal can provide for a reagent. Also the rate of penetrating the reagent to the possible reaction sites in the coal can be affected by the sieving property of coal. Due to its importance, lots of studies have been done on this subject since early 1940's (Berkowitz, 1979).

Usually the porosity is calculated using the amount of coal density, measured by helium and mercury as displacement liquids. Van Krevelen and Zwietering used mercury porosimetry to investigate coal structure. Based on their observations they suggested that coal contains two types of pore system, macropore and micropore. The pores with diameters above 30 nm are considered as macropores, and the ones bellow 4 nm as micropores, and with the diameters in between are mesopores. Mercury can penetrate macropore system, but even with applying high pressures, it cannot penetrate the micro pore system (Harris Jr and Petersen, 1979). And in the case of coal the problem is that it is not rigid and would be deformed under high pressures, making micropore measurements by mercury porosimetry meaningless.

Medeiros et al. did solvent extraction using tetralin and a sub-bituminous coal, the changes in the surface area was investigated. The surface area of raw coal was 99-100 m^2/ g, as the temperature of extraction was increased to 350 °C, the surface area increased, the maximum sureface area obtained 350 °C, 265-269 m^2/g. They also did the progressive extraction at 200 °C for up to 200 hours, the surface area started to increase as the experiment proceeded to 70 hours, but after that as the extraction proceeded, the surface area slightly decreased. They concluded from the surface area variations, the solvents that penetrate the micropores are able to extracts some parts of coal selectively. This result in an increase in the surface area, and the extent of this increase depends on the nature of the solvent and the yield of the extraction (the extracted material from the coal matrix) (Medeiros and Petersen, 1979).

Harris et al. did solvent extraction on Roland Seam coal, and the physical structure of it was studied by measuring the surface area, pore volumes and pore distributions. Their results confirm the macropore and micropore system of the coal, the macropores have large volume and small surface areas without mass-transfer limitations and micropores are characterized by small volume and large surface areas and some mass-transfer limitations. They also observed that the average micropore diameter decrease by extraction, but the micropore surface areas increase, so new micropores should be developing as the extraction proceed. It is stated the factors that play important roles in changing pore structure of coal during extraction are yield, solvent molecular size and chemical nature of solvent (Harris Jr and Petersen, 1979).

In another study on solvent treatments of coal, the effect of extraction with different solvents at ambient temperature has been studied. It is observed that the solvent which extracted more coal also increased the surface area more. These solvents can take out the extractable materials in the pores of a macromolecular network which are bound to it by a donor-acceptor bond, so if the solvent has certain values of acceptor and donor number to make the energy of new bonds between coal and solvent greater than the bond of either coal-coal or solvent-solvent, it can be replaced and extraction happens, so donor acceptor properties appear to be important in extraction of pore material. Based on this work, other important factors are carbon content of the coal and method of extraction (Klotzkin, 1985).

Mercury porosimetry

Mercury porosimetry is a very useful technique for characterizing porous materials. Pores between 3.5 nm to 500 µm can be studied by this method. The pore size distribution, the total pore volume or porosity, the apparent density and the specific surface area of a sample, are examples of the data that this method provides.

In mercury porosimetry it is assumed that the pore shape is cylindrical. With this assumption, a modified Young-Laplace equation known as Washburn is used to relate the pressure difference through curved interface of mercury (the interface curvature can be described by r_1 and r_2) to the associated pore size (r_{pore}) with the use of the mercury surface tension (γ) and the contact angel between mercury and the solid (θ) (Equation 5.1).

$$\Delta \boldsymbol{P} = \boldsymbol{\gamma} \left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \frac{2\,\gamma\,\cos\theta}{r_{pore}} \qquad \text{Equation 5-1}$$

The surface area of the pores can be calculated using the equation 5.2.

$$\boldsymbol{A = -\frac{1}{\gamma_{Hg}\cos\theta}\int_0^V P\,dV} \qquad \text{Equation 5-2}$$

In the system, the sample is evacuated first, and the air and remaining moisture from the pores are removed and the sample is filled with mercury while still under reduced pressure. Then gradually the pressure is increased and mercury penetrates the largest pores in the samples or other void spaces. In this step the pressure would be increased to several atmospheres which make a reasonable cross-over for low and high pressure step. Now high pressure step begins, the hydraulic fluid surround the sample-sell, and it can be pressurized up to 414 MPa.

In mercury porosimitry, compressibility of materials is of a great importance. The fractional change in volume per unit pressure is called compressibility. So for a specific material, considering the compressibility factor and the pore volume of the sample is important and for material like coal, a correction factor might be used.

Some of the limitations of mercury porosimetry can be: (a) This method measure the largest entrance to a pore, it may not be the same as the real pore size. (b) The smallest pore size which can be filled depends on the maximum pressure. (c) The largest pore size that can be measured is limited by the sample height. (d) A powder sample that is not packed suitably can become more compact and it might affect the porosity results. (e) Some irreversible changes might happen to the structure of the sample.

In spite of all these limitations, mercury porosimetry is very useful technique and it can provide information on a wide range of pore diameters, and is well suited for accurate measurement of the true pore volume of macropores (Giesche, 2006).

5.1.2 Problem

If low temperature coal dissolution is used as a pretreatment before other processes like coal liquefaction, the changes in the porous structure of coal can affect that process. As the pore structure of coal plays an important role in the coal utilization processes, it is important to have knowledge about the variations of the pore structure caused by low temperature coal dissolution. So here we want to study the changes coal goes through at low temperature extraction.

5.1.3 Approach

As mentioned before, coal physical dissolution is a fast process and can be finished in few minutes. To see the effect of solvent extraction on coal at low temperatures more clearly, the most extreme conditions was chosen in the scale of our experiments. The temperature was 150 ^{o}C and enough time (7 days) has been given to the solvent to penetrate the coal pores.

5.2 Experimental

5.2.1 Material

Poplar, a lignite coal, was used for all of the solvent extraction experiments. The solvent was 99% pure tetralin (1,2,3,4-tetrahydronaphthalene) provided by Sigma Aldrich and it was used without further purification.

5.2.2 Coal characterization

This section has been discussed in section 3.2.2.

5.2.3 Equipment and procedure

5.2.3.1 Reaction setup

The experiments were carried out in a flask connected to a reflux condenser. The condenser circulates cold water, at 10 °C, to make sure there is no solvent loss. A Heating plate and temperature controller was used to maintain the temperature the setup, and magnetic stirrers were used to provide mixing in the flask.

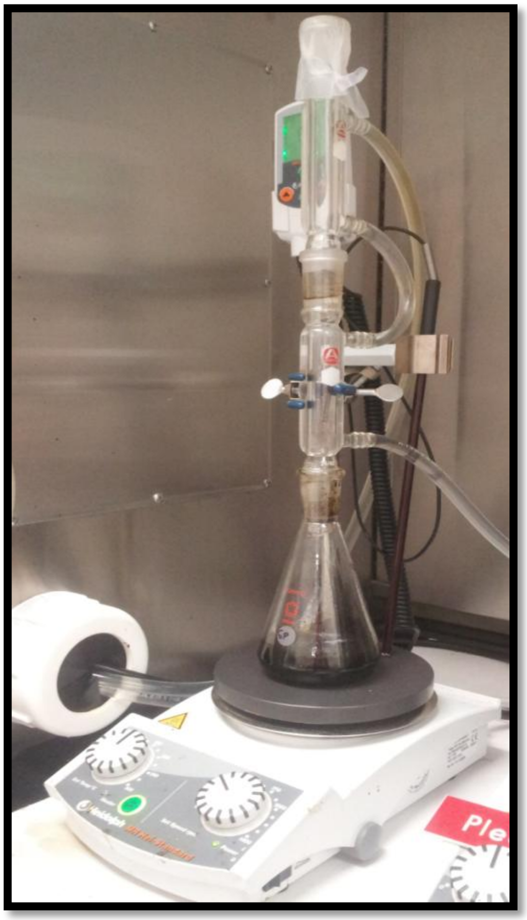

Figure 5-1 Reaction set up

5.2.4 Procedure

The coal particles in size range 250-1000 μm was vacuum dried at 80 °C overnight before the solvent extraction, and kept in plastic bags in a refrigerator to avoid oxidation.

For the experiments the flasks were charged with 3 g coal and 10 ml tetralin and a magnetic stirrer. The hot plates were set to 150 °C and stirrers to 250 rpm. After 7 days the liquid and solid samples were removed.

5.2.4.1 Vacuum filtration

To separate liquid and solid phases, vacuum filtration is used. For this purpose Whatman fiber glass filter media with 1.0 μm opening and a Welch Dryfast vacuum pump were used.

5.2.4.2 Vacuum oven

After filtration, solid samples were dried overnight at 130 °C in a Stable Temp Cole-Parmer vacuum oven, to remove the remaining solvent.

5.2.5 Analyses

5.2.5.1 Mercury porosimetry

The raw coal and extracted samples were analyzed with a Quantachrome PoreMaster mercury porosimetery analyzer. In the porosimeter the pressure went up to approximately 1850 psia, in higher pressures the structure of coal can break down and affect the results. The minimum pressure was 21 psia this pressure range is corresponding to pore with 100 nm to 10.66 µm . The results were analyzed with Quantachrome Intrument Poremaster for windows software.

5.2.6 Calculations

Extraction yield

This part has been discussed in section 3.2.6.

5.3 Results

The extraction yield results are shown in table 5.1. The porosity data gained from the software for raw coal and extracted coal are shown in tables 5.2 to 5.3.

5.3.1 Extraction yields

Table 5-1 Extraction yields for solvent extraction of coal at 150 °C, ash and moisture free bases%

Run number	***Raw coal mass (g)***	***Mass of residue***	***Yield ash –moisture free%***	***Average extraction yield %***	***Standard deviation***
1	3.0849	2.8969	8.38267	8.98	0.39
2	3.0867	2.8913	8.707545		
3	3.0873	2.8792	9.271689		

5.3.2 Total intruded volume and surface area

The total intruded volume is directly determined during mercury porosimetry and it represents the actual pore volume of all pores with diameters

100 nm to 10.66 µm. As the pressure increases the intruded volume corresponding to the pressure is measured.

The surface area is calculated by the software using volume data points and equation 5.2. The total surface area and the total intruded volume for three samples of raw and extracted coal are given in tables 5.2 and 5.3.

Table 5-2 Total surface area (m^2/g) for raw and extracted coal

Run number	*surface area (m2/g) Raw coal*	*Average surface area Raw coal*	*Standard deviation*	*surface area (m2/g) Extracted coal*	*Average surface area Extracted coal*	*Standard devitaion*
1	1.1317	0.9148	0.28	1.832	2.4204	0.72
2	0.5884			2.1927		
3	1.0243			3.2365		

Table 5-3 Total intruded volume (cm^3/g), raw and extracted coal

Run number	*Total intruded volume (cm3/g) Raw coal*	*Average Raw coal*	*Standard deviation*	*Total intruded volume (cm3/g) Extracted coal*	*Average Extracted coal*	*Standard deviation*
1	0.1623	0.1235	0.04	0.3025	0.3542	0.07
2	0.0816			0.3185		
3	0.1268			0.4416		

5.3.3 Changes in pore diameter after extraction

Over the diameter range covered by mercury porosimeter, the amount of mercury volume penetrated into the coal pores, for different diameter ranges, was measured for both raw and extracted coal. The results are shown in table 5.4.

Table 5-4 Intruded volume for pores with different diameter ranges

Diameter Range(µm)	*Intruded volume raw coal(cc/gr)*	*Intruded volume extracted coal(cc/gr)*
10.11	0	0.000587
2.149	0.031019	0.032152
0.6746	0.044287	0.127769
0.3072	0.025373	0.140990
0.1822	0.012335	0.055324
0.1263	0.006987	0.017328
0.1154		0.008121

5.4 Discussion

Solvent extraction is done on Poplar coal using tetralin as solvent, and the changes in the pore characteristics have been studied using mercury porosimetry. As the analyses at high pressures destructed the coal structure, lower pressures used for analyzing. It is not possible to measure pores with diammeters less than 30 nm no matter how high the mercury pressure is. Here as we didn’t use the highest possible pressure, the smallest pore size the mercury porosimeter measured is about 100 nm, which is in macropore size range.

5.4.1 Total surface area and total volume

As mercury porosimeter can only penetrate macropores, the surface area reported here is the surface area belonging to macropores, and as stated before the major part of coal internal surface area is in the micropores, so the scale of the surface areas here are much less than the ones that can be measured using BET and gases like N_2 and Co. But still here we can see the extraction increases the internal surface area of coal (Figure 5.2).

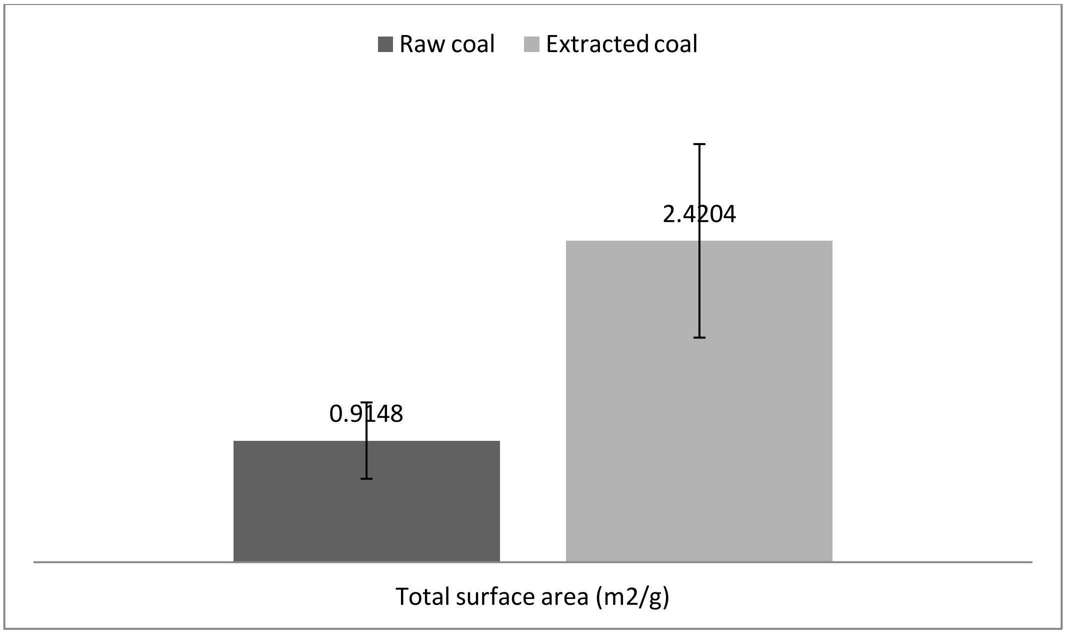

Figure 5-2 Average total surface area (m^2/g) measured by mercury porosimetry for three samples of raw and extracted coal (Table 5.2)

The increase in the total intruded volume in for extracted coal compared to raw coal is shown in figure 5.3.

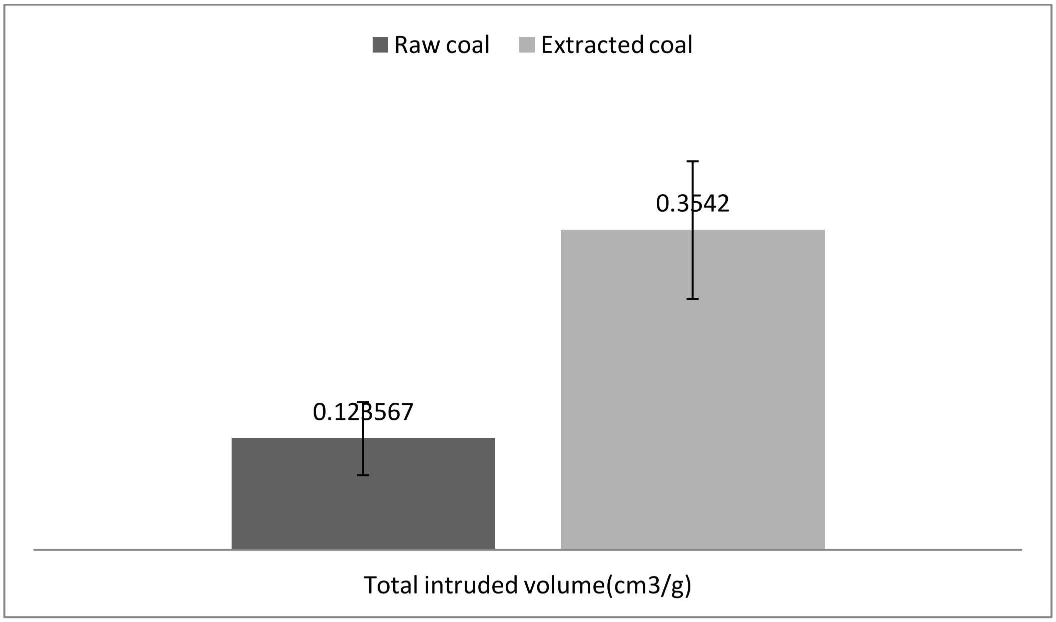

Figure 5-3 Average total intruded volume (cm3/g) measured by mercury porosimetry for three samples of raw and extracted coal (Table 5.3)

5.4.2 Changes in pore diameter after extraction

As mentioned before, in the pressure range applied in the pore volume measurements, the mercury porosimeter was not able to measure the volume changes in pores with diameters less than 100 nm. The average intruded volume for raw and extracted coal is 0.1235 and 0.3542 (cm^3/gr) according to table 5.3, so due to the changes in the pore size, after extraction 0.2307 (cm^3/gr) more mercury can penetrate into the coal pores.

On average 0.1974 gr of coal was extracted during the experiments. With the aid of the changes in the volume of pores with diameters larger than 100 nm, and the volume of total extracted material, the portion which is leached out from the pores with smaller diameters can be calculated. The density of the coal liquid in the extracts is 1.070 (gr/cm^3). Based on the 3 gr coal used for the experiments, this number gives us 0.061 (cm^3/gr) of extracted material from each grams of coal. This amount is less than the extra volume created in the coal pores after the extraction (0.2307 (cm3/gr)), so the portion of material extracted from pores with diameters less than 100 nm cannot be calculated, but these numbers lead us to another observation.

This observation can be explained as, before the extraction there are a portion of pores in the diameter range which mercury cannot penetrate. After extraction when coal molecules are extracted from these pores, the diameter increases to a certain point which is reachable by mercury. This makes the difference between the intruded volume before and after extraction more than what it really is.

The changes in the volume of intruded mercury in the coal pores before and after extraction are shown in figure 5.4. As it can be observed in figure 5.4, in this diameter range, 100 nm to 10.66 μm, the intrusion of mercury into the coal pores increased after the extraction. As the pressure increased and mercury started to penetrate the pores, at a certain pore diameter, more mercury is intruded in the extracted coal samples than raw coal, which means more pores exists in this diameter range after extraction.

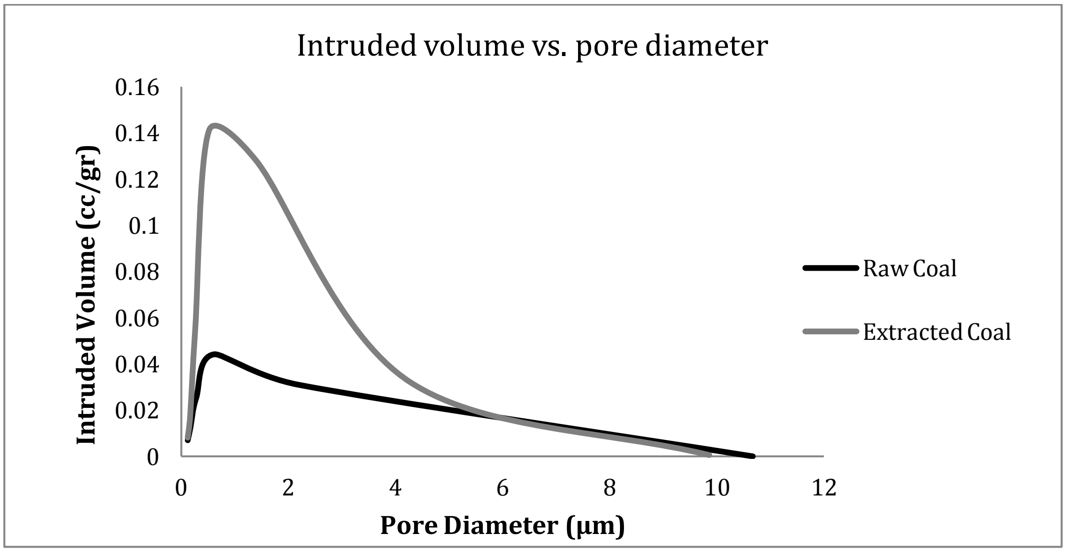

Figure 5-4 Intruded volume (cc/gr) into pores over different diameter ranges, raw and extracted coal

5.5 Conclusion

Solvent extraction of coal has been done using tetralin as solvent at 150 °C to investigate the changes of pore structure of the coal using mercury porosimetry.

a) Solvent extraction of coal at 150 °C takes the material out of the coal matrix and changes the pore structure of coal.

b) Solvent extraction of Poplar coal using tetralin increased the total surface area in the coal structure from 0.91 m^2/g in raw coal to 2.42 m^2/g in the extracted coal, in pore diameter range 100 nm to 10.66 µm.

c) Solvent extraction of Poplar coal using tetralin increased the total pore volume in the coal structure from 0.12 cm^3/g in raw coal to 0.35 cm^3/g in the extracted coal, in pore diameter range 100 nm to 10.66 µm.

5.6 References

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6 Investigation of the effect of heating rate on coal extraction

6.1 Introduction

One of the most abundant fossil fuels and an important source of energy in the world is coal. Among different processes for utilizing this coal, direct coal liquefaction (DCL) can be a good choice for clean and effective coal consumption (Li et al., 2008).

Generally this process consists of dissolving coal in a hydrogen-donor solvent, and can be accompanied by gaseous hydrogen (Şimşek et al., 2001). Coal liquefaction processes taking place in hydrogen-donor solvents, involve different kinds of chemical reactions which yield in active and inactive products. The active species or free radicals can be stabilized in different ways. The type and nature of solvent are important factors in the mechanism of stabilizing free radicals and can determine the yield and type of products in the liquefaction. In laboratory studies, tetralin is usually the solvent used, due to its high ability to donate hydrogen (Mohan and Silla, 1981; Neavel, 1976).

Coal liquefaction is usually done at high temperature and pressure conditions, such as 400 °C and high H_2 pressure. For making the process more economical, research for developing liquefaction technologies under mild conditions have been done. Mild conditions result in less conversion and oil yield. To achieve an acceptable yield at mild conditions, it is necessary to comprehend the main factors that control the liquefaction process (Li et al., 2008). Some of these factors are the nature of the coal and the solvent, temperature, and when used the catalyst.

The purpose of this chapter is to investigate if different time-temperature profiles can affect the extraction yield of coal in a hydrogen- donor solvent. Different time-temperature profiles leads to the formation of free radicals at different stages of liquefaction and at different rates. It also changes the rate of reactions which occur in various pathways and the transport rate of donor solvent needed for stabilizing them. For this purpose, liquefaction using a lignite coal and tetralin has been performed with different heating rates.

6.1.1 Background Literature

For coal liquefaction at high temperatures, chemical dissolution dominates the process. During the process at temperatures more than 350 °C (it can differ for different types of coals, for example 250 °C for lignite) the interactions between solvent and coal play an important role, especially if the solvent has the ability to donate hydrogen. When coal is present at elevated temperature conditions, covalent bonds are cleaved, and this leads to free radical formation. Free radicals need to be stabilized and the liquid yield of liquefaction conversion depends on the efficiency of free radicals stabilization. If sufficient hydrogen is present in the system, the yield will be high, otherwise free radicals will participate in undesirable reactions and low liquefaction yields will be obtained (Şimşek et al., 2001).

In has been reported that when a covalent bond breaks homolytically, for each fragment an unpaired electron would remain on each side of the bond, and this result in two free radicals. As the free radicals are reactive and unstable, they tend to participate in reactions to be stabilized. There are different ways in which the free radicals can be stabilized: rearrangement of atoms in the free radical, combination (addition) with hydrogen or other surrounding molecules and polymerization of the free radicals (Wiser et al., 1967).

For a certain reaction system, in order to maximize the yield and quality of the liquefaction products, and minimize retrogressive reactions, controlling the conditions of the system is important. Reactions such as crosslinking of the radicals formed from thermal decomposition, and condensation of thermally sensitive compounds are retrogressive reactions. The rate of thermal decomposition is mostly determined by parameters such as coal reactivity, temperature and time. By controlling these factors, balance can be provided between the rates of formation of free radicals and capping them by hydrogen, so the favorable conversion and yield can be gained (Song and Schobert, 1992).

The most desirable method for stabilization of a free radical is by capping with hydrogen, i.e. the addition of a hydrogen atom to convert the free radical into a covalent bond with hydrogen. This way the large molecules of coal, after being thermally degraded, react with hydrogen atoms (usually provided by a hydrogen donor solvent) and stabilize as smaller molecules which are also more soluble and also more hydrogen rich. There are two other reactions that can happen when there are not sufficient hydrogen available for free radicals to react with. If in the structure of free radical, a functional group with hydrogen-donor properties is present, an example can be a hydroaromatic unit, the fragment can be capped by itself. If a free radical fragment becomes stabilized by another fragment, polymerization or retrograde reaction can take place and large undesirable molecules can form. This is the way coke, char and some high molecular weight species would form (Whitehurst et al., 1980). Hence, for having a liquefaction process with high conversion and yield, we should provide the conditions in the way the first method can happen.

Song et al. (1992) used a temperature-programmed system for low rank coal liquefaction. They reported in their work, that in low rank coals, bonds can be broken thermally at lower temperatures, and it has been seen that using relatively slow heating rates is effective for low-rank coal liquefaction. In their work they used tetralin as solvent and soaked the coal at 200 °C for 15 minutes, then heated the system up with rate of 7 °C /min to the final desired system temperature. They compared this method to the conventional liquefaction, heating the system rapidly to the liquefaction temperature in 2-3 minutes. The results show, when a hydrogen-donor solvent is used, the temperature-programmed liquefaction leads to noticeably higher conversion than the conventional run at the same or even higher temperatures (Song and Schobert, 1992).

Another study on time temperature profile was done by Wham (1987). He used tetralin as solvent, and the liquefaction was done at 427 °C for 5 minutes without preheating and with preheating at different times and temperatures. It can be seen from this work that preheating of coal at 316 °C for 10 minutes can increase the conversion to pyridine soluble from 32% to 76 %. Preheating at 277 °C and 322 °C for 2.5 minute also show almost the same results. But, process done at 177 °C for 120 minutes and followed by 5 minute liquefaction at 427 °C, showed no significant changes in the conversion. This study shows that different preheating temperature profiles before the liquefaction can affect and improve the extraction yield to a great extent.

In this work, the effect of different heating rates before reaching the final temperature of the reaction was investigated, to see if the path to the liquefaction temperature can change the liquid yield of the experiment.

6.1.2 Problem

For having a favorable yield and conversion in coal liquefaction process and also to prevent the retrogressive reactions, there should be a good balance between the rate of formation of free radicals and the rate of stabilizing them. The rate of free radical formation changes with temperature, so controlling the temperature helps to control this factor.

The aim of this investigation is to see if different time-temperature profiles and different paths to the final reaction temperature can affect the process, and if yes, in which way and to what extent it changes the results.

6.1.3 Approach

To study this problem, different time- temperature profiles have been devised and experiments based on them have been done. These time-temperature profiles consist of three different paths to the desired temperature, first a low heating rate at the beginning, second a high heating rate at the beginning and constant heating rate during the heating up stage. The first set of experiments are followed by an isothermal step, to see if having the same condition for a certain amount of time can cancel the effect of different paths, having the same conditions after that would result in the same conversion.

The second set of experiments has been done with different time-temperature profiles, but the isothermal step is omitted, so the effect on the heating up stage can be seen more clearly.

6.2 Experimental

In the following section, the experimental method to carry out the solvent extraction, the separation of liquid and solid phases of the samples and further processing and analysis of residue and extract are discussed.

6.2.1 Materials

Poplar, a lignite coal (Table 6.1), was used for all of the solvent extraction experiments. The solvent was 99% pure tetralin (1,2,3,4-tetrahydronaphthalene) provided by Sigma Aldrich and it was used without further purification.

Table 6-1 Ultimate and Proximate Analyses of Coal. (Ash free basis)

Description	Poplar (lignite)
Ultimate analysis (wt %)	
carbon	41.07
hydrogen	5.72
nitrogen	0.72
sulfur	0.92
oxygen	51.6
Proximate analysis (wt % daf)	
moisture (wt %)	26.85
Ash	40.5
volatile matter	34.65
fixed carbon	24.94

6.2.2 Coal characterization

The ultimate and proximate analyses have been discussed in section 3.2.2.

6.2.3 Equipment

6.2.3.1 Reaction setup

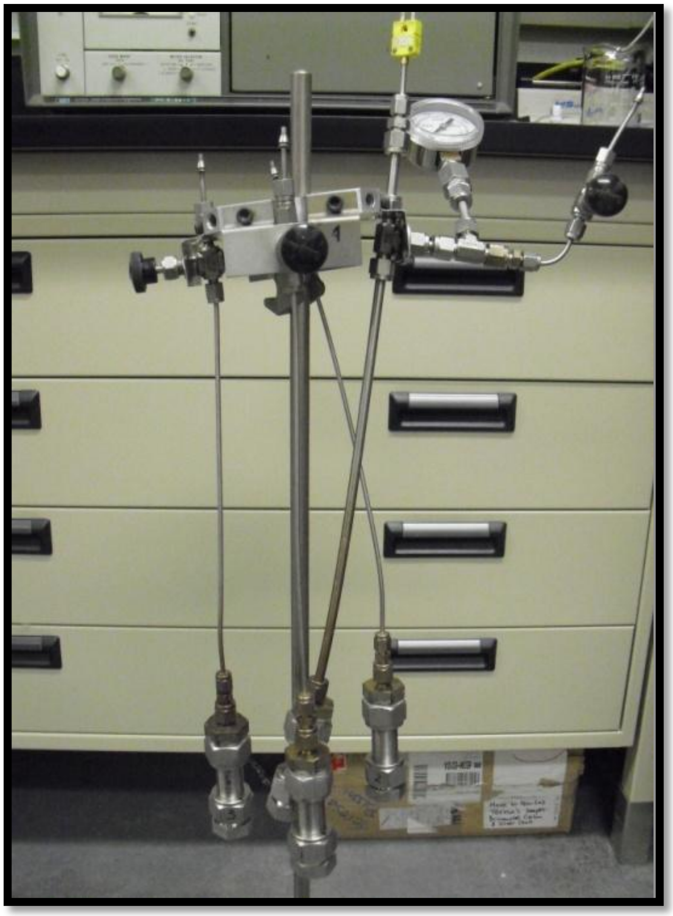

Figure 6-1 The reaction setup, micro-reactors and the holder

The reaction setup (Figure 6.1) includes four micro-reactors, made with 1” nominal diameter of grade 316 L stainless steel seamless pipe and Swagelock fittings. The micro-reactors are connected to 1/8” needle valves using 1/8” nominal diameter stainless steel tubing, and the valves are placed on a holder. One of these micro-reactors is connected to the valve using a 1/4” tubing, so a thermocouple can be placed inside it, it is installed in a way that the end of it, is placed in the center of micro-reactor, a pressure gauge is also attached to the outlet valve of this part, so the conditions inside the micro-reactor during the experiment can be monitored.

Figure 6-2 the sand bath, agitator and the controller

Then the center of the holder is fitted on a rod which is connected to an agitator, it is an eccentric motor that can provide vertical agitation with 173 rpm. The micro-reactors are adjusted in a way that they all submerge completely in the sand bath. The sand bath is a Techne Fluidized Bath (SBS-4) with aluminum oxide and the temperature is controlled with a Techne TC-8D temperature controller (Figure 6.2).

6.2.3.2 Vacuum filtration

After finishing the experiment and cooling down the reactors, the micro-reactors are opened and the solid and liquid phases are separated by vacuum filtration. For this purpose Whatman fiber glass filter media with 1.0 µm opening and a Welch Dryfast vacuum pump were used.

6.2.3.3 Vacuum oven

After filtration, solid samples were dried overnight at 110 °C in a Stable Temp Cole-Parmer vacuum oven, to remove the remaining solvent.

6.3 Procedures

Coal particles in the size range 150-250 µm were vacuum dried overnight at 80 °C before solvent extraction. 2 grams of coal was charged into the reactors, and then 4 stainless steel beads (3/16” diameter) were weighed and added to each micro-reactor to help the agitation during the reaction. Then 6 grams of tetralin (equal to solvent/coal ratio 3) was charged into the micro-reactors. The micro-reactor was closed and pressurized using nitrogen. The micro-reactors were checked for potential leaks using Snoop from Swagelok. When all the leaks were fixed, the gas in the reactor was released and purged four additional times to make sure there is no remaining air in the reactors. Finally, the reactor was pressurized with nitrogen to 4 MPa.

The holder and reactors were placed in the sand bath and adjusted on the eccentric motor rod, it was assured the top of the reactors were always totally submerged in the sand. From this point the heating was started. The sand bath includes two heaters that work separately. If one of them is on, the heating rate is approximately 4 °C/min, by using both of them we can get a heating rate of 8 °C/min. Controlling these heaters manually, different time temperature profiles can be created for the experiments.

After the experiment was finished, the reactors were taken out of the sand bath and cooled down to room temperature using air flow. Afterwards the needle valve was opened and the nitrogen and reaction gases were released inside the fume hood. Then the reactors were opened, the solvent and coal mixture was taken out and placed on the filter media and the solid and liquid phases were separated. The liquid phase was kept in amber vials. The residue, the filter media and stainless steel beads were transferred to an aluminum pan of known weight and dried over night at 110 °C. After drying, the ash content of the residue was determined using the method described in section 6.2.2.2 .

The extraction yield then was calculated using equation 6.1.

$$\boldsymbol{EY}\% = \frac{\boldsymbol{M_{Raw\ coal}}(\mathbf{1}-\boldsymbol{Ash_{Raw\ coal}})-\boldsymbol{M_{\ Residue}}\ (\mathbf{1}-\boldsymbol{Ash_{Residue}})}{\boldsymbol{M_{Raw\ coal}}(\mathbf{1}-\boldsymbol{Ash_{Raw\ coal}})}\mathbf{100} \qquad \text{Equation 6-1}$$

Here EY is the extraction yield in %, $M_{\text{Raw coal}}$ is the mass of the initial coal used, $Ash_{\text{Raw coal}}$ is the ash content of the raw coal, M_{Residue} is the mass of the un-extracted coal and Ash_{Residue} is the ash content of the residue.

6.4 Results

Solvent extraction was carried out using tetralin and Poplar coal, with different time- temperature profiles to 350 °C, to investigate the effect of time-temperature history on the coal liquefaction. The results can be found in this section.

6.4.1 Extraction with isothermal step

The results for the experiments done with different time temperature profiles, including a 20 minutes isothermal step at the end of the experiment can be seen in tables 6-2 to 6-4. The time-temperature plot for the experiments is shown in figure 6.3. The total time for each experiment is 90 minutes.

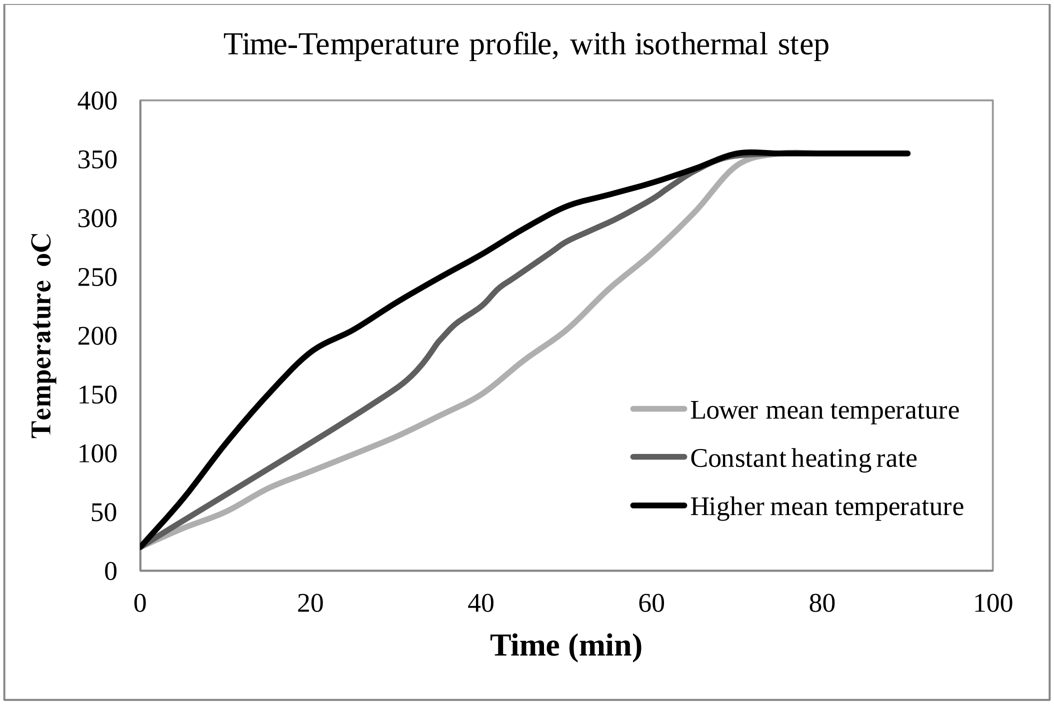

Figure 6-3 Time temperature profile for experiments with isothermal step

Table 6-2 Lower mean heating rate (see Figure 6.3), with isothermal step, at 350 °C for 90 min

Run number	*Raw coal mass (g)*	*Mass of residue*	*Residue ash content%*	*Yield (ash –moisture free %)*	*Average Liquid yield*	*Standard deviation*
1	2.042	1.6428	44.4	25.48	25.94	0.75
2	2.0745	1.6391		26.81		
3	2.0215	1.6251		25.53		

Table 6-3 Constant heating rate (see Figure 6.3), with isothermal step, at 350 °C for 90 min

Run number	*Raw coal mass (g)*	*Mass of residue*	*Residue ash content%*	*Yield ash – moisture free%*	*Average liquid yield*	*Standard deviation*
1	2.0483	1.6368	45.0	26.83	27.57	0.17
2	2.0122	1.5495		29.49		
3	2.0118	1.6052		26.94		
4	2.0219	1.594	45.5	28.39		
5	2.0172	1.6116		27.43		
6	2.0244	1.6398		26.42		
7	2.0165	1.6134	45.9	27.85		
8	2.0351	1.6434		27.18		
9	2.016	1.6178		27.63		

Table 6-4 Higher mean heating rate (see Figure 6.3)**,** with isothermal step, at 350 °C for 90 min

Run number	*Raw coal mass (g)*	*Mass of residue*	*Ash content%*	*Yield ash – moisture free%*	*Average liquid yield*	*Standard deviation*
1	2.0214	1.58	47.7	31.89	31.07	1.25
2	2.028	1.6379		29.62		
3	2.014	1.5785		31.70		

6.4.2 Extraction without isothermal step

The results for the experiments done with different time temperature profiles, to the final temperature 350 ^{o}C is shown in tables 6-5 to 6-7. And the time-temperature plot for the experiments is shown in figure 6.4. The total time for each experiment is 70 minutes.

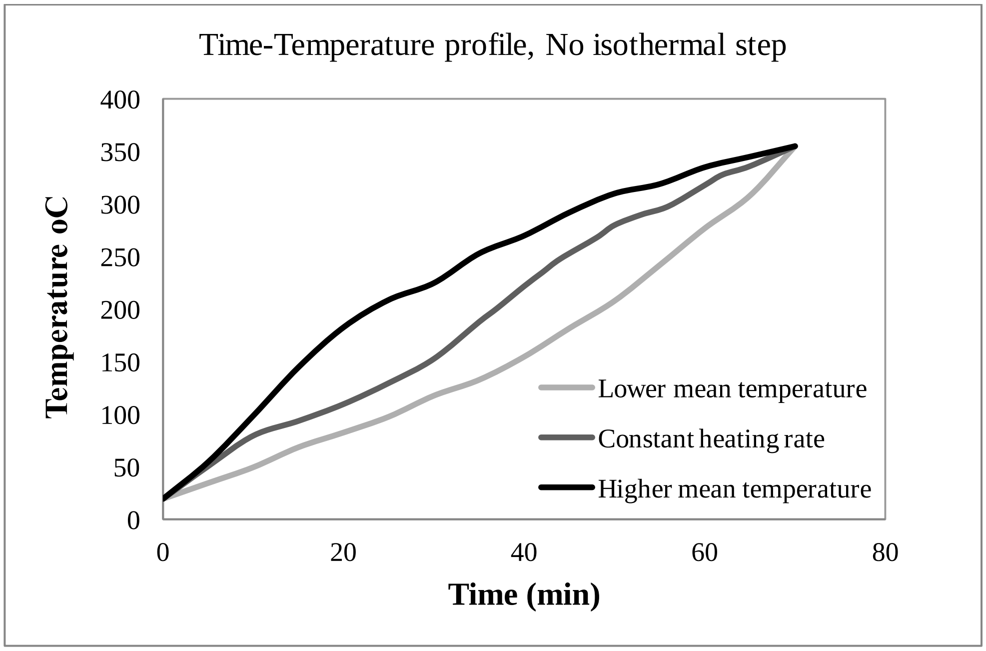

Figure 6-4 Time temperature profile for experiments with no isothermal step.

Table 6-5 Lower mean heating rate (see Figure 6.4), no isothermal step, at 350 °C for 70 min

Run number	*Raw coal mass (g)*	*Mass of residue*	*Ash content%*	*Yield ash – moisture free%*	*Average liquid yield*	*Standard deviation*
1	2.0252	1.6808	45	24.03	22.92	1.02
2	2.0251	1.7097		22.72		
3	2.0281	1.7281		22.00		

Table 6-6 Constant heating rate (see Figure 6.4), no isothermal step, at 350 °C for 70 min

Run number	*Raw coal mass (g)*	*Mass of residue*	*Ash content%*	*Yield ash – moisture free%*	*Average liquid yield*	*Standard deviation*
1	2.0231	1.6907	45.2	23.67	23.83	0.3
2	2.0266	1.6822		24.18		
3	2.0314	1.6979		23.65		

Table 6-7 Higher mean heating rate (see Figure 6.4)**,** no isothermal step, at 350 °C for 70 min

Run number	*Raw coal mass (g)*	*Mass of residue*	*Ash content%*	*Yield ash – moisture free%*	*Average liquid yield*	*Standard deviation*
1	2.0285	1.6624	47.0	27.61	27.57	0.38
2	2.0288	1.655		27.94		
3	2.028	1.6721		27.17		

6.5 Discussion

In this section the results, analyses and the explanation for observations are discussed.

6.5.1 Extraction with isothermal step

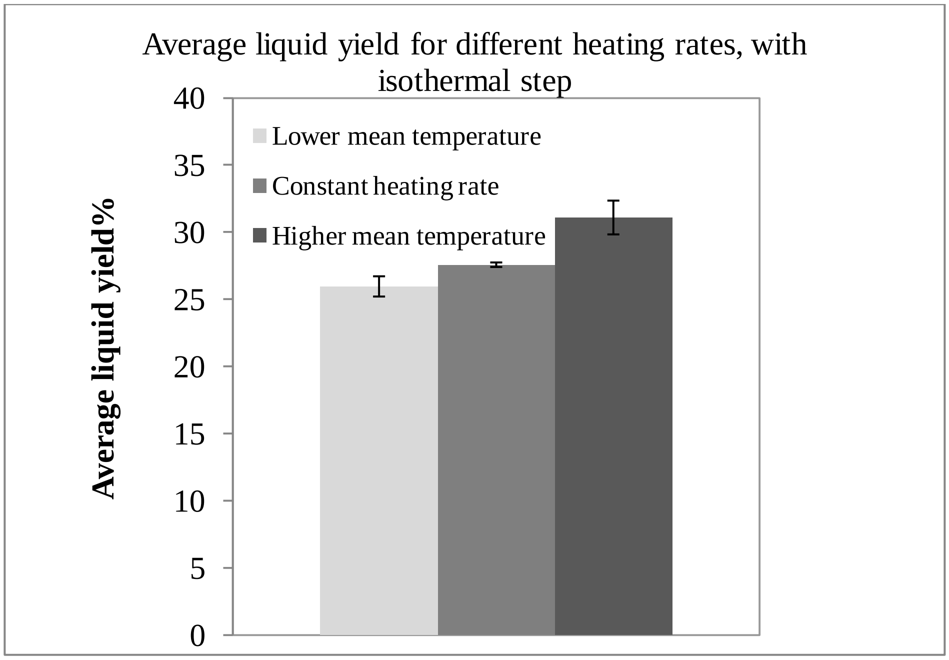

Figure 6-5 Average liquid yields, for experiments with isothermal step and different time-temperature profile

Table 6-8 The Student t-Test results for lower mean heating rate (L), Constant heating rate (C) and Higher heating rate (H) data points with isothermal step

Compared time temperature profiles	L and C	C and H	L and H
p value	0.034	0.025	0.006

As it can be observed in the figure above (Figure 6.5), the extraction yield result for the experiment with the higher mean heating rate is higher than the others, and the yield increased as the mean temperature of the experiment increased. Student t-Test can help to investigate the effect of different time-temperature profiles, the results of the p value is shown in table 6.8. As the results are all less than 0.05, it can be stated that the difference between the liquid yield results for each set of experiment is significant. So despite the same experiment duration and same final temperature the results differ considerably due to different mean temperature caused by different time-temperature profile.

As it was stated before, for lignite the chemical reactions start to happen around 250-300 °C, so in that experiment, after minute 35, the chemical reactions started and continued to the end of the experiment. In the runs with constant and lower mean heating rates, this happened after minute 45 and 55, so the active time for them was less. As it was reported in Wham's (1987) work, extended preheating at temperature ranges before the active regimes does not increase the yield, also when the process is dominated by physical dissolution (Rivolta, 2012).

So, it is obvious that one of the important factors here is the time that passed after the active regime started, not the whole experiment time and not the duration of the isothermal step.

As the conversion is higher for higher reaction rate, it can be concluded there was enough hydrogen in the system to stabilize the active fragments formed, if the solvent was not a hydrogen donor or a donor with low donation ability, and the rate of forming free radicals was not be in balance with capping hydrogen, it could result in forming high molecular weight insoluble molecules, and the extraction yield would decrease.

6.5.2 Extraction without isothermal step

In this section, which the isothermal step is omitted (see figure 6.4), similarly to the last section, the extraction yield increases as the mean temperature of the experiment increase.

Table 6-9 The Student t-Test results for lower mean heating rate (L), Constant heating rate (C) and Higher heating rate (H) data points without isothermal step

Compared time temperature profiles	**L and C**	**C and H**	**L and H**
p value	0.25	0.008	0.0002

Looking at the average liquid yields in figure 6.6 and considering the statistical analyses performed on the results for experiments with different time-temperature profile without isothermal step, it can be stated that as the mean temperature of the experiment increases, the extraction yield also increases. There is not statistically significant difference between the results of extraction with lower mean temperature and experiments with constant heating rate. But, there is a highly significant change in the yield results between experiments with constant heating rate and higher mean temperature.

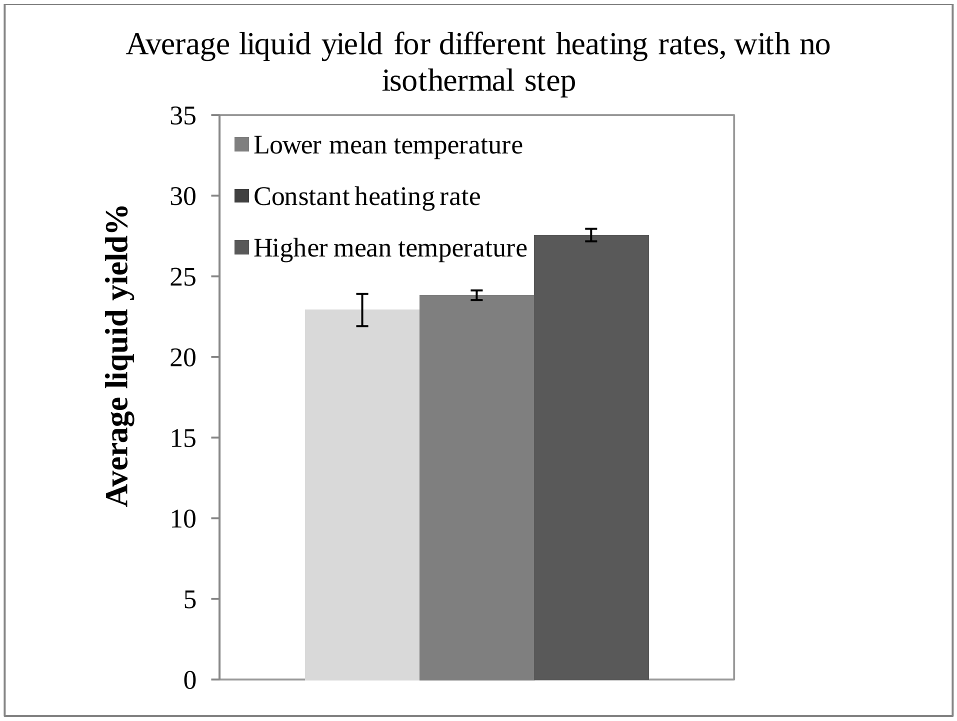

Figure 6-6 Average liquid yields, for experiments without isothermal step.

6.5.3 Comparing extraction yields for with and without isothermal step

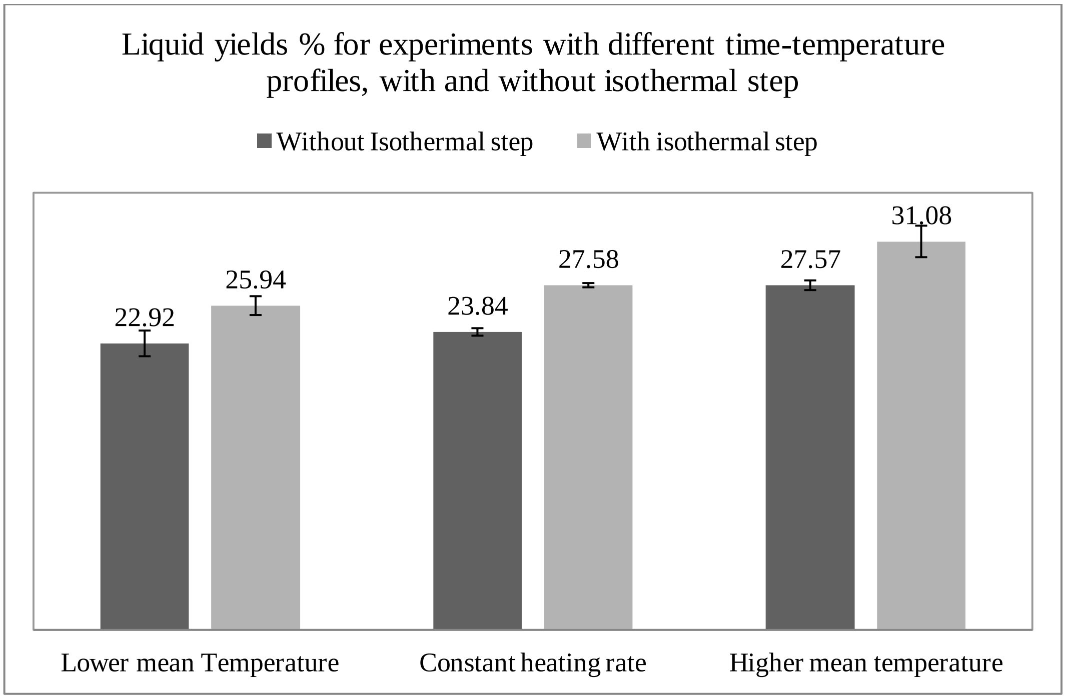

Figure 6-7 Extraction yields for experiments with and without isothermal step.

Having an isothermal step for 20 minutes after reaching the desired temperature of the experiment, here 350 °C, resulted in an increase in extraction yields of about 3-3.7% (absolute difference, see table 6.10). This condition was the same for all the experiments with isothermal step and there is no specific trend in the increase of the yield. It is just the matter of extended time, and as the temperatures are the same, the rates of reactions are the same for experiments with the similar heating rate but with and without isothermal step.

Table 6-10 Absolute difference between liquid yield results for experiments with same heating rate but with and without isothermal step.

	Lower mean heating rate	**Constant heating rate**	**Higher mean heating rate**
Absolute difference%	3.02	3.74	3.51

6.6 Conclusion

Tetralin extraction has been done at 350 °C, with three different time-temperature profiles to investigate the effect of time temperature history on the coal extraction. Two sets of experiments have been done, one with a 20 minute isotherm step at 350 °C and the other one finished when the runs reached 350 °C.

a) At this temperature and using tetralin, a solvent with high hydrogen-donor ability, the yield increases as the mean temperature in the system increases.

b) At the conditions of the experiments here, starting with the higher heating rate and having higher mean temperature, does not interrupt the balance between the rate of forming the radicals and stabilizing them, so the yield increases due to the higher mean temperature during the experiment and more time spent at active temperature regime.

c) Having 20 minutes isothermal step cannot compensate for the lower mean temperatures at the heating up step. After the isothermal step reached, all the runs would have the same rate.

d) The 20 minute isothermal step causes 3-3.7% (absolute) increase in the conversion and no trend is observed for different runs with different temperature profiles.

6.7 References

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7 Conclusion

a) Extraction yield increases with temperature, with a clear increase observed from 25 to 100°C.

b) The extraction yield in the 25-150°C range is determined mainly by extraction temperature.

c) Maximum extraction yield is in < 16 min. Even at 25°C, 75% of the total extraction yield is obtained within 2 min.

d) On cooling the coal extract precipitates are formed. These precipitates can be reversibly dissolved/liquefied with an increase in temperature

e) Physical extraction is not governed by the solubility of the coal molecules in the solvent.

f) As the extraction is not limited by solubility the precipitates formed should be coal liquids which solvent can dissolve as the temperature is elevated, and at room temperature they are not soluble in solvent and precipitate as solid phase.

g) Solvent: coal ratio did not show any significant effect on coal extraction performed at 100°C, both in flow micro-reactor and beakers.

h) Solvent extraction of coal at 150°C increases the surface area and total pore volume of the coal.

i) In the solvent extractions at 350°C with different preheating steps, the extraction yield increases as the mean temperature during the experiment increases.