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Water Conversion of Oil Shales and Biomass

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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.

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Põlevkivi ja biomassi vesikonversioon

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INTRODUCTION

For decreasing the dependence on imported oil-products it is essential to Estonia to find alternative opportunities for obtaining liquid fuels and chemicals from local feedstocks. Among Estonian natural resources there are both fossil and renewable fuels, represented by different kinds of oil shales and biomass. Both the fossilized organic matter (kerogen) accumulated in hundreds of million years into bowels of the earth and different kinds of lignocellulosic organic matter arisen only in some tens of years by photosynthesis are conversible to liquid products. The latter ones could be qualified as unconventional oil. Depending on the methods applied for thermochemical liquefaction the products more or less similar to oil with different yields can be obtained. Shale oil as oil substituent has been produced and used in Estonia already from year 1924. For production of shale oil there has been used industrially only method of semicoking, which is one of the versions of slow pyrolysis. In the course of this the oil shale is heated up to 500 °C without using solvent, so called dry pyrolysis. The mechanism of the Kukersite kerogen thermal decomposition has been accepted as follows (Aarna and Lippmaa, 1958) :

$$\text{Kerogen heating} \xrightarrow{350\ ^\circ\text{C}} \text{Thermobitumen} \xrightarrow{350\text{–}500\ ^\circ\text{C}} \text{Oil, gases, water, semicoke}$$

The process begins with the formation of high-molecular thermobitumen. Final products – oil as liquid product (LP), gas, and solid residue – in their majority form only after thermal decomposition of the primary thermobitumen as the intermediate. Small parts of oil and gas are formed simultaneously with the intermediate. Organic matter (OM) of oil shale contains less than 1% extractables (bitumens extracted by conventional solvents at the temperatures lower than 200^0C) besides the kerogen. Kukersite oil shale belongs to highly oxygenated caustobioliths. The oxygen supply is transferred into liquid and gaseous conversion products. Semicoking gas is characterised by a high concentration of carbon oxides, and in the composition of LPs different groups of compounds can be found as hydrocarbons, phenols and neutral oxygen compounds.

At semicoking the yield of LP – oil – is only 40-45% on the basis of kerogen. The rest is less calorific gas and hazardous semicoke (Urov and Sumberg, 1992).

Shale oil obtained by semicoking is separated in the vertical industrial retort as light- middle and 360^0C+ fractions. The share of the latter one makes up to 50% of the total retort oil. Besides the high proportion of the heavy oil the semicoking oil is especially rich in oxygen. Oxygen compounds are represented in the same amount as hydrocarbons. Also there are many alkenes, which are not represented in natural oil.

The solid residue of the process – semicoke – is a hazardous waste. Accumulated in enormous quantities in the landfills it is related to serious environmental risks.

The facts named above have made a challenge for new sustainable thermal destruction technologies for improving both the yield and the composition of liquid products from Estonian oil shale.

On the other hand, a variety of biomass resources can be used to convert energy (Ni et al., 2006; Akdeniz and Gündoğu, 2007; Goyal et al., in Press). They can be divided into four general categories:

1) Energy crops: herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops.

2) Agricultural residues and waste: crop waste and animal waste.

3) Forestry waste and residues: mill wood waste, logging residues, trees and shurb residues.

4) Industrial and municipal wastes: municipal solid waste, sewage sludge and industry waste.

Biomass (BM) consists of cellulose, hemicellulose and lignin, and a small amount of other extractives (Goyal et al., in Press; Hon, 1996; Heredia et al., 1995). Cellulose is a polymer, consisting of linear chains of 1,4-D-glucopyranose units, in which the units are linked 1-4 in the alpha-configuration, with an average molecular weight of around 100,000. Hemicelluloses are complex polysaccharides present in the cell wall, which consists of branched structures and vary with BM-s. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methylglucuronic and galaturonic acids, with an average molecular weight of <30,000. Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the certain BM, especially woody species, and are often adjacent to cellulose fibers to form a ligno-cellulosic complex. Lignin is regarded as a group of amorphous, high-molecular weight, chemically related compounds. The building blocks of lignin are believed to be a three-carbon chain attached to rings of six carbon atoms, called phenyl-propanes. In BM, cellulose is generally the largest fraction followed by hemicellulose and lignin. BM energy – the energy stored in plants, actually, originates from solar energy through the photosynthesis process. This energy can be recovered by burning BM as a fuel. During combustion, BM releases heat and carbon dioxide that was absorbed while the plant was growing, so the use of BM is the reversal of photosynthesis, carbon dioxide recycling. In contrast to fossil fuels, utilizing BM energy does not add extra carbon dioxide to the environment; besides, BM is the only renewable source of carbon and it can be converted into convenient fuels (Hon, 1996; Heredia et al., 1995; World Energy Council, 1994; Demirbas, 2001).

BM in its availability, variety, and abundance is a practically inexhaustible resource of feedstock for energy and chemical needs. BM is a term for all organic material that stems from plants (including algae, trees, and crops). The BM resource is also considered to be a combustible natural high molecular matter, in which the energy of sunlight is stored in chemical bonds (McKendry, 2002). Coals and oil shales could also be termed BM, since they are fossilized remains of higher plants and marine fauna that grew and lived tens and hundreds of millions of years ago. There are determinations where BM is generally defined as any hydrocarbon material, mainly consisting of carbon, hydrogen, and nitrogen, sulphur being also present in less proportions (Yaman, 2004).

As the energy density in BM is low, hence comes the necessity to increase it. The energy enclosed in different ingredients of terrestrial and aquatic plants as well as in technological and decaying residues of those and in other renewable resources of biological origin can be released either by direct use like in combustion or converted by thermochemical or biochemical upgrading into synthetic liquid and gaseous fuels or higher value products for the chemical industry. Semicoking, liquefaction and gasification of BM lead to the formation of liquid, gaseous, and solid products with higher energy density than the original.

The mechanism of semicoking of BM and fossilized organic matter like oil shale and the final products are notably similar. The thermal decomposition of BM begins with formation of a high-molecular intermediate, following decomposition of which gives oil, gas and solid residue. Simultaneously with the intermediates small parts of oil and gas are formed. Organic matter of BM also contains a small amount of extractables. BM is more oxygenated than Kukersite, usually containing up to 50% oxygen. The oxygen supply is also transfered into liquid and gaseous aim products and gas consists mainly of carbon oxides and the LPs contain the same groups of compounds as the LP obtained from Kukersite. Depending on the conditions used the yields of LP obtained on BM feed vary from 8% to 80% (Graham et al., 1984). It was demonstrated that practically at any temperature sufficient for BM decomposition a high LP yield can be obtained by varying solid and gas phase residence times.

Flash and fast pyrolysis LP obtained from wood in high yields has often been characterized as a dark and fairly viscous (10–55 cP at 70 °C) tarry liquid, having density around 1.2 g/ml and molar H/C ratio 1.46-1.70. Such LP obtained in yields 50-80% on woody feed by semicoking contains 30-50 wt.% oxygen, 15-20 wt.% water, 4-7 wt.% organic acids, and 10 wt.% char in suspension, water being dissolved in the oily phase as a constituent of the part that cannot be separated

(Gust, 1997). The higher the yield of LP, the higher its oxygen concentration. Therefore these liquids cannot be used as fuel and must be upgraded by further processing.

Depending on BM pyrolysis conditions charcoal in varied yields can be obtained. Compared to hazardous semicoke obtained from oil shale, charcoal is environmentally safe and requested product in the world. In slow pyrolysis the main product is specifically charcoal.

It should also be possible to produce the oil-like liquid from biomass, if to find the adequate conditions for thermochemical processing and using the same technology as for processing of oil shale and co-processing oil shale and biomass.

Hence the aim of this Ph.D is to work out an alternative method for expiring semicoking – thermal dissolution, to find suitable solvent, to carry out comparable liquefaction for Estonian fossil and renewable fuels, to obtain modified oils – with better composition than in semicoking. For this purpose there were carried out experiments with Kukersite oil shale kerogen as the most researched, in the presence of several superheated solvents: benzene, diethyl ether, ethanol, n-hexane, dimethyl ketone and water in order to find the most suitable solvent for both oil shales and BM. As the most oils obtained from BM by thermal destruction are water soluble and BM itself contains water, the liquefaction was carried out with supercritical water. Water conversion was made for two main Estonian oil shales: Kukersite and Dictyonema, and for two representatives of BM: pinewood and reed as the most typical for Estonia. As the products of water conversion were fractionated to gas, water soluble oil, benzene soluble oil, acetone soluble oil and solid residue. The benzene soluble fraction as the most valuable was separated thoroughly by thin layer chromatography and its composition was investigated by gas chromatographic and spectroscopic methods. Also there was carried out co-liquefaction of Kukersite and pinewood in order to investigate the bilateral interaction.

The present dissertation is base of the following papers, which are referred to in the text by their Roman numerals I-V.

I. Luik, H., Palu, V., Bityukov, M., Luik, L., **Kruusement, K**., Tamvelius, H., Pryadka, N. 2005. Liquefaction of Estonian Kukeriste oil shale kerogen with selected superheated solvents in static conditions. – Oil Shale, vol 22, no 1, p 25-36.

II. Veski, R., Palu, V., Luik, H., **Kruusement, K**. 2005. Thermochemical liquefaction of reed. – Proceedings of the Estonian Academy of Sciences Chemistry, vol 54, no 1, p 45-56.

III. Luik, H., Palu, V., Luik, L., **Kruusement, K**., Tamvelius, H., Veski, R., Vetkov, N., Vink, N., Bityukov, M. 2005. Trends in biomass thermochemical liquefaction: global experience and recent studies in Estonia. – Proceedings of the Estonian Academy of Sciences, vol 54, no 4, p 194-229.

IV. Luik, L., Luik, H., Vink, N., **Kruusement, K**., Veski, R. 2007. Thermochemical co-liquefaction of woody biomass and fossil fuel in supercritical water. – Proceedings of the International Conference held in Berlin, Germany, 7-11 May 2007 [DVD], p 1955-1959.

V. Veski, R., Palu, V., **Kruusement, K**. 2006. Co-liquefaction of Kukersite oil shale and pinewood in supercritical water. – Oil Shale, vol 23, no 3, p 236-248.

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1. LITERATURE REVIEW ON THE LIQUEFACTION AND GASIFICATION OF NATURAL FEEDSTOCKS

Energy conversion methods from feedstock are divided into the thermochemical methods (direct combustion, semicoking, pyrolysis, gasification and liquefaction) and the biological/biochemical methods (direct and indirect biophotolysis, biological water–gas shift reaction, photo-fermentation, dark fermentation, methane fermentation, alcoholic fermentration) (Qian et al., 2007; Ni et al., 2006; Goyal et al., in Press). In this work the thermochemical liquefaction methods were applied.

1.1.Thermochemical liquefaction methods

1.1.1. Pyrolysis

The oldest and industrially applied slow pyrolysis method since twenties of last century for obtaining oil from Kukersite is semicoking. Fast and flash pyrolysis regimes have been applied mostly for biomass. Pyrolysis like other thermochemical destruction processes yields also solid and gaseous products. At laboratory standard tests for semicoking of Kukersite in Fischer assay the feedstock is heated at the rate of 5 °C/min up to the final temperatur 520 °C and then isothermally for 20 minutes (ISO 647:1974). Semicoking of raw Kukersite gives 23.3% oil, 1.9% pyrogenetic water, 71.0% semicoke and 3.8% gas on the basis of dry matter (65.6%, 5.4%, 18.3% and 10.7%, on the basis of organic matter (OM)) (Urov and Sumberg, 1992; Arro and Klesment, 1984). The oil obtained in semicoking contains 8% fraction, boiling point up to 200 °C, 8% fraction, boiling point 200-250 °C, 10% fraction, boiling point 250-300 °C (Urov and Sumberg, 1992), and over 70% fraction, boiling point over 300 °C. The most characteristic components of shale oil are n-hydrocarbons and n-alcanones. If in destruction cracking of the first bond of the nucelus of kerogen occurs (α-cleavage), parafine is formed, in case of cracking of the second bond (β-cleavage) olefine is formed. So in semicoking oils odd-numbered parafines and even-numbered olefines are dominating (Klesment, 1984; Luik and Klesment, 1984). The oil is particularly rich in phenols and ketones. The phenols are predominantly of the resorcinol series (Mölder, 2004).

The oil-shale-processing industry in Estonia is facing some difficult choices despite all the riches of the Fischer assay method. The first one is to select the retorting technology to extract oil from raw oil shale. There are three possible technologies (Mölder, 2004):

1) processing in gravitational shaft retorts, so-called ’gas generators’. This process accepts only large-particle feed. The combustion products play the role of heat carrier. The yield of crude oil lies between 14 and 17% on raw shale basis. The oil contains only a small amount of low-boiling fractions. Solid residue – semicoke – contains 4-6% organic carbon. This causes environmental concern, as spent shale piles continue to leach toxic substances. Another drawback of this process is a large quantity of process water. The majority of oil-shale-originated resorcinol-series phenols end up in this water. Further processing of the water to extract phenols and decompose other toxic compounds is expensive.

2) the solid heat carrier (SHC) process uses a rotary kiln-type retort. Solid shale ash is used as the heat carrier. The process can accept shale fines. The oil yield is approximately 12% on raw shale basis. The oil contains 15-20% low-boiling fractions. The process produces only small amounts of phenol-contaminated water at low concentrations. Further processing of the water would be expensive. Most of the phenolic compounds generated in the retorting process remain in the oil and may be easily removed by water extraction. Carbon is burned out from spent shale in a special furnace. However, even the burning residue, so-called black ash, causes environmental concerns, as it contains some organic carbon and decomposable calcium sulphide.

3) the *Alberta Taciuk* process (ATP) uses also a rotary kiln-type retort and accepts shale fines. A combined retort-heating system is used: internal heating with shale ash and external heating with combustion gases generated from burning carbon available in semicoke. The oil contains up to 30% low-boiling fractions. The process produces only small amounts of contaminanted water with low concentration of phenols. When retorting Estonian oil shale, the ATP has been tested only in small-scale trials and the results are preliminary.

The second challenge is to decide what commercial products will be made from the raw shale oil and how (Mölder, 2004). The selection depends on the production method of oil. SHC and *Alberta Taciuk* processes produce oil rich in low-boiling fractions. These oils should be first upgraded by treating with hydrogen to remove sulphur, nitrogen and oxygen and to saturate the unsaturated hydrocarbons. If upgrading is not used, it is difficult to find a commercial market for fractions boiling below 200 °C. Upgraded oil, a light sweet crude, can be further processed like any crude petroleum. In this case, the main products are gasoline, kerosene and gas oils. The phenols could be removed from oil by water extraction before upgrading.

In semicoking oil there is quite big amount of aromatic compounds, despite this structure is not characteristic for sapropelites. The majority of aromatic compounds are forming during semicoking by the result of dehydrogenation of cyclohexanic structures. It’s known, that aromatisation runs easily in occurence of one olefinic bond in the cycle. This bond may occur already in kerogen or may be formed either by regrouping of hydrogen from the cycle to side chain which cleaves in the form of parafine or by dehydration of hydroxyl groups. The easiest way for forming of aromatic structures is tautomeric changing of cycloketones to phenolic ones (Klesment, 1984). As far the components of heavy fraction are less volatile and are hardly subject to gaschromatographic analysis, this fraction was investigated by pyrolysis (Luik and Klesment, 1984; Arro and Klesment, 1984). Also the composition of phenols formed by pyrolysis was investigated. In their structure occurence of majority of unbranched hydrocarbon chains was found. Comparing the semicoking oil fraction with lower boiling point and pyrolyse product of heavy fraction there was made a conclusion that the heavy fraction of semicoking oil functions as transfer product of incomplete destruction of kerogen.

Elemental composition of Kukersite is shown in Table 1.

Table 1. Elemental composition of Kukersite, % (Urov and Sumberg, 1992)

Object	C	H	N	O (from difference)	H/C atomic ratio
Kukersite	79.32	9.5	0.3	10.88	1.44

The residue of distillation of phenols constitutes the most polar part of semicoking oil (Luik and Klesment, 1984).

The stocks of fossil resources (mineral oil, gas and coal) in the world have essentially decreased during last three decades due to development of technics and the increasing of world population and urbanization, which cause more intensive consumption of these resources (Goyal et al., in Press). So the present era of a chemical industry based on fossil resources will gradually come to an end in the course of the 21st century as the stocks of fossil resources are finite (Karagötz et al., 2004). It was estimated that oil sources might be depleted till 2050. The process of obtaining energy from the fossil fuel sources caused atmospheric pollution, resulting in problems like global warming, acid rain etc (Goyal et al., in Press).

There have been made several researchworks in order to find alternative energy sources for fossil fuels from species of biomass or from the components of biomass (cellulose, lignin etc), converting them into methanol, ethanol, hydrocarbon fuels or hydrogen, getting more independent on exhaustible fossil energy resources (Kumabe et al., 2007; Akdeniz and Gündoğu, 2007). BM is being used from the ancient times as a combustion fuel for cooking, keeping warmth in houses etc. Biomass is available in abundance and is cheap and its better utilization is to convert it to energy rich products using suitable processes (Goyal et al., in Press). Biomass, which contributes about 10-14% of the world’s energy supply (in many developing countries 40-50% of total energy supply) today (Lu et al., 2006; Qian et al., 2007; Ni et al., 2006), as an energy source, has two striking characteristics. Firstly, biomass is the only renewable organic resource and is also one of the most abundant resources. Secondly, biomass fixes carbon dioxide in the atmosphere by photosynthesis. The use of biomass as energy source founds mostly on transfering it into gas (mostly hydrogen) (Ji et al., 2006; Furusawa et al., in Press) or liquid (Wang et al., in Press; Wang et al., 2007), because the energy density of biomass is lower than of fossil fuels.

Biomass, a diversified resource in its colossal majority is permanently regenerated directly or indirectly by plant growth, is generally of lignocellulosic nature. Unused biomass and reminders of biomass used as material or food accumulate as natural and processing wastes. The cost of such feedstocks often does not surpass transportation costs. Processes such as mining, flotation, drying, or assorting are usually not necessary in biomass procurement and further combustion or liquefaction. Hence, availability, productivity, renewability, sustainability, and similarity in main building blocks are the important factors making the use of biomass as a feedstock attractive.

Biomass as a feedstock can be successfully used for the production of synthetic liquid fuels similar to conventional petroleum fuels and non-petroleum chemicals. Biomass contains negligible amounts of sulphur and nitrogen and has a low ash content. Compared with fossil fuels, biomass generates far less harmful air emissions and its use will considerably reduce the amount of solid waste sent to landfills.

Conversion processing of biomass leads to the formation of fuels with a higher energy density than the original. Oxygen-containing chemicals can be separated as well. Water conversion is one of the methods often used in biomass thermal and thermochemical liquefaction. Operating at temperatures around 380 °C with water liquid products can be obtained in various yields and chemical compositions. Due to large amounts of oxygenated compounds present, the biomass-derived liquids have a polar nature and do not mix readily with hydrocarbons but they do mix with water and other polar solvents. This is one of the specific features of biomass-derived liquids compared with those originating from fossil fuels. As a result of effective reductive deoxygenation the yield of upgraded liquid products decreases proportionally with the decreasing oxygen concentration, which can be diminished to the level meeting transportation fuel specification.

It is obvious that deoxygenation, a strongly desired process, occurred intensively in water conversion in spite of feedstock under investigation was used though the oxygen concentration was reduced insufficiently – only by half. To furhter reduce the oxygen amount to achieve the concentration comparable with that in Kukersite shale oil (6-10 wt.%) and to enhance hydrocarbon yield, upgrading in a second stage seems unavoidable.

Pyrolysis of BM, according to the temperature, includes three principal stages as follows (Arpiainen et al., 1986):

1) below 300 °C – dehydrogenation processes; water and carbon oxides formation; charcoal is the main product;

2) 300-600 °C – fragmentation reactions, primary tar is the main product;

3) above 600 °C – depolymerization, cracking, and reforming reactions of primarily formed products and their reactions with free radicals; gas is the main product.

The other important parameter for pyrolysis after temperature, in particular in gas phase, is the residence time (Arpiainen et al., 1986). In the temperature region 450-600 °C preferably charcoal formation was noticed at lower heating rates while elevated heating rates and a short residence time in the same temperature region favoured tar yield. Temperature higher than 700 °C and a long residence time in the gas phase favoured tar cracking and gas formation. At a slow heating rate and low pyrolysis temperature (less than 10 °C/min and below 500 °C, respectively) formation of solid residue and liquid is favoured.

According to the heating rate pyrolysis is classified into slow pyrolysis, fast pyrolysis and flash pyrolysis. Slow pyrolysis is the main industrial technology used in liquefaction, gasification, semicoking and coking of fossil solid fuels – e.g. oil shale (Luik et al., 2006). The heating rate in slow pyrolysis is 5-7 °C/min (Luik et al., 2006; Ni et al., 2006; Goyal et al., in Press; Apaydin-Varol et al., 2007). This leads to less liquid and gaseous and more semicoke (char) production. For oil production from biomass by slow pyrolysis the most suitable temperature is 550-600 °C (Goyal et al., in Press).

In fast pyrolysis the biomass feedstock is heated rapidly (300 °C/min) in the absence of air, to form vapour and subsequently condensed to a dark brown mobile bioliquid (Goyal et al., in Press). Gaseous products include hydrogen, methane, carbon oxides and other gases depending on the feedstock. Liquid products include tar and oils containing components that remain in liquid form at room temperature like acetone, acetic acids etc. Solid products are mainly composed of char being almost pure carbon plus other inert materials.

Flash pyrolysis is the process in which the reaction time is only several seconds or even less, which requires that the particle size would be fairly small: 105-250 μm (Goyal et al., in Press). The heating rate is very high.

So, temperature, heating rate, residence time and type of catalyst used are important pyrolysis control parameters (Ni et al., 2006). High temperature, heating rate and long volatile phase residence time are required in order to favor to get more gaseous products.

The technical requirements for pyrolysis (e.g. high temperature, absence of air) make the process financially expensive. The low yield of oil and high quantity of oxyen compounds in the oil, as well as difficulties for gas chromatographic analysis and high content of organic matter in semicoke give challenge for more efficient liquefaction technology.

Investigations initiated in Estonia have focussed on working out the fundamentals of individual and co-processing of biomass and oil shales on the basis of not only the existing industrial facilities but also on those that have to be introduced to modify the oil shale industry in Estonia keeping space with scientific progress. The technologies applied allow obtaining liquid products close to shale-derived syncrude quality.

1.1.2. Thermal dissolution

In biomass liquefaction, biomass is heated 525-600 K in the presence of solvent under a pressure 5-20 MPa in the absence of air (Ni et al., 2006). Also catalyst can be added in the process. The disadvantages of biomass liquefaction are difficulty to achieve the operation conditions and low production of hydrocarbons. Therefore, liquefaction is not favorable for hydrogen production (Ni et al., 2006). For oil production from biomass water conversion is a good method (Watanabe et al., 2006; Feng et al., 2004a; Feng et al., 2004b). To avoid evaporation an increased pressure is necessary. The oil should have a low oxygen content and should be liquid under ambient conditions, because in this case, the hydrophobic oil spontaneously separates from water. The best-known method for concentrating wet biomass into oil is so-called 'hydrothermal upgrading' process, originally developed at Shell Research B. V. (Amsterdam). Treated in water at the aforenamed conditions biomass is depolymerised to a hydrophobic liquid product so called „biocrude“. Gases are also produced, consisting of CO_2, H_2, methane and CO. Other products include water and organic compounds (Feng et al., 2004a; Feng et al., 2004b). Some of the latters are oxygenated compounds, which lead to quality and stability problems (Akdeniz and Gündoğu, 2007). Indirect liquefaction methods convert lignocellulosic materials to a synthesis gas and then recombine components to form quality hydrocarbon fuel products that are free of oxygenated compounds (Akdeniz and Gündoğu, 2007).

Watanabe et al. (2006) researched oil formation from glucose with formic acid and cobalt catalyst in hot-compressed water. Liquefaction of glucose into oil was examined in hot-compressed water at 300 °C and 30 or 60 min in tumbling batch reactor. The effects of alkali ($KHCO_3$), an acidic agent (HCO_2H), and a cobalt catalyst (Co_3O_4) were studied. Also the combinations of these additives were investigated. HCO_2H and $KHCO_3$ showed a positive effect on oil formation. Co_3O_4 was found to be an advantageous additive as well, increasing the oil formation from glucose, but the stability of this catalyst under reaction conditions was quite low. The catalytic activity of Co_3O_4 worked as a solid base material under these conditions. In the presence of HCO_2H, oil formation was further increased by Co_3O_4.

Qian et al. (2007) liquefied silver birch by water in an autoclave in the reaction temperature range of 280-420 ^{0}C with sodium carbonate as the catalyst. The experimental results show the following:

1) Both yield and characteristics of heavy oil from woody biomass are dependent on the direct liquefaction conditions.

2) The maximum yield of the main liquefaction product (heavy oil), 53.3%, was obtained at reaction temperature 380 ^{0}C, when reaction temperature was higher or lower than this temperature, the heavy oil yield decreases.

3) The analytical results (by FTIR and GC/MS) show the heavy oil is complex compound that contains hydrocarbons, aldehydes, ketones, hydroxybenzene and esters.

Karagöz et al. (2004) explored the effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass (280 ^{0}C for 15 min) products in the presence and absence (thermal) of the bases by using an autoclave. Rb and Cs carbonates increased the conversion of wood from 58.3% to 84 and 88%, respectively. At the same time content of solid residue decreased from 41.7% to 12 and 16.2%, respectively. Catalytic hydrothermal treatment (Rb and Cs carbonates) of sawdust produced mainly phenolic compounds and benzenediol derivatives. In thermal case 4-methyl-phenol, 2-furan carboxaldehyde and 2-methoxy-phenol were major compounds. 2-Furan carboxaldehyde and 4-methyl-phenol were not observed in catalytic runs. The use of base catalysts hindered the formation of char and favored the formation of oil products.

Akdeniz and Gündoğdu (2007) analysed direct and alkali medium liquefaction of *Laurocerasus officinalis* Roem. Ground *Laurocerasus officinalis* Roem wood was liquefied in an autoclave with or without alkali additives such as Na OH and Na_2CO_3 at temperatures 523 ± 5 and 623 ± 5 K. The liquid products were extracted by a liquid-liquid extraction procedure using benzene, diethyl ether and 1-butanol as solvents. Maximum oil yields were obtained as 68.9% and 43.1% by using NaOH and Na_2CO_3, respectively at 3/5 alkali additive/sample ratios at 623 ± 5 K.

Hashaikeh et al. (in Press) investigated hydrothermal dissolution of willow in hot compressed water as a model for biomass conversion. The dissolution was carried out in the 200-350 °C temperature range. The process was studied using batch-type and a continous flow reactor. An overall 95% dissolution of willow was achieved. The lignin and hemicellulose in willow were fragmented and dissolved at a temperature as low as 200 °C and a pressure of 10 MPa. Cellulose dissolved in the 280-320 °C temperature range. A dissolution mechanism was proposed, which involves a rapid fragmentation and hydrolysis of lignin, hemicellulose and cellulose to form oligomers and other water-soluble products, such as glucose. The re-condensation behavior of the dissolved oligomers is the main challenge for efficient dissolution. A continuous flow process was more effective in this regard than a batch process.

Rezzoug and Capart (2002) applied thermal dissolution method for wood liquefaction. Ethylene-glycol or some recycled solvent was used for the solvolysis step, being limited by the acidity of reactant media and by the formation of a coke-like residue. A kinetic model of solvolysis was proposed accounting for the production of the coke-like residue. When using recycled solvolytic oil instead of fresh ethylene-glycol, the conversion into liquid was also reduced and the viscosity of the solution strongly increased. The step of hydrogenation was investigated by varying different parameters, i.e., the nature of the catalyst, the initial hydrogen pressure (30-60-90 MPa), the maximal temperature of plateau (from 330 to 400 °C) and the ratio tetralin/solvolytic oil. A slightly better deoxygenating rate was obtained by using a Ni-Mo bi-functional catalyst. The deoxygenation rate increased with the tetralin/solvolytic oil ratio and a minimum value of 0.5 for this ratio was necessary to prevent the unwanted formation of a solid residue. Also increasing the hydrogen pressure increased the removal of oxygen, independently on the type of tested catalyst. After hydrogenation, an upgraded oil was obtained with a heating value similar to that of a usual petroleum fuel, at oxygen content less than 2%.

Shui et al. (2006) investigated the effect of hydrothermal treatment of the extraction of coal in the CS_2/NMP mixed solvent. The extraction of four Chinese different rank bituminous coals with the carbon disulfide/N-2-pyrrolidione (CS_2/NMP) mixed solvent was carried out in room temperature. It was found that one of middle bituminous raw coal of the four coals gave more than 74% extraction yield, suggesting an associative structural model for the coal. The coals were hydrothermally treated under different conditions (10 g sample with 10 or 20 g water, with 0.1 or 5 MPa of pressurized nitrogen at room temperature, working temperature 423 and 513 K), and it was found that the extraction yields of the treated coals increased. FTIR measurements showed the removal of minerals after the hydrothermal treatment of coals suggesting the dissociation of the coal aggregation structure.

1.1.2.1. Supercritical fluid extraction (SFE)

Superheated and supercritical solvent, mainly water and aqeous solutions, have been effectively used in thermal decomposition and chemical transformation of a wide range of complicated organic molecules in areas as diverse as recycling of polymeric wastes, extraction of thermally unstable food constituents (with supercritical CO_2), synthesis of chemicals, and generation of liquid fuels from both natural and technological source materials (Luque de Castro et al., 1994; Smith, 2002; Siskin and Katritzky, 2000; Palma et al., 2001; Qu et al., 2003; Feng et al., 2004a; Demirbas, 2000; Sovová, 1994; Sovovà et al., 1994a and b; Sovovà, 2001; Temelli, 1992; Froning et al., 1990; Hwang et al., 1996; Borch-Jensen and Mollerup, 1997a and b and 1999; Borch-Jensen et al., 1994; Staby et al., 1994; Penninger and Rep, 2006). Thermal debituminization of the fossilized organic matter of kerogen and kerogen-like formations can also be significantly accelerated in the presence of solvents, and not only water but many other solvents can be successfully used in thermosolvolytical extraction and thermochemical conversion processes of fossilized and renewable high-molecular organic matter.

A supercritical fluid is a state where matter is compressible and behaves as a gas (i.e. it fills and takes the shape of its container), but has the typical density of a liquid (0.1-1.0 g/ml) and hence its characteristic dissolving power. A supercritical fluid can also be defined as a heavy gas with a controllable dissolving power or as a form of matter in which the liquid and gaseous state are indistinguishable (Luque de Castro et al., 1994).

Every matter has critical point, which could be defined as a point in the phase diagram which is determined by critical temperature (T_c) and critical pressure (P_c) above which no liquefaction of the matter will take place on raising the pressure and no gasification of the matter will come about on increasing the temperature. The latter property gives also a definintion of supercritical fluids: one that is above its critical pressure and temperature. Above T_c and P_c the density of liquid and gas are identical so they occur as a single phase. The region of pressures and temperatures above P_c and T_c is called supercritical region. The region bellow these values is called subcritical region (Luque de Castro et al., 1994).

Figure 1 summarizes the basic properties of supercritical fluids. First, the density of a supercritical fluid depends on the pressure and temperature to which it is subjected, even though it is always close to the typical values for the liquids. Hence the good dissolving properties of supercritical fluids, where the interactions between the fluids and solute molecules are strong.

Viscosity values of supercritical fluids lie between those of liquids and gases, which enables for the SF more favourable hydrodynamic properties than liquids have. On the other hand, very low surface tension allows SF to penetrate readily porous solids and packed beds.

The diffusion coefficients of solutes in supercritical fluids lie between those they display in liquids and gases. As the diffusion coefficients in supercritical fluids are higher than those in liquid, mass transfer is usually more favourable in supercritical fluids.

Good compressibility allows to vary density of fluid and by this parameter also solvent power.

In conclusion supercritical fluids are not neither liquids nor gases, but exhibit the properties of both them: high diffusivity and low viscosity of gases and density and solvent power of liquids.

In fact, the dissolving power of a supercritical fluid only approaches that of a liquid solvent at a high enough density. Also the maximum solubility in most liquids surpasses that in supercritical fluids. Even though supercritical fluids offer no advantage over liquid solvents in terms of dissolving power, some other properties of theirs make supercritical fluid extraction the ideal alternative to analytical leaching. Because solute diffusivities in supercritical fluids are typically higher than those of liquid solvents by one of magnitude and their viscosity is lower by one order of magnitude, their mass transfer properties are much more favourable than those of liquids. As a result, SFE is much faster than liquid extraction: a quantitative SFE can be finished in 10-60 min, whereas a liquid extraction usually takes from a few hours to several days.

The dielectric constant of supercritical water is much lower, and the number of hydrogen bonds is much lower and their strength is much weaker than those values of liquid water. As a result, supercritical water behaves like many organic solvents so that organic compounds have complete miscibility with supercritical water. Moreover, gases are also miscible in supercritical water, thus a supercritical water reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under conventional conditions (Lu et al., 2006; Calzavara et al., 2005).

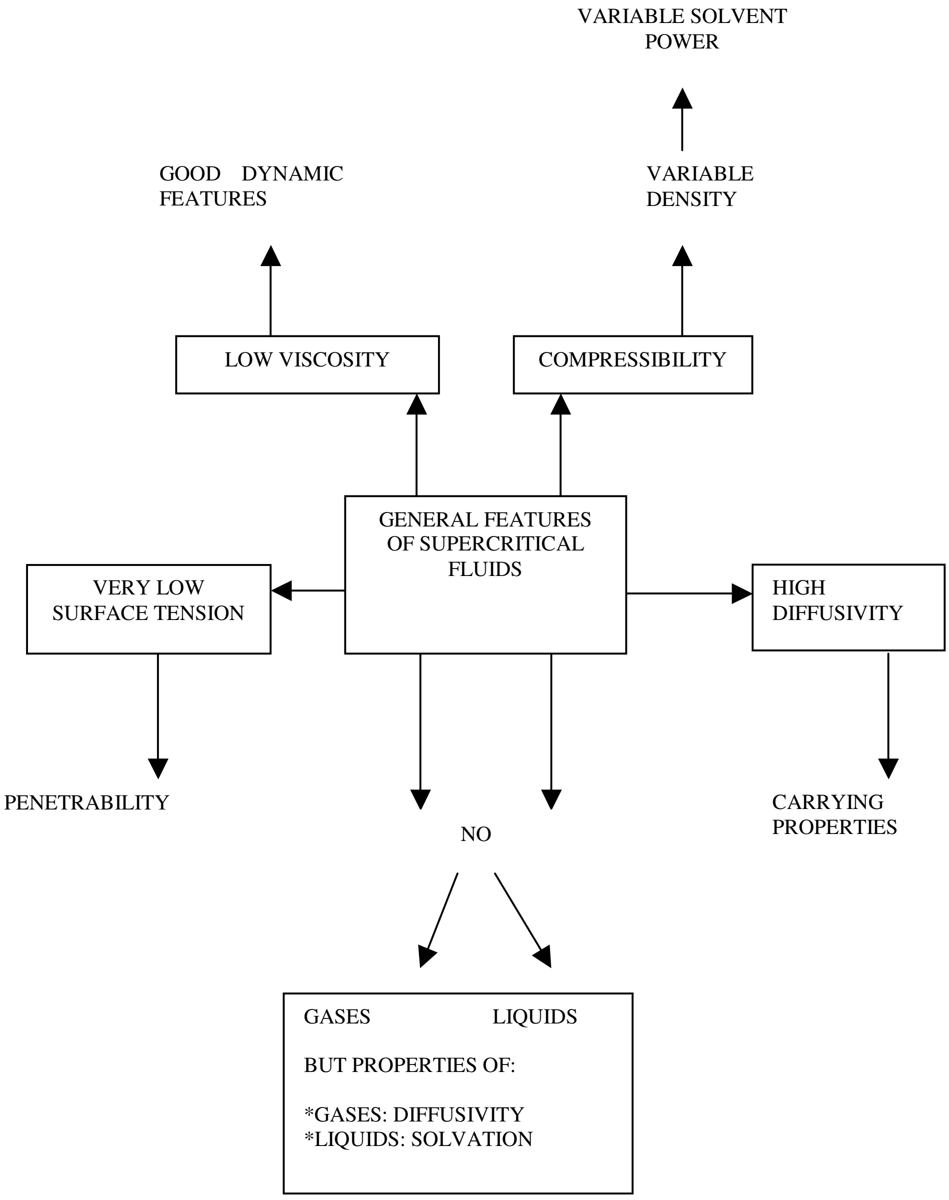

Figure 1. Most salient features of supercritical fluids

Critical pressure and critical temperature for most used solvents are listed in Table 2, as well as critical density (ρ_c) which could be defined as the fluid density at the critical point.

Table 2. Features of various solvents at the critical point

Solvent	Critical temperature (^{0} C)	Critical pressure (bar)	Critical density (g/ml)
CO_2	31,1	72	0,47
Diethyl ether*	193,6	63,8	0,267
n-Hexane*	234,2	28,9	0,23
Dimethyl ketone*	235	47,0	0,279
Isopropyl alcohol	235,3	47,6	0,273
Methanol	239	78,9	0,27
Ethanol*	243,4	72	0,276
Thetrahydrofurane	267	50,5	0,32
Benzene*	288.9	98.7	0.302
Toluene	319	41,1	0,292
Water*	374,2	214,8	0,32

* Applied in this work

1.1.3. Hydrogenisation

In hydrogenisation (hydroliquefaction) the feedstock is hold in the presence of pure hydrogen or hydrogen-rich solvent such as tetralin or hydrogen-rich gas such as syngas (Wang et al., in Press). The last one could be taken from outside or at first produce from the feedstock which is liquified, and then to use the syngas for production of liquid products

Wang et al. (In Press and 2007) investigated liquefaction of sawdust directly under syngas and studied the effects of temperature (200-350 °C), initial syngas pressure, reaction time, solvents (tetralin and toluene) and catalysts (Mo catalyst prepared by different methods). The results were also compared by product distribution and analyses of GC-MS, TG, IR and GPC. Sawdust loaded with 1 wt.% Mo catalyst was liquefied in a 250 ml autoclave at 300 °C, initial gas pressure 2.0 MPa and reaction time of 30 min in attempt to produce more liquid fuels. The effects of different catalysts preparation methods including mechanical mixing, impregnation and ultrasonic treatment with or without solvents on liquefaction were compared. The effect of atmosphere and temperature was also examined. It was found that tetralin as hydrogen donor solvent showed remarkable effect than either toluene as non-hydrogen donor solvent or without presence of solvent and its hydrogenation ability was much higher than gaseous hydrogen. Non-donor solvent increased remarkably the yield of preasphaltene (PA) and asphaltene (A) and decreased the gas yield. Among various atmospheres H_2 displayed higher activity than syngas and both of them were better than Ar and CO, while CO did not give the favorable influence. With increasing temperature and reaction time (10-30 min) the oil yield increases, while less effect with increasing initial syngas pressure. The thermal decomposition of sawdust to form PA + A was a fast step, while longer reaction time was necessary for conversion of PA + A to oil as the 2nd step. The results also indicated that syngas can replace hydrogen in sawdust liquefaction. The highest yield of oil and the lowest yield of PA + A were obtained using the sample loaded catalyst with ultrasonic treatment than those with impregnation or mechanical mixing no matter with or without solvents due to the well dispersion of the catalyst. Solvent, especially a hydrogen donor, played an important role in sawdust liquefaction, while gaseous hydrogen itself displayed less action in promoting hydrogenation reaction and enhancing catalyst ability. Gaseous hydrogen and catalyst do show signifficant functions in the presence of solvent. Higher temperature was favorable of thermal decomposition, hydrogenation and hydrocracking reactions. Based on the experimental results, a two-step liquefaction mechanism was proposed. BM liquefaction was roughly divided into two steps: the formation of PA + A as well as residue 1 by thermal decomposition of BM as the first step and conversion of PA + A and residue 1 into oil and gas by hydrogenation/hydrocracking reactions or into gas 2 and residue 2 by polycondensation as the second step.

At certain conditions (600 °C and over critical pressure) supercritical water acts as hydrogen donor due to decomposition. Oxygen atoms are transferred to the carbon atoms of the feedstock, forming carbon oxides. The hydrogen atoms of water can form H_2 (Feng et al., 2004a and b) or react with the feedstock. The latter phenomenon can be used for hydrogenation.

1.2. Gasification and combustion

Feedstock can be gasified at high temperatures (above 1000 K) (Ni et al., 2006). The feedstock particles undergo partial oxidation resulting in gas and charcoal production. The charcoal is finally reduced to form hydrogen, carbon oxides and methane. This conversion process can be expressed as follows:

$$\text{Biomass} + H_2O \xrightarrow{t^\circ} H_2 + CO + CO_2 + CH_4 + \text{light and heavy hydrocarbons} + \text{char}$$

Unlike pyrolysis and liquefaction, gasification of solid feedstock is carried out in the presence of oxygen. The gases produced can be steam reformed to produce hydrogen and this process can be further improved by water−gas shift reactions.

As a large portion of biomass is wet biomass containing up to 95% water and this wet biomass causes high drying costs if classical gas-phase gasification or liquefaction process is used. Using supercritical water for those purposes these high costs could be avoided (Lu et al., in Press; Feng et al., 2004a and b; Yan et al., 2006; Furusawa et al., in Press; D’Jesùs et al., 2006; Ni et al., 2006). At the temperature and pressure higher than the critical point of water it becomes a strong oxidant, and oxygen in water can be transferred to the carbon atoms of the biomass (Feng et al., 2004a and b; Ni et al., 2006). Biomass reacts with water according to the ideal reaction:

$$C_6H_{12}O_6+6H_2O \rightarrow 6CO_2+12H_2$$

The expected advantages of gasification in supercritical water compared to atmospheric pressure gasification processes, are the following:

1) The homogenous medium, which is supercritical water, allows to lower the impact of resistance caused by transport phenomena in a heterogenous reaction.

2) The high solid conversion, i.e. a low level of organic compounds and low level of solid residue, has crucial importance when considering the effect of the residual chars and tars on continuous reactors.

3) Hydrogen is produced at thermodynamic equilibrium due to the operating conditions, which means higher conversion yields and higher proportion of hydrogen in the formed gas phase.

4) The hydrogen is produced at high pressure directly, which means a smaller reactor volume and a lower energy to pressurize the gas in a storage tank (Calzavara et al., 2005).

However, in the real case, all of the biomass does not react with supercritical water, although its reactivity is higher in this specific medium than in atmosphere pressure steam (Calzavara et al., 2005). Every organic molecule is not transformed into hydrogen and carbon dioxide. Significant amounts of tars and chars can be formed during the reaction. This shift from thermodynamic expectations could be reduced by the use of catalyst.

Ji et al. (2006) found appropriate operating conditions for hydrogen purification and recovery in supercritical water gasification of biomass. The gas product from biomass gasification in supercritical water (at >600 ^{0}C and 300 bar) contained about 55% H_2 and 33% CO_2 in mole fraction. Also there were CH_4 and CO. As hydrogen was the target product, it needed to be purified. Water was used as solvent for purification of hydrogen by separating CO_2 and other gases from the gas product. These gases dissolved into the water phase, and the hydrogen went into the vapour phase and was purified. The room temperature of 25 ^{0}C was suggested as the appropriate operating temperature for the hydrogen purification in the high-pressure separator.

Combustion is the direct burning of fossil fuels and biomass in air to convert the chemical energy of their OM into heat, mechanical power or electricity using equipment such as stoves, furnaces, boilers or steam tuebines, respectively (Ots, 2006; Ni et al., 2006; Goyal et al., in Press). In most of the cases the process requires some pretreatment like drying, chopping, grinding, etc., which in turn is associated with financial cists and energy expenditure (Goyal et al., in Press).

1.3. Review on the feedstocks applied

The fossil and renewable objects chosen for this Ph.D thesis were two Estonian oil shales: Kukersite and Dictyonema, and pine sawdust and reed as the representatives of typical and most available biomass. These biomass forms were chosen as the most typical in Estonia and due to their inexhaustibility.

1.3.1. Kukersite

By its genesis Kukersite oil shale is sedimentary rock (Eesti maapõuerikkusi, 1993). It is one of the richest burning matter by OM: 35-50% on the basis of dry matter (Urov and Sumberg, 1992). The OM of Kukersite consists of remainders of microscopic algae *Gloeocapsomorpha prisca*. Occurrence of the remainders of fossils like trilobites, graptolites etc is characteristic for the OM of Kukersite. The content of heteroatoms in OM is 12.9%. The *in situ* formation of the OM of Kukersite has allochtonic origin. From the geological viewpoint it is quite possible that the formation of allochtonic shales could take place not only via transport by water essentially simultaneously with its formation as it possibly happened during the formation of Kukersite, but also as a result of a later alluvial deposition of the OM into the preformed deposits of shale (Urov and Sumberg, 1999). On the other hand, the insignificant solubility of the OM of oil shales in low-boiling organic solvents (benzene, chlorogorm, etc.) appears to be an important distinguishing property as it allows to differentiate typical (pyrobituminous) oil shales from the rocks impregnated with organic compounds that are essentially soluble (natural asphalts, oil sands, etc.)

1.3.2. Dictyonema

The content of OM in Dictyonema is 10-20% (Eesti maapõuerikkusi, 1993; Urov and Sumberg, 1992). Compared with Kukersite the organic matter in Dictyonema contains more heteroatoms: 22.1% (Urov and Sumberg, 1992).

1.3.3. Pinewood

The resources of pinewood (*Pinus sylvestris*) in Estonia are 642.8 millions cubic meters of solid volume (Statistical Yearbook of Estonia, 2002). Pinewood consists of 45-52% cellulose, until 20% hemicellulose, unil 30% lignin and under 10% solvent extractables and minerals (Saarman, 1998; Rustamov et al., 2002).

1.3.4. Reed

Reed (*Phragmites communis*) is a tall perennial grass of the family Poaceae that grows in both salt and freshwater marshes, in swamps, ditches, and along shoreline around the world. In Estonia: 26 000 ha in total (Kask, L. and Kask, Ü., 2003). OM of reed contains 27.1% lignin, 15.5% α-cellulose, and 43.3% cellulose.

1.3.5. Application of fossil fuels and renewables

Due to the origin of OM in oil shales they can be also qualified as fossilized biomass. As Kukersite contains more OM than Dictyonema, it is used for energy production in Estonia. The main consumers of Kukersite are heatpower stations where there are used 12-15 millions tons annually (Statistical Yearbook of Estonia, 2002). Also shale oil and gas are produced from Kukersite. From crude oil there have been produced heating oil, petrol, diesel fuel, epoxide resins, bitumens etc. Dictyonema has still not been used industrially, but as there are about 50 milliards of tons Dictyonema resources – about 50 times more than Kukersite in the bowels of the earth, it could be alternative for Kukersite in energy and oil production.

The main application for pinewood is its usage in building of houses, but application of pinewood wastes is direct combustion with the purpose of heating. Reed has been mostly used in making of roofs for houses. As both pinewood and reed are profoundly lignocellulosic, their resources are inexhaustible and so they afford alternative to oil shales for oil production.

2. EXPERIMENTAL PART

2.1. Feedstocks

Table 3 and 4 summarize the characteristic compositions of the objects. Moisture was measured by drying 2 h at 105 °C. Ash was measured by ignition 2 h at 825 °C. Carbonates were determined by processing with hydrochloric acid. Elemental composition was determined with Elementar Vario EL Analyser.

Table 3. Feedstocks' chemical composition, %

	Moisture	Ash (A^d)	Carbonate $(CO_2)^d$	Organic matter (OM)
Kukersite	0.6	37.2	12.8	50.5
Dictyonema shale	1.4	81.2	0	16.0
Pine sawdust	9.1	0.4	0	99.6
Reed	7.5	3.0	0	97.0

Table 4. Feedstocks' elemental composition, % OM based

	C	H	N	O^*	H/C	O/C
Kukersite	79.32	9.5	0.3	10.88	1.44	0.10
Dictyonema shale	73.02	9.19	2.66	15.13	1.51	0.16
Pine sawdust	50.22	7.12	0.14	42.52	1.70	0.64
Reed	43.74	6.50	0.62	49.14	1.78	0.84

*Calculated by difference

2.2. Analytical methods

2.2.1. Ultimte analysis

Oil fractions obtained from feedstocks were analysed for C, H, N, and S elemental composition using an Elemental Vario EL Analyser. Oxygen was determined by the difference.

2.2.2. Infrared Spectroscopy

Infrared (IR) spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole.

The far IR (1000-30 µm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-IR (30-1.4 µm), may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, (1.4-0.8 μm), can excite overtone or harmonic vibrations.

The IR spectra of a sample is collected by passing a beam of IR light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelenhth (or frequency). This can be done with a monochromatic beam, which changes in wavelengths over time by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance of absorbance spectrum is produced, showing at which IR wavelenghths (or frequencies) the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample; so every functional group has its own absorbance.

In this thesis IR spectra were taken on an Interspec 2020 spectrometer.

2.2.3. Thin layer chromatography

Liquid products were separated by preparative thin layer chromatography (TLC). For this there were used plates 24 X 24 cm coated with a silica gel 40 (2 mm) layer. For analyse there was taken 0.5 g sample, which is spotted near the bottom of this plate, and n-hexane was used for eluent. The plate was placed into a shallow pool of the eluent in a developing chamber so that only the very bottom of the plate was in the liquid. The principles of TLC are as follows. The eluent is the mobile phase, which slowly rises up tp the plate by capillary action. As the solvent moves past the spot that was applied, an equilibrium is established for each component of the sample between the molecules of that component which is adsorbed on the solid and the molecules which are in solution. These components will differ in solubility and in the strength of their adsorption to the adsorbent and some components are carried farther up the plate than others. When the solvent has reached the top of the plate, the plate is removed from the developing chamber, dried, and the separated components of the sample were visualized. If the components are colored, visualization is straightforward. Usually the compounds are not colored, so a UV lamp is used to visualize the plates. (The plate itself contains a fluor which fluoresces everywhere except where an organic compound is on the plate).

In TLC, the stationary phase is polar, and the polarities of both the component of the sample and the solvent used as the mobile phase are the determing factors in how fast the component travels.

Since these factors are difficult to keep constant from experiment to experiment, relatively Rf values were considered. "Relative Rf" meant that the values are reported relative to a standard, or it meant that the Rf values of compounds run are compared on the same plate at the same time.

The larger an Rf of a compound, the larger the distance it travels on the TLC plate. When comparing two different compounds run under identical chromatography conditions, the compound with the larger Rf is less polar because it interacts less strongly with the polar adsorbent on the TLC plate.

The sample was devided by polarity into 5 groups: 1) non-aromatic hydrocarbons, 2) monoaromatic hydrocarbons, 3) polyaromatic hydrocarbons, 4) low polar heteroatomic hydrocarbons, 5) high polar heteroaromatic hydrocarbons. The last ones (the most polar) remain on the startline. The groups were extracted with diethyl ether and their amount was determined by weighting. TLC fractions, were analysed by gaschromatography. The content of asphaltenes in benzene-solubles are determined as the share of insoluble in n-hexane compounds.

Phenols were extracted from the liquid products with 10% sodium hydroxide.

2.2.4. Gas chromatography

Gas chromatography (GC) is a chromatographic technique that can be used to separate volatile organic compounds. Gas chromatography – especially gas-liquid chromatography – involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.

A gas chromatograph consists of a flowing mobile phase, an injector port, a separation column containing the stationary phase, and a detector. The organic compounds are separated due to differences in their partitioning behaviour between the mobile gas phase and the stationary phase in the column.

Mobile phases are generally inert gases such as helium, argon, or nitrogen. The injection port consists of a rubber septum through which a syringe needle is inserted to inject the sample. The injection port is maintained at a higher temperature than the boiling point of the least volatile component in the sample mixture. Since the partitioning behaviour is dependent on temperature, the separation column is usually contained in a thermostat-controlled oven. Separating components with a wide range of boiling points is accomplished by starting at a low oven time to elute the high-boiling components. Most columns contain a liquid stationary phase on a solid support. Separation of low-molecular weight gases is accomplished with solid adsorbents.

GC columns are of two designs: packed or capillary. Packed columns are typically a glass or stainless steel coil (typically 1–5 m total length and 5 mm inner diameter) that is filled with the stationary phase, or a packing coated with the stationary phase. Capillary columns are thin fused-silica (purified silicate glass) capillary (typically 10-100 m in length and 250 µm inner diameter) that has the stationary phase coated on the inner surface. Capillary columns provide much higher separation efficiency than packed columns but are more easily overloaded by too much sample.

The thermal-conductivity (TCD) and flame-ionization (FID) detectors are the two most common detectors on commercial gas chromatographs. The requirements of a GC detector depend on the separation application. For example, one analysis might require a detector that is selective for chlorine-containing molecules, another analysis might require a detector that is non-destructive so that the analyte can be recovered for further spectroscopic.

The FID is extremely sensitive with a large dynamic range, its only disadvantages is that it destroys the sample.

An FID consists of a hydrogen/air flame and collector plate. The effluent from the GC column passes through the flame, which breaks down organic molecules and produces ions. The ions are colleted on a biased electrode and produce an electrical signal. The FID is extremely sensitive with a large dynamic range. Its only disadvantage is that it destroys the sample.

The TCD is not as sensitive as other detectors but it is non-specific and non-destructive. Two pairs of TCDs are used in gas chromatographs. One pair is placed in the column effluent to detect the separated components as they leave the column, and another pair is placed before the injection or in a separate reference column. The resistances of the two sets of pairs are then arranged in a bridge circuit. The bridge circuit allows amplification of resistance changes due to analytes, passing over the sample thermoconductors and does not amplify changes in resistance that both sets of detectors produce due to flow rate fluctuations.

The ECD is a sensitive as the FID but has a limited dynamic range and finds its greatest application in analysis of organic molecules that contain electro-negative functional groups, such as halogens, phosphorous, and nitro groups.

Gas chromatograph Chrom 5 (completed with integrator CI 100A) with programming was used for determination of the individual composition of aliphatic hydrocarbons, isolated by TLC. The conditions applied for gas chromatography are given in Table 5.

Table 5. Conditions for gas chromatography

Column	25 × 0.2 mm fused silica
Stationary phase	Methyl silicone (cross-linked) (OV–101)
Carrier gas	Helium
Detector	Flame ionization
Detector temperature	170°C
Injector temperature	230°C
Temperature programming	25-350 °C

Individual composition of gaseous compounds was analysed by GC in packed columns (molecular sieves, sepharon) under isothermal conditions.

2.3. Procedure of thermal dissolution

Papers I, II, III, IV, V

For liquefaction of feedstocks there was chosen thermal dissolution in supercritical conditions. As at first it was necessary to find optimal solvent for both oil shale and biomass, there were carried out experiments with Estonian Kukersite oil shale kerogen (kerogen-70) in the presence of following solvents: benzene, diethyl ether, ethanol, n-hexane, dimethyl ketone and water.

The features of the solvents at their critical point are presented in Table 2. The liquefaction process was carried out in batch autoclave (Fig. 2), volume of which was 500 cm^3, variable temperature (maximum 400 °C) and pressure maximum 40 MPa. The autoclave is supplied with manometer, thermocouple and gas valve. The autoclave was filled with sample and solvent at room temperature, sample-to-solvent ratio (wt.%) 1 : 3 (60 g : 180 g). After filling the autoclave it was placed and fixed into electric heater, which was by lever connected to electric engine, thanks to which all the system rocked. In every 5 minutes starting from switching on of the heater pressure (measured to an accuracy of ± 2%) and temperature (measured to an accuracy of ± 5 °C) were fixed. The time account of process started as soon as 380 °C was reached. The pressure vs. time diagramm is shown in Figure 3. Duration of the process was 4 h. At the end of the process the heater was switched off and the autoclave was cooled down to room temperature, the residual pressure was fixed, the gas valve was opened and gaseous products were captured in a gas receiver, measured and analysed.

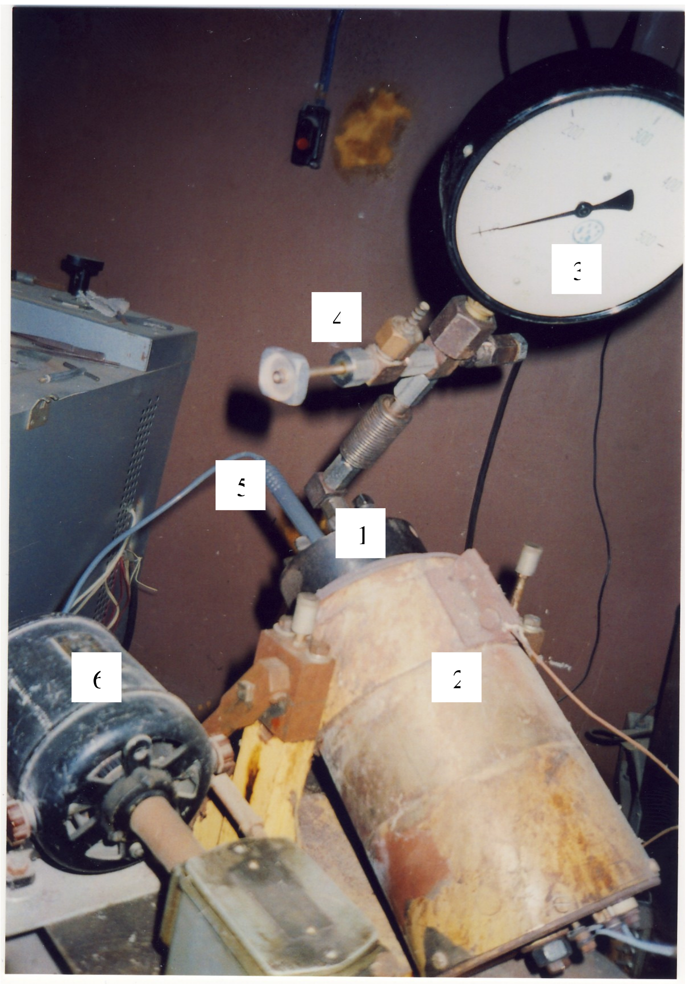

Figure 2. Rocking autoclave in heater: 1 – autoclave, 2 – heater, 3 – manometer, 4 – gas valve, 5 – thermocouple, 6 – electric engine for rocking

The pressure vs. time diagram in Fig. 3 represents water conversion generally. The respective curves of Kukersite, Dictyonema, pinewood and reed individually differ in the fluctuating amplitude ±5% only.

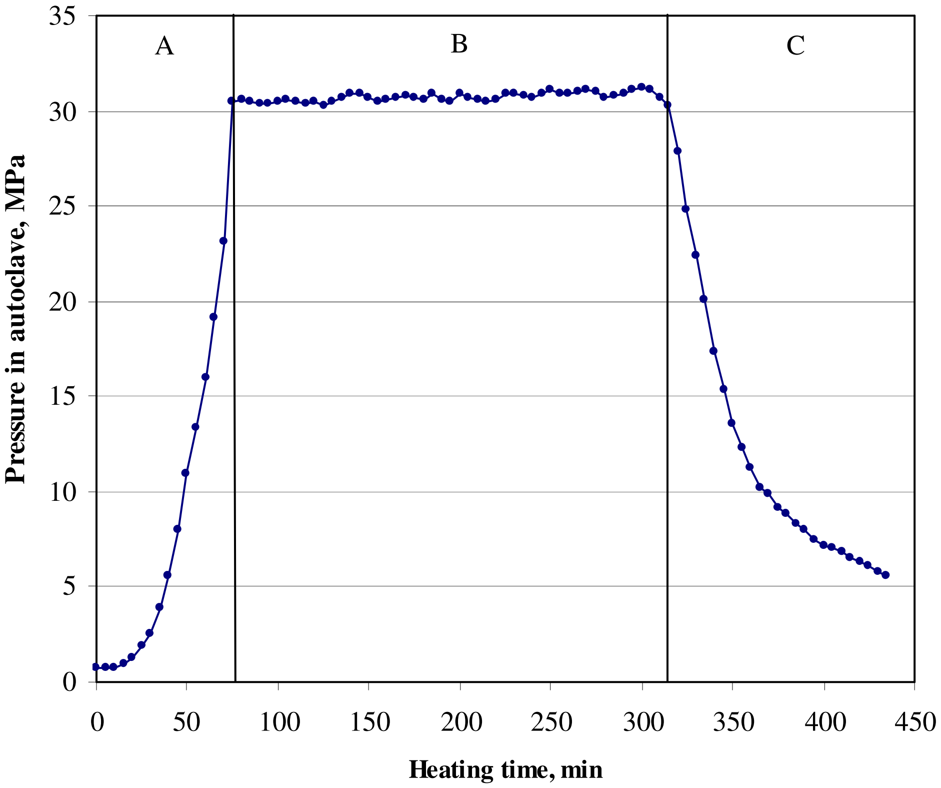

Figure 3. Pressure versus conversion time: A – temperature rise from ambient to 380 °C, 75 min; B – temperature constant, 240 min; C – temperature drop from 380 °C back to ambient, 120 min

Liquid and solid products remaining in the autoclave were diluted with benzene, and the liquid products were separated from solid ones by filtration. The yield of liquid was determined as the amount of benzene-soluble compounds.

3. RESULTS AND DISCUSSION

All the results and their discussion concerning this Ph.D work have been published and added in Appendix 1. So, only the main results obtained will be described below.

3.1. Results of liquefaction of Kukersite oil shale kerogen

Paper I

Yields of liquid, solid and gaseous products obtained are given in Table 6.

Table 6.Yield of liquefaction products, mass %, on kerogen concentrate organic matter basis

No.	**Solvent**	**Products**		
		Liquid	Gas	Solid
1	Benzene	81.5	3.5	13.4
2	Diethyl ether	106.3	134.9	0.1
3	Ethanol	99.0	27.6	0.5
4	n-Hexane	72.8	8.6	16.7
5	Dimethyl ketone	145.7	19.3	0.3
6	Water	69.6	14.5	16.0

The yields of single products were determined by direct weighting. The sum differs from 100% due to direct determination of the products, and/or incorporated solvents. The data in table show exceptionally high yields of liquid and gaseous products in several cases, surpassing the total liquid or gas generation potential of kerogen. The yield of liquid product was in all cases, despite the solvent used, higher than that at semicoking (66%), being 69-145%, on the basis of organic matter weighted into the autoclave. Gas yields calculated by the same way varied in a large range – 4-135%.

So, the data in table show very marked effect of not only solvent's solvolytical power but just its stability qualities and chemical activity towards kerogen and kerogen liquefaction products during the liquefaction process. Data in Table 7 indicate the decomposition of some of the solvents used.

Forming chemically active fragments begin to react with kerogen and kerogen fragmentation products incorporating into liquid, gaseous and even solid products finally formed. So, chemically modified final products can be obtained depending on the type of superheated solvent used.

Table 7. Gas yield, on (kerogen concentrate organic matter + solvent) basis, and solvent recovery, mass%

Superheated solvent			Gas
Used (120 g = 100%)	Recovered	Transformed*	
Benzene	99.5	-	0.7
Diethyl ether	52.1	0.4	26.4
Ethanol	74.0	1.7	5.4
n-Hexane	98.2	-	1.7
Dimethyl ketone	72.9	-	3.8
Water	100.2	-	2.8

*Liquids insoluble in parent solvent were determined

Solvents used are partially or completely soluble mutually and with transformed ones. Besides, diethyl ether, n-hexane and dimethyl ketone are volatile at room temperature already. Being blended and repeatedly submitted to evaporation, condensation and other chemical separation techniques causing losses at every stage, the amounts of solvents recovered or transformed are not reliable enough for precise material balances, but urgently needed to give insight into general tendencies. Basing on the data in Tables 6 and 7, hydrocarbon-type solvents as benzene and n-hexane seem to maintain their stability and inertia even at superheated state and do not react with kerogen structural elements. After evaporation those solvents are recovered as benzene or n-hexane only. Differences in the liquid product and gas yields have been caused by differing solvolytical and destructive power of superheated benzene and n-hexane under the conditions created.

The market of liquid fuels and solvents should judge the benefit from the waste of a solvent to increase the liquid yield at liquefaction of kerogen.

In the experiments with different solvents benzene was used both as solvent for separation of liquid products and as one of the superheated solvents. To compare solvolytical efficiency of benzene with other superheated solvents, the benzene-soluble liquid product was dissolved once more at room temperature in the solvent used at kerogen liquefaction (Tab. 8).

The data in Table 8 indicate that the solubility of liquid products in the solvents used at their formation during thermosolvolytical liquefaction is uncomplete varying between 12.2-77.6%, being lowest for water and highest for dimethyl ketone. The similar regularities can be observed in Table 6. The most unexpected results concerning benzene-soluble liquid products are their poor solubility in ethanol, and, in particular, high yield of hydrophilic compounds obtained at liquefaction with superheated water. The content of water-soluble acids and alkalis in kukersite shale oil, hydrogenisate or thermal dissolution oils is usually low, and mainly water-soluble phenols are presented.

Table 8. Solubility of benzene-soluble liquid products in the parent superheated solvent used at liquefaction in its state

No	**Superheated solvent used at liquefaction**	**Solubility in the parent solvent, mass %**
1	Benzene	100.0
2	Diethyl ether	57.3
3	Ethanol	31.7
4	n-Hexane	55.0
5	Dimethyl ketone	77.6
6	Water	12.2

Data in Tables 6 and 8 demonstrate that benzene, compared with other solvents used, is actually an extra-effective solvent to remove liquid products obtained at kukersite kerogen liquefaction from the solid residue.

3.1.1. Group composition of liquid products

Group composition of liquid products is presented in Table 9.

Table 9. Chemical group composition of liquid benzene-soluble products (mass%) obtained from Kukersite kerogen using various superheated solvents at 360 ^{0}C

Solvent	Compound groups						
	Asphaltenes*	High polar heteroatomic compounds	Oxygen compounds		Hydrocarbons		
			Neutral	Acidic**	Aromatic		Aliphatic
					Poly-	Mono-	
Benzene	45.6	23.7	10.4	1.4	10.3	2.4	6.2
Diethyl ether	48.8	21.4	10.0	3.2	8.8	0.4	7.4
Ethanol	36.1	31.2	10.8	1.9	9.5	2.7	7.8
n-Hexane	45.0	24.7	8.4	1.4	11.3	2.0	7.2
Dimethyl ketone	31.0	22.2	23.5	4.0	10.9	2.9	5.6
Water	37.3	36.2	7.0	4.7	2.7	1.3	10.8

* Insoluble in n-hexane

** Phenols extracted by 10% sodium hydroxide

Irrespective of solvent used the benzene-soluble compounds separated are characterized by very little flowability in normal conditions caused by high content of bituminous fractions – asphaltenes and high-polar heteroatomic compounds – the constituens forming almost 70% of the total liquid. The highest content of bituminous fractions was fixed in the liquid product obtained in aqueous medium (73.5%), but exceptionally low content of those fractions was found in the product obtained in dimethyl ketone (53.2% only) thanks to incorporation of the solvent in lower fractions. By physical and chemical qualities and chemical composition, the liquid products obtained are similar to thermobitumen – the primary product of kukersite kerogen pyrolytical decomposition, whose formation begins at 250 ^{0}C already, and whose decomposition is observable over 350 ^{0}C. Depending on the type of solvent used the velocities of not only thermobitumen formation but also of its decomposition (oil formation) differ determining solvent efficiency. Asphaltenes and a part of high-polar compounds obtained at thermal dissolution are similar to those in thermobitumen, and are characterized as primary fragments of not completely decomposed kerogen. The compounds being susceptible to temperature and solvent action, yield secondary products typical of semicoking oil on further decomposition.The latters belong to less- or non-polar compounds and are aliphatic and aromatic hydrocarbons, neutral oxygen compounds and phenols. So, the higher the ratio of maltenes-to-bituminous fractions, the higher the decomposition degree of thermobitumen, and the higher thermosolvolytical destruction power of the solvent towards both kerogen and thermobitumen, resulting in oil formation. The solvents used can be arranged by their destructive power towards kerogen as follows: dimethyl ketone (0.88) > ethanol (0.49) > benzene (0.44) > n-hexane (0.43) > diethyl ether (0.42) > water (0.36).

The regularities demonstrated in Table 6 show that solvent attacks not only kerogen, but subsequently, high-molecular fragments in thermobitumen formed from kerogen.

Thermobitumen decomposition degree depends on both pyrolysis temperature and time. In the experiments with different solvents these parameters were unified: 360 °C and 4 h in all experiments, but different solvents in equal quantities were added resulting, nevertheless, in individual and different decomposition degree of thermobitumen.

The regularity indicates that the different solvents act differently. Based on the data in Table 9 one can assert that thermobitumen having been formed in also to maximum yields, was not subjected to significant conversion. The total yield of asphaltenes and high-polar compounds as thermobitumen constituents, measured in most cases 67-74%, indicates that thermobitumen decomposition had not been complete in the experimental conditions used. That fact is confirmed by low content of acidic oxygen compounds (1-5% only), being usually 25% in semicoking oil which is a thermobitumen decomposition product as well. Low phenol content in the liquid benzene-soluble products obtained indicates that phenols form in final stages of thermobitumen decomposition.

The content of neutral oxygen compounds and hydrocarbons did not achieve even a half of that present in semicoking oil (except liquid product obtained in superheated dimethyl ketone medium) indicating their sufficient reserve in nondecomposed thermobitumen.

The data in Table 8 indicate that the solubility of liquid products in the solvents used at their formation during thermosolvolytical liquefaction is incomplete varying between 12.2-77.6%, being lowest for water and highest for dimethyl ketone. The similar regularities can be observed in Table 6. The most unexpected results concerning benzene-soluble liquid products are their poor solubility in ethanol, and, in particular, high yield of hydrophilic compounds obtained at liquefaction with superheated water. The content of water-soluble acids and alkalis in Kukersite shale oil, hydrogenisate or thermal dissolution oils is usually low, and mainly water-soluble phenols are represented.

Date in Tables 6 and 8 demonstrate that benzene, compared with other solvents used, is actually an extra-effective solvent to remove liquid products obtained at Kukersite kerogen liquefaction from the solid residue.

3.1.2. Characterization of benzene soluble liquid

IR spectra of the liquid benzene-soluble products are presented in Figure 4. One can see that spectra obtained in the medium of solvents stable and chemically inert under superheated conditions (benzene, n-hexane, water) are similar and noticeably differ from the spectra recorded when labile and chemically active solvents (diethyl ether, ethanol, dimethyl ketone) were used.

All spectrea have common absorption bands at 725, 750, 1380, 1460, 2860, 2930 and 2690 cm^{-1}, and at 745, 770, 820, 880, 1020, 1080, 1600, and about 3000 cm^{-1} indicating, respectively, the presence of CH_3-, -CH_2- and CH-groups in aliphatic chains and aromatic ring systems of different degree of condensation and substitution. Broad absorption bands with a maximum at 3450-3500 cm^{-1} indicating various OH groups and absorption at 1700-1720 cm^{-1} belonging to the C=O groups are common, too.

Besides those groups there are some other absorptions indicating specific effects caused by the action of chemically active solvents. Absorptions at 2290-2970, 2860, 1430 and 1300-1100 cm^{-1} originate from C–O and C–O–C and C=O groups incorporated from diethyl ether and dimethyl ketone. Also absorption at 1720 cm^{-1}, belonging to the C=O groups in dimethyl ketone and diethyl ether liquids, is considerably amplified as compared with that in other liquid products. In the case of ethanol liquid one can notice an increase in absorptions at 2930 and 2960 cm^{-1} and appearance of narrow absorption at nearby 1740 cm^{-1}, the former absorptions belonging to methylene and terminal methyl groups in mainly cycloalkanes and aliphatic heterocompounds, and the latter one being a result of incorporation of acetaldehyde into the liquid product composition.

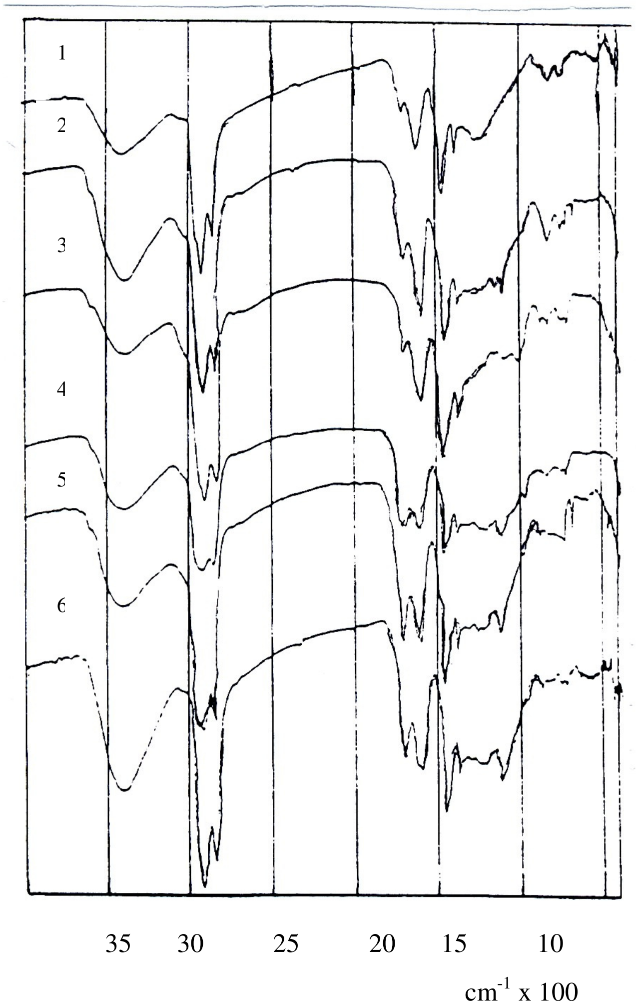

Figure 4. Infrared spectra of liquid products obtained on Kukersite kerogen liquefaction in following superheated solvents: Benzene (1), n-hexane (2), water (3), ethanol (4), diethyl ether (5), dimethyl ketone (6)

3.1.3. Gas composition

Gas composition is characterized in Table 10. Discussing the data one can make following conclusions. Gas formed in the presence of chemically stable C_6-hydrocarbons and water is of similar composition, and strongly differs from that obtained in the presence of unstable and chemically active solvents. Liquefaction of kerogen in both hydrocarbon and aqueous superheated solvents yielded only kerogen-derived gaseous components while gas produced in superheated diethyl ether, ethanol or dimethyl ketone consisted mainly of thermal and thermochemical decomposition products of the solvents.

Table 10. The main gaseous components formed at liquefaction of Kukersite kerogen, vol%

Component	Superheated solvent used at liquefaction					
	Benzene	Diethyl ether	Ethanol	n-Hexane	Dimethyl ketone	Water
Hydrogen	5.9	0.9	0.1	5.6	2.6	9.8
Carbon monooxide	12.3	16.3	11.2	9.8	19.0	-
Carbon dioxide	20.2	9.7	15.7	22.5	23.0	27.5
Methane	25.8	25.3	31.6	23.0	38.6	18.0
C_2-C_4 alkanes	10.5	42.4*	29.3**	12.7	9.7	14.1
C_2-C_4 alkenes	0.9	1.3	6.5	1.3	1.2	0.8

* Ethane content 99.5%

** Ethane content 92.2%

Gases, particularly those obtained using reactive solvents, were rich in alkanes C_1-C_4, whose yield reached even 60-67%. Considerable amounts of both carbon oxides and methane were yielded (26-32 vol.%), but their maximum yields, 42 and 39 vol.%, respectively, were produced in the case of dimethyl ketone decomposition. Outstandingly high is the share of ethane among saturated C_2-C_4 hydrocarbons, reaching 92-99% when superheated ether and alcohol were used. The content of unsaturated hydrocarbons C_2-C_4 is extremely low (0.9-1.3 vol.%) in all cases except ethanol (6.5 vol.%). One can suppose that decomposition of diethyl ether and ethanol both resulted in abundant formation of ethylene radicals which can stabilize reacting with active hydrogen from the same solvent decomposition and, in addition, with hydrogen from kerogen decomposition, forming ethane and other saturated hydrocarbons. Low content of both hydrogen and unsaturated hydrocarbons in gas indicates active consumption of hydrogen formed during kerogen destruction reactions.

3.2. Selection of the solvent for liquefaction of feedstocks and the extraction scheme for the water conversion products

Paper II, III

Despite the yield of liquid products from Kukersite oil shale kerogen in liquefaction with supercritical water was the lowest compared to the other solvents used, water was chosen for further experiments with oil shales and BM. The reasons why supercritical water was of interest as liquefaction agent are following:

1) Water is cheap, easily available and chemically safe.

2) Water dissolves the phenols with short akyl-substituents – alternative for dephenolation of oil with alkali solutions.

3) As BM itself contains water (Lu et al., in Press; Feng et al., 2004 a and b; Yan et al., 2006; Furusawa et al., in Press; D'Jesùs et al., 2006; Ni et al., 2006), there is no necessity for drying of the samples (additional expense).

As the LPs from BM are of hydrophilic caracter and shale oils are hydrophobic, their solubility in conventional solvents is different. As it is known, thermobitumen and shale oil formed as a result of its decomposition are both hydrophobic and totally soluble in benzene and practically insoluble in water while the solubility of hydrophilic liquid products from biomass, on the contrary, is low in benzene and significant in water. In order to estimate the liquefaction potential of various materials and the efficiency of different liquefaction processes, comparable data on liquid yield and its composition should be obtained. That is why the following extraction scheme, depicted in Figure 5, was worked out. The scheme was originally used for oil shales, but as the data obtained from oil shales and BM should be comparable, it is applied also for BM. According to this scheme the content of autoclave after water conversion was treated consequently with solvents with different polarity. The yield of LPs was determined as the total weight of solubles in water, benzene, and acetone. Basing on solution principles the scheme enables to compare adequatly the liquefaction potential of all kinds of fossil and renewable fuels when water conversion is used as thermochemical liquefaction method.

Water solubles are represented by polar hydrophilic, oxygeneous compounds, probably of different alcohols, phenols which may have short alkyl-substituents, carboxylic acids, aldehydes and sugars. The lower oxygeneous homologues formed, such as methanol, formic and acetic acids, formaldehyde and acetaldehyde, acetone, and several simple ketoaldehydes, being in contact with other decomposition fragments and influenced by high temperature and pressure for a long time can initiate different reactions, including chemical incorporation, reductive decomposition, synthesis gas reactions and others.

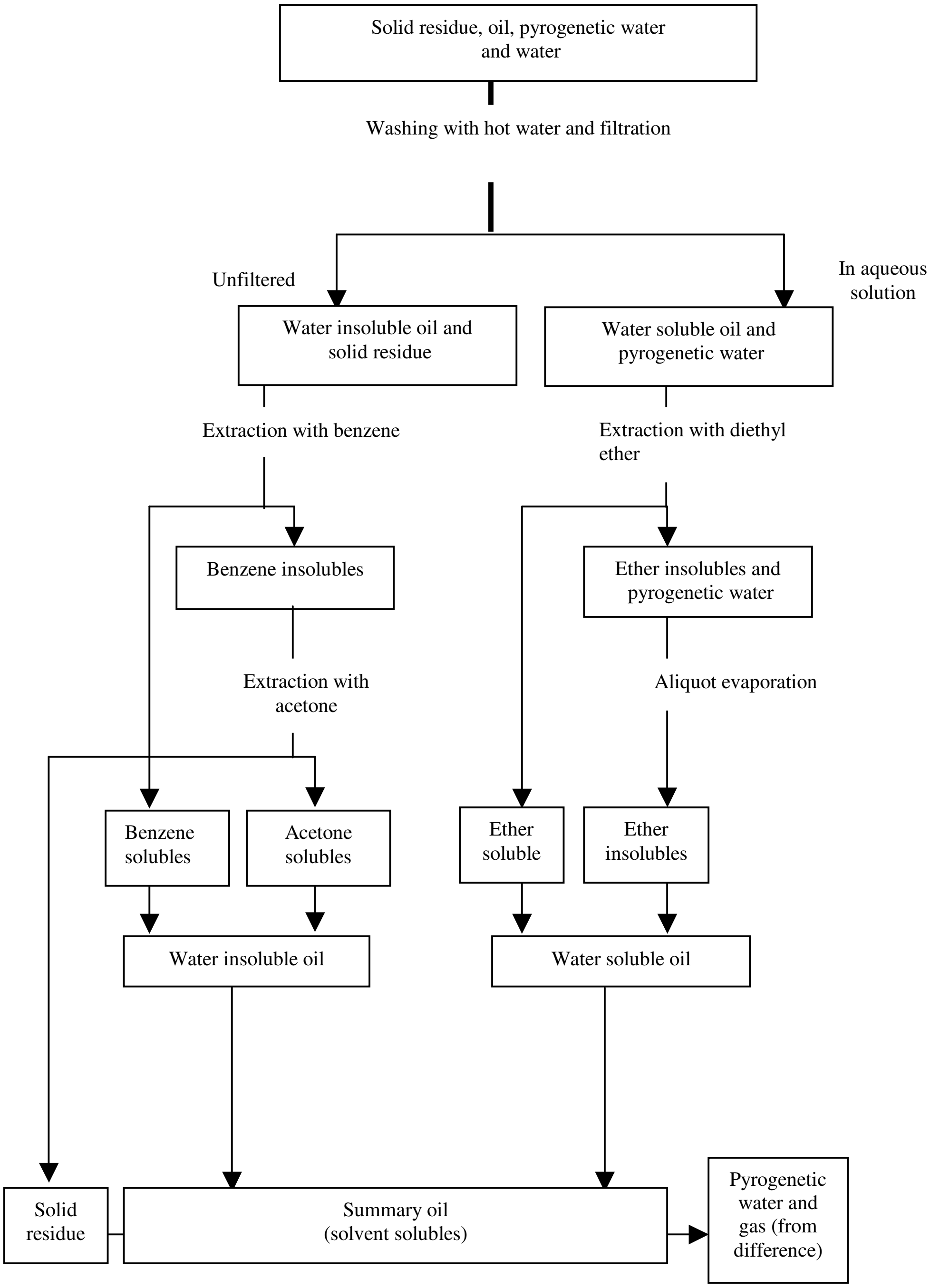

Figure 5. **Separation scheme for solid, liquid, and gaseous products obtained as a result of water conversion**

Into benzene solubles there are concentrated mainly non-polar compounds: hydrocarbons, water insoluble phenols and also asphaltenes. From these there were later determined the group composition by TLC.

Acetone soluble matter is represented by polar hydrophobic compounds and hetero-atomic structures insoluble in nonpolar solvents. This fraction, closer to solid than to liquid, probably consists of large polyfunctionalized fragments of the initial macromolecules not decomposed entirely. Due to their low volatility and poor solubility in conventional solvents, these fragments cannot be analysed by chromatographic methods. Meier et al. (1986) demonstrated that the acetone soluble part of the thermochemical decomposition products of lignocellulosic materials consists mainly of lignin-derived ones while the cellulosic part yields mainly water solubles. However, by C, H, and O concentrations the acetone extract manifests itself as an in-between water and benzene soluble, but it contains significantly more N and S than both these.

Specifying water solubles as chemicals and acetone solubles as transition compounds, the goal of the investigation includes maximizing the yield of benzene solubles and minimizing that of acetone solubles. The idea of this Ph.D thesis is limited to obtaining liquid petroleum-like oily products and phenols. Other products obtained were regarded as by-products. Only such limitation can create a basis to further developing processes of co-liquefaction of Estonian oil shale and biomass to obtain chemically modified syncrude and valuable phenolic compounds. The balance of water conversion is shown in Table 11.

Table 11. Yields of water conversion of feedstocks (1 – % from dry matter, 2 – from OM)

Product	Kukersite		Dictyonema		Pinewood		Reed	
	1	2	1	2	1	2	1	2
Total oil	32.54	62.70	4.0	20.46	15.86	15.92	14.17	14.62
Gas and pyrogenetic water	18.51	30.80	7.46	46.64	51.32	51.90	52.01	52.90
Solid residue	48.95	6.50	88.54	32.90	32.82	32.18	33.82	32.48

3.3. Liquefaction with supercritical water of fossil fuels

Papers I, IV, V

3.3.1. Yields of oil fractions

From the balance of water conversion (Tab. 11) one can see that almost all OM of Kukersite was transferred to oil and gas (62.7 and 30.8%, respectively). Only

6.5% OM remained in solid residue. From total oil the biggest fraction – 84.89% from total oil (Fig. 6) – is the benzene soluble oil. Semicoking of Kukersite gave 56.24% oil, 98.35% of which is benzene soluble. 14.88% of OM remained in solid residue and 28.88% was transferred into gas. From the comparision of water conversion and semicoking one can conclude that water conversion transfers more organic matter to oil and remains less into solid residue.

From Dictyonema only 20.46% of OM transferred to oil and 46.64% to gas. 32.90% OM remained in solid residue. The poor oil formation from Dictyonema could be related to the structure of its kerogen. The content of benzene soluble oil is 59.29% from total oil (Fig. 6).Semicoking of Dictyonema gave 12.92% oil, 76.47% of which is benzene soluble. 45.6% remained in solid residue and 41.48% was transferred into gas. Comparision of the processes shows also better tranfering of OM into oil in water conversion.

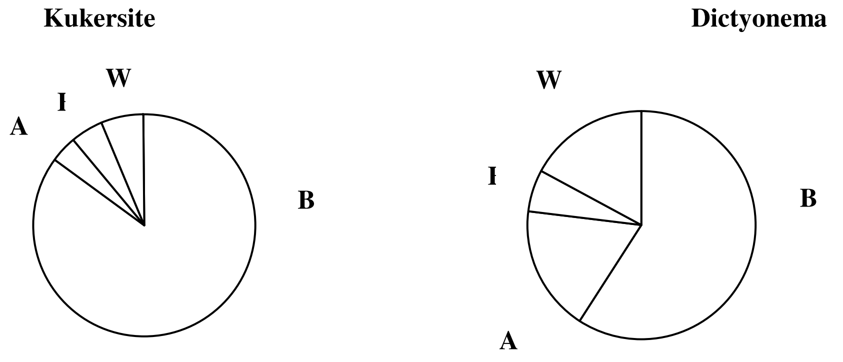

Figure 6. Composition of total oil from Kukersite and Dictyonema according to solubility, % (fractions: E – ether soluble part of water soluble oil, W – ether insoluble part of water soluble oil, B – benzene soluble part of water insoluble oil, A – acetone soluble part of water insoluble oil)

3.3.2. Functional groups of liquid products

The common absorption bands in case of both oil shales (Fig. 7) are at 750, 1380, 1460, 2860, 2930 and 2960 cm^{-1}, and at 745, 1020, 1145, 1380, 1600 cm^{-1}, indicating, respectively the presence of CH_3–, –CH_2– and CH– groups in aliphatic chains and substitution.

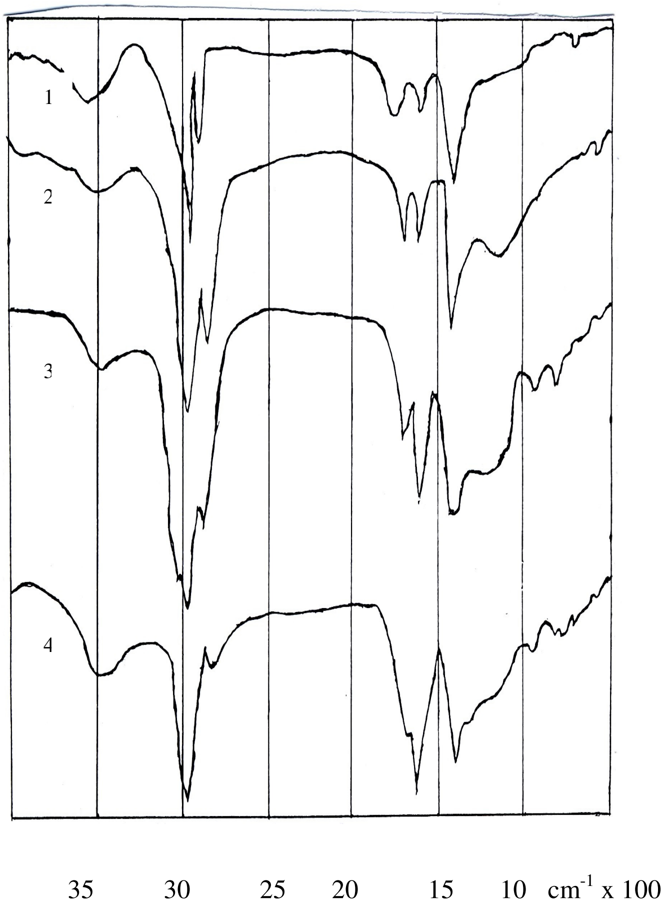

Figure 7. Infrared spectra of benzene soluble (1 and 2) and acetone soluble (3 and 4) fractions obtained in water conversion of Kukersite (1 and 3) and Dictyonema (2 and 4)

The broad absorption band at 3230-3340 cm^{-1} and 1700-1760 cm^{-1} indicate hydroxyl and carbonyl groups, respectively. In the same region also N–H, C–N, C–N–C and C–S groups can be found. Long alcyl chains (~725 cm^{-1}) are practically absent in the composition of the acetone soluble fraction. Absorptions at 2960, 2872, 1460, and 1380 cm^{-1} caused by CH_3– groups in different positions as well as those at 2930, 2860, and 790-720 cm^{-1} (–CH_2– groups) are considerable. As the absorption band 3020, 3050, 860, 815 and 769 cm^{-1} is less intensive, the content of aromatic C–H bonds is low. Benzene nucelus manifests itself at 1600 and 1500-1515 cm^{-1}. Cyclic hydrocarbons and their derivatives manifest themselves by absorption at around 3040 an 1462-1452 cm^{-1}, more or less intensively.

3.3.3. Group composition of benzene soluble oil

52.9% of the benzene soluble oil obtained by liquefaction with supercritical water from Kukersite consists of fraction of polar heterocompounds (Fig. 8).

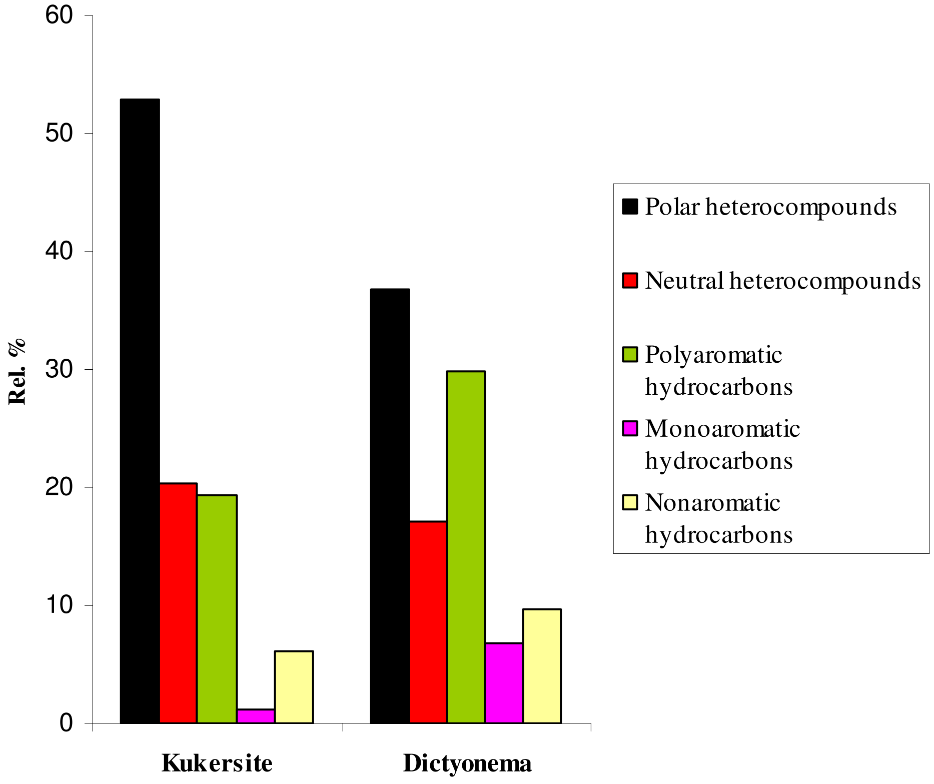

Figure 8. Composition of benzene soluble oil from Kukersite and Dictyonema by thin-layer chromatography

Only 6.1% of this oil constitutes fraction of nonaromatic hydrocarbons. For comparision the Kukersite semicoking oil was treated according to scheme in Figure 5. The benzene soluble oil consisted 36.6% of polar heterocompounds and 13.7% of nonaromatic hydrocarbons. So, the composition degree at liquefaction with supercritical water is higher than at semicoking.

Polar heterocompounds constitute 36.7% of the benzene soluble oil from Dictyonema, while 9.1% of it consists of nonaromatic hydrocarbons, whereas

42.4% of benzene soluble semicoking oil consists of polar heterocompounds and 8.9% of nonaromatic hydrocarbons.

3.3.4. Composition of parafines of benzene soluble oil

The percentages of alkanes in benzene soluble oils are presented in Figure 9. One can see that n-alkanes C_{12}-C_{23} were formed. In benzene soluble oil from Kukersite C_{14} and C_{15} prevail and in the oil from Dictyonema C_{16} and C_{18} dominate.

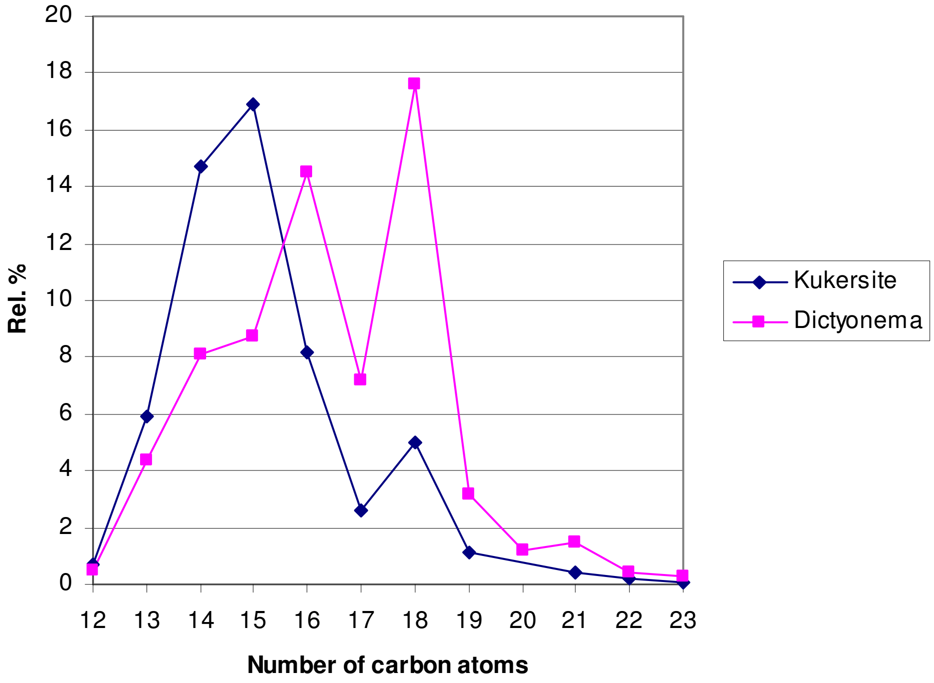

Figure 9. Relative concentration of n-alkanes in benzene soluble oil

3.3.5. Elemental composition of total oil

The elemental composition of total oil from Kukersite and Dictyonema is presented in Table 12.

Table 12. Ultimate analysis of total oil obtained from Kukersite and Dictyonema

Object	Concentration, wt. %				
	C	H	N	S	O*
Kukersite	82.5	10.0	0.2	0.7	6.6
Dictyonema	83.7	9.0	1.2	1.8	4.3

* By difference

3.3.6. Gas composition

In water conversion one part of OM transfers to gas and pyrogenetic water. Composition of gases formed in water conversion of Kukersite and Dictyonema is shown in Figure 10. CO_2 prevails in case of both fossil fuels – until 70% of total gas amount from Kukersite. The main hydrocarbons formed from dictyonema are methane, ethane, propane and buthane. Ethane and propane are relatively much formed also from Kukersite.

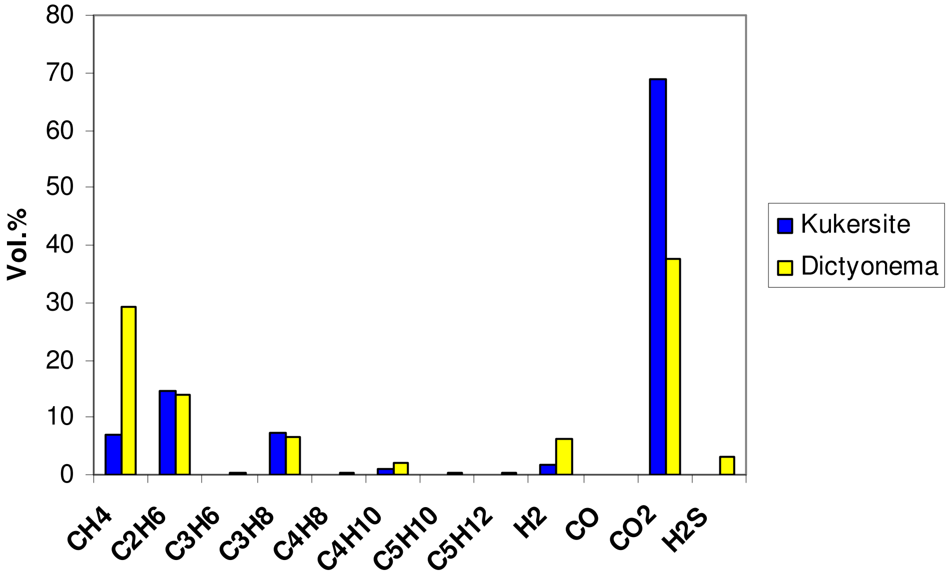

Figure10. Gas composition of water conversion of fossil feedstocks

3.4. Liquefaction with supercritical water of renewable feedstocks

Papers II, III

3.4.1 Yields of fractions

According to Table 11, from pinewood and reed even less OM transferred to total oil (15.92 and 14.62%, respectively) than from Dictyonema. The biggest amount of OM from pinewood and reed is transferred to gas (51.90 and 52.90%, respectively). 32.18% of OM from pinewood and 32.90% from reed remained in solid residue. The content of benzene soluble oil from pinewood is and 37.44% and from reed 44.53% from total oil (Fig. 11).

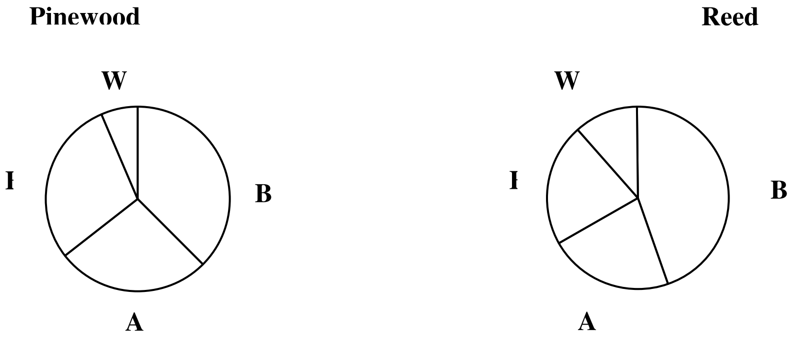

Figure 11. Composition of total oil from pinewood and reed according to solubility, %. For abbrevations see Fig. 6

In semicoking of pinewood and reed more OM transferred to oil: 25.62 and 25.73%, respectively. 46.04% OM from pinewood and 45.83% from reed was transferred to gas and 28.34% from pinewood and 28.44% from reed remained ins olid residue. The content of benzene soluble oil from total oil is 30.95 and 28.45%, respectively.

Comparing semicoking and water conversion one can see that the latter method transfers less OM to oil, but the content of benzene soluble oil as the most valuable in total oil is higher.

3.4.2. Functional groups of liquid products

In Figure 12 there is presented infrared spectra of different LP fractions. Various oxygen functionalities occuring in abundance are the most characteristic in the composition of BM LP fractions. According to the absorptions at 1034, 1078, 1118-1123, 1154, 1200, 1223-1229, 1265-1278, 1648-1652, 1675-1685, 1696-1702, 3016, 3050-3069, and the region 3324-3416 cm^{-1} one can find C–O, O–H, C–O–H, C–O–C, C=O, C–C–O, S=O and also N–H, C–N, C–N–C, and C–S groups surviving not only thermolytical but also chemical attacks of protons and supercritical water.

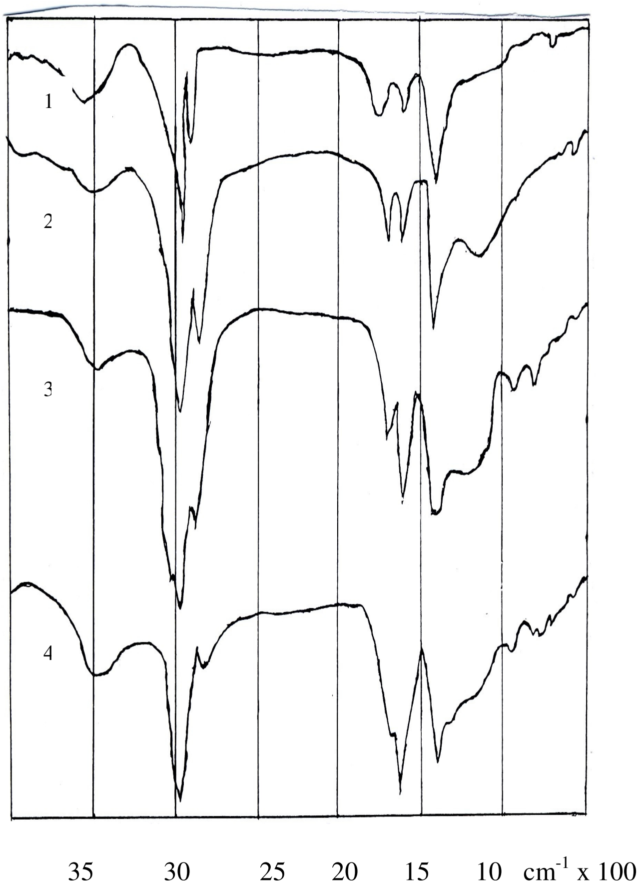

Figure 12. Infrared spectra of benzene soluble (1 and 2) and acetone soluble (3 and 4) fractions obtained in water conversion of pinewood (1 and 3) and reed (2 and 4)

Formation of intermolecular hydrogen bonds between polar compounds such as ethers, ketones, or amides, preferable multi-shifts of absorption bands of certain functional groups, overshadowing and covering up broad absorptions with those in minority and often complicate identification. Absorptions typical of methyl, methylene, and methyne groups in alkyl chains appear at 3000-2800, 1400-1300, and at around 725 cm^{-1}. Asi t was expected, long alkyl chains (~725 cm^{-1}) are practically absent from the composition of the acetone soluble fraction.

Absorptions at 2960, 2872, 1460, and 1389 cm^{-1} caused by CH_3– groups in different positions as well as those at 2930, 2860, and 790-720 cm^{-1} (–CH_2– groups) are considerable. The most of methylene and methyne groups are bounded into different ring structures such as cyclic hydrocarbons and aromatic compounds. Absorption in the region 3010–3070 cm^{-1} refers to the presence of =C–H groups. The absorption in 815-960 cm^{-1} belongs to vinyl and terminal methylene groups in unsaturated compounds. In the same regions also aromatic C–H absorptions (3020, 3050, 860, 815, 760 cm^{-1}) are visible.

Absorptions at 1170 and 1145 cm^{-1} typical of isoprenoid groups derived from lignin decomposition are less visible. Mono- and triterpenes such as 2-pinene, limonene, and suberine can be expected to be present. Cyclic hydrocarbons and their derivatives manifest themselves by absorption at around 3040 and 1462-1452 cm^{-1}, more or less intensively.

Note that the use of severe thermal destruction contributing to the supercritical or chemical agents leading to the formation of products changed beyond recognition not mild depolymerization resulting in the formation of recognizable links of the original polymers in parent lignocellulosic matter (such as sugars and other carbohydrates from holocellulose, phenylpropanes from lignin, and others) in this Ph.D thesis was intentional. Severe processing variables caused large-scale but not exhaustive deoxygenation and cracking of the initial BM. This was inevitably accompanied also by undesired secondary reactions between primary products. That is why among the intentionally obtained oily products polymeric remnants survived, and oligosaccharidic fragments and various re-structured and distorted derivatives exist. LPs, in particular woody ones, are known as very unstable and internally reactive even at ambient temperature. So, during thermochemical liquefaction (TCL), isolation, and storage in contact with air oxygen the final composition of solvent solubles submitted to analysis can be affected by a series of concurrent and consequtive secondary reactions such as dehydrogenation, condensation, denaturation, oxidation, sedimentation, re-polymerization, coagulation, resin formation, and other spontaneous alterations and interactions. In spite of being submitted to large destruction and transformations, the initial matter of BM manifests itself in infrared spectra by oxygeneous and cyclic character. Though oxygen-containing compounds are re-distributed into all fractions: hydroxyl functionalities were mainly separated by polar solvents (especially mighthy absorptions at 3300-3500 cm^{-1} in water solubles) while –C=O containing compounds with the absorption maximum between 1648 and 1702 cm^{-1} are considerably soluble in benzene. A spectrum of benzene solubles is clearly recognizable by a low hydroxyl concentration and amplified aliphatic, aromatic, and cyclic hydrocarbonaceous functionalities (especially in the regions 720 cm^{-1} (long alkyl chains), 1462-1452 cm^{-1} (cyclic structures), and 1515, 1600, and 1450 cm^{-1} (complex referring to skeleton vibrations of benzene nuclei)). The compounds present in solvent solubles can be expected to include compounds of varied molecular weight, besides low-molecular oily products and monomers also polyfunctionalized compounds, oligomeric derivatives, and polymeric remnants being present.

In the infrared spectra absorptions belonging not only to −C−N, −C=N, −C−S, −N−H, and −C=S but also to functional groups such as P−H, P=S, −S=O, P−O−aromatic (or aliphatic) radical, −N−CS, −N−CS=N, N−N=O, and C−N=O can be found. As heteroatoms other than oxygen are concentrated into the composition of acetone solubles, the presence of pyrrolic, pyranic, sulphoxidic, metallorganic, lecitinic and other phospholipidic, tioketonic, tioalcoholic, tiouretanic, amidic, and many other fragments containing one or more heteroatoms in the form of remnants, substitutes, derivation or recombination products in this fraction is probable. Often absorption bands for some radicals and of those containing substitutes differ only slightly. For example, the characteristic absorption of the phenyl group in organic compounds and that of linked to different elements in the periodical system are close. Most metal-phenylic compounds have absorption bands in the spectrum region 1050–1120 cm^{-1} and these are visible in acetone solubles in Figure 12.

On the basis of the above observations acetone solubles can be qualified as nonaliphatic polar hydrophobic polyfunctionalized heteroatomic compounds of different origin. Having a sufficient reserve of hydrogen, acetone solubles can give an additional amount of both water and benzene solubles in further decomposition.

3.4.3. Group composition of benzene soluble oil

In the benzene soluble oil from BM liquefaction with supercritical water the biggest fraction is also fraction of polar heterocompounds (63.9% for pinewood and 58.3% for reed) (Fig. 13). Neutral heterocompounds are another dominating class of compounds. Their percentage is considerably lower than that of high polar heterocompounds but never lower than that of any hydrocarbonaceous fractions obtained. Only 8% of benzene soluble oil of pinewood and 5.7% of that of reed consists of nonaromatic hydrocarbons. The higher the content of hydrocarbons, the closer the product to natural petroleum. The content of benzene soluble oil from total oil in semicoking of pinewood and reed is 30.95 and 28.45%, respectively. Polar heterocompounds consist 58.0 and 58.3% of benzene fraction and nonaromatic hydrocarbons 2.5 and 4.4%, respectively.

Comparing the yields of oil between fossil and renewable feedstocks one can conclude that in water conversion of renewable feedstock there is formed less oil, but the composition by TLC of the benzene soluble fraction is similar.

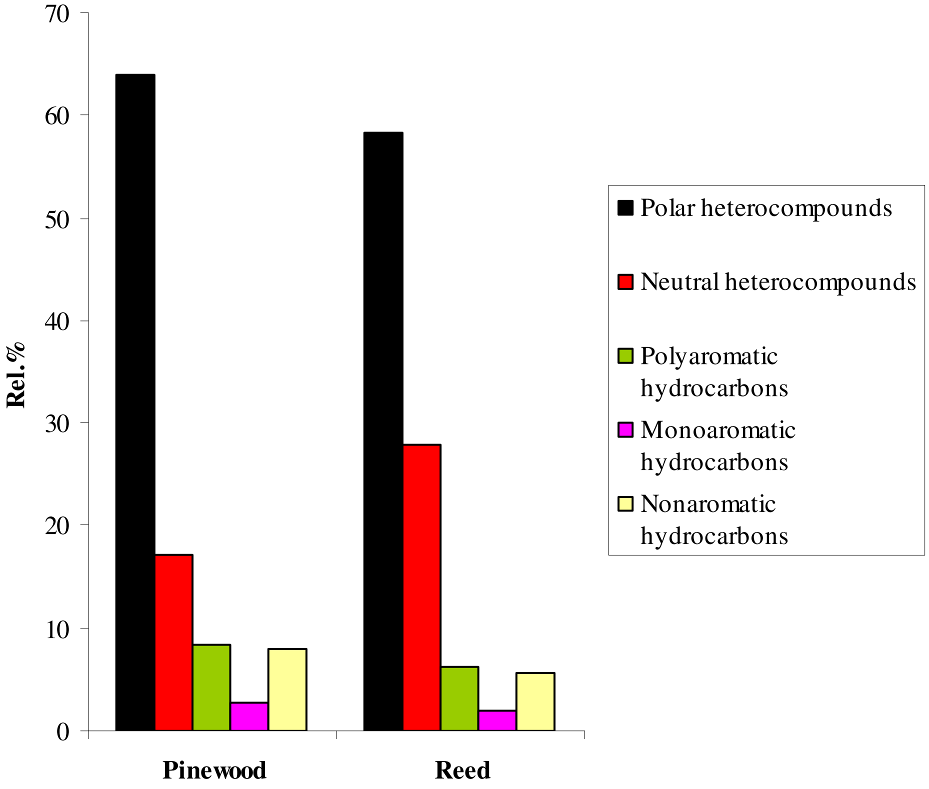

Figure13. Composition of benzene soluble oil from pinewood and reed by thin-layer chromatography

3.4.4. Composition of parafines of benzene soluble oil

The percentages of alkanes in benzene soluble oils are presented in Figure 14. One can see that n-alkanes C_{13}-C_{33} were formed and the regularities of those distribution are generally similar in both oils. In case of pinewood even numbered n-alkanes prevail over odd numbered ones and in case of reed vice versa. Particularly visible are maximums at C_{17}, C_{18}, C_{21}, C_{23} and C_{24}.

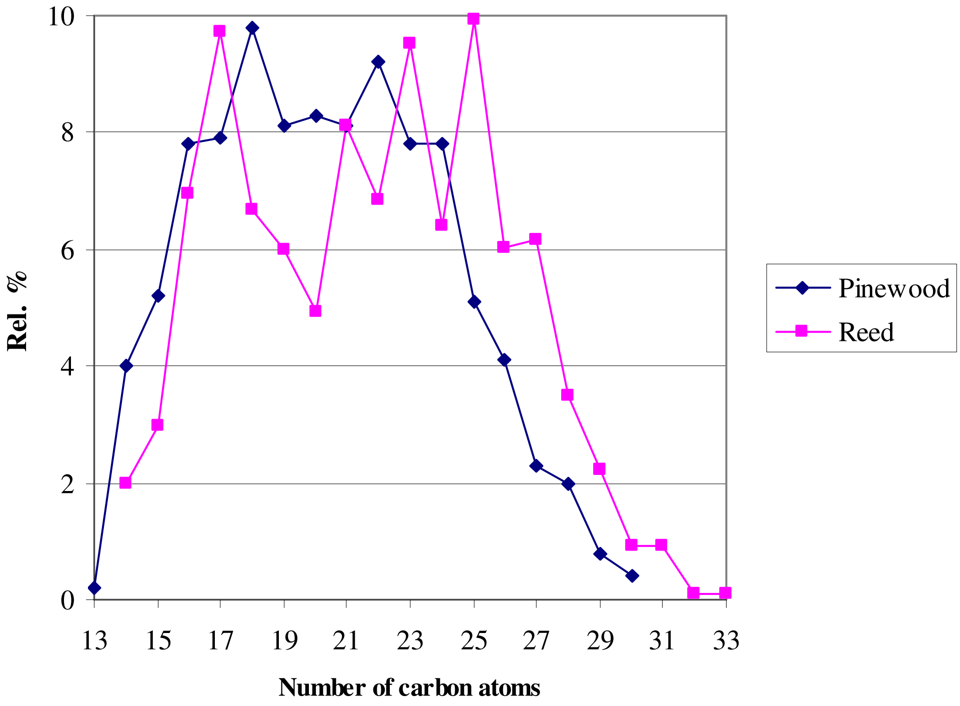

Figure 14 . Relative concentration of n-alkanes in benzene soluble oil

3.4.5. Elemental composition of total oil

The elemental composition of total oil from pinewood and reed is presented in Table 13.

Table 13. Ultimate analysis of total oil obtained from pinewood and reed

Object	Concentration, wt. %				
	C	H	N	S	O*
Pinewood	73.7	7.1	0.3	0.2	18.7
Reed	75.1	7.2	0.5	0.3	16.9

* By difference

3.4.6. Gas composition

The main gaseous compound formed from both objects was also CO_2 (Fig. 15), being until 80% of total gas amount, which arises from large quantity of oxygen in initial samples. The main hydrocarbons are methane and ethane.

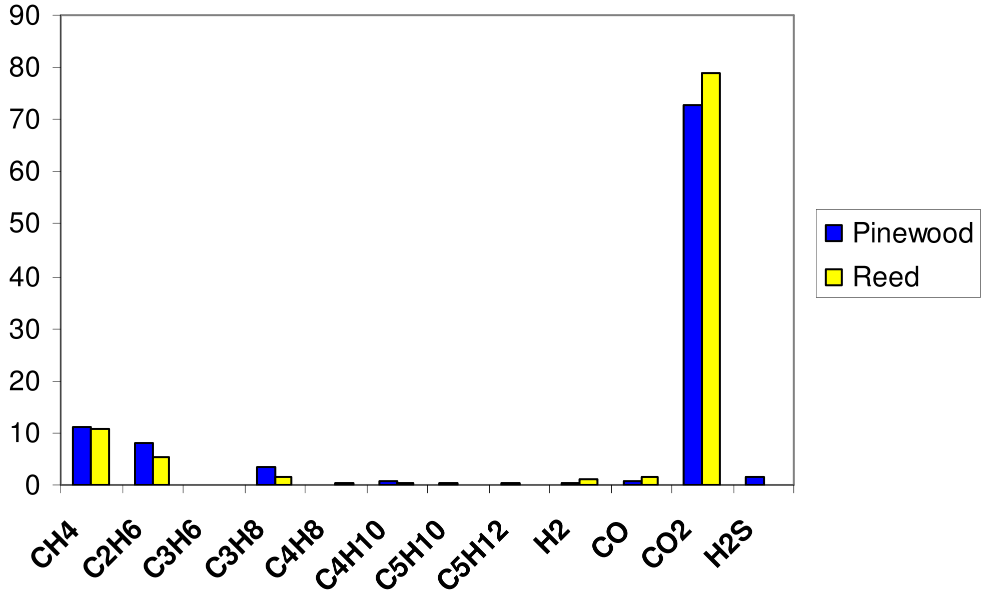

Figure 15. Gas composition of water conversion of renewable feedstocks

3.4.7. Comparision of the oils obtained from fossil and renewable fuels

The yield of total oil obtained in water conversion of BM was 1.5-4 times lower than obtained from oil shales. From BM majority of OM transfers to gas and pyrogenetic water. The content of benzene soluble oil in total oil obtained from BM is until 2 times lower than obtianed from oil shales, while the content of water and acetone soluble oil in case of BM is higher. In group composition of benzene soluble oil from all feedstocks is similar – the polar heterocompounds dominate: 37-63% from the oil. Comparing the numbers of carbon atoms in alkanes in the benzene soluble oil one can see that in the oil obtained from BM contains more alkanes with longer chain. The IR spectra taken from the liquid products obtained from all feedstocks bear great resemblance. The oil obtained from BM contains more oxygen due to higher oxygen content in initial sample. In gas composition in case of all feedstocks carbon dioxide prevails.

3.5. Co-liquefaction with supercritical water of Kukersite and pinewood

Papers IV, V

The aim of co-liquefaction of oil shale and biomass in supercritical water is to find wether biomass could substitute fossil fuel and wether there is synergy between them in conversion process. There were made different mixtures of Kukersite and pinewood: 25, 54 and 75% pinewood on OM basis, which were liquefied at the same conditions as pure components described in Chapter 2.3. Separation, calculation of products and preparative TLC were also carried out as for pure components, described in Chapter 2.2.

The highest yield of total oil (74.6%) was obtained at liquefaction of the mixture containing 75% Kukersite and 25% pinewood on OM basis. The corresponding data for pure Kukersite was 62.70% and for wood – 15.92% (Tab. 14). The yield of the most desirable product – benzene soluble oil – was highest (63.7%), too (Fig. 16). It is worth mentioning that 25% of Kukersite in feed on OM basis, gave sharp increase in the yield of total oil (50.1%) as well as of oil soluble in organic solvents (45.3%), incl. water insoluble portion (38.3%).

Table 14. Yield of products obtained by water conversion of Kukersite, pinewood and their mixtures

Product	Wood in feed, % on OM basis				
	0	25	54	75	100
Total oil	62.70	74.60	57.50	50.10	15.92
Gas and pyrogenetic water	30.80	18.30	29.90	33.80	51.90
Solid residue	6.50	7.10	12.60	16.10	32.18

The maximum yield of oil was accompanied with the minimum yield of gas and pyrogenetic water. According to TLC data, component composition of the fraction soluble in benzene varied slightly, but differed from that of Kukersite semicoking oil (Tab. 15); polar heterocompounds prevailed upon the other components, unlike those of semi-coking oil.

Experimental and calculated data presented in Figure 17 demonstrate very strong synergic effect of co-liquefaction. Then yields of products or their combinations (numeral data) are compared with additive ones (straight lines) on OM basis. There are some exceptions considering water soluble oil (E and W), acetone soluble part of the water insoluble oil (A), and their sum (E + W, E + W + A) – almost no synergy when the share of wood was low and, as for acetone soluble part additionally, when the share of Kukersite was low, too (Fig. 17).

It must mention that synergy worked in desired direction: the yield of solid residue and gas with pyrogenetic water was lower – 0.5-0.6 and 0.5-0.7 of additive ones, respectively, whereas the yield of the most expected component of oil – benzene soluble part was 1.5-1.9 times higher than additive yields. Higher yields compared with additive ones were also in case of water insoluble oil (B + A) and of oil soluble in organic solvents (E + B + A) – 1.6-1.8 and 1.5-1.7 times, respectively. The yield of more polar components of oil separately compared with additive ones was up to 2.5 times higher, while their sum (E + W + A) did not exceed the value obtained for the compounds solubles in benzene.

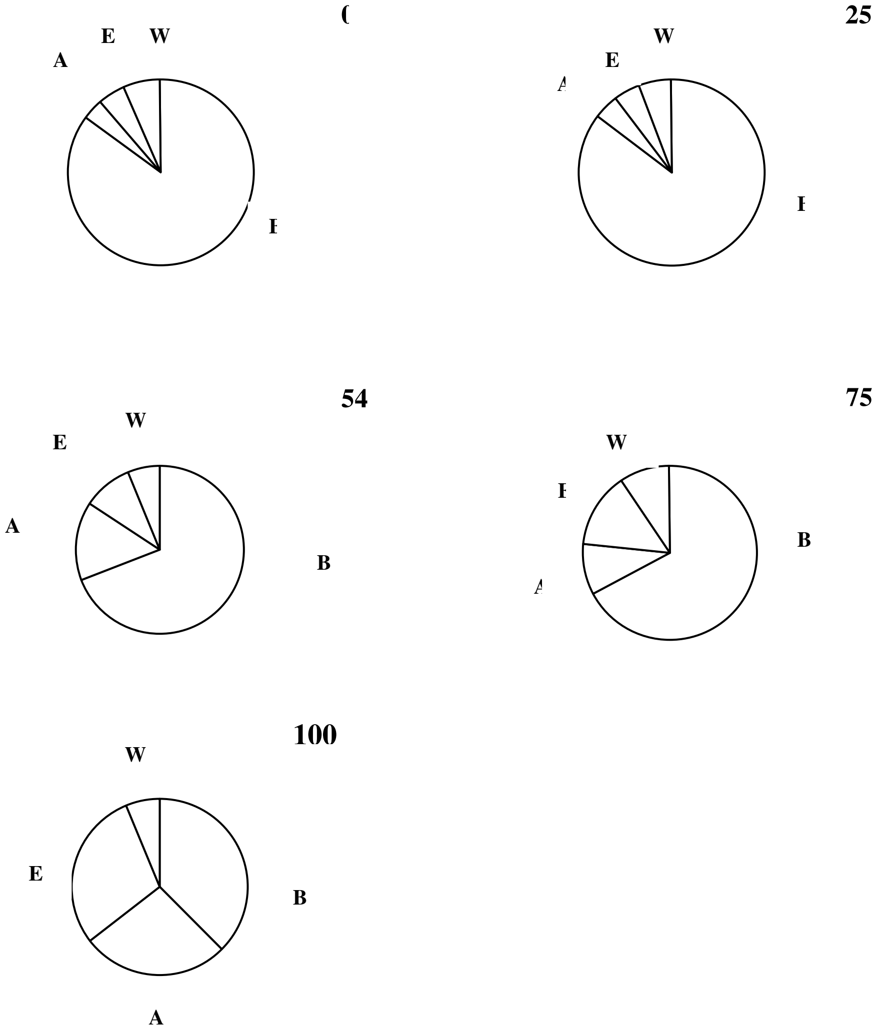

Figure 16. Composition of total oil from Kukersite, pinewood and their mixtures (by wood in feed, % on OM basis) according to solubility, %. For abbrevations see Fig. 6 and 11

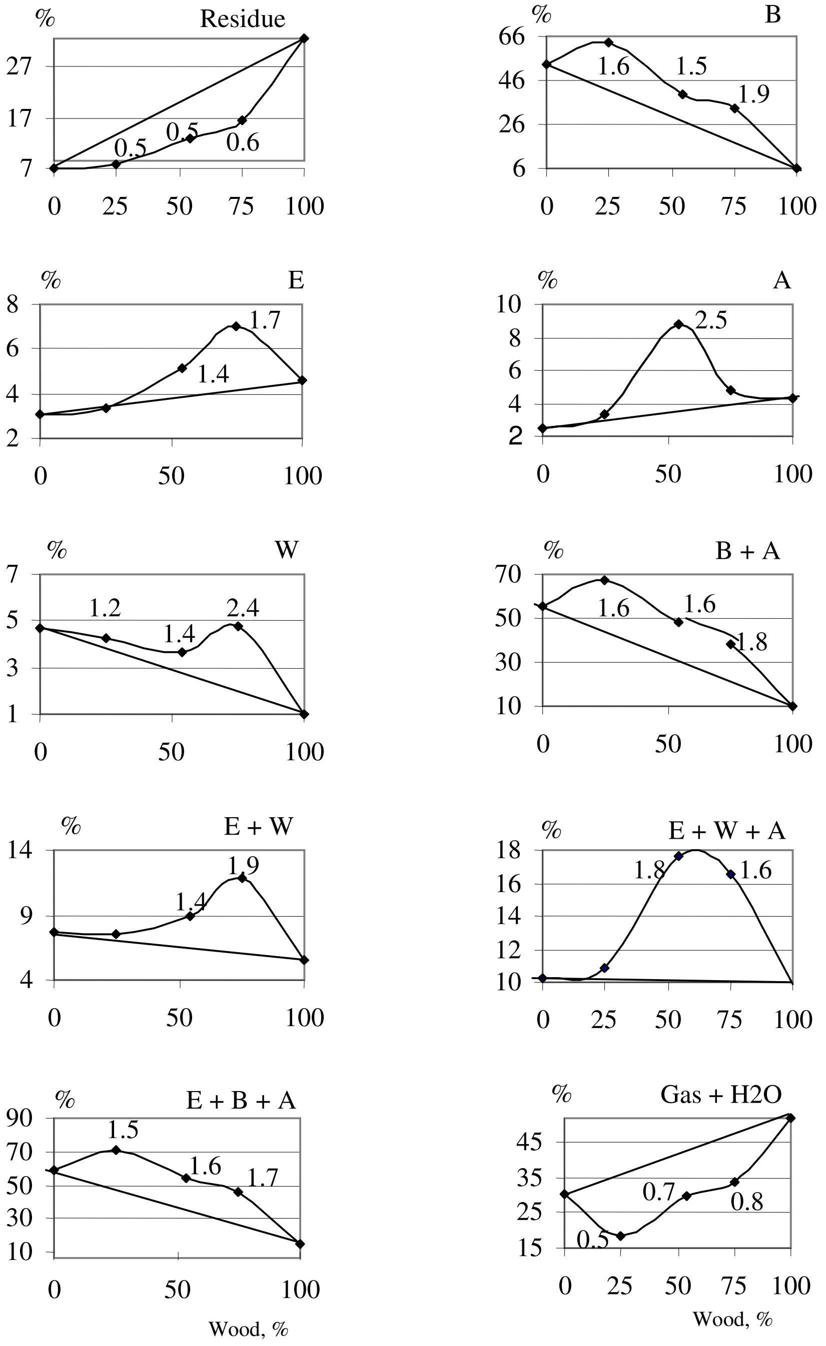

Figure 17. Yield of products obtained by water conversion and calculated additive ones (straight lines) on OM basis, %. For abbrevations see Fig. 6 and 11, for the numbers on the plot area see the text

Table 15. Component composition of benzene soluble oil by TLC

Compo-nent	Semi-coking oil		Water conversion oil. Wood in feed, % on OM basis				
	Kukersite[1]	Wood	0	25	54	75	100
1	23*	58.0	52.9	66.6	70.6	71.9	63.9
2	34**	36.1	20.4	18.9	14	16.6	17.1
3	17	2.9	19.4	8.6	10	7.9	8.4
4	8	0.5	1.2	1.3	2.2	1.2	2.7
5	18	2.5	6.1	4.6	4.3	2.4	8

Fractions: 1 – polar heterocompounds, 2 – neutral heterocompounds, 3 – polyaromatic hydrocarbons, 4 – monoaromatic hydrocarbons, 5 – nonaromatic hydrocarbons, %

[1] Urov and Sumberg, 1999

* Phenols – polar heterocompounds separated previously.

** Neutral heterocompounds with a portion of polar heterocompounds remained after dephenolizing

CONCLUSIONS

Thermal dissolution – the liquefaction method of the fossil fuels, BM and their mixtures in the medium of sub- or supercritical solvents as an alternative to semicoking has been used to elevate the conversion efficiency and to modify the conversion products chemical composition.

Amongst tested solvents – benzene, water, ethanol, n-hexane, dimethyl ketone and diethyl ether – just the water as thermal dissolution solvent was selected out as:

- environmentally safe
- the cheapest one
- the solvent concentrating oil-insoluble phenols and a great deal of other oxygeneous oil constituents

Resulting from supercritical water conversion at unified experimental conditions the comparable data on liquid, gaseous and solid conversion products yield and composition formed of the most available Estonian fossil and renewable natural feedstocks – Kukersite and Dictyonema oil shales, pine wood and reed were obtained.

The common scheme for shale oils and bioliquids separation basing on their subsequent dissolution in water, benzene and acetone as solvents of different polarity has been worked out and used to gain the total liquid determined as a sum of the solvent solubles.

Compared with conventional semicoking, the oil shales give higher liquid yield in supercritical water conversion while biomass types give higher benzene soluble fraction yield concentrating compounds similar to those in natural petroleum.

Biomass-derived liquids differ from shale oils by significantly higher contents of water-soluble and acetone-soluble oxygen compounds the group composition of the most valuable benzene fraction being similar.

In supercritical water conversion of both fossil and renewable feedstocks considerable yields of methane and other gaseous hydrocarbons, carbon monoxide and hydrogen as extra-valued by-products can be also obtained and used as fuel or producer gas.

Both kerogeneous and lignocellulosic types of fossilised and renewable BM can be converted individually or blended in the same facilities.

Replacing Kukersite oil shale partly with the same amount of pinewood the synergistic effects in total liquid yield as well as in specific solvent-soluble fractions were detected.

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ABSTRACT
Water Conversion of Oil Shales and Biomass

The main goals of the present research were to study alternative to semicoking liquefaction method – thermal dissolution, to find suitable solvent to carry out comparable liquefaction. For Estonian fossil and renewable fuels and their blends with the aim to obtain modified oils – with better yield and composition than in semicoking.

For this purpose there was at first carried out liquefaction of Estonian Kukersite oil shale kerogen with selected superheated solvents (benzene, diethyl ether, ethanol, n-hexane, dimethyl ketone and water) in order to find the best one for both oil shales and biomass. Despite water gave low yield of liquid products, it was chosen for liquefaction of the feedstocks due to cheapness, good availability, safety and its high content in biomass (no need for previous drying). Also water dissolves the phenols with short alcyl-substituents, which is good alternative for oil dephenolation with alkali solution.

Liquefaction with supercritical water of two Estonian oil shales: Kukersite and Dictyonema, and two representatives of biomass: pinewood and reed as the most typical for Estonia was studied. The product of water converison was separated by consequent fractional dissolution into gas water soluble oil, benzene soluble oil, acetone soluble oil, and solid residue. The yields of total oil (sum of water, benzene and acetone soluble oil) from oil shales were higher than the oil yield obtained in semicoking. From biomass the total oil yield in water conversion was lower than in semicoking, but the proportion of benzene soluble oil as the most desirable product was higher. In the benzene soluble oil according to thin layer chromatographic analysis, the biggest fraction was fraction of polar heterocompounds.

Co-liquefaction of Kukersite and pinewood was carried out in different ratio of components. At every feed blend under the chosen liquefaction conditions synergic effect was evident and the yield of benzene soluble oil was higher than additive yields, the yields of solid residue and gas with pyrogenetic water were lower than additive yields.

KOKKUVÕTE

Põlevkivide ja biomassi vesikonversioon

Töö eesmärk oli uurida poolkoksistamisele alternatiivset vedeldamismeetodit – termilist lahustamist, leida selleks sobiv solvent, viia läbi võrdlev vedeldamisprotsess Eesti fossiil- ja taastuvkütuste ja nende segudega saamaks modifitseeritud õli – parema saagise ja kvaliteediga kui poolkoksistamisõli.

Esmalt viidi läbi Eesti kukersiidi kerogeeni vedeldamine superkriitilises olekus solventidega (benseen, dietüüleeter, etanool, n-heksaan, dimetüülketoon, vesi) leidmaks neist sobivaim nii põlevkividele kui biomassile. Hoolimata madalast vedelprodukti saagisest vee puhul valiti vesi kütuste vedeldamiseks tema odavuse, hea kättesaadavuse ning biomassis kõrge sisalduse tõttu (puudub vajadus eelnevalt kuivatada). Samuti lahustuvad vees lühikeste alküülasendajatega fenoolid – hea alternatiiv õli defenoleerimisele leelise lahusega.

Vesikonversioon teostati kahe Eesti põlevkivi – kukersiidi ja diktüoneemakildaga ning kahe Eestile enim tüüpilise biomassi esindaja – männipuidu ja pillirooga. Vesikonversiooni produkt jaotati gaasiks, vees, benseenis ja atsetoonis lahustuvaks õliks ning tahkeks jäägiks. Superkriitilise veega oli summaarse õli (vees, benseenis ja atsetoonis lahustuva õli summa) saagis põlevkividest suurem kui poolkoksistamisel. Biomassi puhul oli summaarse õli saagis väiksem kui poolkoksistamisel, kuid benseenis lahustuva õli kui kõige enam soovitavama õli osakaal selles oli suurem. Benseenis lahustuvast õlist tehti õhekihi kromatograafiline analüüs. Suurim fraktsioon iga objekti puhul oli polaarsete heteroühendite fraktsioon.

Viidi läbi kukersiidi ja männipuidu koosvedeldamine komponentide erinevatel koostistel. Valitud vedeldamistingimustel esines sünergeetiline efekt komponentide iga koostise puhul: benseenis lahustuva õli saagis oli suurem kui aditiivsed saagised. Samas moodustus tahket jääki ning gaasi ja pürogeneetilist vett vähem kui on nende aditiivne saagis.

ELULOOKIRJELDUS

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