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Solvent Swelling of Estonian Oil Shales: Low Temperature Thermochemical Conversion Caused Changes in Swelling

NATALJA SAVEST

TUT PRESS

TALLINN UNIVERSITY OF TECHNOLOGY
Faculty of Chemical and Materials Technology
Department of Chemical Engineering

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Supervisor: Professor Vahur Oja, Department of Chemical Engineering, Tallinn University of Technology

Opponents: Professor Emeritus Olev Träss, Toronto University, Canada
Professor Tiit Kaps, Tallinn University of Technology, Estonia

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

Natalja Savest

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Eesti põlevkivide pundumine lahustites: termokeemilise konversiooni mõju pundumisprotsessile

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LIST OF PUBLICATIONS

The thesis is based on the following papers referred to in the text by the Roman numerals:

I. **N. Savest**, V. Oja, T. Kaevand, Ü. Lille, Interaction of Estonian kukersite with organic solvents: a volumetric swelling and molecular simulation study, Fuel, 86 (2007) 17-21.

II. **Savest, N**., Hruljova, J., Oja, V. Characterization of thermally pre-treated Kukersite oil shale using the solvent swelling technique. Energy Fuels, 23 (2009) 5972-5977.

III. K.Kilk, **N. Savest**, J. Hruljova, E. Tearo, S. Kamenev, V. Oja, Solvent swelling of Dictyonema oil shale, Oil Shale (accepted 2009).

THE AUTHOR'S CONTRIBUTION TO PUBLICATIONS

The contribution by the author to the papers included in the thesis is as follows:

I. Carrying out the experimental work, developing experimental procedure, participation in data processing and the results analyzing.

II. Carrying out a major part of the experimental work, participation in data processing, analysis of the results and summing up the research work.

III. Participation in data processing and in the discussion of the results, minor role in the experimental work; co-supervising.

LIST OF ABBREVIATIONS AND SYMBOLS

amu	atomic mass unit
CPD	Chemical Percolation Devolatilization model
DMF	dimethylformamide
EAN	electron acceptor number
EDN	electron donor number
FG-DVC	Functional Group – Depolymerization, Vaporization and Crosslinking model
H-bonding solvent	hydrogen-bonding solvent
$\mathbf{M_C}$	number average molecular weight between cross-links
MEK	methyl ethyl ketone
NMP	N-methyl-2-pyrrolidinone
Py-FIMS	pyrolysis field ionization mass spectrometer
Q	swelling ratio
$\mathbf{Q_{dmmf}}$	swelling ratio on dry mineral matter free basis
THF	tetrahydrofuran
$\boldsymbol{\delta}$	solubility parameter
$\boldsymbol{\chi}$	polymer-solvent interaction parameter

INTRODUCTION

Utilization of oil shales has gained considerable interest in recent years due to increasing global energy demand and also the strategic domestic energy visions of countries with considerable oil shale resources. Oil shale has been used since ancient times and can be used as fuel just like coal. Mostly, oil shale is used for manufacturing oil, electricity production [Brendow, 2003] and chemicals [www.easac.org.]. Solid residues from oil shale processing (for example, ash) can also be used for production of cement [Koel, 1999] or different construction materials [www.easac.org.].

Oil shales, ranging in age from Cambrian to Tertiary, are located in many parts of the world; over 600 deposits are known [Arro *et al*., 2003]. Deposits occupy thousands of square miles and contain many billions of barrels of potentially extractable shale oil. Total world resources of oil shale are conservatively estimated at 2.9 trillion barrels of recoverable oil [Arro *et al*., 2003; http://en.wikipedia.org/wiki/Oil_shale]. Estonian oil shale kukersite deposits account for just 17% of total deposits in the European Union and 0.4% of worldwide deposits. There are two kinds of oil shales in the Baltic Basin: the Middle Ordovician kukersite, and lower Ordovician Dictyonema argillite (claystone). Kukersite oil shale resources are about 5 billion tons, among these mineable (active) resources about 1.5 billion tons. The Dictyonema shale reaches 64 billion tons. In Estonia, the oil shale kukersite is the most important source of primary energy and thermo-chemical conversion based oils and chemicals. Although the reserves of the Dictyonema shale considerably surpass those of kukersite, the quality of Dictyonema is poor. The relatively low oil yield (3-5 %) and a high sulfur content (2-4 %) prevents Dictyonema utilization for energy production and processing into oil. However, it has been historically of interest because of some commercially important elements, e.g. uranium, vanadium, molybdenum [Maremäe *et al*., 2003].

Oil shale can be described as a complex and heterogeneous material which consists of sedimentary inorganic material containing organic matter. Oil shale organic matter is known to a large extent consist of kerogen, a macromolecular network, which is largely insoluble in solvents and that swells when immersed in certain organic solvent. This organic macromolecular network structure of the kerogen must somehow be broken down in order to release lower molecular weight compounds (oil material) from this matrix. Because of this reason knowledge of the macromolecular structure of oil shale kerogen and of the changes caused by different types of treatments of the network (heat-treatment, solvent penetration) can be useful information to guide upgrading process development.

Among many available techniques for characterizing macromolecules, volumetric solvent swelling is one of the simplest methods, which has had some success when applied to fossil fuels such as coals and also oil shales [Solomon *et al*., 1990 (a, b); Turpin *et al*., 1996; Ballice, 2004 (a, b); Larsen and Li, 1994;

Ballice, 2003]. When a cross-linked macromolecular system is brought into contact with a solvent, the system absorbs the solvent and swells. The information obtained from solvent swelling has been used to characterize cross-linked structures, to determine solubility parameters (square root of cohesive energy density), molecular weights between cross-links or cross-link densities of fossil fuels with cross-linked macromolecular structures. Solvent swelling has been a useful technique for gaining insights into geochemical process of maturation [Ballice, 2004] or changes occurring during thermo-chemical conversion processes of coal [Solomon *et al.*, 1990; Solomon *et al.*, 1993]. There is a specific connection between swelling and extraction; extraction always being accompanied by coal swelling [Szeliga and Marzec, 1983].

Our literature review has shown that for Estonian oil shales only one dataset on kukersite swelling in watery trichloromethanol could be found [Zalessky, 1917] and no other studies on organic solvents have been conducted. Generally, there is a considerable amount of data on swelling studies of various oil shale kerogens [Larsen and Li, 1994 (a, b); Larsen and Li, 1997; Larsen *et al.*, 2002; Ballice, 2003] where the solubility parameter is estimated or number average molecular weight and cross-link density are calculated. However, no data were found on the use of solvent swelling to investigate changes in oil shale organic matter structures up to temperatures of oil shale thermobitumen formation (up to 350 - 400 ^{o}C) - before the onset of major pyrolytic processes.

There has been use of solvent swelling to get information on changes in macromolecular structure during thermal processing of coals - the swelling extent has been used as an indicator for evaluating changes in crosslink density in the pyrolysis process. Thermochemical conversion of the organic matter in coal is shown to be a complex phenomenon which includes (among other processes) depolymerization (breaking of cross-linked macromolecular networks) and repolymerization (cross-linking) processes. The importance of the extent and timing of cross-linking in the pyrolytic processing of coals has been shown elsewhere [Solomon *et al.*, 1990b]. It is emphasized here that the cross-linking behavior influences tar yield and tar molecular weight distribution. It has been concluded, based on coal solvent swelling results in pyridine, that some lower rank coals have already undergone cross-linking at low temperatures before the onset of major pyrolytic processes, and that this cross-linking process is one of the reasons for the relatively lower tar yields of these coals [Solomon *et al.*, 1990a]. There have been remarkable advances in the modeling of coal pyrolysis in the past three decades. There has been a shift from utilizing simple kinetic models to the development of more complex models, network coal devolatilization models, for example the Functional Group – Depolymerization, Vaporization and Crosslinking model (FG-DVC model) [Solomon *et al.*, 1990; Solomon *et al.*, 1993; Smith *et al.*, 1994], the Chemical Percolation Devolatilization model (CPD model) [Smith *et al.*, 1994], and the FLASHCHAIN model [Smith *et al.*, 1994]. These models all rely on coal structural parameters as input data. Relative to coal pyrolysis studies, oil shale pyrolysis has not been studied as systematically, especially with respect to the development of predictive models applicable to a wide variety of oil shales under a variety of pyrolysis conditions. Therefore, also the study of cross-linking in the pyrolysis process is a somewhat specialized topic in the oil shale pyrolysis field. However, based on the success achieved in coal studies one can assume that the same methodology should be useful to treating oil shale kerogen pyrolysis process.

In this study the volumetric solvent swelling procedure was used to investigate kukersite oil shale taking into account the specification of this shale (macromolecular cross-link network, insolubility, inhomogeneity, complexity and diversity of kerogen). To compare two types of oil shale of Baltic Basin solvent swelling of Dictyonema oil shale was also performed. The present thesis addresses to two specific aspects in the solvent swelling area of oil shale kerogens:

1) The first aspect is concerned with the changes in kerogen swelling capacities during low temperature heat treatment (below 400 ^{o}C) and the aim is to see whether the significant difference in kukersite and Dictyonema oil yields is relative to the nature of cross-linking processes. The examination is performed in a light of a qualitative approach: the lower the swelling capacity, the higher the degree of cross-linking and the other way around. The scope of study has also been extended to evaluate corresponding changes in solubility parameter values.
2) The second aspect is concerned with the use of simple classic solvent swelling models (the Regular Solution Theory based swelling models) and is aimed at recommending values of number average molecular weight between cross-links (or cross-link densities) for two Estonian oil shale kerogens. The number average molecular weight between cross-links is an input parameter for the Functional Group – Depolymerization, Vaporization and Crosslinking model, i.e., for the advanced pyrolysis model.

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Tallinn, February 2010

Natalja Savest

1. LITERATURE REVIEW

1.1 Summary of fossil fuel solvent swelling

The solvent swelling is a simple low-cost method to characterize the macromolecular organic structure of solid fossil fuels such as oil shale, coal. It is a technique that takes advantage of the fact that in contact with a solvent a cross-linked macromolecular system will absorb the solvent and swell. The volumetric swelling is characterized by the swelling ratio, Q, defined as a final swollen volume divided by the initial unswollen volume. In heterogeneous macromolecular networks, such as oil shale kerogens, swelling is considered a complex phenomenon. Different processes can occur simultaneously: adsorption, pore filling, breakage of non-covalent bonds, dissolution (and possible removal) of extractables, and formation of different type of gels.

A considerable number of papers dealing with oil shale kerogen-solvent interactions are available in literature. Table 1 lists the published oil shale swelling studies.

Table 1. Published oil shale solvent swelling data

Oil shale	**Sample Used**	**Number of solvents used**	**Swelling technique**	**Reference**
Kukersite (Type I/II)		Mixture of watery trichloro-methanol		Zalessky M., 1917
Colorado shale (Type I)	Acid demineralized	6	Gravimetric solvent swelling	Shadle *et al.*, 1989
New Albany shale (Type II)	Acid demineralized	6	Gravimetric solvent swelling	Shadle *et al.*, 1989
Draupne shale (Type II)	Acid demineralized	11	Volumetric solvent swelling	Ertas *et al.*, 2006
Göynük shale (Type I)	Raw shale	10	Volumetric solvent swelling	Ballice, 2003
Beypazari shale (Type II)	Raw shale	10	Volumetric solvent swelling	Ballice, 2003
Paris Basin Toarcian (Type II)	Acid demineralized	20	Volumetric solvent swelling	Larsen *et al*, 2002
Uinta basin (Type I)	Acid demineralized	10	Volumetric solvent swelling	Larsen and Li, 1997a
Green River (Type I)	Acid demineralized and $(NH_4)_2SO_4$	28	Volumetric solvent swelling	Larsen and Li, 1994

	demineralized			
Rundle (Type I)	Acid demineralized	23	Volumetric solvent swelling	Larsen and Li, 1997b
Rundle Ramsay crossing (Type I)	Raw shale	9	Volumetric solvent swelling	Siskin *et al*, 1989
Type II kerogens	Acid demineralized	11	Volumetric solvent swelling, mean values of 8 samples	Kelement *et al*., 2006
Type III kerogens	Raw coaly shales	11	Volumetric solvent swelling, mean values of 5 samples.	Kelement *et al*., 2006

From Table 1 it is seen that different types of oil shale kerogen (classified as Type I, II, III) were investigated by using solvent swelling. This classification of kerogens is usually based on Van Krevelen diagram [Vandebroucke, 2003; Vandebroucke *et al*., 2007], where kerogens tend to form groups when the ratios of hydrogen to carbon and oxygen to carbon are compared (see Table 2a and 2b). It can be seen that the kerogens are grouped as Type I, II, III or IV with further sub-grouping according to sulfur content. The types I and II can be described as oil-prone, the type III as gas-prone and the Type IV corresponds to something called as "inert carbon" (due to oxidation or advanced maturity). Estonian oil shale kukersite kerogen can be classified as Type I kerogen (some data/classifications suggest II/I kerogen [Derenne *et al.,* 1989]) and Dictyonema kerogen as Type II kerogen according to Van Krevelen diagram [Vandebroucke *et al.,* 2007].

Table 2a. Kerogen classification according Van Krevelen diagram [Vandebroucke *et al*., 2007]

Type of kerogen	H/C	O/C	Tendency
I	> 0.25	< 0.15	To produce oil
II	< 1.25	0.03-0.18	To produce a mix of gas and oil
II – Sulfur	Similar to type II but high in sulfur		
III	< 1	0.03-0.3	Tend to produce gas. Material is thick, resembling wood or coal.

Table 2b. Kerogen classification according Van Krevelen diagram [Walters, 2006]

Type of kerogen	H/C	O/C	S/C
I	> 1.4	< 0.1	< 0.02
IS	> 1.4	< 0.1	> 0.04
II	1.2 – 1.4	~ 0.1	0.02 – 0.04

IIS	1.2 – 1.4	~ 0.1	> 0.04
III	0.7 -1.0	> 0.1	< 0.02
IIIC	1.0-1.2	> 0.1	< 0.02
IV	< 0.5	< 0.15	< 0.02

The literature review of oil shale swelling studies was performed before applying solvent swelling method to Estonian oil shale. The following is a literature based examination of specific aspects of oil shale swelling studies. The examples of coal swelling studies have been shown for comparison.

1.1.1. Examination of experimental swelling procedures

In order to perform swelling experiments more precisely one should take into account the composition of the oil shale. Oil shale is commonly defined as organic rich shale. For a very rich oil shale the organic content is about 70% and for very lean oil shale its content is about 5%. The oil shale consists of organic and inorganic (or mineral) matter. The organic matter of oil shale is composed mostly of kerogen with small percentage of bitumen. Kerogen is a three-dimensional cross-linked heterogeneos macromolecular substance insoluble in organic solvents. The soluble portion of the organic matter is known as bitumen. The bitumen content in oil shales may vary from 1 to 20% in oil shale organic matter basis [Lee, 1991]. The inorganic matrix of oil shales is mainly composed by minerals such as quartz, feldspars, clays, carbonates and pyrite. The oil shales, both by their organic and inorganic matter, have greatly various compositions and properties, depending on the location of the deposits and the type of formation. Geologically, oil shale can be categorized into three different kinds: carbonate-rich shale, siliceous shale, and coaly shale. Carbonate-rich oil shales are the higher-grade shales that contain substantial amounts of carbonate minerals (calcite and dolomite may be dominant mineral constituents). Siliceous shales do not contain substantial amounts of carbonate minerals and may have detrial minerals (quartz, feldspar or clay) as their main inorganic constituent. Coaly shale generally contains so much impurity that it is excluded from commercial categories of coal [Lee, 1991].

Estonian oil shale kukersite, for example, is mainly a carbonaceous shale which is distinguished by the following composition: inorganic matter is 67% (41% of carbonate and 26% of sandy-clay part), organic matter (kerogen) is 30% and bitumen is 1-3% [Koel, 1999]. The predominant mineral phase in this shale is limestone. The extraction yield of organic matter from the kerogen by H-bonding solvents reaches 1.1% and only 1.57% by using non-H-bonding solvents [Oja, 2005].

Dictyonema shale is a low-grade oil shale with a content of organic matter of about 20% which is rich in nitrogen, sulphur and oxygen. The inorganic part of this shale is primarily clay (76%) with a small part of carbonate (3%) [Maremäe *et al.*, 2003; Koel *et al.*, 2001; Kohh *et al.*, 1982 (in Russian)].

Before applying solvent swelling methods to kukersite the examination of swelling experiments was performed (Table 4a and 4b). Table 4a focuses on some experimental related aspects such as reversibility, accuracy and technical problems. Table 4b presents observations on the behavior of kerogen, bitumens and mineral matter in the swelling process.

Table 4a. Examination of published oil shale swelling studies: experiment - related aspects. The facts from coal/polymer swelling studies are shown for comparison

	Parameter	**Literature data on oil shale**	**Literature data on coal / polymers**
1.	*Swelling reversibility*	**1)** Three consequent swelling experiments of Göynük (Kerogen Type-I) and Beypazari oil shale (Kerogen Type-II) showed reversible behavior and the height of dry bed for oil shale samples did not change due to re-swelling [Ballice, 2003]. **2)** Control experiments of Type I kerogens from the Uinta basin have demonstrated that the solvent swelling measurements are reversible [Larsen and Li, 1997]. **3)** The swelling experiments of Paris Basin Toarcian acid demineralized kerogen (Type II) have shown irreversibility. A trend of decreasing swelling from the first to the third measurements was observed [Larsen *et al*., 2002]. **4**) Acid demineralized Kimmeridge kerogen (Type II) showed reversibility: the consequent swelling ratios were the same or the second swelling was slightly larger [Larsen and Flores, 2008]. 5) Acid demineralized Green River kerogen (Type I) exhibited irreversibility [Larsen and Flores, 2008].	**1)** Soma lignite (Turkey) samples after swelling measurements swelled reversibly, and the height of dry bed of coal samples did not change due to re-swelling [Ballice, 2004]. **2)** The char swellings are reversible within the error limit of +/- 0.1 determined by duplicate swelling measurements [Ballice, Larsen, 2003]. **3)** The solvent swelling of coal investigated by Ke-Chang Xie *et al*. was shown to be irreversible and coal structure was explicitly rearranged to form a lower energy conformation in comparison with raw coal. The latter was concluded according the activation energy data of the functional groups [Xie *et al*., 2000].
2.	*Swelling ratio Q dependence of temperature*	**1)** The ultimate swelling level of kerogen in most solvents used does not appear to be very sensitive to temperature. The experiments found no statistical difference in the Q values for Type II and III kerogens at 30 and 90^{0}C, and the mean Q at 150^{0}C is only slightly greater than that at lower temperature (3.0 and 2.1 %, respectively). The weak temperature dependence of the swelling data indicates that kerogen –solvent systems have nearly equilibrated after 24h at 30^{0}C [Kelemen *et al*., 2006].	**1)** The equilibrium extents of low rank coals swelling are independent of temperature within the temperature range studied (25-70^{0}C) [Otake and Suuberg, 1997]. **2)** The ultimate extent of coal swelling was not a strong function of temperature, which implies that the swelling process was essentially thermo-neutral in character. There was no significant effect of temperature on the extent of swelling, at least in the range from 10 to 60^{0}C [Otake and Suuberg, 1997].

3.	*Others influences on swelling*		**1)** The extent and method of drying of a coal can have major impacts on the equilibrium solvent swellability of the coal and its rate of swelling [Suuberg *et al*., 1993].
4.	*Reproducibility / accuracy*	**1)** The results of Green River kerogen swelling have demonstrated the reproducibility of the technique. The scatter was usually about 2-3% of the reported value [Larsen and Li, 1994]. **2)** The mean of volumetric swelling ratio of Draupne Type II kerogen and the standard error for each solvent was in the range of 0.056-0.062 (ANOVA ± 95%) [Ertas *et al*., 2006].	**1)** It is shown in the coal study by Otake *et al*. that the particle size effect on swelling behavior of coals due to artifacts associated with particle packing was observed to lead to irreproducible results of swelling when samples of a broad particle-size range were examined [Otake and Suuberg, 1997].
5.	*Specific experimental problems*	**1)** In the study of Göynük (Kerogen Type-I) and Beypazari oil shales (Kerogen Type-II) it was often necessary during the course of the swelling measurements to change the solvents, as it became visibly extract-laden. It was done by removing extract-laden solvent and replacing with fresh one [Ballice, 2003].	**1)** Sometimes the amount of extractable material of Soma lignite was significant and in such cases it was necessary to add fresh solvent to the tubes by removing the contaminated solvent after centrifugation with a syringe, and then adding the fresh one. Measurements were repeated until equilibrium [Ballice, 2004].
6.	*Specific technical problems*	In some experimental procedure samples were centrifuged at 1000 rpm for 20 min [Kelemen *et al*., 2006], 3000 rpm for 5 min [Ballice, 2004; Önal and Ceylan, 1997; Önal andAkol, 2003].	**1)** Although the constant height of Turkish lignite (h_2) was reached within 8h for most of the samples, the mixing and centrifugation was repeated for 48h to allow a sufficient time to reach the equilibrium since swelling proceed gradually [Önal and Ceylan, 1997]. **2)** Some shrinking instead swelling has been observed in swelling of petroleum asphaltenes, the phenomenon was explained by non-uniformity of the sample particle size [Carbognani and Rogel, 2002].

Table 4b. The examination of published oil shale swelling studies: behavior of kerogen, bitumen and mineral matter in swelling process. The facts from coal/polymer swelling studies are shown for comparison

	Parameter	Literature data on oil shale	Literature data on coal / polymers
1.	*Kerogens behavior*	**1)** In the case of Green River kerogen, it was suggested that in the swelling process the kerogen is plasticized and may become rubbery. It is then no longer “frozen” in its unstable structure and can rearrange to a more stable structure. The occurrence of a rearrangement is demonstrated by a decrease in solvent swelling [Larsen and Flores, 2008]. **2)** Paris basin Toarcian kerogen (Type II) swelling indicates that the keorgen may not be in the most stable thermodynamic state what is indicated by swelling decrease on the 2nd and 3rd repetitions. Being swollen and free to adopt its most stable conformation, kerogen may rearrange to a more highly associated structure that leads to less swelling in repetitions [Larsen *et al*., 1997]. **3)** In the case of Kimmeridge kerogen, there was no evidence about a kerogen structural rearrangement to a structure with lower free energy during swelling [Larsen and Flores, 2008].	**1)** Kerogen of coals may rearrange to more stable state when made rubbery through solvent swelling [Larsen et al., 1997]. **2)** It is shown that coals as mined are strained – coal is a glassy solid and the macromolecular chain segments have very limited freedom of motion [Larsen *et al*., 1997].**3)** Orthogonal microscopic image analysis experiments showed that in two kinds of coals (Witbank, Canada; bituminous coal, USA) the coal particles had tendency to maintain their initial shape during swelling [Gao *et al*., 1998].**4)** The presence of compatible swelling agent such as pyridine is resulted in an expansion of the coal network leading to significant solvent swelling [Peppas, 1997]. **5)** It is shown in the study of Fushun coal that during the solvent swelling process, the coal network is expanded and forms a more stable free energy conformation. The greater the swelling ratio, Q, of the coal was, the more relaxed the coal structure was fixed [Xie *et al*., 2000]. **6)** The cleavage of cross-links allows the coal macromolecule structure to rearrange and the solvent swelling process becomes controlled by the coal molecular structural relaxation rather than controlled by solvent diffusion [Nomura and Thomas, 1998].
2.	*Bitumen influence on kerogen swelling*	**1)** Although the amount of solvent extractables from oil shale kerogens is low, still the solvent swelling measurements are often carried out on previously extracted materials [Larsen, Flores, 2008]. **2)** The data on	**1)** The extraction of soluble materials from the coal during swelling could result in a decrease in the thermodynamic activity of the swelling solvent that therefore in less swelling than would be observed with the pure liquid [John W.

		Kimmeridge shales swelling demonstrate that the organic material involving from the kerogen during the swelling experiments lower solvent activity, thus reducing swelling [Larsen and Flores, 2008].	Larsen, Carsol Islas Flores, 2008]. **2)** The activity decrease reduces the driving force for swelling and therefore reduces the welling ratio [Larsen and Flores, 2008].
3.	*Inorganic matter caused effects on kerogen swelling*	**1)** The inorganic content of Green River oil shale seems not having a large effect on solvent swelling of kerogen. Extensive studies with partially demineralized Green River oil shale demonstrated that inorganic content had no effect on the solvent swelling ratios. The high rock content Green River kerogen had essentially the same swelling behavior as the fully demineralized kerogen providing the justification for using the high mineral content demineralized kerogen samples [Larsen and Li, 1997]. **2)** The swelling of Paris Basin Toarcian kerogens (Type I and II) with high mineral content (up to 40% kerogen based) was the same as the swelling of the demineralized kerogen [Larsen *et al.*, 2002].	Swelling can be performed on deminerilized sample or on the sample mineral matter free. **1)** Solvent swelling studies of lignite and of a subbituminous coal revealed no changes whether they were demineralized or not [Larsen, 1989]. **2)** To presume the mineral matter to be unswellable its contribution to the dry and swollen volumes should be subtracted. As it has been seldom done in practice [Suuberg *et al.*, 1994], the correction was used to take into account the unswellable mineral content of the sample. The correction was calculated as $Q_{dmmf} = (Q_{measured} - y)/ (1-y)$, where $y = [(\rho_{dry\ coal}/\rho_{minerals})]$ [mass fraction minerals in coal].
4.	*The influence of sample pretreatment on swelling*	*Pretreatment by acids* Acid demineralization reveals no obvious changes after HCl and HF treatment. For example, the swelling results of Green River kerogen demineralized in HF/HCl provide no evidence for strong acid-induced cross-links [Larsen and Li, 1997]. *Pretreatment by solvents* **1)** After swelling of Kimmeridge shale in tetrahydrofuran (THF), extracted organics were isolated from the THF and the recovered kerogens were swollen a second time in fresh THF. The second solvent swelling ratios were	*Pretreatment by acids* **1)** The results have indicated that Turkish lignites swelling generally increased after the samples pretreatment with HCl (1N) or solution of sodium ethanolate in ethanol (EtONa in EtOH, 20% by weight) [Önal, Ceylan, 1997].**2)** The Turkish lignites (Beypazari LGN-1), Gölbasi (LGN-2) and Kangal (LGN-3) have been pretreated with the solutions of 0.1N HCl, 10% HCl, HCl-HF or with air oxidation at 2000C. The pretreatment increased the swelling values of the lignites by all solvents used [Önal and Akol, 2003].**3)** The acid treatment has no effect on swelling of Ermenek lignite

		slightly larger than the first one [Suuberg *et al*., 1993]. **2)** Swelling of Green River Kerogen in three solvents before and after the chlorobenzene treatment was studied. Exposure to the chlorobenzene has significantly reduced the solvent swelling. This may be due to a conformational rearrangement analogous to that observed with coals [Larsen and Li, 1994]. **3)** In the study of Paris Basin Toarcian kerogen it has been shown that the most effective extraction solvents are the best swelling solvents [Larsen *et al*., 2002].	except for the samples swollen with pyridine and ETDA [Kiraz et al., 2004]. **4)** The removal of some of the mineral matter by acid treatment may have resulted in a relaxation in the organic structure of lignite, which might have played a role in the increase in the swelling ratio of the coal [Azik and Yürüm, 1994]. *Pretreatment by solvents* **1)** Amount of Taiheiyo and Witbank coals particles, which swell via anomalous diffusion mechanism, increased by O-Acetylation pretreatment [Murata *et al*., 2008].

Tables 4a and 4b examine the published studies of oil shale volumetric swelling with an emphasis on the so called "glass tube" method as the procedure was adapted for this study. In short, the general procedure is as follows: a finely powdered substance is placed in a constant diameter cylindrical glass tube and then centrifuged at a selected constant speed for a selected time period to obtain reproducible compaction of the sample; the dry sample height is measured; the sample is then exposed to the desired solvent; the swollen sample height is measured again after centrifugation for a selected speed and time period; thereafter the swelling ratio, Q, is calculated as the final swollen height divided by the initial unswollen height. The volumetric swelling method using a glass tube was proposed by Green and co-workers [Green *et al.,* 1984] for coal samples and since then has been widely applied. Although this method is a simple and widely used general procedure, still, in the case of fossil fuel studies the specific experimental procedure can be quite variable, depending on the behavior of the sample studied, and also on the preference of authors or the aim of research. Table 4a demonstrates that when specific technical / experimental problems are taken into account, then reliable / reproducible results can be obtained.

Table 4b shows that the behavior of different Types (I, II, III) of kerogens may vary in the swelling process [Larsen and Li, 1994; Larsen and Li, 1997a; Ertas *et al.,* 2006]. There are some evidences that when being in contact with organic solvents kerogen may rearrange to a more stable structure that is demonstrated by a decrease in solvent swelling. This trend was observed in the cases of Green River kerogen (Type I) and Paris Basin kerogen (Type II), but not in Kimmeridge kerogen (Type II) [Larsen and Flores, 2008].

Table 4b also reveals that for oil shale cross-linked organic matter swelling it is necessary to evaluate the influence of other constituents (bitumen and inorganic matter) of oil shale to kerogen swelling. Several studies have demonstrated that the bitumen (more precisely the extractable compounds of bitumen under experimental conditions) lowers solvent activity, thus reducing the swelling [Larsen and Flores, 2008]. The presence of bitumen in a sample may cause also experimental problems (see Table 4a, row 6). Therefore, the removal of the bitumen by extraction is often considered important to oil shale sample preparation for swelling experiments.

The inorganic matrix of oil shales is mainly composed of minerals such as quartz, feldspars, clays, carbonates and pyrite. With regard to mineral matter swellability in organic solvents, only clay minerals have been shown to swell / shrink. For example, mixed layer clays with 70% clay content, mostly illite and smectite, [Graber and Mingelgrin, 1994] have shown to swell / shrink in solvents with solubility parameter values between 15 to 25 $MPa^{1/2}$ (for example, the swelling ratios measured were 0.99 in hexane, 1.11 in acetone, 1.13 in acetonitrile or 1.19 in N,N-dimethylformamide). In connection with mineral-kerogen interaction, the clay-organic matter associations have been identified as the most dominant [Siskin *et al*., 1989] and most investigated [Michel *et al*., 2007]. However, there are also some indications on the possibility of carbonate-kerogen and silicate-kerogen associations [Jeong and Kobylinski, 1983].

Therefore, in principle, the swelling study of oil shale kerogens requires first its isolation from solvent solubles (bitumen) and minerals. Although different procedures are available, there are no standard protocols, neither for the extraction of solvent solubles no for the demineralization by physical or chemical methods. In the view of the complexity of kerogen preparation from oil shale and limited knowledge on accompaning side effects, that could alter isolated kerogen swelling behavior from non-treated kerogen (see Table 4a, row 4), the rationale approach could be a compromise. For example, (1) In the case of kukersite and Dictyonema oil shales it may not be so critical to utilize the extraction process to isolate bitumen as the organic matter of these oil shales contains a very small amount of solvent extractables at room temperature. For example, the extraction yield from kukersite using organic solvent tetrahydrofuran is 0.40 wt% and only 0.01 wt% by using hexane. The extraction yield from Dictyonema is estimated to 0.50 wt% using methanol and 0.01 wt% by using hexane [Koel *et al.*, 2001]. (2) Acid based demineralization of carboneus oil shales with a low clay content could be avoidable as the mineral matter can be assumed un-swellable. It is known that slight changes in kerogen structure during acid based demineralization process can not be outruled as acids may react with organic functional groups of kerogen. Instead, the swelling capacity of kerogen or the swelling ratio on dry mineral matter free basis can be obtained as $Q_{dmmf} = (Q_{measured} - y)/ (1\text{-}y)$, where $y = [(\rho_{kerogen}/\rho_{minerals})]$ [Suuberg *et al.,* 1994].

In summary, the review of swelling investigations presented in Table 4a and 4b and the study described above shows that the specific swelling procedure may vary when being applied to fossil fuels (coal, oil shales) and that the swelling procedure can be to some extent less or more modified when applied to the definite sample of a fossil fuel.

1.1.2. Examination of literature - based oil shale swelling results

The discussion above has indicated that the volumetric solvent swelling is a simple and quite reliable experimental procedure. In the present chapter the outcome of the review of published oil shale swelling studies is presented (see Table 5). Coal and polymer swelling studies are shown for comparison.

Table 5. The examination of interpretations of oil shale swelling data. Coal and also polymer swelling studies are shown for comparison

	Parameter	Literature data on oil shale	Literature data on coal / polymers
1.	*Suggestions for application of Regular Solution Theory approaches*	**1)** Experimental results from solvent swelling measure-ments of Göynük (Kerogen Type I) and Beypazari (Kerogen Type II) oil shales show that there are some deviations from the Regular Solution Theory. Polar solvents behave similar to non-polar solvents and hydrogen-bonding solvents except ethyl alcohol show enhanced swelling [Ballice, 2003]. **2)** The volumetric solvent swelling of Green River acid demineralized kerogen (Type I) roughly follows the predictions of the Regular Solution Theory for almost all of the solvents including good hydrogen bond acceptors [Larsen and Li, 1994]. **3)** The less polar low O/C Type I Green River acid demineralized kerogen follows the Regular Solution Theory and there appear to be no specific intermolecular interactions serving as non-covalent cross-links. There were a few troubling deviations from regular solution behavior [Larsen and Li, 1994]. **4)** The more polar O/C Type I Rundle acid demineralized kerogen showed deviation from regular solution behavior, however it was brought out that, depending on the goal and need, regular solution approaches based predictions could suffice [Larsen and Li, 1997a]. **5)** A good match between the Regular Solution Theory and experiment is obtained for Draupne Type II kerogen. The results imply that this kerogen behaves like a cross-linked elastomer network and that the interaction with the solvents	**1)** The volumetric solvents swelling of Soma lignite samples in non-polar solvents roughly follow the the Regular Solution Theory [Ballice, 2004b]. **2)** Swelling of Illinios No. 6 coal in non-polar solvents follows the Regular Solution Theory. Polar solvents fall well off the curve [Larsen, 1985]. **3)** The complex structure of coal gives rise to solvent swelling behavior which often deviates from the theories that describe the swelling of conventional polymers in solvents. That is why it is important to understand the factors which affect the solvent swelling characteristics [Ndaji and Thomas, 1995].

		used involves nonspecific interactions [Ertas *et al.*, 2006]. **6)** Acid demineralized Uinta Basin Type I kerogen swelling behavior was found to be close enough to the prediction of the Regular Solution Theory [Larsen and Li, 1997b]. **7)** Acid demineralized Type II kerogens from the Paris Basin: ther was no evidence for any specific interactions between kerogens and solvents; it was suggested that the Regular Solution Theory was followed [Larsen *et al.*, 2002]	
2.	*Swelling characterized by means of* $Q_V \sim f(\delta)$	Swelling of oil shales has been characterized by solubility parameter: but in most cases scatter plot was observed and the bell shaped curve was drawing by eyes [Larsen and Li, 1994; Ballice, 2003; Kelemen *et al.*, 2006].	In the case of coals solubility parameter was determined either drawing the curve by eye or using Gee methods approach [Gee, 1943; 29. Yagi *et al.*, 1992]. It is a graphical determination of solubility parameter, based on the assumption that the solubility parameter of a macromolecule matches the solubility parameter of solvents of maximum swelling. The formula of Gee is given as: $Q/Q_{max} = \exp[-a\ Q\ (\delta_s - \delta)^2]$, where Q and Q_{max} are the swelling ratio and the maximum swelling ratio respectively, δ_s and δ are the solubility parameters of solvent and macromolecule respectively.
3.	*Swelling characterized by scale Q ~ f(EDN), f(EAN-EDN) or f(EAN/EDN*)	There were not found the data on the use of these scales for characterization of oil shale swelling behavior.	*Scale Q ~ f(EDN), f(EAN-EDN) or f(EAN/EDN*) is considered the better approach for description the swelling behavior. For example, **1)** It has been concluded that the degree of coal swelling is strongly correlated with the electron donor stength of the swelling solvent. With increasing solvent donor number swelling ratios increase [Önal and Ceylan, 1997]. **2)** Solvent donor number (DN) seems to be the determining factor in swelling. Larger DN is, there is sharper increase of

			Q in hvB coal swelling [Szeliga and Marzec, 1983]. **3)** Swelling of Ermenek lignite (Turkey) in the solvents that have donor numbers between the range of 15-30 occurs more rapidly than that in the solvents of DN between 0-15 [A. Kiraz et al., 2004].
4.	*Swelling models to predict number average molecular weight between crosslinks, M_C*	The swelling models such as Flory-Rehner model and its extension, Kovac model, [Lucht, Peppas, 1981; Larsen and Li, 1994] has been used to characterize the macromolecule structure of oil shale by estimating number average molecular weights between cross-links, M_C. The results of M_c were found as following: **1)** Green River oil shale kerogen (Type I) (1): M_c (Fl.-R.) 207 and 242, M_c by Kovac was 808 and 879 (N=1), respectively. **2)** Göynük (Kerogen Type-I) and Beypazari oil shale (Kerogen Type-II): M_c (Fl.-R) 274 (GOS) and 208 (BOS), M_c by Kovac 790 (BOS/GOS) (N=1.93). **3)** Type I kerogen from Uinta basin: M_c (Fl.-R.) 300-2000 (depending on kerogen maturation).	**1)** The swelling models such as Flory-Rehner model and its extension, Kovac model, or modified model by Peppas-Lucht [Lucht, Peppas, 1981; Larsen and Li, 1994] have been used to characterize the macromolecule structure of coal by estimating number average molecular weights between cross-links, M_C. For example, Soma lignite (Turkey): M_c (Fl.-R.) 361 and M_c by Kovac 1361 (N=1), respectively. **2)** To take account specific interactions others models have been proposed, but not used [Lucht and Pappas].
5.	*Swelling in solvent mixtures*	**1)** Swelling of Draupne kerogen (Type II) is dominated by the aromatic solvent in each mixture. The predicted Q values for the three-component solvent mixtures fall in a narrow range (1.30-1.36). It was stated that in all cases studied, there was strong preference for aromatic solvent to be retained in the swollen kerogen network [Ertas *et al*., 2006]. **2)** Good correlations are observed between the predicted and the observed swelling of Type II and III kerogens in binary mixtures of n-hexadecane/solvent mixtures. These results indicate that this theoretical framework can be used to determine the multicomponent equilibrium for kerogen and	Mixtures of a pair of solvents can be used to generate a range of solubility parameters and the interaction of coal with these mixtures [Green and Larsen, 1984]. The swelling experiments in binary mixture are characterized by selective solvent uptake [Green and Larsen, 1984]. **1)** The addition of small amount of H-bonding solvent (pyridine) to the mixture with chlorobenzene increases Illinois No. 6 coal swelling because it reduces the coal cross-linking [Green and Larsen, 1984]. **2)** Acetone-water mixtures give a swelling spectrum which displays a maximum in the region of the swelling parameter

		complex mixtures representative of those thermally generated by kerogen [Kelemen *et al*., 2006].	of the German brown coal, whereas methanol-water mixtures have swelling parameters too high to encompass that of the coal [Jones *et al*., 1997]. **3)** Illinois No. 6 coal swelling in pyridine-chlorobenzene mixture: the addition of very small amounts of pyridine leads to an enormous increase in the uptake of chlorobenzene by the coal. Bruceton coal swelling in N,N-dimethylaniline-alcohol mixture was also performed. Swelling maxima in mixtures was in certain cases higher than were the swelling ratios in the individual solvents of the mixture. However, these experiments were characterized by selective solvent uptake [Green and Larsen, 1984].

It is seen from Table 5 that there are abundant data on the swelling of oil shale and coal where the results of fossil fuel swelling have been interpreted, basing first of all on the Regular Solution Theory approaches.

The first attempt to quantify coal structure cross-link density using the Regular Solution Theory based approach, solvent swelling together with the Flory-Rehner equation, was published by Sanada and Honda in 1966. Since then, despite several fundamental difficulties, but mostly due to convenience, the Regular Solution Theory based swelling models became “a standard tool” in coal science in the eighties and nineties [Lucht and Peppas, 1981; Suuberg *et al*., 1994; Azik and Yürüm, 1994; Ndaji and Thomas, 1995; Turpin *et al*., 1996; Otake and Suuberg, 1998; Peppas, 1998]. When fossil fuel swelling capacity (swelling ratio) is to be plotted as a function of Hildebrand solubility parameter of solvents, then the Regular Solution Theory predicts a bell shaped curve with no swelling for solvents energetically quite unlike the crosslinked macromolecular substance and reaching the maximum when solubility parameters of solvent and macromolecular substance are nearly equal [Larsen and Li, 1994; Larsen and Li, 1997]. In coal solvent swelling studies, the existence of clearly defined bell shaped curves is only sometimes seen (with particular choices of solvents), and scattered behaviors are usually observed. This indicated that the use of a single parameter, such as Hildebrand solubility parameter, was clearly not sufficient to describe the swelling in these systems. Other polarity scales, for example Guttmann’s donor number (EDN), acceptor number (EAN) or their combinations, were found to be better to describe the swelling behaviors of coals (see Table 5 raw 3). Solvent EDN was shown to be the determining factor indicating that relatively strong non-covalent interactions play an important role in the coal swelling process [Önal and Ceylan, 1997; Szeliga and Marzec, 1983]. Because of this many studies of coal swelling have indicated the necessity to a further development of swelling models for coal where it should be important to understand the factors affecting the solvent swelling characteristics [Ndaji and Thomas, 1995; Otake and Suuberg, 1998; Xie *et al.,* 2000]. It has been concluded that the analysis of coal swelling is by no means a simple task as coal “kerogens“ are not “homopolymers”- instead of being built of repeating regular structural units, they are composed of highly irregular segments, both by size and chemical character. Furthermore, due to heteroatomic nature, coals are capable of forming specific kerogen-solvent interactions and of selective solvent uptake (see Table 5 for swelling experiments of coal in binary mixtures). All this makes quantitative application of the simplest, the Regular Solution Theory based, approaches questionable. Despite the complications shown above, there has been still extensive use of the Regular Solution Theory based approaches on coals [Lucht and Peppas, 1981; Ndaji and Thomas, 1995; Peppas, 1997; Önal, Ceylan, 1997; Otake and Suuberg, 1998].

Referring back to Table 5, it can be seen that swelling of Type I and Type II kerogens roughly follows the Regular Solution Theory, i.e. the randomly distributed weak interactions, which are the basis for the Regular Solution Theory, are of primary importance. The results presented in Table 5 show that the predictions of the Regular Solution Theory and the corresponding solvent swelling models (Flory-Rehner, Kovac's one) could be a useful tool for analyzing the basic behavior of solvents, even with such a complex material like oil shale. For example, Green River Kerogen, Uinta Basin Type I kerogen, Draupne Type II kerogen and Paris Basin Type II kerogen have shown to follow the Regular Solution Theory based approaches for almost all of the solvents, including strong hydrogen bond acceptors (see Table 5, row 1). The swelling of Rundle Type I kerogen and Turkish oil shale kerogens (Beypazari and Göunük oil shales) was found to occur somewhat differently: hydrogen bonding solvents have shown more enhanced swelling than it could be assumed by the Regular Solution Theory [Larsen and Li, 1997a, b; Ballice, 2003]. Such evidence was explained by Larsen and Li by the solvent ability to disrupt macromolecule hydrogen bonding. Despite some deviations from the Regular Solution Theory, which have been observed and actually not explained fully, it was concluded that predictions based on this theory could suffice depending on the aim and need (see Table 5 raw 1). So far the swelling behavior of oil shales has been only correlated with Hildebrand solubility parameter of solvents (the swelling agents used). This is a typical way of presentation of swelling results for solubility parameter estimation purposes, as the solubility parameter concept would lead to a bell-shaped distribution of the swelling ratio, with the maximum value matching the macromolecular solubility parameter. However, again scattered behaviors are usually observed. The solubility parameters found for various oil shale kerogens are presented in Table 6.

Table 6. Solubility parameters given by authors from literature for oil shales

Oil shale	**Solubility parameter [MPa$^{1/2}$] ([(cal/cm^3)$^{1/2}$])**	**Determination method**	**Reference**
Draupne kerogen (Type II)	24.3 (11.9)	Determined from swelling	Ertas *et al.*, 2006
Green river (Type I)	19.8 (9.7)	Determined from swelling	Larsen and Li, 1997b
Rundle (Type I)	20.5 (10) 20.3 (9.9)	Determined from swelling. Calculated from Siskin's structure [Siskin *et al.*, 1995] and van Krevelen method.	Larsen and Li, 1997b
Uinta basin (Type I)	19.4-20.5 (9.5-10.0)	Determined from swelling	Larsen and Li, 1997a
Green River (Type I)	19.4-20.5 (9.5-10) 19.4 (9.5)	Drawing curve by eye, from swelling. Calculated using Siskin's structure and van Krevelen	Larsen and Li, 1994

		method	
Göynük shale (Type I)	20.0-21.1 (9.8-10.3)	Drawing curve by eye, from swelling	Ballice, 2003
Beypazari shale (Type II)	20.0-21.1 (9.8-10.3)	Drawing curve by eye, from swelling	Ballice, 2003
Type II kerogens Type IIIC kerogens	22.5 (11.0) 23.3 (11.4)	Determined from experimental swelling data	Kelement *et al.*, 2006

Table 6 reveals that the solubility parameters were mostly estimated according to the plots swelling ratio as a function of Hildebrand solubility parameters of solvents and upon visual observation. It can be seen from Table 6 that the solubility parameter of most of the kerogens investigated was determined within the range of 9.5-10 $(cal/cm^3)^{1/2}$. Only the solubility parameter of Draupne kerogen was found to be 11.9 $(cal/cm^3)^{1/2}$, which is larger than the others. This value was higher than the solubility parameter values of solvents used in this work [Ertas *et al.*, 2006].

Table 5 shows that applying the Regular Solution Theory related swelling models, such as Flory-Rehner and Kovac's [Lucht and Peppas, 1981; Larsen and Li, 1994] the macromolecule structure of oil shales has been characterized by estimating the number average molecular weights, M_C, between the cross-links (see Table 5, row 5). The main advantage of these models is that the structure properties can be estimated from the swelling data using a few key parameters: the interaction parameter (from solubility parameter for example) and the macromolecule volume fraction in the swollen network (from swelling ratio). The data found on the number average molecular weight, M_C, of oil shale between cross-links show that M_C calculated from Flory-Rehner equation is lower than the values calculated using Kovac equation (see Table 5 raw 5). It can be explained by the tightly cross-linked macromolecular network of kerogen, and application of the Flory-Rehner equation is then questionable [Ballice, 2003].

The Flory treatment assumes that there are no specific interactions, such as hydrogen bonding, have occurred and the Regular Solution Theory is followed. In this case, assuming the affine elastic network with a Gaussian chain distribution Flory-Rehner equation [Lucht and Peppas, 1981] can be applied to estimate number average molecular weight between crosslinks:

$$M_c = -\frac{V_1 \nu_2^{1/3} \rho - 1/2 V_1 \nu_2 \rho}{\ln(1-\nu_2) + \nu_2 + \chi \nu_2^{2}} \quad (1),$$

where M_C is the number average molecular weight (mass) of the part between cross-links; V_1 is the solvent molar volume; υ_2 is the volumetric fraction of polymer at the swelling equilibrium (it is measured in terms of the volumetric swelling ratio Q, defined simply as the swollen sample volume divided by the unswollen sample volume). It is simple to show that $\upsilon_2=1/Q$ [Turpin *et al.*, 1996]; ρ is the polymer density. When the distance between cross-links is not large and no longer follows Gaussian distribution, this equation does not hold. Another theory developed by Kovac and Peppas [Lucht and Peppas, 1981] for coals could be used. Kovac and Peppas extended their theory removing the assumption of Gaussion distribution of chain lengths and introducing an additional parameter N, the number of rotatable segments between branch points [Ballice, 2004b]. Kovac's equation is

$$M_c = -\frac{V_1 v_2^{1/3}\rho + N^{-1} V_1 v_2^{-1/3}\rho}{\ln(1-v_2) + v_2 + \chi v_2^{2}} \quad (2)$$

Finally, the analysis of experimental swelling results presented in Table 5 shows that thermodynamic parameters used to interpret solvent swelling of coal or oil shale kerogen can, in turn, be applied to predict the swelling behavior in other solvents or mixtures of solvents. Also mixtures of a pair of solvents can be used to generate a range of solubility parameters and to study the swelling with these mixtures [Green and Larsen, 1984]. Table 5 shows that the swelling experiments of coal in binary mixture have been characterized by a selective solvent uptake [Green and Larsen, 1984; Ertas *et al.*, 2006]. In the case of oil shales, swelling in solvent mixtures has not been used extensively (see Table 5 raw 5).

1.2 Examination of oil shale low temperature pyrolysis in relation to solvent swelling - literature overview

The importance of the extent and timing of cross-linking in the pyrolytic processing has been shown in coal studies by Solomon and co-workers where it is emphasized that the cross-linking behavior influences tar yield and tar molecular weight distribution [Solomon *et al.*, 1992]. It has been concluded that the cross-linking process before the onset of major pyrolytic processes is one of the reasons for the relatively lower tar yields of lower rank coals. It has also been shown that one of the causes for low temperature cross-linking reactions is the decomposition of carboxyl groups and possibly hydroxyl groups [Solomon *et al.*, 1990b].

In Estonia there are two kinds of oil shales: kukersite and Dictyonema oil shale. One of the main differences of two oil shales is the yields of retorting products. The corresponding comparison of kukersite and Dictyonema is presented in Table 7. It is seen that the dictyonema shale, compared to kukersite, yields considerably less oil (dictyonema 19.6%, kukersite 61.3%, organic matter basis).

Table 7. Retorting yields (wt%) organic matter basis [Elenurm *et al.*, 2008]

Retortig products	**Kukersite**	**Dictyonema**
gas	16.72	16.44
oil	61.32	19.64
char	16.75	45.42
water	5.21	18.50

Kukersite is a high tar (or from industrial viewpoint, oil) yield oil shale and kukersite shows softening behavior during pyrolysis [Oja, 2005]. Although, it has a high oxygen content (above 10%) on an organic matter basis, the content of carboxyl functional groups is relatively low. Therefore, based on what is seen in coal studies [Solomon *et al*., 1990; Solomon *et al*., 1992a,b], one could expect structural relaxation rather than tightening of the structure during the low temperature (pre-pyrolytic) thermal treatment.

On the other hand, Dictyonema oil shale is a low tar yield non-softening oil shale. It contains functional groups known to be responsible for the low-temperature cross-linking. For example, the following distribution of oxygen containing functional groups has been presented in the literature on a total oxygen basis for the Dictyonema oil shale organic matter: carboxyl 2.36%, carbonyl 33.05%, hydroxyl 9.63% and ester 54.96% [Siirde, 1956]. Therefore one could expect tightening of the structure rather than structural relaxation during the low temperature (pre-pyrolytic) thermal treatment.

1.3 Estonian oil shales

Oil shale is the most important mineral resource of Estonia. Estonia oil shale deposits account for just 17% of total deposits in the European Union but the country generates 90% of its power from this source.

There are two kinds of oil shales in the Baltic Basin: the Middle Ordovician kukersite mined in the Estonia and St.Petersburg fields (Russia), and lower Ordovician Dictyonema argillite (claystone) that distribution area in Western and Northern Estonia is over 11000 km^2. Kukersite oil shale resources are about 5 billion tons, among these mineable (active) resources about 1.5 billion tons. The Dictyonema shale reaches to 64 billion tons.

1.3.1. Kukersite

Kukersite is a light-brown marine-type oil shale of the lowest Upper Ordovician formation, named after the Kukruse settlement in Estonia [Lille, 2003]. It was discovered in the North of Estonia more than 200 years ago. Oil shale is used as a fuel in electricity, but also proceeded thermally to produce oil. The organic matter of kukersite is considered to be entirely of marine origin.

The organic matter is composed mostly of kerogen with few percent of bitumen. Due to quite inert kerogen matrix oil shale kukersite gives very little extractables with different solvents at normal conditions [Koel *et al.,* 2001]. The extraction yield of organic matter from kerogen by H-bonding solvents attains 0.1%, and by non-H-bonding solvents only 0.01% [Johannes *et al.,* 2009]. Typical elemental composition range of kukersite kerogen is (%): C 76.0-77.5; H 9.4-9.9; S 9.4-9.9; N 0.2-0.5; O 9.0-11.0 ; Cl 0.5-0.9 [Koel, 1999]. The kukersite kerogen has low H/C (about 1.48) and high O/C (about 0.14) ratios and therefore is classified as

Type I / Type II kerogen according to van Krevelen diagram [Koel, 1999; Vandebroucke *et al.,* 2007]. According to the literature data the average density of the kukersite kerogen is 1.11±0.05 g/cm^3 [Rikken *et al.,* 1971].

At the very beginning of investigations of kukersite organic matter the following simplified formula of kerogen was proposed $C_{10.5}H_{15}O_{1.5}$. Later, the chemical structure of kerogen unit was presumed by Dobrjanski to be $C_{72}H_{104}O_8$ [Aarna, 1989]. Underway structural analysis of kukersite kerogen the following formula was presented $C_{100}H_{150}O_{10}S$ [Turenko, 1987]. Lille presented kukersite kerogen as a mixture of high-molecular poly-functional organic compounds with an empirical formula $C_{421}H_{638}O_{44}S_4NCl$ and molecular mass 6581 Dalton [Lille, 2003]. In the same paper the molecular model of Estonian kukersite kerogen was also given.

The inorganic matter of kukersite is a complex mineral suite, which consists mainly of carbonate. For example, the following composition of kukersite mineral matter was presented by Utsal [Utsal, 1984]: calcite 43%, clay minerals 20 %, dolomite 13%, quartz 11%, feldspars 7% and pyrite 6%. The density of inorganic part is 2.75-2.81 g/cm^3 [Rikken *et al.,* 1971].

1.3.2. Dictyonema

The marine-type Estonian Dictyonema argillite (also known as Dictyonema oil shale) of an Early Ordovician age is a brown lithified claystone belonging to the formation of black shales of sapropelic origin [Veski, 2003]. The origin of the Dictyonema shale goes about 500 million years back. The lower Ordovician Dictyonema shale occurs on area of about 11000 km^2 in the north-western parts of Estonia at a depth of 10-90 m. The reserves of the Dictyonema shale considerably surpass those of kukersite. Its supplies are enormous – more than 60 billion tons. But the quality of Dictyonema is poor.

In the study by Kohh *et al.* an empirical formula $C_{324}H_{376}O_{39}N_7S_4$ of the Dictyonema shale kerogen was offered with the following contents: C – 76.00%, H – 7.40%, O+Cl – 12.22%, S – 2.50% and N – 1.88% [Kohh *et al.*, 1982 (in Russian)]. The H/C and O/C suggest Type II kerogen according to van Krevelen diagram. According to the literature data the density of the Type II kerogens could be taken as 1.15g/cm^3 [Okiongbo, 2005; Seftle *et al.*, 1991; Stankiewicz et *al.*, 1994].

The inorganic part of this oil shale is primarily sand-clay (76%) with small part of carbonate (3%). The density of oil shale related clay mineral illite is 2.6 g/cm^3 [Smith, 1986].

1.3.3. Comparison of kukersite and Dictyonema oil shales

Kukersite and Dictyonema oil shale differ considerably in their mineral and organic composition. Kukersite is one of higher oil-yield and Dictyonema one of lower oil-yield oil shales basing on characterization by the Fischer Assay method.

Kukersite is a carbonate-rich oil shale while dictyonema is a carbonate-lean oil shale. To see the difference between these two types of Estonian oil shales the comparison of kukersite and dictyonema is presented in Tables 9, 10a, 10b and 11.

Table 9. The comparison of kukersite and Dictyonema organic matter elemental composition [Klesment, 1985]

Organic Matter, %	**Kukersite**	**Dictyonema**
C	74-78	67-75
H	9.3-9.9	7.4-7.6
N	0.3-0.4	1.9-3.6
S	1.6-1.9	2.0-2.8
O	9-11	12-19

Table 10a. Functional groups in the organic matter of kukersite and Dictyonema based on kerogen

Functional groups, %	**Kukersite**	**Dictyonema** ***
Carboxyl [-C(=O)OH]	(1.5)* / (0.16)**	0.47
Hydroxyl [-OH]	(1.3-3.7)* / (3.52)**	1.92
Carbonyl [>C=O]	(0.3-0.5)* / (1.60)**	6.56
Ester [-OC(=O)-]	(is present)* / (1.92)**	10.93

[*] It was found by Semenov [Durand, 1980].

[**] It was found by Aarna and Lippmaa [Durand, 1980].

[***] It was found by Siirde [Durand, 1980].

Table 10b. Functional groups in the organic matter of kukersite and Dictyonema based on total oxygen

Functional groups, %	**Kukersite**	**Dictyonema** ***
Carboxyl [-C(=O)OH]	(1.33)* / ()**	2.36
Hydroxyl [-OH]	(29.34)* / (42)**	9.63
Carbonyl [>C=O]	(13.33)* / (13.00)**	33.05
Ester [-OC(=O)-]	(16.00)* / (17.00)**	54.96

[*] It was found by Aarna and Lippmaa [Durand, 1980].

[**] It was found by Lille [Lille, 2003].

[***] It was found by Siirde Durand, 1980].

Table 11. The comparison of the ash composition of kukersite and Dictyonema [Klesment, 1985]

Inorganic Matter, %	**Kukersite**	**Dictyonema**
SiO_2	19-27	60-64
Al_2O_3	4-5	12-20
Fe_2O_3	1.4-6.0	2.6-7.0
K_2O	2.1-2.7	6-8
Na_2O	0.2-0.3	0.2-2.0
MgO	1.5-5.0	0.7-1.7

CaO	30-37	0.7-1.3
CO_2	27-31	0.3-0.9
P_2O_5	-	3.2-7.0
FeS_2	1.5-3.0	2.3-8.0
SO_3	0.2-0.6	0.7-1.4

2. EXPERIMENTAL PART

2.1 Oil shale samples

2.1.1. Kukersite oil shale

The main part of the experimental research of this thesis was performed with kukersite samples of 38 wt% of organic content (ash 46.5 wt%, carbonate CO_2 16.5 wt%, SO_4^{2-} in ash 3.2 wt%) (Paper II). As the content of solvent extractables in kukersite oil shales is low, below 1.5% on the organic matter basis, then the oil shale was not treated for removal of solvent solubles. The sample was ground to a particle size below 100 µm. The oil shale was characterized by an elemental composition of C 36.3 wt%, H 4.1 wt% and N 1.1 wt% determined using an elemental analyzer Exeter Analytical model CE440.

For comparison, kukersite oil shale sample of 91% organic matter was used (Paper I). This sample was isolated from the parent oil shale by a flotation technique [Koch *et al.*, 1973]. The elemental composition of the organic matter was 73.3 wt. % C, 8.wt. % H, and 1.6wt% O+ S (by difference). The samples were ground to <100 µm particle size.

All samples were pre-dried 1 hour at 100 ^{0}C in air (a standard oil shale drying procedure) before swelling experiments.

2.1.2. Dictyonema oil shale

Dictyonema oil shale with organic content of 13% from a layer about 10 m underground was used in this thesis. It was characterized as follows: ash 86%, carbonates 2% and elemental analysis results C 6.7%, H 0.9%, N 0.3%, residue 92.1% (giving H/C ratio of 1.56). The elemental composition of the organic matter was determined by an elemental analyzer Exeter Analytical model CE440.

Dictyonema oil shales are known to contain significant amounts of clay minerals, mostly illite and smectite [Loog *et al.*, 2001] that can swell/shrink in organic solvents [Graber and Mingelgrin, 1994]. Therefore, in order to eliminate the effect of clay minerals, acid treatment with hydrogen fluoride (HF) was used to treat original shale minerals into an unswellable form. Details of the pretreatment experiments are available elsewhere (Paper III).

The samples were pre-dried 1 hour at about 100 ^{0}C in air (a standard oil shale drying procedure) before swelling experiments.

2.2 Solvents

All solvents used in the swelling experiments were reagent grade solvents without further purification and are listed in Table 12a and 12b together with their key characteristics: solubility parameters (Hildebrand or total) [Karger *et al.*, 1976; Larsen and Li, 1994; Belmares *et al.*, 2004; Larsen *et al.*, 2002]; Hansen three dimensional solubility parameters (dispersion, polar and hydrogen bonding) [Hansen, 2002], Guttmann's donor and acceptor numbers [Behbehani *et al.*, 2001; Malavolta *et al.*, 2002; Marcus, 1984].

Table 12a. Solvent parameters

Solvent	**Hildebrand solubility Parameter, MPa$^{1/2}$**	**Hansen dispersion solubility parameter, MPa$^{1/2}$**	**Hansen polar solubility parameter, MPa$^{1/2}$**	**Hansen hydrogen-bonding solubility parameter, MPa$^{1/2}$**
Acetone	20.3	15.5	10.4	7.0
Acetonitrile	24.3	15.3	18.0	6.1
Aniline	21.3	19.4	5.1	10.2
Cyclohexanol	20.3	17.4	4.1	13.5
DMF	24.5	17.4	13.7	11.3
Ethanol	26.0	15.8	8.8	19.4
MEK	19.0	16.0	9.0	5.1
Methanol	29.3	15.1	12.3	22.3
NMP	23.1	18.0	12.3	7.2
n-propanol	24.5	16.0	6.8	17.4
Propylamine	18.2	16.9	4.9	8.6
Pyridine	21.9	19.0	8.8	5.9
Tetrahydrofuran	18.6	16.8	5.7	8.0
1-methylnaphthalene	20.3	20.6	0.8	4.7
Benzene	18.8	18.4	0.0	2.0
Hexane	14.7	14.9	0.0	0.0
o-xylene	18.0	17.8	1.0	3.1
Tetralin	19.4	19.6	2.0	2.9
Toluene	18.2	18.0	1.4	2.0
Nitrobenzene	20.5	20.0	8.6	4.1
Nitroethane	22.7	16.0	15.5	4.5
Nitromethane	26.0	15.8	18.8	5.1

DMF stands for dimethylformamide; NMP stands for N-methyl-2-pyrrolidinone; MEK stands for methyl ethyl ketone.

Table 12b. Solvent parameters

Solvent	Electron donor number (EDN)	Electron acceptor number (EAN)
Acetone	17.0	12.5
Acetonitrile	14.1	18.9
Aniline		
Cyclohexanol		
DMF	26.6	16.0
Ethanol	19.2	37.1
MEK		
Methanol	19.1	41.3
NMP	27.3	13.3
n-propanol	19.8	37.7
Propylamine		
Pyridine	33.1	14.2
Tetrahydrofuran	20.0	8.0
1-methylnaphthalene		
Benzene	0.1	8.2
Hexane	0.0	0.0
o-xylene		
Tetralin		
Toluene	0.1	3.3
Nitrobenzene	4.4	14.8
Nitroethane		
Nitromethane	2.7	20.5

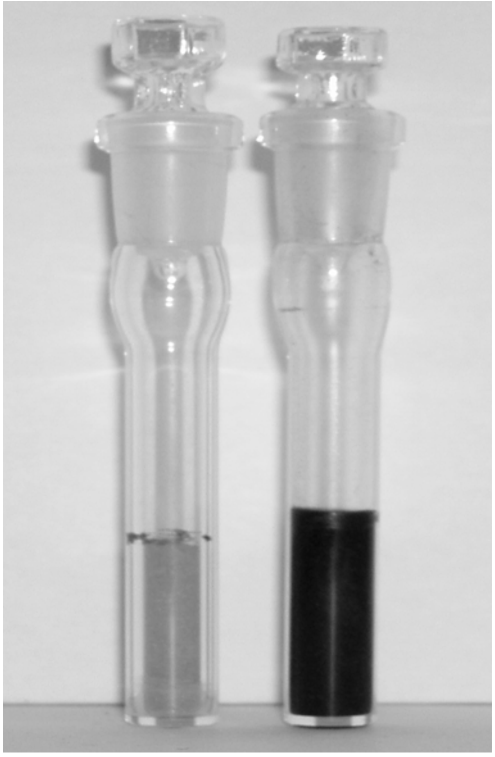
DMF stands for dimethylformamide; NMP stands for N-methyl-2-pyrrolidinone; MEK stands for methyl ethyl ketone.

2.3 Thermal pretreatment of kukersite oil shale

The experimental setup consisted of a sealable cylindrical stainless-steel tube with an inner diameter of 1 cm and with a length of 10 cm. This sealed sample holder, containing the oil shale sample in nitrogen atmosphere, was heated in a circulating air bath from room temperature at a fixed heating rate of 10 ^{o}C/min. When the sample reached a selected temperature, it was maintained there for the desired time, and then cooled to room temperature. The thermal pre-treatment temperatures were varied between 150 and 375^{o}C. The pre-heat temperature range did not exceed 375 ^{o}C, in order to avoid the significant decomposition of kerogen.

2.4 Volumetric solvent swelling

The swelling behavior of Estonian oil shale samples was studied by using the volumetric swelling technique [Green *et al.,* 1984]. All swelling experiments of oil shale were performed on 30-40 mg samples.



Picture 1. The performance of Estonian oil shale solvent swelling experiments. The left taste-tube corresponds to the beginning of the experiment when the oil shale sample is introduced into the tube. The right taste-tube corresponds to the swollen sample

A certain amount of the sample was introduced into a constant diameter glass tube, fitted with a cap to minimize solvent loss during the experiment. The glass tube had an inside diameter of 5.5 cm and length 8cm, excluding the cap. The tube was repeatedly centrifuged three times at 6000 rpm for 5 minutes until the oil shale sample bed reached a minimum height, H_1. The reason for this was that it was found that shifting the position of the tube relative to the rotor in between spinning periods gave an easier to read the initial height. The initial height, H_1, of the oil shale sample was determined after the third centrifugation using a caliper ruler.

Organic solvent in excess was added to the tube, the content of the tube was thoroughly mixed with a thin wire in order to wet the oil shale sample and get the complete mixing. Then the tube was again centrifuged three times at 6000 rpm for 5 minutes until the oil shale sample bed had reached a minimum height, H_2. The height of the sample, H_2, was measured again. The actual reported final height for each sample was then measured in 24h and 48 hours of swelling in solvent until there was no further volume change, indicating that the equilibrium had been reached. It was found that the extra time rarely resulted in additional oil shale swelling at room temperature beyond that what was observed in the first few minutes, but only the longer time results ensure that all samples were truly equilibrated.

Concerning with oil shale samples pretreated by heating at various temperatures (especially at higher temperatures) it was found that the extra time resulted in additional swelling beyond that what was observed in the first few minutes. Significant changes were fixed in 24 hours and in some cases in 48 hours.

In the case of the heat-treated samples, there was also trouble with the adding organic solvent. Air bubbles appeared in the tube after adding excess organic solvent and mixing the content with a thin wire. To remove the air from the sample the tube was placed into supersonic bath after adding organic solvent and there the content of the tube was carefully mixed for 5 min.

The solvent swelling behavior was presented by volumetric swelling ratio. The volumetric swelling ratio, Q, is defined as the final swollen volume divided by the initial unswollen volume. For the constant diameter tube, the swelling ratio can be calculated from the equilibrium height of swollen oil shale in the tube relative its initial unswollen height: $Q = H_2/H_1$, where H_1 is the initial height of unswollen sample of oil shale and H_2 is the equilibrium height of swollen oil shale. The correction to dry mineral matter free basis was performed accordingly: $Q_{dmmf} = (Q - y)/(1-y)$, where $y = [(\rho_{dry\ coal}/\rho_{minerals})]$. In order to present the results more conveniently as a function of donor number in some cases, molar solvent uptakes calculated as $(Q -1)/V_m$ or $(Q_{dmmf}-1)/V_m$ were used, where V_m stands for solvent molar volume. The molar solvent uptake is used instead of the swelling ratio in order to eliminate solvent molar volume effect on solvent absorption extent.

For the swelling in binary mixtures the binary mixtures of solvents were prepared with the desired concentration and were applied in excess so that each solvent in the applied mixture volume was present in an amount larger than the previously determined solvent uptake volume in the pure solvent swelling. This was done in an attempt to minimize any change in solvent mixture composition associated with possible selective absorption of solvent components by the kerogen. Only a simple global behavior of swelling extent was investigated as a function of initial mixture composition or the solubility parameter of initial mixture. The compositional changes caused by selective solvent uptake inside the swollen network were not studied and also the extent of association between binary solvent mixture components was not evaluated with the aid of solution thermodynamics.

The reproducibility of the swelling ratio (Q) determinations was in the range of 0.015for swelling in pure solvents and of 0.02-0.03 for swelling in solvent mixtures.

2.5 The methods for determination of oil shale solubility parameter applying swelling procedure

2.5.1. The Regular Solution Theory

The Regular Solution Theory predicts that there should be a maximum in the plot of swelling vs. solubility parameter, and that the maximum should occur at the solubility parameter of the polymer:

- if the combination of the polymer sample and solvent follows the Regular Solution Theory, there will be a maximum in the solvent uptake, and thus will be a maximum in polymer swelling when the solubility parameter of solvent matches that of the polymer;
- as the solubility parameters of the polymer and different solvent diverge, swelling will be less.

In the case of the swelling in binary mixtures, the solubility parameter concept suggests that at maximum swelling the solubility parameter of the macromolecule and, in this case of the solvent mixture, should match - in the other words, the solvent mixture and the macromolecule should have energetic similarity.

- The combination of solvents with lower and higher solubility parameters than that of the macromolecule can result in a maximum at higher swelling than in either solvent alone.
- Swelling in binary solvent mixtures, which have solubility parameters lower or higher than the macromolecular network do not show swelling maxima [Tershatov and Senichev, 2001].

2.5.2. Gee methods

Gee equation is a Gaussian error function based on the approach of the principle that the maximum swelling occurs in the solvent with solubility parameter equal to that of the cross-linked macromolecule. The formula of Gee:

$$\frac{Q}{Q_{max}} = exp[-a\,Q\left(\delta_{solvent} - \delta\right)^2\,] \quad (3)$$

where Q and Q_{max} are the swelling ratio and the maximum swelling ratio respectively, $\delta_{solvent}$ and δ are the solubility parameters of solvent and macromolecule respectively and *a* is a constant. The macromolecule solubility parameter can be determined from a rearranged equation (1) by plotting $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus $\delta_{solvent}$ [Gee 1943; Yagi *et al.*, 1992; Alli *et al.*, 2006]

2.6 Field Ionization Mass Spectrometric experiments

The raw data for the field ionization mass spectrometric experiments were generated at Rostock University and the data processing and analyses were carried out in our laboratory. In FIMS experiments about 0.5 to 1.1 mg of the air-dry sample was transferred to a quartz micro-oven and introduced into the fore-vacuum chamber of a double-focusing Finnigan MAT 900 mass spectrometer (Finnigan, MAT, and Bremen, Germany). When the pressure had dropped below 1.5×10^{-2} hPa, the quartz micro-oven with sample was inserted into the ion source and heated under high vacuum (10^{-6} hPa) from 50 to 710 °C in steps of 10°C per min. During about 30 min of total measurement time, 67 magnetic scans were recorded for the mass range 15 to 900 Dalton (single spectra).

3. RESULTS AND DISCUSSION

3.1 Swelling of oil shale Kukersite and Dictyonema at room temperature – evaluation of applicability of the Regular Solution Theory based approaches

3.1.1. Equilibrium swelling of kukersite and Dictyonema oil shales in single solvents

The experimental results of kukersite oil shale swelling in 22 solvents are presented in Figure 1 (data from Paper II). The swelling behavior of the isolated kerogen (91 wt% of organic matter) was found to behave in a similar manner of kukersite oil shale (in detail the results are presented in Paper I).

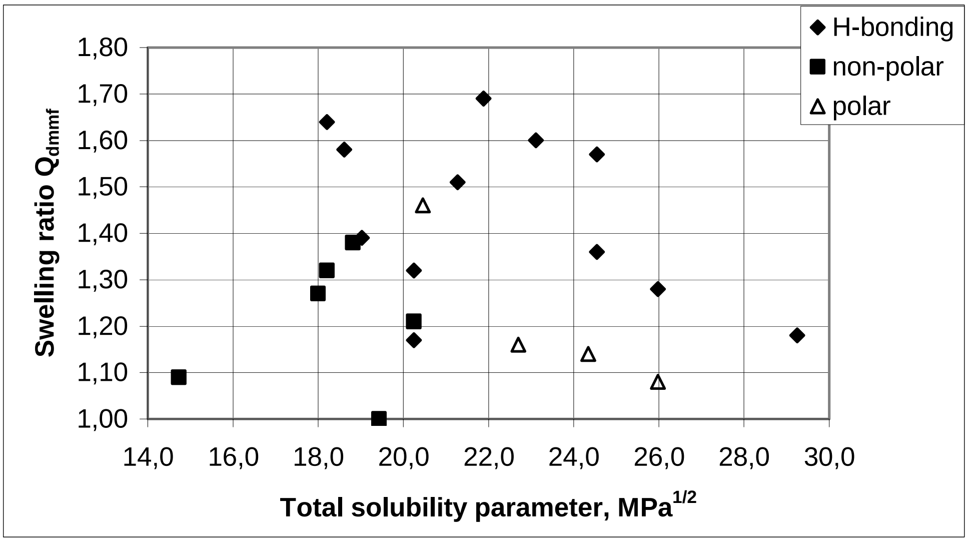


Figure 1. Equilibrium swelling ratios of kukersite oil shale measured at room temperature as a function of the solvent solubility parameter (Hildebrand solubility parameter). The results are given in dry mineral matter free basis

Figure 1 illustrates graphically the variation of swelling ratios with Hildebrand solubility parameters of solvents. This is a traditional way to presents the swelling results for solubility parameter estimation purposes. The formation of a bell shaped curve should be expected when randomly distributed weak non-specific interactions dominate in the swollen network. The plot swelling ratios of kukersite sample and the corresponding solubility parameters of the solvents in Figure 1 show scattering pattern suggesting that the chemical character caused specific interactions between solvents and kerogen play an important role in the swelling process. Kerogen contents a lot of functional groups (see Table 10a and 10b) that are capable of interacting both with other kerogen functional groups and also with solvent. From Figure 1 it is seen that kukersite kerogen swelling ratios are in the range of 1.00 -1.70 depending on the solvent used. The most enhanced swelling occurs in hydrogen-bonding solvents such as pyridine, propylamine and 1-methyl-2-pyrrolidone (NMP). These solvents are also high electron donor number (EDN) solvents (see Table 11). The maximum extent of the volumetric swelling in dry mineral matter free basis was about 1.6-1.7 in the case of these solvents. Such kind observation implies that kukersite kerogen has a tighter, more cross-linked structure than do the coals that generally exhibit swelling ratios around 2 to 2.5 in strong swelling agents. The observation of the highest swelling extents in specifically interacting solvents emphasizes the concern regarding the use of the Regular Solution Theory based approaches.

In the case of Dictyonema (see Figure 2), considerably lower swelling capacity comparing to kukersite is observed indicating the existence of even more tighter cross-linked structure of the Dictyonema shale kerogen (data from Paper III).

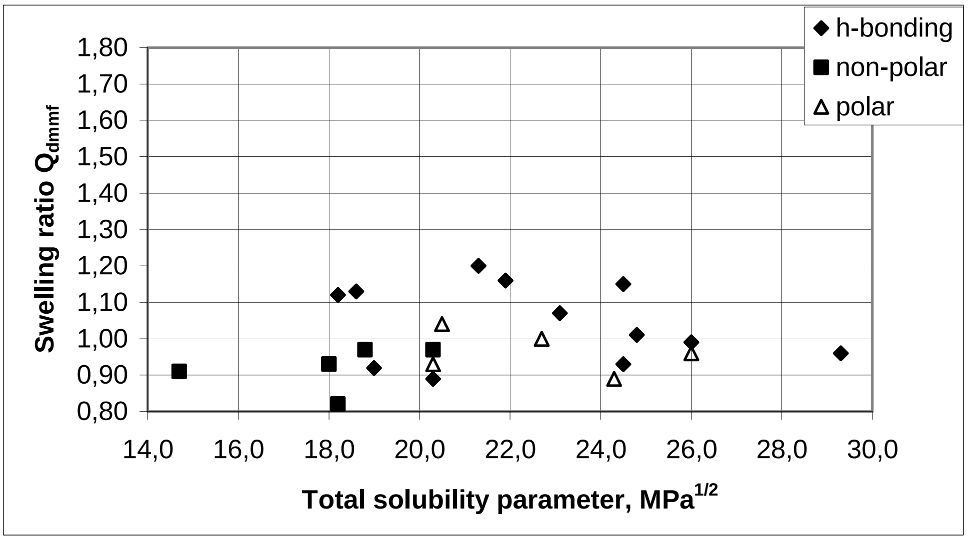


Figure 2. Equilibrium swelling ratios of dried acid treated Dictyonema oil shale measured at room temperature as a function of the solvent solubility parameter (Hildebrand solubility parameter). The results are given in dry mineral matter free basis

Figure 2 shows that the maximum swelling ratios of acid treated Dictyonema oil shale in dry mineral matter free basis were as low as 1.2. It is also seen from Figure 2 that the Dictyonema oil shale does not practically swell in non-polar solvents and considerable swelling can be observed mostly in hydrogen-bonding solvents with high EDN. Moreover, a noticeable shrinking of Dictyonema shale, instead of swelling, is observed with several non-polar and polar solvents (see Figure 4). Although the shrinking is not a common experimentally seen behavior, still, it is not the unusual phenomena in solvent swelling studies and a slight shrinking has been observed also in other occasions: for example, in the case of petroleum asphaltenes [Carbognani and Rogel, 2002], explained based on non-uniformity of the sample size, or in the swelling of clay minerals [Graber and Mingelgrin, 1994]. One plausible reason for shrinking behavior of Dictyonema oil shale could be the rearrangement of kerogen structure in the present of a swelling agent assuming that the dry state may not be thermodynamically most stable structure [Larsen and Flores, 2008].

Again, Figures 1 and 2 suggest that the highest swelling occurs in high electron donor number (EDN) solvents. Therefore in Figures 3 and 4 the data are reploted by means of solvent molar uptake, $(Q_{dmmf} - 1)/V_m$, as a function of electron donor number, EDN. Such kind presentation of the results was offered by Suuberg *et al.* [Suuberg *et al.*, 1994] to describe coal-solvents interactions. The solvent molar uptake was used instead of swelling ratio to eliminate solvent molar volume effect on solvent absorption extent. These Figures 3 and 4 reveal that there exist better correlations with swelling capacity than in the case of the solubility parameters (see Figures 1 and 2). Figures 3 and 4 also indicate that the molar solvent uptake increases with solvent EDN up to some limiting value - the limiting molar solvent uptake is reached at about solvent EDN value of 25. These Figures (3 and 4) demonstrate that the high EDN solvents are effective in breaking kerogen-kerogen non-covalent bond interactions resulting in maximum swellability in such solvents.

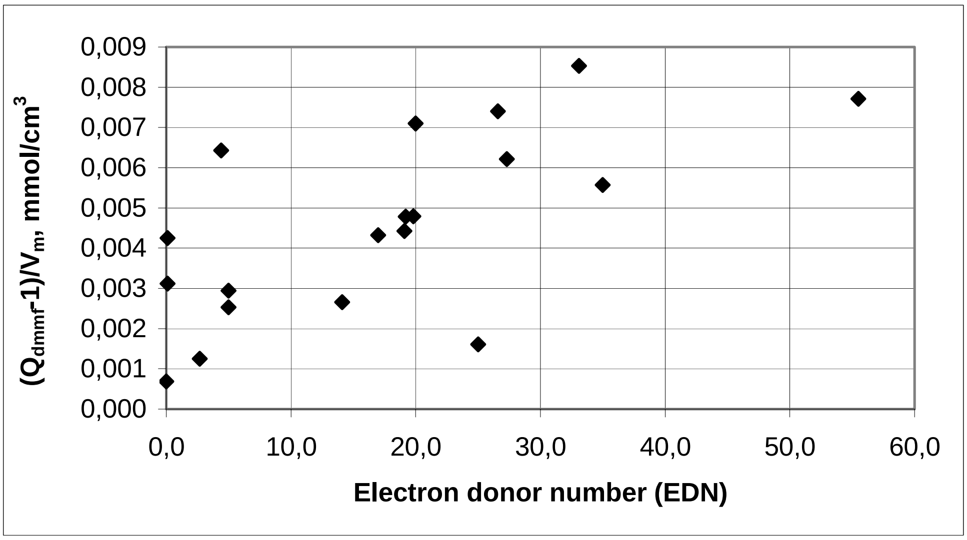


Figure 3. The degree of kukersite swelling represented as a molar solvent uptake, $(Q_{dmmf}-1)/V_m$, versus solvent EDN

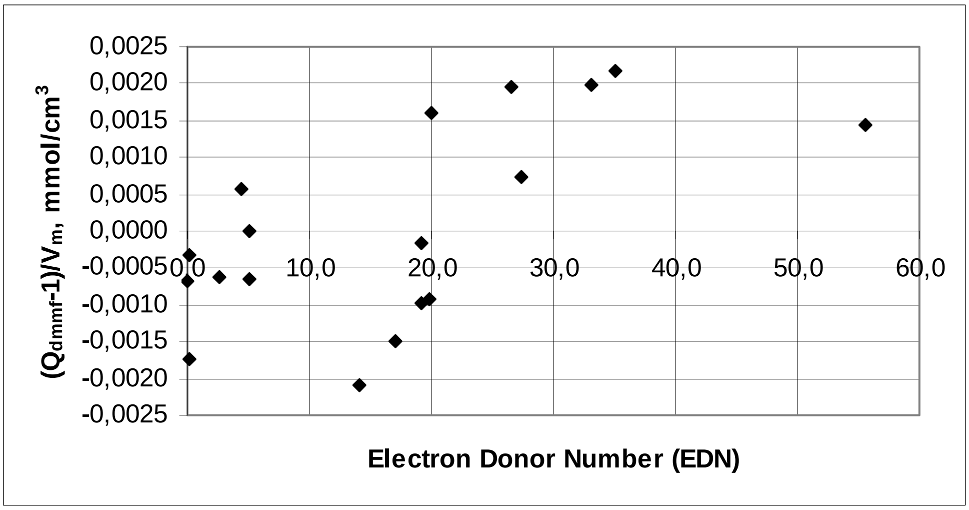
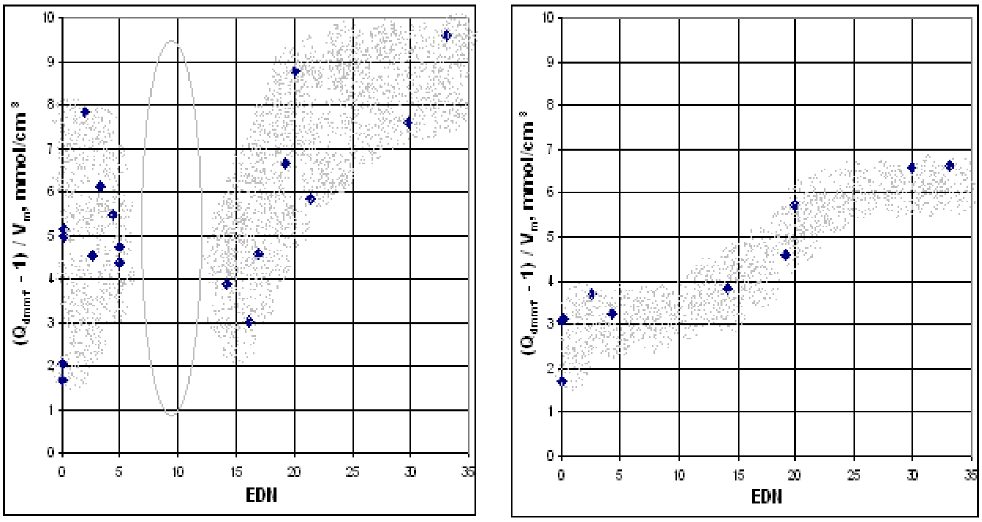


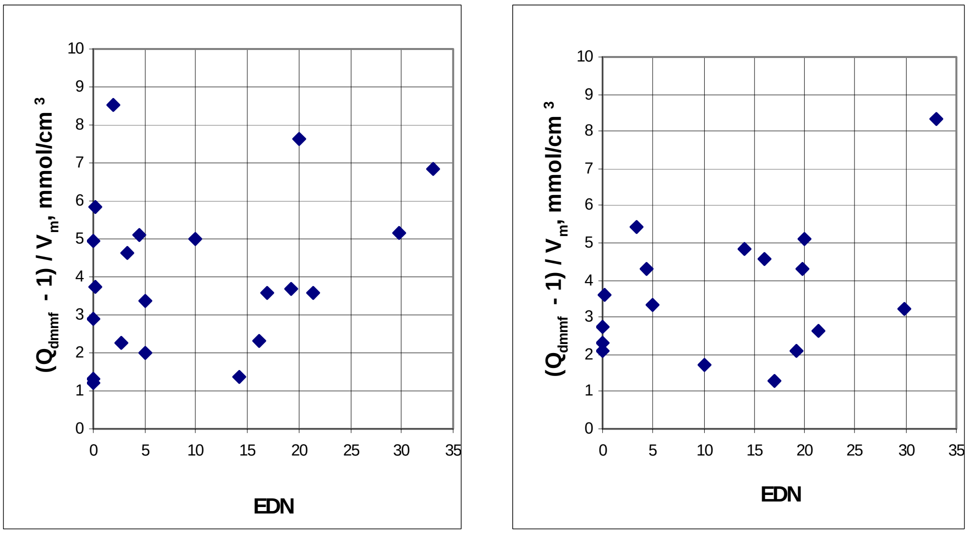
Figure 4. The degree of Dictyonema swelling represented as a molar solvent uptake, $(Q_{dmmf}-1)/V_m$, versus solvent electron donor number. The shrinking behavior is the reason for the negative values of the molar solvent uptake in the case of several solvent

To evaluate the general importance of specific interactions in oil shale kerogens in the solvent swelling process some literature data [Göynük oil shale, Rundel kerogen, Green River and Paris Basin Toarcian kerogens] are reploted in Figure 5 (a, b, c and d) by means of molar uptake as a function of electron donor number, EDN.



a) Göynük oil shale [Ballice, 2003]

b) Rundle HCl/HF demineralized kerogen [Larsen and Li, 1997]



c)Green River HCl/HF (48h) demineralized Kerogen [Larsen and Li, 1994]

d) Paris Basin HCl/HF demineralized Toasrcian kerogen [Larsen et al., 2002]

Figure 5. The degree of some oil shale kerogens (Göynük oil shale, Rundel kerogen, Green River and Paris Basin Toarcian kerogens) swelling represented as a molar solvent uptake, $(Q_{dmmf}-1)/V_m$, versus solvent electron donor number

From Figure 5a it is seen that the swelling behavior of Göynük oil shale is similar to kukersite one (see Figure 3). The swelling extent of these oil shales is more determined by solvent EDN. The more enhanced swelling occurs in “strong” solvents, which suggests that macromolecular network – solvent interactions are higher than by using solvents with lower electron donor number in swelling.

Green River and Paris Basin Toarcian kerogens behave differently. It is clearly seen in Figure 5c and 5d that solvent molar uptake does not depend on EDN. Green River and Paris Basin Toarcian kerogens follow the Regular Solution Theory reasonably well and the swelling here is rather determined by the match between kerogen and solvent solubility parameters than by solvent EDN.

The lack of experimental data on Rundle kerogen (see Figure 5b) in the EDN range of 5-14 makes it difficult to analyze the swelling behavior properly. Although, the swelling results of Rundle kerogen in the range of EDN > 14 show the analogous tendency that is observed in kukersite swelling (see Figure 3).

Outcome: There are oil shale kerogens that follow the Regular Solution Theory reasonably well (for example, Green River kerogen), but there are also other data showing that for some oil shale kerogens the deviation from this theory can be observed (for example, Göynük oil shale, Kukersite oil shale, Dictyonema oil shale). These latter oil shale kerogens show a tendency to exhibit the swelling maxima in polar solvents and to show an increase in solvent uptake with increase in Gutmann’s electron donor number for the solvent. Thus, the application of the Regular Solution Theory based approaches to analyze swelling of kukersite and Dictyonema oil shales should be done with caution. However, the use of the classical Regular Solution Theory-based approaches might still offer semi-quantitative estimates of the number average molecular weights between cross-links, and the cross-link density, in the kukersite and dictyonema kerogens.

3.1.2. Kukersite oil shale swelling in binary mixtures

Another way of gaining insights into the process occurring in kerogen network is through the use of the swelling in binary mixtures. While a large number of studies are available on oil shale kerogen swelling in a single solvent, much less attention has been directed to swelling in multicomponent solvent mixtures, despite the potential that such information might offer the understanding of the macromolecular structure.

In total nine binary mixtures were used to investigate kukersite kerogen swelling under a research program (the present thesis was the part of the program). The results are not presented here and only the general outcomes are shown. The results from the swelling in binary mixtures confirmed the important role of specific interactions in the swelling of kukersite kerogen by solvents. The highest swelling values (upper limit) for Kukersite kerogens observed in high donor number solvents could not be significantly increased by the use of mixed solvents; the usual electron donor solvents gave the highest swelling, though their effect could be decreased in mixture with non-specifically interacting solvents. The results also showed that the role of solvent solubility parameter was of secondary importance in the determining of the swellability of kukersite kerogen. It was the disruption of strong non-covalent cross-links that resulted in a roughly two-fold increase in swellability, as compared with non-specifically interacting solvents.

3.2 Thermal pretreatment induced changes in swelling of kukersite and Dictyonema – room temperature swelling experiments

To track changes in kukersite oil shale swelling, induced by the thermal pretreatment, six solvents with different polarity, namely, NMP, THF, benzene, acetone, acetonitrile and nitroethane, were used (Paper II). The samples of kukersite were pre-treated from 175 to about 375 ^{0}C with the residence times of 1 and 3 hours, respectively. Figure 6 corresponds to a treatment time of 1 hour. The results of 3 hour thermal pretreatment are not shown here (see Paper II, Figure 2). The trends of those results are in principle similar to those seen in 1 hour thermal pretreatment. Kukersite swelling behavior, seen in these figures, shows that the six solvents appear to group into three pairs: NMP and THF, acetone and benzene, and acetonitrile and nitroethane.

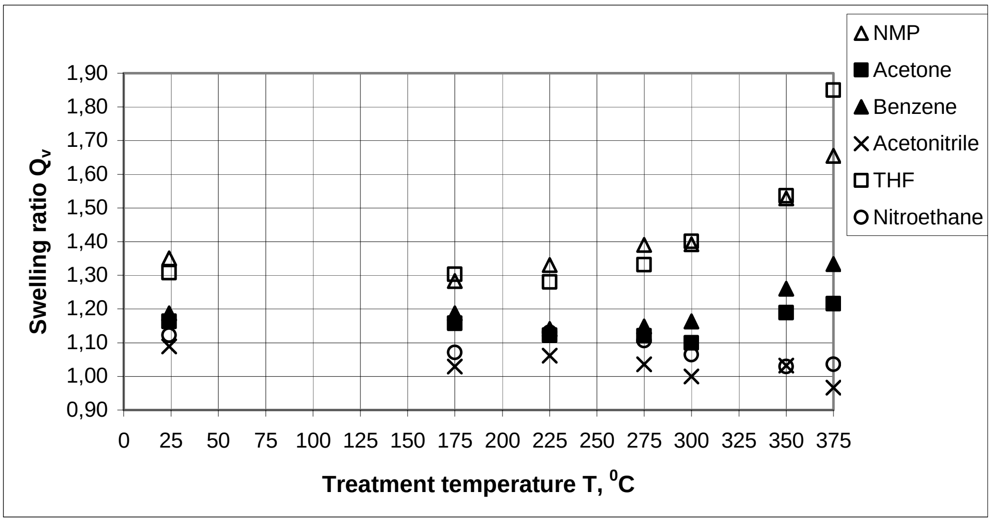


Figure 6. The comparison of solvent swelling ratios in six solvents resulting from different pretreatment temperatures. Heat treatment time of 1 hour was used. (Figure 1, Paper II)

From Figure 6 it is seen that the pair of highest donor number solvents, NMP and THF, shows the highest swelling ratios over the entire pre-treatment conditions studied. These are solvents with strong hydrogen bond capabilities and both are able to break kerogen-kerogen non-covalent interactions and form new solvent-kerogen non-covalent interactions. The swelling ratios in these solvents behaved similarly when the pretreatment temperatures were in the range from 175 ^{o}C to 350 ^{o}C, however, at 375 ^{o}C THF gave greater swelling than NMP. The latter temperature was already in the range of a considerable thermobitumen formation, as shown by a change in solvent color to dark brown, due to an increased amount of soluble formation.

In the context of this study, the swelling in NMP and THF are expected to be similar to that in pyridine, which has been used as the qualitative indicator of cross-link density in coal swelling studies [Suuberg *et al.*, 1987; Solomon *et al.*, 1990]. Based on this, if swelling in these solvents is the indicator of the extent of cross-linking, then kukersite is showing a tendency to relax before the major pyrolysis (devolatilization) onset. It is similar to the trend seen in high tar yield softening coals.

The second pair of solvents, benzene and acetone shows to a lesser extent of similar trend than NMP and THF. The swelling in these solvents is characterized by lower swelling and a delayed onset of relaxation – the noticeable increase in swelling ratio appears at higher temperatures, above 300 ^{o}C compared with the 225 ^{o}C in NMP and THF.

Swelling in the last pair of solvents, nitroethane and acetonitrile, shows much different behavior than do the other pairs - swelling capacity decreases with heat treatment temperature and time. Note that these are poor swelling agents for kukersite; both are characterized by stronger electron acceptor than electron donor properties.

Outcome: The kukersite kerogen shows the tendency towards structural relaxation in the low temperature pre-pyrolysis region.

With comparison to kukersite kerogen which has shown the tendency towards structural relaxation in the low temperature region, Dictyonema oil shale behaves differently. The results of the room temperature swelling of Dictyonema heat treated samples as a function of isothermal heat-treatment temperatures are shown in Figure 7. The samples were heat-treated 1 hour at 125, 150, 200, 250, 350 and 380 ^{0}C. The comparative swelling was performed in four solvents: two hydrogen bonds forming high EDN solvents (aniline and NMP) and two low EDN solvents with the EDN is lower than EAN, one polar (nitrobenzene) and one non-polar (toluene). From Figure 7 one can observe the increasing trend in the degree of the swelling in aniline, NMP and nitrobenzene for pre-heated temperatures in the region of 125-150 ^{0}C. This increase in the swelling extent could be a thermally produced physical relaxation as the “original” fossil fuel structure may not be in a relaxed equilibrium state [Yun and Suuberg, 1992; Otake and Suuberg, 1997]. It also can be seen from Figure 7 that the swelling extents in high EDN solvents were significantly higher than in the lower EDN solvents in temperature region up to about 200 ^{0}C of heat-treatment indicating the importance of non-covalent cross-links in the swelling process. When the preheating temperature has reached 380 ^{0}C

– the region of major pyrolysis event, devolatilization, the swelling in all solvents indicates almost no swelling, even shrinking in toluene (Figure 7). The decrease in the swelling extent with thermal pretreatment intensity observed in Figure 7 suggests the increase in crosslink density due to low-temperature cross-linking reactions.

Outcome: The Dictyonema oil shale kerogen shows the tendency towards structural tightening in the low temperature pre-pyrolysis region.

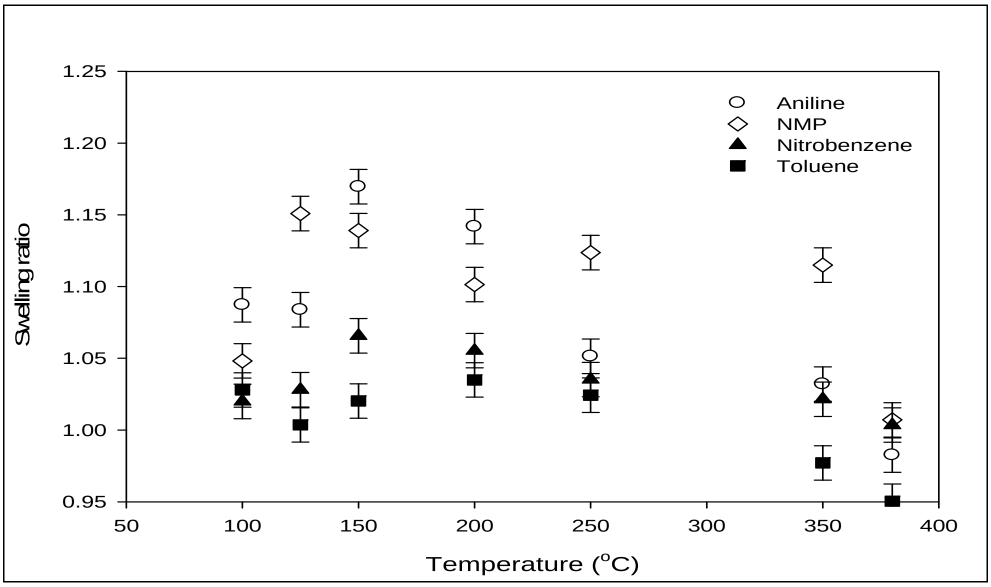


Figure 7. The equilibrium swelling ratios of thermally pre-treated Dictyonema oil shale acid treated samples measured at room temperature as a function of pretreatment temperature. Pre-treatment time of 1 hour was used. Open points are for swelling in high EDN solvents and solid points in low EDN solvents. Error bar values are included

3.3 Swelling of thermally pre-treated kukersite oil shale samples – evaluation of applicability of the Regular Solution Theory based approaches

3.3.1. The ambient temperature swelling of thermally pre-treated kukersite oil shale samples in single solvents

Three pre-treatment conditions were selected for more detailed study of kukersite swelling using 22 solvents (Paper II). The conditions were as follows: 1 hour at 275 °C, 3 hours at 300 °C and 1 hour at 350 °C. The highest temperature of 375 °C in Figure 6 was considered too close to the onset of active pyrolytic reactions, based on the visual observation of solvent extraction. Figure 8 illustrates the variation of swelling ratios with the Hildebrand solubility parameters of the solvents where the non-treated samples (open points) are compared with 350 ^{0}C 1 hour heat-treated samples (solid points). Data from the other thermal pre-treatment conditions (275 °C for 1 hour and 300 °C for 3 hours) differed only slightly from the results of the non-treated sample and are not shown here.

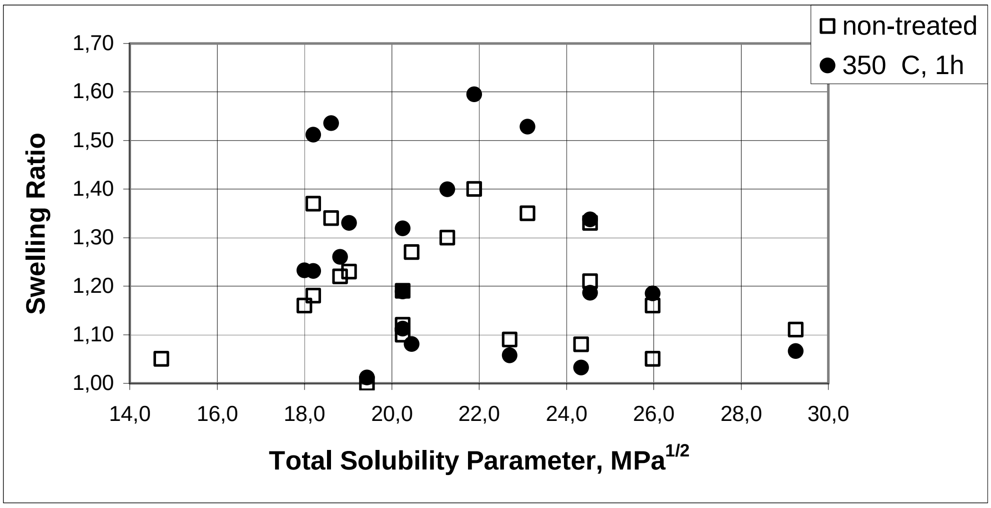


Figure 8. Solvent swelling of kukersite oil shale at room temperature. The results are compared for the non-treated sample and the sample that has undergone the thermal treatment at 350 °C for 1 hour. See Table 12a to identify solvents with solubility parameter values. (Figure 4, Paper II)

As it is seen in Figure 8 scattered swelling behavior of both untreated and heat-treated kukersite samples is observed. The open and solid points in Figure 8 show the similar patterns, only the swelling extent magnitudes vary depending on a solvent character. High swelling values in strongly polar solvents (THF, NMP, pyridine, propylamine, DMF for example) can be seen in both cases (treated and untreated).

The re-plotted data presenting molar uptake as the function of solvent donor number have demonstrated that in kukersite exist the specific interactions (between moderately to strongly polar solvents and macromolecule structural units) in both the non-treated and the heat-treated samples (see Paper II, Figure 5), and that randomly distributed weak interactions, which are the basis for the Regular Solution Theory are of secondary importance.

3.3.2. *The ambient temperature swelling of kukersite oil shale pre-treated by heating samples in solvent mixtures*

Based on the elaborated study of swelling in binary solvent mixtures, referred in *Chapter 3.1.2,* two types of mixtures (benzene-propanol and benzene-NMP) were selected for the swelling experiments of heat-treated kukersite samples (Paper II). The basis for selecting these particular binary mixture components was that there should be a non-associative behavior between each other (they were assumed not to be attracted to each other, which of course, is not entirely true).

The results from swelling experiments with benzene-NMP mixture presented in Figure 9 show the typical behavior that was observed in kukersite kerogen swelling in the binary mixture of non-polar solvent and strong electron donor. 10 to 20% of NMP in the mixture (points corresponding to the total solubility parameter values below 20 MPa$^{1/2}$ in Figure 9) is sufficient to raise the swelling ratio to a level comparable to that in pure NMP, the high donor number solvent. In the case of the non-treated sample, additional NMP does not change the swelling extent significantly. A somewhat different pattern emerges for NMP swelling of the pre-treated samples, especially of the 350 ^{o}C sample. In the case of the 350 ^{o}C sample, after a sharp increase at low NMP concentrations, for concentrations from 20% to 100% the swelling ratios change smoothly with mixture solubility parameter: first, there is a slight increase and then after passing through a maximum (at about 21 MPa^{½}) there is a decrease to a lower value corresponding to swelling in pure NMP. The swelling ratio at the maximum is considerably higher than that in pure NMP, about 1.64 relative to 1.53 in pure NMP. This might indicate that although the specific interactions in the system of NMP with the kukersite are essential for breaking the non-covalent cross-links, the binary mixture solubility parameter match with kerogen segments contribute to finalize the extent of swelling.

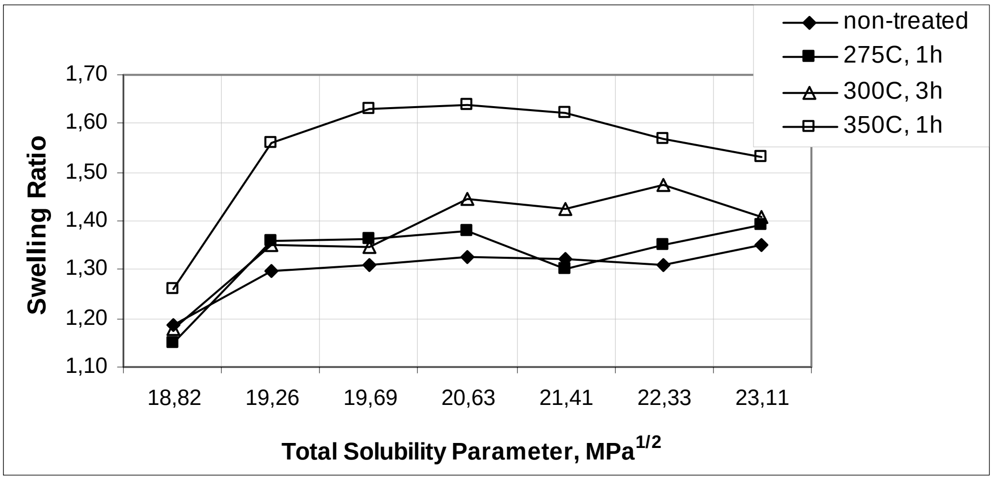


Figure 9. Swelling of raw and thermally pre-treated samples in benzene-NMP mixtures as a function of binary mixture solubility parameter. Solubility parameters of pure solvents are 18.8 and 23.1 MPa$^{1/2}$ for benzene and NMP. (Figure 6, Paper II)

Figure 10 shows the curves obtained from the swelling experiments with benzene-propanol mixtures: a non-polar solvent in mixture with a moderate electron donor. The swelling behavior, indicating something that is close to "ideal" thermodynamic swelling theories, is observed from this figure. An especially nicely shaped parabolic curve emerges in the case of 350 °C sample. It is also seen, that there is a variation in maximum with pre-treatment conditions, and that the deviation between the swelling ratios at the curve maximum and those in pure solvents increases with pretreatment temperature increasing. For example, the thermal pre-treatment at 350°C results in the maximum swelling (Q= 1.52) close to the swelling in pure NMP (Q= 1.53) or pure THF (Q=1.54).

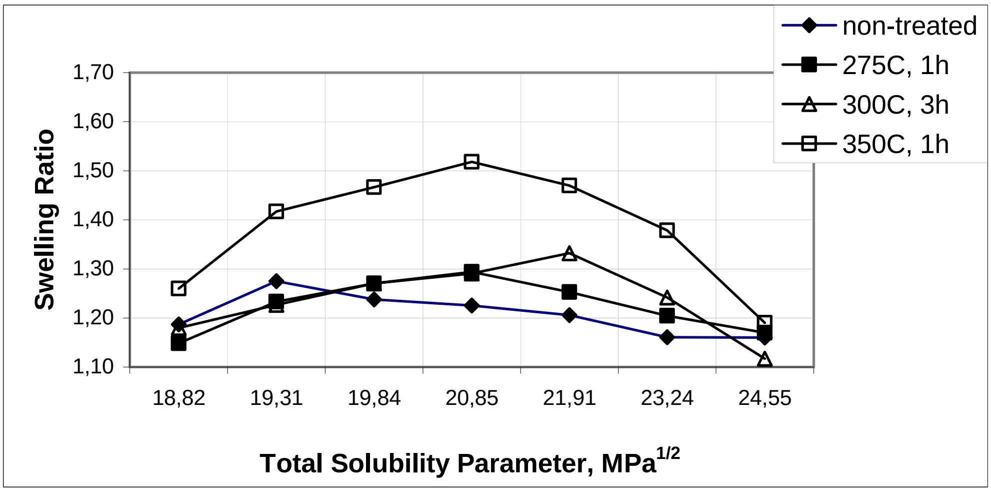


Figure 10. Swelling of raw and thermally pre-treated samples in benzene-propanol mixtures as a function of binary mixture solubility parameter. Solubility parameters of pure solvents are 18.8 and 24.5 MPa$^{1/2}$ for benzene and n-propanol respectively. (Figure 7, Paper II)

Examine the data in Figure 9 and 10 there seems to be similar trends with the pre-treatment temperature in both figures: 275 °C pretreatment shows behavior close to the non-treated sample, 300 °C pretreatment indicates a swelling ratio increase at concentrations richer in the solvent with better donor properties, and in the case of 350 °C, the pretreatment of the network structure is clearly most relaxed, and beginning to approach the "ideal" swelling behavior (at least to something that resembles it). These results show the combined importance of specific and non-specific interactions in swelling, and suggest that the influence of the specific interaction decreases with increasing the severity of the pretreatment.

3.4 Solubility parameter estimation from swelling data

Despite the importance of specific interactions, for illustrative purposes, kerogen solubility parameters of kukersite oil shale, thermally pretreated kukersite oil shale and Dictyonema oil shale were estimated by applying Gee's approach [Gee, 1943]. Figure 11 shows an exemplary evaluation of the solubility parameters based on Gee's approach for Hildebrand solubility parameter. The Hildebrand solubility parameter value of 22 MPa$^{1/2}$ (see Table 15, column 2, row 2) corresponds to the linear regression line interception of the horizontal axis or the ratio of intercept and slope. The data of scattering seen on the plot indicates that the randomly distributed weak interactions, which are the basis for the Regular Solution Theory, are of secondary importance.

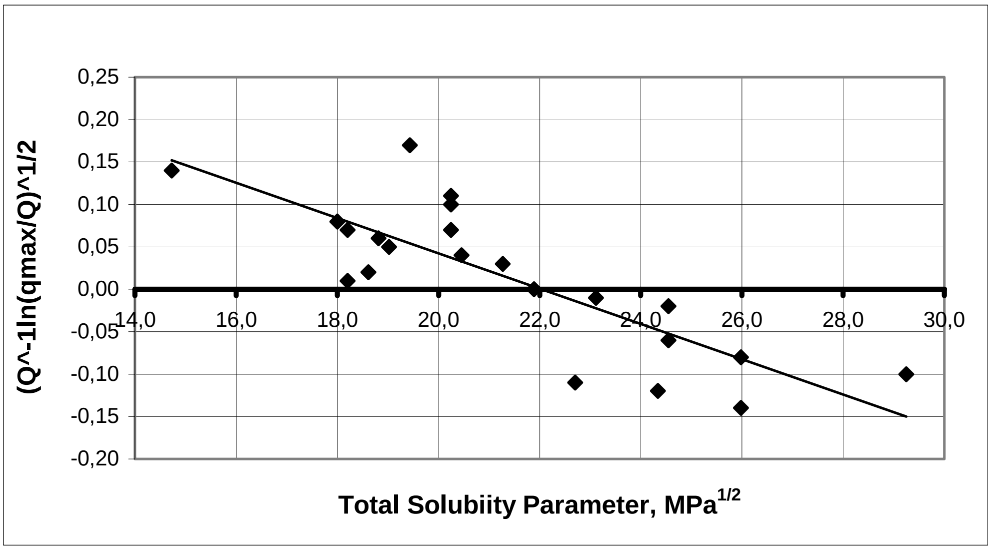


Figure 11. The determination of Hilderbrand solubility parameter of oil shale kukersite by applying Gee's approach

The three-dimensional Hansen solubility parameters were similarly determined. The results are given in Table 15.

Table 15. Total and Hansen solubility parameters obtained for non-treated and thermally pre-treated kukersite kerogens using Gee's equation. The total solubility parameters δ_{calc} (in principle the same as the Hildebrand solubility parameter) were calculated from three determined Hansen solubility parameters. Units are MPa$^{1/2}$

	Dictyonema	**Kukersite**			
	non-treated	*non-treated*	*275 °C, 1 h*	*350 °C, 1h*	*300 °C, 3 h*
Hildebrand or total, δ	22	22	22	22	22

$\delta_{calc} = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$	23	23	23	22	22
Hansen dispersion, δ_d	19	18	19	18	19
Hansen polar, δ_p	6	9	9	8	8
Hansen h-bonding, δ_h	12	11	10	9	8

Table 15 demonstrates that the total solubility parameters of Dictyonema and kukersite were estimated about 22 MPa$^{1/2}$. It is consistent with literature data (see Table 6). However, more solvents must be used to estimate the solubility parameter of oil shales more precisely. The results presented in Table 15 also illustrate that the thermal pre-treatment does not have significant effect upon solubility parameter values, or in other words, the thermal pretreatment conditions applied do not change considerably the basic chemical nature of kukersite.

Finally, the determined solubility parameters of kukersite are also in quite good agreement with the results presented by Lille using the method of atomistic simulation (Paper I). The comparison is shown in Table 6. The total solubility parameter was calculated to be 19.3 ± 1.82 MPa$^{1/2}$ using this method, which is somewhat lower than the value obtained from the experimental data by Gee's method. However, the dispersion solubility parameter was calculated to be 18.9 ± 0.55 MPa$^{1/2}$, which is just the same as obtained experimentally. Therefore the difference in the total solubility parameter comes from electrostatic component. It is seen in Table 16 that H-bonding and polar solubility parameters were not separately calculated by the method of atomistic simulation because this model applied did not account electrostatic components (sum of polar and H-bonding interactions) with reasonable error limits.

Table 16. The comparison of the results of solubility parameters determined by using Gee's method and the method of atomistic simulation. The units of δ are MPa$^{1/2}$

Solubility parameter	**Experimental Gee's method**	**Atomistic simulation**
Hildebrand or total, δ	22	19.3 ± 1.82
Hansen dispersion, δ_d	19	18.9 ± 0.55
$\delta = \sqrt{\delta_p^2 + \delta_H^2}$	13.4	4
Hansen polar, δ_p	6	
Hansen H-bonding, δ_H	12	

3.5 Estimation of input parameters for Functional Group-Depolymerization, Vaporization and Crosslinking model (FG-DVC model)

Several decades ago the Functional Group-Depolymerization, Vaporization and Cross-linking model (FG-DVC model) was developed to predict yields and compositions of coal pyrolysis products, such as gas, tar and char, under a wide variety of pyrolysis conditions. As one can note the FG-DVC model consists of two sub-models: the FG model which describes the gas evolution and the elemental and functional group composition of both tar and char, and the DVC one, which describes the depolymerization of the macromolecular network combining bridge breaking, cross-linking, and tar formation subject to transport and vaporization processes [Smith, 1994]. The FG-DVC model has three coal (more generally, fossil fuel) description files (coal data file, kinetic file, polymer file) as wide set of coal physical / chemical parameters are needed for calculations. The aim is to evaluate two oil shale specific parameters for the „polymer file“ that contains macromolecular network data. The parameters of interest are: (1) the number average molecular weight between cross-links and (2) the molecular weight of monomers. For the model originally, the former was evaluated from experimental swelling data using simple swelling models (Regular Solution Theory based models) and the latter was estimated from pyrolysis-field ionization-mass spectrometric measurements. For the model the molecular weight distribution of monomers was assumed to follow Gaussian distribution and was described with a mean and a standard deviation. In this chapter of the present thesis the approach based on the same techniques is chosen.

3.5.1. Application of swelling models (Flory-Rehner and Kovac) to estimate the number average molecular weight between crosslinks for kukersite and Dictyonema

The major implication of the results shown in previous chapters, is that for kukersite and Dictyonema oil shales, the highest swelling extent can be seen in specifically interacting solvents (in hydrogen bonding solvents with high EDN values, such as pyridine, NMP, tetrahydrofuran, propylamine), and this emphasizes the concern regarding the use of the Regular Solution Theory based approaches. However, at present, there is no consensus as to what degree of the non-ideality one should use the Regular Solution Theory based approaches. Therefore, the simple swelling models have been extended to quite complex systems, including coals [Solomon *et al.*, 1992] and oil shales [Larsen and Lee, 1994], to estimate at least semi-quantitatively useful properties. Thus, the following is pursued only for comparative purposes as information for some other shales are available from literature: for Green River [Larsen and Li, 1994], Beypazari [Ballice, 2003] and Göynük [Ballice, 2003] oil shales using the Flory-Rehner model (Gaussian distribution network model) and its extension, the Kovac model (modified Gaussian distribution network model) [Lucht and Peppas, 1981; Barr-Howell and Peppas, 1985].

The main advantage of these models is that the structure properties can be estimated from swelling data using a few key parameters: the macromolecule volume fraction in swollen network and the Flory-Huggins interaction parameter. The Kovac model, relative to the Flory-Huggins model, has one more parameter N, the number of repeating units between junction points (connection points). The parameter describes deviation from Gaussian behavior as in the case of large N the Kovac equation approaches to the Flory-Rehner equation. The Kovac swelling model was developed especially for coals as the coal structure (also the structure between junction points) was assumed to consist of "rigid" clusters (condensed aromatic or hydro-aromatic structures) with molecular weight much larger than the connecting short flexible links or bonds.

The macromolecule volume fraction in the swollen network can be found from swelling ratio as it is equal to the reciprocal value of the swelling ratio. This is a strightforward approach to kukersite kerogen (no shrinking was observed). In order to get reasonable estimate on volume fraction of Dictyonema kerogen in swollen network from swelling data for this oil shale, the lowest swelling ratio (Q_{dmmf} = 0.89 for acetone) was taken to be 1 and others were corrected accordingly by adding 0.11 to corresponding swelling ratios Q_{dmmf}. It could be assumed that the shrinking was caused by re-arrangement of molecular structures, and thus the lowest swelling ratio was taken to be so called "reference state". Of course, this assumption is debatable (Paper III).

The largest source of the uncertainty comes from the Flory-Huggins interaction parameter (χ) as the choice of proper value of χ is not presently clear. The interaction parameter is an empirical measure of interactions between solvent and macromolecule. There has been a very limited amount of work found on the coal-solvent [Peppas and Lucht, 1986], and not at all for oil shale kerogen-solvent, interaction parameters. For coal-solvent pairs the interaction parameters are shown to be in the range from – 0.4 to about 2 [Suuberg *et al.*, 1994; Lucht and Peppas, 1981]. In this study the solvent-kerogen interaction parameters were calculated from solubility parameter values of the macromolecule and the solvent in accordance of the suggestive equation [Farve, 1996]:

$$\chi = \chi_s + \chi_h = \chi_s + \frac{V_s}{RT}(\delta_s - \delta)^2 \quad (4)$$

where χ is interaction parameter, χ_h is the enthalpy term, χ_s is the entropy term and taken constant with a value of 0.35, R is ideal gas constant, T is temperature, V_s is molar volume of the solvent, δ_s is solubility parameter of solvent and δ is solubility parameter of macromolecule, here of kerogen. The determination of solubility parameter of kukersite and Dictyonema kerogens using Gee's method was explained in Chapter 3.4 and values were given in Table 15. The same value of 22 $MPa^{1/2}$ can be seen for both oil shales. It is only to emphasize, that the determination of the number average molecular weight between cross-links is sensitive to the choice of the interaction parameter value. For example, it has been shown based on the computer simulation that the changes in the interaction parameter with ± 0.1 can result the changes in the number average molecular weights with several hundred units [Lucht and Peppas, 1981].

Tentative calculations for the hypothetical number average molecular weights between cross-links are presented in Table 17 for two equations (swelling models): Flory-Rehner model and Kovac model [Lucht and Peppas, 1981].

Table 17. Average values of the calculated number average molecular weights per cross-links for kukersite and Dictyonema oil shales. Literature values for other oil shales (Green River [Larsen and Li, 1994], Göynük [Ballice, 2003], Beypazari [Ballice, 2003]) are shown for comparison

Oil shale	**Flory-Rehner**	**Kovac N=1**	**Kovac N=2**	**Kovac N=3**
Kukersite	229	861	621	541
Dictyonema (Paper III)	80	370	270	240
Göynük	247	933	678	593
Beypazari	208	790	576	504
Green River (5.2% mineral)	215	808	581	505

3.5.2. Evaluation of reliability of obtained number average molecular weights

The values of number average molecular weight between the cross-links in Col. 2 of Table 17, predicted by the classical Flory-Rehner equation, are in the range from 80 to 247 molecular weight units. The results seem to be rather low in view of the fact that the tarry products of the thermo-chemical conversion of oil shale, both thermo-bitumen (pyrolysis intermediates) and pyrolysis tar, are believed to have much higher number average molecular weight values [Oja, 2005; Suuberg *et al.*, 1987].

To evaluate this statement, a direct pyrolysis in Field Ionization Mass Spectrometer (FIMS) was carried out on kukersite and dictyonema oil shale samples. The pyrolysis in FIMS (also referred as Py-FIMS) is a low-heating rate pyrolysis in a high vacuum - at a pressure 10^{-4} torr at a heating rate of 10^{o}C/min in this study. Field ionization is a soft ionization resulting in molecular ions, therefore providing molecular weight distribution of pyrolysis products from kerogen. On the basis of the rapid evaporation and detection of the formed tarry material under a deep vacuum condition, the following can be assumed: (1) there are structural similarities between tar constituents and kerogen (macromolecular network); (2) the tarry material could represent "hypothetical structures" between the cross-links resulting from the destruction of weakest bonds – kerogen is composed of a large variety of structures with a large distribution of bond strengths, and the weaker bonds are broken earlier in pyrolysis process.

Figures 12 and 13 present mass spectra of the pyrolysis-field ionization of the two Estonian oil shales. To evaluate the molecular weight distribution of kerogen decomposition products, and not that of the vaporizing bitumen, only the magnetic scans in the temperature region from 360 to 710 ^{o}C are shown in Figures 12 and 13. The application of the three parameter Gaussian distribution function results in number average molecular weight values of 408 and 383 amu, and standard deviation values of 141 and 128 for kukersite and Dictyonema oil shales respectively. This suggests that the molecular weight of Dictyonema vacuum pyrolysis tar is slightly lower and the distribution slightly narrower than that of the kukersite vacuum pyrolysis tar, but the difference is, from a practical viewpoint, quite insignificant. This observation is interpreted to indicate that when the weakest bonds are broken, the evolving tarry products are statistically (molecular weight basis) similar for both oil shales.

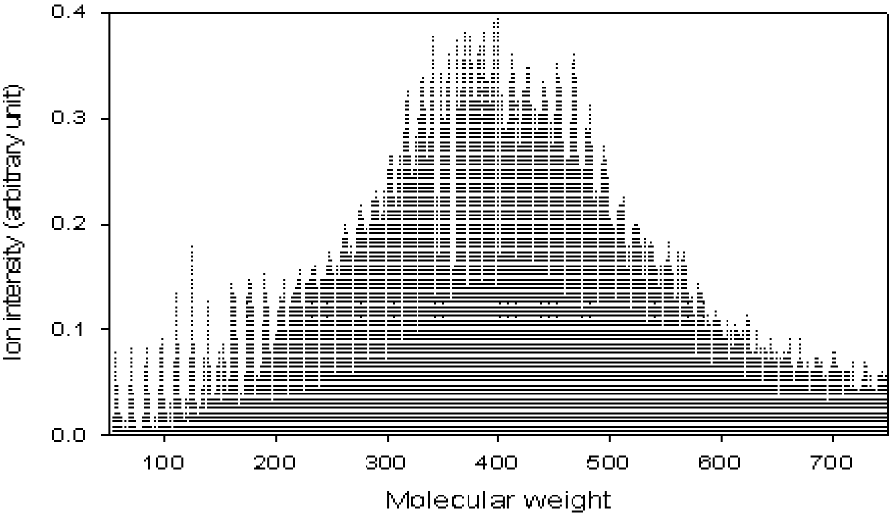


Figure 12. Py-FIMS spectrum of kukersite kerogen obtained by heating kerogen under 10^{-4} Torr at 10 °C/min heating rate

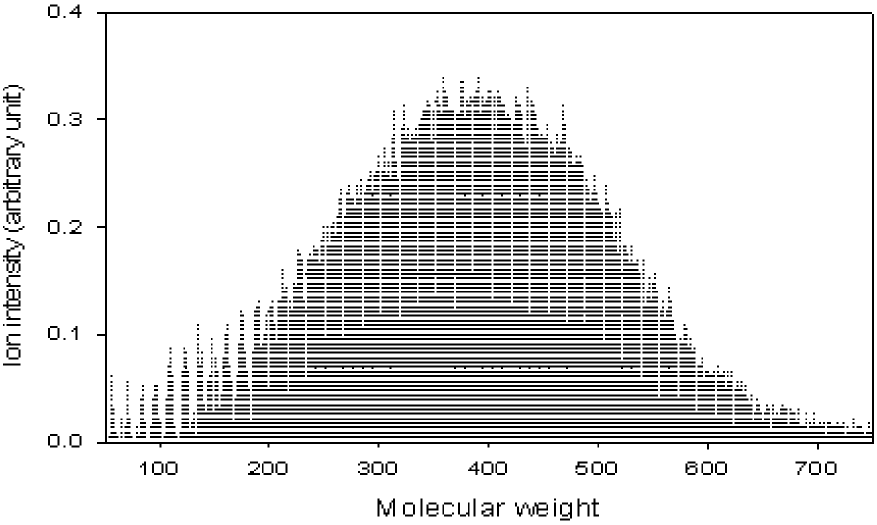


Figure 13. Py-FIMS spectrum of Dictyonema kerogen obtained by heating kerogen under 10^{-4} Torr at 10 °C/min heating rate

The non-gaussian Kovac model requires one more additional parameter N, the average number of repeating units between crosslink points. Lately, a comprehensive study on the characterization of kerogens was carried out using X-ray photoelectron spectroscopy and the solid-state ^{13}C nuclear magnetic resonance technique (unfortunately, Estonian oil shales were not studied) [Kelemen *et al.,* 2007] to evaluate the average chemical compositions of 18 oil shale kerogens. We have selected some characteristics of two kerogens, Rundle (Type I) and Oxford Clay (Type II), that are shown in Table 18. Table 19 has been compiled to compare the elemental composition of these kerogens with kukersite and Dictyonema kerogens.

Table 18. Selected structural characteristics of Rundle and Oxford Clay oil shales [Kelemen *et al.,* 2007]

Kerogen	**Average carbon per organic cluster**	**Fraction of aromatic carbon with attachments**	**Average aliphatic carbon chain length**	**Percent of aromatic carbon**
Rundle, Type I	10	0.42	15	19
Oxford Clay, Type II	13	0.4	12.5	32

Table 19. The elemental composition of the kerogens [Kelemen *et al.,* 2007; Klesment, 1985].

Kerogen	**C**	**H**	**O**	**S**	**N**	**H/C**	**O/C**
Rundle, Type I	100	164	11.1	0.6	1.8	1.64	0.11
Kukersite, Type I-II	100	151	10.4	0.95	0.24	1.51	0.1
Oxford Clay, Type II	100	123	13.7	3.2	2.4	1.23	0.14
Dictyonema, Type II	100	117	12	1.23	2	1.17	0.12

Table 18 shows that the “average repeating structural unit” of these kerogens consists of a 2-3 ring hydro-aromatic/aromatic cluster (Table 18, Col. 2) with a significant number of short attachments (Table 18, Col. 3) and a long roughly linear alkyl-chain (Table 18, Col. 3). It also indicates that the number average molecular weight of the “average repeating structural unit” could be around 400 amu. It is the range detected for the molecular weight of tar from FIMS spectra. Supported by the Py-FIMS data shown in Figures 12 and 13 one over-all observation can be drawn: the Flory-Rehner model strongly underestimates the number average molecular weights between cross-links, including oil shale kerogens that are expected to follow the Regular Solution Theory reasonably well (for example, Green River kerogen); therefore the reason for underestimation might be related to the elastic term of the classic Flory-Rehner theory.

In a light of the structural characteristics shown in Table 18, it is not easy to interpret the Kovac model which expects existence of “rigid” clusters (condensed aromatic structures with 3 to 5 rings) with a molecular weight much larger than that of the connecting short flexible links or bonds. Therefore, neither of the theoretical models (Flory-Rehner or Kovac) is sufficient to enable us to propose reliable values of the number average molecular weight between the cross-links. The evaluation of number aevarge molecular weight between crosslinks of oil shales using classical swelling theories requires re-examination of underlying principles of both the elastic network and the mixing terms. Although experimental data foe making final conclusions are missing, the author is intuitively led to recommend the number average molecular weight values for Estonian oil shales. Swelling of Dictyonema kerogen (Type II kerogen) in organic solvents shows the existence of a very tightly crosslinked structure. The size of „average repeating structural unit“ was estimated from FIMS experiments to be ca. 380 amu. This is close to that suggested by structural analysis for Oxford Clay kerogen (Type II kerogen) [Kelemen *et al.,* 2007]. It appears, therefore, that Dictyonema oil shale has an average molecular weight between crosslinks of at least about 380 amu. This value is significantly higher than that predicted by the Flory-Rehner equation, however, close to that predicted by Kovac equation with one repeating unit between crosslink points (N=1). Swelling of kukersite kerogen in organic solvents is characterized by a considerably higher swelling capacity (than the Dictyonema kerogen) indicating the existence of a lower cross-link density (larger molecular weights between crosslinks). However, both FIMS experiments and structural analysis [Lille, 2003; Kelemen *et al.*, 2007] suggest the size of „average repeating structural unit“ to be around 400 amu, close to that of Dictyonema kerogen. This reveals that there could be more than one “average repeating structural unit“ between crosslink points. The Kovac model predicts the value of number average molecular weight between cross-links to be as high as 860 (if N=1, see Col. 3 Table 17). Again, the Flory-Rehner equation clearly underestimates the number average molecular weight between crosslinks. Since neither model can be regarded as being suitable for establishing reliable numerical values of hypothetical “average molecular weight between crosslinks” (cross-linked via covalent bonds) then the following is recommended: the numerical value of ca 400 amu for Dictyonema oil shale kerogen and between 700-900 amu for kukersite oil shale kerogen (assuming a molecular weight increase with increasing the swelling ratio; and that the value should be higher than that of Dictyonema kerogen and lower than that of bituminous coals).

SUMMARY

The object-matter of the present thesis was to apply a volumetric solvent swelling technique to study kukersite and Dictyonema oil shale kerogens. This work was undertaken in the belief that the Regular Solution Theory based techniques could result in useful information (at least semi—quantitative), especially in the regards of determining the number average molecular weight between cross-links. As a matter of fact, the suggestions that this might be so were found in the literature for other oil shales. It will be recalled that no similar experimental studies have been conducted previously on Estonian oil shales. The experimental study has been peformed to examine the influence of thermal pre-treatment in the low temperature pre-pyrolysis region on the solvent swelling behavior of Estonian oil shale kukersite: on the extent of swelling, on the importance of the specific interactions in the swollen network and on the solubility parameter of kerogen. Similar study on other Estonian oil shale, Dictyonema shale, was performed for comparison.

The main results of the present thesis can be summarized as follows:

1. The sensitivity of swellability to solvent donor numbers indicates the occurrence of specific kerogen-solvent interactions and thus an application of the Regular Solution Theory based approaches to analyze swelling of kukersite and Dictyonema oil shales should be done with caution. It was shown that generally, there are oil shale kerogens that follow the Regular Solution Theory reasonably well (Green River oil shale kerogen, for example), but there are also other data showing that for some oil shale kerogens, the application of this theory can be considered only a crude approximation (kukersite and Dictyonema oil shales, for example). These latter oil shale kerogens show the tendency to exhibit the swelling maxima in polar solvents and to show the increase in solvent uptake with increase in Gutmann's electron donor number for the solvent.

2. The kukersite and Dictyonema kerogens appear to have very tight macromolecular network structures, with significant non-covalent cross-link density. In terms of maximizing swelling, binary solvent mixtures do not offer particular advantage relative to pure, strong electron donor solvents.

3. The thermal pretreatment in the low temperature pre-pyrolysis region (up to 300 ^{o}C with time scale of few hours) does not have significant effect upon solubility parameter values in the case of kukersite, or in other words, the thermal pre-treament conditions applied did not change considerably the basic chemical nature of kukersite. The total solubility parameter was estimated (based on Gee's method) to be roughly the same (ca. 22 MPa$^{1/2}$) for all samples of oil shale.

4. The evaluation of the number aevarge molecular weight between crosslinks of oil shales using classical swelling theories (Flory-Rehner swelling model and Kovac swelling model, applied in this study) requires the re-examination of underlying principles of both, elastic network and thermodynamic, terms. Since neither model can be regarded as being suitable for establishing reliable numerical values of "average molecular weight between cross-links", then only the tentative values were proposed.

5. The results of this investigation indicate that the kukersite kerogen shows the tendency towards structural relaxation in the low temperature pre-pyrolysis region. This observation is qualitatively compatible with those seen in high tar yield softening coals. It is also seen that the thermal pretreatment causes no drastic changes in a general pattern of swelling behavior: kukersite still swells to the greatest extent in high donor numbers solvents (with strong hydrogen bond forming capabilities); the swelling ratio reaches to upper limit, although of somewhat different value, above certain donor number values; the solubility parameter approach is of secondary importance in describing swellability. The experiments performed to track the swelling ratio changes with mixture composition (mixture solubility parameter) indicate that the importance of the energetic compatibility (solubility parameter approach) might increase due to the caused changes in kerogen structures by the thermal treatment.

6. The results of this investigation indicate that the Dictyonema kerogen shows the tendency towards structural tightening in the low temperature pre-pyrolysis region. This observation is qualitatively compatible with those seen in low tar yield non-softening coals. The decreasing pattern in swelling extent with pretreatment temperature severity holds for the swelling in both high and low donor number solvents.

7. It is shown that molecular weight of vacuum pyrolysis tarry products follow Gaussian distribution with the number average molecular weight values of 408 and 383 amu, and with standard deviation values of 141and 128 for kukersite and Dictyonema oil shales respectively. This suggests that the molecular weight of Dictyonema vacuum pyrolysis tar is slightly lower and the distribution slightly narrower than of the kukersite vacuum pyrolysis tar, but the difference is from practical viewpoint quite insignificant. This observation is interpreted to indicate that when weakest bonds are broken, then the evolving tarry products are molecular weight basis similar for both oil shales.

ABSTRACT

In the present thesis a volumetric solvent swelling technique was applied to study Estonian oil shale kerogens. Equilibrium swelling experiments were used to gain insight into structural changes of kerogens during low temperature heating, in the pre-pyrolysis region up to 350 ^{0}C.

The swelling experiments were performed at room temperature on non-treated and previously preheated samples in different organic solvents and binary solvent mixtures. The objective was to examine the influence of thermal pretreatment severity on solvent swelling behavior of oil shale kukersite: on the extent of swelling, the importance of specific interactions in swollen network and solubility parameter of kerogen. The extent of swelling and solubility parameter are input parameters in swelling models that can be used to estimate kerogen crosslink density or at least qualitatively track changes in this parameter in the pre-pyrolysis region. For comparison, the swelling of other Estonian oil shale, Dictyonema shale, was carried out. To evaluate the number average molecular weight between cross-links of these oil shales classical swelling theories (Flory-Rehner swelling model and Kovac swelling model, applied in this study) were applied.

Based on the swelling in high donor number solvents, kukersite oil shale kerogen shows structural relaxation before the onset of active pyrolysis. Otherwise the thermal pretreatment severity applied caused no drastic changes in a general pattern of swelling behavior of kukersite kerogen: the kukersite kerogen still swelled to the greatest extent in high donor numbers solvents (indicating importance of specific interactions such as hydrogen bonds); these solvents also determined the upper limit of swelling in mixtures of solvents; there was not significant effect upon solubility parameter values. Using Gee's method the total solubility parameter was estimated to be the same (about 22 MPa$^{1/2}$) for all samples of oil shale. The results of the swelling of thermally pretreated Dictyonema samples indicated that the Dictyonema kerogen had shown the tendency towards structural tightening in the low-temperature pre-pyrolysis region.

KOKKUVÕTE

Antud doktoritöös rakendati Eesti põlevkivide (kukersiit ja diktüoneema) kerogeeni uurimiseks kerogeeni pundumist lahustites. Pundumine lahustites on suhteliselt lihtne ja laialdaselt kasutatav meetod võrkstruktuursete fossiilkütuste uurimiseks, mille tulemused võimaldavad iseloomustada lahusti-makromolekuli vastastikmõjusid, määrata lahustuvusparameetrit ning hinnata ristsidemete vahelist keskmolekulaarmassi kasutades sobivaid teoreetilisi pundumismudeleid. Kuigi see on vajalikku informatisooni pakkuv meetod, ei oldud seda varem rakendatud Eesti põlevkivide uurimiseks. Peamiseks eesmärgiks oli hinnata termilise eeltöötlemise mõju pundumismeetodiga määratavatele kukersiitse põlevkivi kerogeeni kirjeldavatele parameetritele (kerogeeni lahustuvusparameetrile, kerogeen-lahusti vastasmõjudele, ristsidemete tihedusele). Võrdluseks uuriti ka teist Eesti põlevkivi – diktüoneemakilta.

Antud doktoritöö pundumismetoodika valik ja eksperimentaalse osa läbiviimine baseerus põlevkivi- ja kivisöealase kirjanduse ülevaate detailsele uuringule. Pundumiskatsed viidi läbi nii termiliselt eeltöötlemata kui ka termiliselt eeltöödeldud põlevkivi proovidega. Pundumiskatseid teostati toatemperatuuril kasutades erinevaid orgaanilisi lahusteid ning nende binaarseid segusid.

Termiliselt eeltöötlemata kukersiidi prooviga sooritatud pundumiskatsete tulemused näitasid, et suurim pundumine toimus kõrgema elektrondoonori numbriga lahustites. Diktüoneemakildaga sooritatud pundumiskatsetes on näha märgatavalt madalamat pundumist võrreldes kukersiidi tulemustega.

Termiliselt eeltöödeldud kukersiidi proovidega sooritatud pundumiskatsete tulemused viitavad sellele, et kukersiidi struktuur muutub lahtisemaks (pundumine suureneb) eelpürolüüsi piirkonnas (kuni 350 ^{0}C). Samas võis näha, et kasutatud termilise eeltöötlemise ulatus eriti ei mõjutanud pundumismeetodi kaudu hinnatavat kukersiitse põlevkivi käitumismustrit: kerogeen pundus kõige paremini kõrgema elektrondoonori numbriga lahustites (viidates vesiniksidemete tähtsusele); esines ikka toetav elektrondoonori numbri piirväärtus (kui teostati pundumist lahustite segudes), mille ületamisel solvendi molaarse neeldumise suurenemist elektrondoonori numbri suurenemisega enam ei toimunud. Termiliselt eeltöödeldud diktüoneemakilda proovidega saadud pundumiskatsete tulemused viitavad selle, et diktüoneemakilda struktuur muutub tihedamaks eelpürolüüsi piirkonnas.

Lahustuvusparameetri hinnang näitas, et kerogeeni lahustuvusparameetrid praktiliselt ei sõltunud kasutatud termilise eeltöötlemise ulatusest. Pundumiskatsete alusel määratud põlevkivi erinvate proovide üldlahustuvusparameetri väärtused olid 22 MPa$^{1/2}$.

Ristsidemete vahelise arvkeskmise molekulaarmassi suurusjärgu hindamiseks kasutati kahte klassikalist pundumismudelit: Flory-Rehneri mudelit ja Kovac'i mudelit. Uurimistöö tulemusena hinnati kukersiidi kerogeeni ristsidemete arvkeskmise molekulaarmassi väärtuseks 700-900 amu ja diktüoneemakilda kerogeenile 400 amu.

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APPENDIX A

Publication I

N. Savest, V. Oja, T. Kaevand, Ü. Lille. Interaction of Estonian kukersite with organic solvents: a volumetric swelling and molecular simulation study, Fuel, 86 (2007) 17-21.

APPENDIX A

Publication II

Savest, N., Hruljova, J., Oja, V. Characterization of thermally pre-treated Kukersite oil shale using the solvent-swelling technique. Energy Fuels, 23 (2009) 5972-5977.

APPENDIX A

Publication III

K. Kilk, **N. Savest**, J. Hruljova, E. Tearo, S. Kamenev, V. Oja. Solvent swelling of Dictyonema oil shale, Oil Shale (accepted 2009).

APPENDIX B

Curriculum Vitae

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi	Natalja Savest
Sünniaeg ja -koht	07.04.1981, Tallinn
Kodakondsus	Eesti

2. Kontaktandmed

Aadress	Kalevipoja 11-134, 13265 Tallinn
Telefon	+372 52 38 393
E-posti aadress	nataly_29@hotmail.com

3. Hariduskäik

alates 2005	Tallinna Tehnikaülikool, doktoriõpe, keemia- ja materjalitehnoloogia eriala
2005	Tallinna Tehnikaülikool, Tehnikateadute magistri kraad
2003	Tallinna Tehnikaülikool, Tehnikateaduste bakalaureuse kraad
1999	Tallinna Lasnamäe Gümnaasium

4. Keelteoskus

vene	kõrgtase (emakeel)
eesti	kõrgtase
inglise	kõrgtase
hispaania	algtase

5. Teenistuskäik

2005-	Assistent, TTÜ, Keemiatehnika instituut

6. Teadustegevus

Alates 2005 – Eesti Keemia Seltsi liige.

7. Kaitstud lõputööd

„Tekstiilvärvaineid sisaldavate mudellahuste ja heitvete värvuse eemaldamine”, bakalaureusetöö, juhendaja vanemteadur Sergei Preis

„Eesti põlevkivi kukersiidi pundumine lahustites”, magistritöö, juhendaja Prof. Vahur Oja

8. Teadustöö põhisuunad

Põlevkivi kukersiidi kerogeeni struktuuri ning füüsikaliste ja keemiliste omaduste uurimine kasutades pundumismeetodit erinevates lahustites. Termilise eeltöötlemise mõju põlevkivile (kuni 350 ^{0}C) rakendades pundumisprotsessi. Võrdluseks teise Eesti põlevkivi – diktüoneema kilda uurimine rakendades pundumismetoodikat. Klassikaliste pundumismudelite (Flory-Rehner mudeli ja Kovac'i mudeli) kasutamine ristsidemete vahelise arvkeskmise molekulaarmassi suurusjärgu hindamiseks. Kaasaegse kivisöe pürolüüsi mudeli FG-DVC (Functional Group-Depolymerization Vaporization Crosslinking Coal Pyrolysis Model) rakendamine Eesti põlevkivile (kukeriidile).

9. Teised uurimisprojektid

G7222 Termilise lagunemisega kaasnevate Eesti põlevkivi struktuuri ja soojusfüüsikaliste omaduste muutmiste uurimine.

SF0142628s04 Kütused ja kütuste komponendid, nende termodünaamilis-füüsikalised omadused.

CURRICULUM VITAE

1. Personal data

Name	Natalja Savest
Date and place of birth	07.04.1981, Tallinn

2. Contact information

Address	Kalevipoja 11-134, 13265 Tallinn
Phone	+372 52 38 393
E-mail	nataly_29@hotmail.com

3. Education

since 2005	Tallinn University of Technology, Faculty of Chemical and Materials Technology, doctoral study
2005	Tallinn University of Technology, Faculty of Chemical and Materials Technology, MSc
2003	Tallinn University of Technology, Faculty of Chemical and Materials Technology, BSc
1999	Tallinn Lasnamäe Gymnasium, Secondary Education

4. Language competence/skills

Russian	fluent
Estonian	fluent
Inglish	fluent
Spanish	basic

5. Professional employment

2005-	Assistent, Tallinn University of Technology, Department of Chemical Engineering

6. Scientific work

Since 2005 – the member of Estonian Association of Chemistry.

7. Defended theses

"Discoloration of synthetic solutions and wastewaters containing textile dyes", bachelor thesis, supervisor senior researcher Sergei Preis

"Estonian oil shale kukersite solvent swelling", master thesis, supervisor Prof. Vahur Oja

8. Main areas of scientific work/Current research topics

The application of solvent swelling technique to study Estonian oil shales and to gain insight into structural changes of kerogens during low temperature heating, in the pre-pyrolysis region up to 350 ^{0}C. For comparison, swelling of other Estonian oil shale, Dictyonema shale. The application of classical swelling theories (Flory-Rehner swelling model and Kovac swelling model) to evaluate number average molecular weight between cross-links of kukersite and Dictyonema.

9. Other research projects

Project: G7222 "Investigation of thermally induced changes in structure and thermal properties of Estonian oil-shales."

Project: SF014268s04 „Thermodynamic and transport properties of fuels and fuel components."

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and destruction of polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase transformations in hydrothermal sintering processing of phosphate rock. 1995.

4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi apatites. 1995.

5. **Anu Hamburg**. The influence of food processing and storage on the N-nitrosamines formation and content in some Estonian foodstuffs. 1995.

6. **Ruth Kuldvee**. Computerized sampling in ion chromatography and in capillary electrophoresis. 1999.

7. **Külliki Varvas**. Enzymatic oxidation of arachidonic acid in the coral *Gersemia fruticosa*. 1999.

8. **Marina Kudrjašova**. Application of factor analysis to thermochromatography and promotion studies. 2000.

9. **Viia Lepane**. Characterization of aquatic humic substances by size exclusion chromatography and capillary electrophoresis. 2001.

10. **Andres Trikkel**. Estonian calcareous rocks and oil shale ash as sorbents for SO_2. 2001.

11. **Marina Kritševskaja**. Photocatalytic oxidation of organic pollutants in aqueous and gaseous phases. 2003.

12. **Inna Kamenev**. Aerobic bio-oxidation with ozonation in recalcitrant wastewater treatment. 2003.

13. **Janek Reinik**. Methods for purification of xylidine-polluted water. 2003.

14. **Andres Krumme**. Crystallisation behaviour of high density polyethylene blends with bimodal molar mass distribution. 2003.

15. **Anna Goi**. Advanced oxidation processes for water purification and soil remediation. 2005.

16. **Pille Meier**. Influence of aqueous solutions of organic substances on structure and properties of pinewood (*Pinus sylvestris*). 2007.

17. **Kristjan Kruusement**. Water conversion of oil shales and biomass. 2007.

18. **Niina Kulik**. The application of Fenton-based processes for wastewater and soil treatment. 2008.

19. **Raul Järviste**. The study of the changes of diesel fuel properties a its long term storage. 2008.

20. **Mai Uibu**. Abatement of CO_2 emissions in Estonian oil shale-based power production. 2008.

21. **Valeri Gorkunov**. Calcium-aluminothermal production of niobium and utilization of wastes. 2008.

22. **Elina Portjanskaja**. Photocatalytic oxidation of natural polymers in aqueous solutions. 2009.

23. **Karin Reinhold**. Workplace assessment: determination of hazards profile using a flexible risk assessment method. 2009.