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Trends in biomass thermochemical liquefaction: global experience and recent studies in Estonia

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Abstract. Investigations on thermochemical liquefaction of various renewable resources of biomass carried out in many countries over the world during the last 25 years are shortly reviewed. As a rule, all kinds of the renewable biomass used as liquefaction feedstock were characterized by extremely high oxygen contents, amounting to 50 wt.%. It was found to be one of the main specific features of the chemical composition of lignocellulosic biomass. Until 1990 short contact time fast pyrolysis methods were favoured as these give a high liquid yield from renewables. As a result of fast pyrolysis the most of oxygen was transformed into the composition of pyrolysis liquids and therefore these were not fit to replace even conventional light fuel oil. Improvements to fuel products quality were badly needed. That is why during the last decade one- or two-stage upgrading processes were preferred including in situ upgrading using H-donor agents in the liquefaction or supplementary deoxygenation of fast pyrolysis primary liquids. In Estonia fundamental studies on renewable biomass liquefaction basing on both the pre-existent technologies developed as a result of prolonged kukersite oil shale processing experience and on the improved and novel ones have been initiated. Partial substitution of oil shale for renewables and their wastes and co-processing of fossil and renewable biomass can create a basis to sustainable oil shale utilization and shale oil production. Opportunities to continue production of liquid fuels and chemicals simultaneously decreasing the proportion of oil shale as a feedstock, as well as modifying both liquid composition and qualities closer to those of natural petroleum and, concurrently, decreasing environmental risks are the main goals of those studies being carried out at the Department of Oil Shale Technology at Tallinn University of Technology since 2001. Forest waste biomass as an abundant local and global renewable resource is represented as one of the most promising alternative feedstock. The results obtained in the liquefaction of sawdust, bark, and needles using semicoking, hydrogenation, and water conversion methods and chemical characterization of liquids obtained are reported as well. It was concluded that thermochemical liquefaction of forest waste biomass using methods known from oil shale processing results in the formation of significantly deoxygenated liquid products compared with the initial feedstock while in the benzene soluble part of those liquids (38–86% of the total liquid product) several similarities with kukersite shale oil were found.

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Key words: biomass, lignocellulosic wastes, pyrolysis, hydrogenation, water conversion, biomass-derived liquid product, chomatographic separation, infrared spectroscopy.

Abbreviations: BM – biomass, FWB – forest waste biomass, IRS – infrared spectroscopy, LP – liquid product, TCL – thermochemical liquefaction, TLC – thin layer chromatography.

INTRODUCTION

Biomass (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 [1]. Coals and oil shales can 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, oxygen, and nitrogen, sulphur being also present in less proportions [2]. Most often BM refers to forestry (trees, plants, purposely grown crops) and biological wastes (agricultural, agro-industrial, and domestic). 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. Liquefaction, gasification, and coking of BM lead to the formation of liquid, gaseous, and solid products with higher energy density than the original. From that point of view bioresource can be observed as a promising alternative to both crude petroleum and fossil fuels.

Chemically, the cell walls of plants contain varying amounts of three main biopolymers – cellulose, hemicellulose, and lignin – and a small amount of other extractives. So, the main building blocks in BM are carbohydrates and the role of lignin is to reinforce the cell walls, to make them waterproof, and it is deposited in wounds as a barrier to pathogen ingress [3, 4]. 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 [5, 6]. BM differs from other alternative energy resources in that the resource as a feedstock is varied. Organic material from trees, plants, and crops available everywhere in its individual multitude and obtained as a whole or ingredients has been submitted to thermochemical liquefaction (TCL) using different processes and facilities. Comparison and parallels with fossil BM using data obtained for kukersite oil shale have been drawn further here and there.

Usually, BM in large quantities is easily available unsorted and blended, which influences less direct combustion but more the liquefaction process. Forest waste biomass (FWB) includes whatever direct and indirect forest-originating wastes such as logging residues, brushwood, ingredients of different trees, forestry residues, the remains of the wood-working industry, and others. Those used in mass or separately do not generate much differing amounts of ash and air emissions. At the same time softwood and hardwood, bark and needles, leaves and cones etc. of individual strains of BM submitted to TCL can produce quite different yields and compositions of products though the same liquefaction conditions are used.

WORLD PRACTICE IN BM CONVERSION: RECENT 25 YEARS

Thermal destruction is, indubitably, the main technology used for BM liquefaction. Numerous methods and facilities are being applied to upgrade waste BM into products of higher value [6]. Fundamentals concerning BM thermal destruction and regularities of products formation have been described [7–9]. Since the early 1980s much attention has been paid to the BM thermal transformation in Canada, USA, Finland, Sweden, Italy, Germany, Switzerland, Spain, United Kingdom, France, and Belgium. The principal results and developments on investigations in these countries during the period 1983–1990 have been highlighted in [10, 11]. Pyrolysis, thermal destruction without using pressure, any solvent, or chemical, was the basic process used while wood and peat were the main materials pyrolysed as BM representatives. Minor attention has been paid to thermal destruction in pressurized solvents and other BM species.

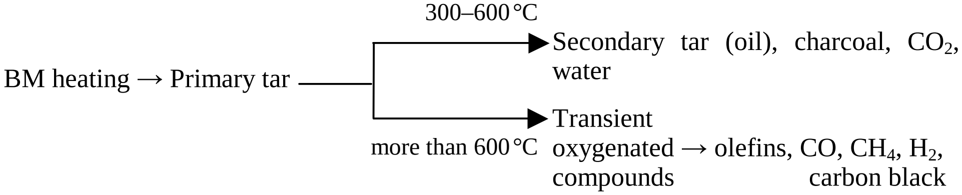
Pyrolysis

Pyrolysis of BM yields liquid, gaseous, and solid products. Like in the case of fossilized high-molecular organic matter the mutual ratio of these is strongly dependent on pyrolysis conditions. Each of the products obtained from BM – liquid product (LP, in the literature often termed also as “bio-liquid”, “bio-oil”, “bio-crude”, “oil”, “tar”, “black liquor”), bio-gas, and charcoal can be regarded as an upgraded one having higher energetical density and broader use value compared with the initial feedstock. Varying pyrolysis conditions closer to coking, gasification, or liquefaction, a desired product of market value in high yield can be obtained.

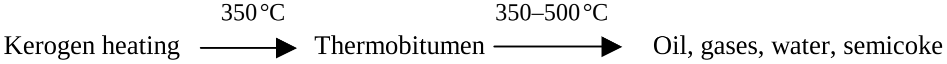
The yield and composition of BM conversion products mainly depend on pyrolysis conditions such as temperature, heating rate, residence time, and products evacuation conditions from the hot zone (measured as residence time in the gas phase), particles size, and presence of additives and less on the composition of BM subjected to pyrolysis [7–9]. As for feedstock, consisting mainly of holocellulose and lignin, BM variety is often determined as lignocellulosic matter and both the yield and the composition of pyrolysis products primarily depends on the cellulose/hemicellulose/lignin ratio in the pyrolysis feedstock. Temperature has been considered the main parameter among process variables determining products distribution between liquid, gaseous, and solid phases. Pyrolysis of BM, according to the temperature, includes three principal stages as follows [7]:

(1) below 300 °C – dehydrogenation processes; H_2O, CO_2, and CO 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.

It was demonstrated that the residence time, in particular that in the gas phase, has also a significant effect on the above reactions. So, the residence times of solid feedstock and gaseous primary products in the hot zone at pyrolysis temperature as well as condensation velocity of the vaporized products strongly affect the disproportion regularities of pyrolysis products between liquid, gaseous, and solid phases. Several regularities between process variables were fixed. 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. Temperatures 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) both the gas and solid state residence times are long (the former one more than 5 s) favouring solid residue and liquid formation. The mechanism of BM pyrolysis was described to occur via several consecutive and parallel stages [7]:



The mechanism of renewable BM pyrolysis bears notable resemblance to that of fossilized organic matter like kerogen in oil shales. Estonian kukersite oil shale has been thoroughly investigated during more than 80 years and the mechanism of its pyrolysis has been accepted as follows:



Both the BM and kerogen pyrolysis process begins with the formation of high-molecular LP. In the case of kerogen the product is known as thermobitumen and for BM as primary tar. Final products of renewable and fossil BM pyrolysis – oil, gas, and solid residue – in their majority form only after thermal decomposition of those primary intermediates. Small parts of oil and gas are formed simultaneously with intermediates. Both feeds – organic matter of oil shale and BM – contain a small amount of extractables (bitumens extracted by conventional solvents). Kukersite belongs to highly oxygenated caustobioliths while growing BM is extra highly oxygenated. The oxygen supply in both ones is transferred into liquid and gaseous aim products. Gas, be it obtained from kukersite shale or BM pyrolysis, is characterized by a high concentration of carbon oxides, and in the composition of LPs numerous groups of similar compounds can be found.

The most promising industrial applications are processes producing tarry or oily LP for use as fuel oil or for further processing. Numerous pyrolysis methods and facilities have been applied for BM liquefaction since 1990 such as slow pyrolysis, low-temperature pyrolysis, vacuum pyrolysis, entrained-flow pyrolysis, fast pyrolysis, flash pyrolysis, vortex ablative pyrolysis, mill pyrolysis, fluid-bed pyrolysis, pyrolysis with partial combustion, and updraft fixed-bed pyrolysis [10]. Depending on the conditions used the yields of LP obtained on BM feed varied from 8% to 80%. The highest LP yields from peat and wood, 50–80%, were obtained by the flash pyrolysis method, first reported by Graham et al. [12]. Samples of BM were heated up as quickly as possible (usually within 0.5–5 s up to 400–600 °C) followed by quick evacuation and condensation of gaseous products (residence time in the gas phase less than 2 s). 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. For instance, at 500–600 °C the residence time in the gas phase must be short to avoid cracking but long enough for solid matter. Fast pyrolysis operating with heating rates of 1000–10 000 °C/s and residence times in the gas phase less than 0.5 s usually results in yielding valuable gases (lower olefines and other hydrocarbons) when temperatures from 600 to 1000 °C are used.

Flash 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 flash pyrolysis 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 [13]. The higher the yield of LP, the higher its oxygen concentration. “Liquid wood” as a reactive mixture is unstable even at room temperature and has a heating value only about half of that of conventional light fuel oil. Products of similar composition and in comparable yields as in flash pyrolysis can be obtained also in vacuum pyrolysis at slower heating rates. Neither individual nor group composition of wood-derived tars has been properly characterized, also several aspects of tar recovery are uncertain. Nevertheless, several pragmatic conclusions can drawn basing on the results of investigations on BM liquefaction from the period since 1990:

- BM species, kinds, and ingredients in their global multitude have been defined similarly as consisting of three main polymers – cellulose, hemicellulose, and lignin;
- BM has been brought into prominence as an alternative to fossil fuels for producing petroleum substitutes;
- LP yields from pyrolysis of cellulose, hemicellulose, and lignin taken singly under different conditions have been reported; as a result, the LP yield from

any lignocellulosic material can be approximately predicted knowing the concentration and ratio of these components in a material not pyrolized before;

- the liquefaction potential of BM in pyrolysis units has been estimated and LP yields as high as up to 80 wt.% from wood and 50 wt.% from peat have been obtained using, respectively, flash pyrolysis and the fluidized bed technology;
- LPs from BM pyrolysis have been characterized as rich in oxygen but containing poor amounts of commercially interesting chemicals. Therefore BM-derived liquids obtained meet hardly fuel oil qualities and must be upgraded by further processing;
- an impulse has been given to developing solvolytical and hydrotreating processes with the aim to upgrade and deoxygenate BM-derived LPs.

Thermochemical liquefaction (TCL) and upgrading

Pyrolysis liquids from BM, though obtained in high yields, urgently need upgrading (deoxygenation) to be used as petroleum substitutes and directly marketable hydrocarbon fuels [13–15]. For upgrading one- and multi-stage methods with solvents and chemical agents used have been developed. One-stage upgrading processes such as liquefaction via solvolysis, high-pressure liquefaction, catalytic hydroliquefaction, hydrotreating, steam/water liquefaction, iron-catalysed pressurized aqueous pyrolysis, thermochemical solvolytic processes at elevated temperature used to be mainly conducted in autoclave-type reactors. Multi-stage upgrading processes involved BM decomposition in several consecutive steps such as pyrolysis, stabilization, and upgrading. As a typical example a two-step hydrotreating process for the production of hydrocarbon fuels from BM pyrolysis oils was developed by D. C. Elliot and co-workers from the Pacific Northwest Laboratories, USA [10]. In the first stage, a low-temperature catalytic treatment (270 °C, 13.8 MPa, sulphided cobalt–molybdenum on aluminia) was used to convert unstable pyrolysate into a tar similar to the high-pressure liquefaction product. This tar was then hydrodeoxygenated and hydrocracked at elevated temperature by conventional hydrotreating techniques (400 °C, 13.8 MPa) to produce petrol. Single-step processing of the pyrolysate in the same conditions, except that temperature was elevated up to 350 °C, produced only limited quantities of the hydrocarbon product before the catalytic bed plugged with a coke-like material. One-stage processes developed were characterized by low efficiency while technically feasible multi-stage ones were regarded as too expensive. The higher the efficiency of oxygen removal, the lower the yield of the liquid upgraded. The yield of upgraded oil from BM, containing 1–10% of residual oxygen, was usually in the range 15–30% on the initial feedstock basis.

Since 1990, in particular during the last 10 years, the geography of investigations dealing with BM liquefaction and the assortment of BM species used have been significantly widened, emphasis being strongly displaced from pyrolysis towards thermochemical methods. At present investigations on BM liquefaction and upgrading are being carried out in the EU, USA, Canada, Japan, China, Indonesia, Turkey, Azerbaidjan, Russia, New Zealand, and other countries. Liquid biofuels, such as wheat, sugar-cane, rapeseed, and sunflower oil are already being used in some member states of the European Union, for example in Austria, Belgium, France, Germany, Italy, and Spain [6]. Practically, BM of all kinds from various geographical areas belonging to different botanical families of both terrestrial and aquatic origin have been submitted to TCL to estimate their prospects of yielding energy carriers and upgraded (hydrocarbon) liquids. BM samples tested include a wide range of materials, among them forest products (wood residues, branches, shrubs, sawdust, bark, needles, leaves, cones, etc. from forest cleanings and logging) and energy crops (short rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops) as well as wastes (agricultural production wastes, agricultural processing wastes, urban wood wastes, crop residues), and aquatic plants and organisms. Forest waste BM is currently not used in the traditional forest products industries; this concerns both unused wild and residual materials, including forest residues left after forest harvesting, residual trees, and shrubs. Presently under-managed woodland is dominating and therefore forest residues alone account for some 50% of the total forest BM and are currently left in the forest to rot [6].

Graminaceous BM (cereal stalks, straw), grasses (weeds, clovers, alfalfa), starch (maize, wheat, barley), sugars (cane, beet), and other high moisture herbaceous and aquatic plants (vegetables, sorghum, cotton, rushes, plankton), animal wastes, and municipal solid wastes have mainly been submitted to biological degradation via microbic digestion and fermentation to produce bio-alcohols while those BM wastes deposited in landfills were demonstrated to be promising for biogas (methane) in situ production [16–20]. Considering the oxygeneous character of LPs from BM efforts have been made to convert BM into dimethyl ether usable as a new ultraclean alternative fuel for diesel engines [21, 22].

The list of individual samples submitted to TCL is long and steadily lengthening. Reported data include algae (*Betryococcos braunii*, *Dunaliellu ferriolecta*, *Microcystis viridis*); oriental beech and spruce, ailanthus, northern poplar, birch, and oak, reed (*Phragmites australis*), tea waste, wheat and rye straw, corncob, olive husk, hazelnut shells, hazelnut seedcoat, corn stover, tobacco stalk, tobacco leaves, sunflower stalk, unhusked rice, wastes from oil-palm, cotton, and banana plantations, *Cunninghamia lanceolata*, polysaccharides, *Verbascum* stalk, cotton plant and cotton gin, proteins, garbage, sugar cane bagasse, pine and spruce needles, and many others [2, 23–42]. Solvent extraction methods, mainly using water and H-donating solvents with and without catalysts or additives, are preferred [43–72]. It was demonstrated that cellulose material, all other carbohydrates, wood wastes, urban wastes, sewage sludge, agricultural wastes, etc. can be converted to oil with CO and H_2O for the H_2O-gas shift reaction and Na_2CO_3 as catalyst. In [26] a liquefaction process in hot compressed water around 300 °C and 10 MPa using sodium carbonate as the catalyst, without any reducing gas such as H_2 and CO, was developed. Water conversion, as well as several other liquefaction processes, has the significant merit of not requiring a drying process for feedstock and those processes can be conducted at high moisture content.

Water is the most conventional, the cheapest, and an environmentally safe solvent. Water, in smaller or larger amounts, is always present in TCL processes of solid fuels, particularly in BM liquefaction even when absolutely dry feedstock is used, forming in situ during liquefaction as a result of the decomposition of BM organic matter. In an aqueous medium with water used as the solvent or co-solvent, high enough LP yields characterized by a moderate oxygen content have been obtained. The addition of alkalis (hydroxides, carbonates, and formates) increases the solvolytical power of water towards BM, accelerates hydrolysis of high-molecular constituents in BM at lower temperatures and thermal degradation at higher temperatures. As a result, higher liquid yields are obtained as compared with those using only water. That is why BM liquefaction processes using sub- and supercritical water (the latter often activated by adding additives or catalysts) are favoured in modern BM processing methods [23, 25, 26, 32, 43–58]. In [23] water conversion of algae into oil at 300–340 °C and 20 MPa during 30–60 min with and without Na_2CO_3 as catalyst was conducted and the oil yield was increased from 28–32 up to 38–40 wt.%. In [26] 18 kinds of Indonesian BM were submitted to liquefaction in hot compressed water at 300 °C and 10 MPa using Na_2CO_3 as catalyst and the oil was obtained in the range of yields 21–36 wt.% on organic basis. In alkali-catalysed aqueous liquefaction the liquid yields as high as up to 65 wt.% in the liquefaction of BM wastes or unused BM [32] and even over 90 wt.% in the liquefaction of oriental beech, *Ailanthus*, tea wastes, and hazelnut seed-coats [25] are reported. In spite of the high liquefaction efficiency the LPs obtained were characterized as heavy oils with a very high oxygen content similar to flash-pyrolysis oils. Such products are classified into unupgraded ones and have to be submitted to additional processing. Significantly high liquid yields have been obtained also by using instead of water other solvents in the supercritical state, such as alcohols C_1–C_4, acetone, and glycerol [25, 30, 31, 59–64]. As they are strongly influenced by mass transfer from the solvent into the LP composition, these processes should be regarded as specific ones. The above-listed solvents often decompose under supercritical conditions in close contact with bio-organic material and incorporate chemically via their fragments into the LP composition. Similarly to water conversion the presence of alkalis contributes to increasing the liquid yield in BM liquefaction with alcohols and acetone [25, 30, 31, 60]. As it was mentioned above BM flash and fast pyrolysis yield LP containing up to 50% of oxygen while the content of oxygen in those of sub- and supercritical extraction of different BM species is usually in the range 20–25 wt.%. Even liquids obtained in BM reductive liquefaction (BM liquefaction and hydrogenation in one stage) using tetralin and other H-donor solvents can often contain excessive oxygen, which has to be removed. To compete with petroleum crude, LPs obtained as synthetic bio-crudes in different processes of pyrolysis, extraction, and hydro-liquefaction badly need oxygen removal, visbreaking, and stabilization. Hydro-deoxynation is the main process used in BM-derived LPs upgrading, actually involving all the processes that have been used in BM upgrading practice in different manner such as catalytically activated hydropyrolysis, hydroliquefaction, and catalytical hydrocracking using in situ hydrogenation or hydrogen from outside. Sometimes common (vapour) cracking or cracking over zeolites has been used in upgrading leading to redistribution of BM internal hydrogen and oxygen and disproportion in the transformation of those into desired products, respectively into liquid and gas composition [13, 14, 64–70]. Two-stage processes involving obtaining primary liquids in as high yield as possible accompanied by successive catalytic hydrotreatment have been performed with bi-functional Ni–Mo and dispersed iron catalysts used to obtain upgraded oils with a low oxygen content (less than 2%) and a heating value of the same magnitude as that of conventional petroleum fuels [71, 72]. In BM catalytic hydroliquefaction hydrogen is consumed mainly in hydrodeoxygenation reactions and Co–Mo or red mud, known as powerful catalysts in the processing of fossil BM, can be successfully used [69].

Chemical composition of BM

BM includes a large variety of different lignocellulosic materials. Containing small amounts of extractives and mineral matter, the main organic matter of trees, purposefully grown coppices, crops, grasses, and wastes from the agricultural and forest industries consists of polymerized lignin, cellulose, and hemicellulose molecules in different proportions (see Table 1).

Table 1. Some kinds of BM and their main constituents

Type and reference number	Concentration, wt.%			
	Cellulose	Hemi-cellulose	Lignin	Solvent extractables, solvent used
Wood [6]	43	22	36	No data
Softwood [73]	40–44	24–29	26–33	1–5 (not specified)
Hardwood [73]	43–48	27–35	16–24	2–8 (not specified)
Pine (*Pinus sylvestris*) wood[a] [74]	45	20	28	6 (not specified)
Pine wood [75]	52	No data	28	0.6 (water)
Spruce wood [73]	43	26	29	1.6 (acetone)
Spruce (*Picea abies*) wood[a] [74]	41	26	29	3 (not specified)
Birch (*Betula pendula*) wood[a] [74]	38	37	20	4 (not specified)
Poplar wood [73]	44	30	21	2.4 (acetone)
Scots pine[a] [76]	50	21	26	2.7 (hot water)
Scandinavian and Baltic softwood bark[b] [74]	20–30	15–20	25	5
Pine (*Pinus pinaster*) bark[a] [77]	24	15	44[c]	17 (dichloromethane, ethanol, water)
Pine bark[a] [9]	34	16	34	14 (not specified)
Pine (*Pinus halepensis*) needles [78]	24	No data	18	21 (ethanol, toluene)
Mullein (*Verbascum*) stalk [29]	50.3	17.6	31.4	0.7 (petroleum ether)
Common reed (*Phragmites australis*) [30]	43.3	15.5	27.1	No data
Wheat straw [25]	28.8	39.1	18.6	8.0 (alcohol–benzene)
Corncob [25]	52.0	32.0	15.0	1.3 (acetone)
Hazelnut shell [25]	25.9	29.9	42.5	4.2 (acetone–water)
Corn stover [25]	51.2	30.7	14.4	1.9 (diethyl ether)
Tobacco leaf [25]	36.3	34.4	12.1	10.0 (dichloromethane)

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[a] Ash and moisture included. [b] Tannin concentration 10–15% included. [c] Other polyphenols included.

Ultimate analysis data (Table 2) characterize BM representatives as having an extraordinarily high oxygen concentration (40–50 wt.%) and a negligible concentration of sulphur and nitrogen (less than 2% usually).

Table 2. Ultimate analysis of various kinds of forest BM

Type and reference number	Concentration, wt.%				Molar ratio[a]	
	C	H	N+S	O[b]	H/C	O/C
Wood[c] [6]	52	6.3	0.4	40.5	1.45	0.58
Wood [7]	48–50	6.0–6.5	0.5–2.3	38–42	1.44–1.63	0.57–0.66
Pine (*Pinus pinaster*) wood [72]	52.5	5.2	0.8	41.5	1.19	0.59
Poplar wood [73]	50.1	6.0	0.5	43.4	1.44	0.65
Spruce wood [73]	52.1	6.1	0.3	41.5	1.40	0.60
Spruce wood [79]	49.9	6.2		43.9	1.49	0.66
Pine branches (Ø >0.5 cm) [80]	47.9	6.2	0.3	45.6	1.55	0.71
Pine branches (Ø <0.5 cm)[c] [80]	45.4	6.8	0.3	47.4	1.80	0.78
Blended forestry wastes (spruce 80%, pine 10%, birch 10%) [81]	51.1	5.9	0.5	42.5	1.38	0.62
Blended forestry wastes (spruce 86%, pine 9%, birch 5%) [81]	51.4	6.0	0.5	42.1	1.38	0.62
Pine sawdust, bark free [81]	51.0	6.2	0.1	42.7	1.46	0.63
Variation limits	45.4–52.5	5.2–6.8	0.1–2.3	38–47.4	1.19–1.80	0.57–0.78
Pine bark[c] [9]	55.9	5.3	0.4	37.1	1.14	0.50
Pine (*Pinus brutia*) bark [82]	50.2	5.4	0.4	44.0	1.29	0.66
Pine bark [79]	55.9	5.5		38.6	1.18	0.52
Japanese red pine bark[c] [83]	46.9	5.3		46.0	1.36	0.74
Bark waste [7]	51–56	6.0–8.5	0.3–0.8	24–40	1.41–1.82	0.32–0.59
Variation limits	46.9–56	5.3–8.5	0.3–0.8	24–46.0	1.14–1.82	0.32–0.74
Pine needles[c] (*Pinus pinaster*) [80]	46.9	6.7	1.9	44.6	1.71	0.71
Cellulose [79]	43.7	6.4		49.9	1.76	0.86
Spruce holocellulose [79]	47.1	6.0		46.9	1.53	0.75
Birch holocellulose [79]	45.4	6.0		48.6	1.59	0.80
Birch Willstätter lignin [79]	61.3	5.8		32.9	1.13	0.40
Spruce lignin [79]	66.7	5.9		27.4	1.06	0.31
Lignin [83]	63.9	5.8		30.3	1.09	0.35
Xylan[c] [83]	43.5	6.2		49.9	1.71	0.86
Rye straw[c] [69]	45.5	6.5	1.9	42.0	1.71	0.69
Wheat straw[c] [25]	45.5	5.1	1.8	34.1	1.34	0.56
Corncob[c] [25]	49.0	5.4	0.4	44.6	1.32	0.68
Hazelnut shell[c] [25]	52.9	5.6	1.4	40.1	1.27	0.57
Corn stover[c] [25]	49.5	5.4	0.6	41.8	1.31	0.63
Tobacco leaf[c] [25]	43.0	4.5	0.5	35.8	1.25	0.62

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[a] Calculated by the authors.

[b] Often calculated by difference.

[c] Ash content reserved.

Liquefaction products

As a result of TCL the macromolecules in the initial BM are decomposed into fragments of lighter molecules. Depending on TCL conditions, gaseous, solid, and liquid products in different yields and of different composition can be obtained.

The gas obtained in BM pyrolysis contains large amounts of CO, H_2, and CH_4 and therefore it can be used as synthesis gas or fuel gas. BM-derived fuel gas is characterized by the heating value of 10–20 MJ/Nm^3, which is lower than that of natural gas (29–38 MJ/Nm^3). BM gasification was particularly popular in the 1970s and several technologies such as Peatgas, Hy-gas, and Hyflex processes, with mainly peat used, were developed to pilot plant level with the aim to produce either a rich in CH_4 substitute to natural gas or low boiling hydrocarbons (mainly olefines) for further conversion. Naval process uses wood and its ingredients to obtain olefines and from those petrol. Of the olefines C_2–C_4 9–10% was obtained at 750 °C, the ethylene content was 4% on dry wood basis.

Carbon-rich charcoal obtained in pyrolysis has a high heating value comparable with that of coal coke (~25 MJ/kg), and due to its low sulphur and nitrogen concentrations its combustion does not generate poisonous oxides in considerable amounts. Because of its scanty ash content charcoal can be used as metallurgic coke or in the preparation of active charcoal. The chemical character of the oxygen containing functional groups on the char surface revealed that they are polyfunctional cationites. Thus, charcoals have hydrophilic surfaces and are suitable for removing metal ions and other pollutants from water [2].

The LP obtained in BM pyrolysis as organic condensable is oxygeneous and contains a large amount of water and polyfunctional oxygen compounds and less simple phenols, alcohols, acids, ketones, and aldehydes. The concentration of hydrocarbons, typical constituents in natural petroleum and shale oil, is low.

Fragments formed as unstable and reactive can repolymerize into solvent soluble compounds with appropriate molecular weights. Depending on the operating conditions, which determine liquefaction severity, various compounds in different concentrations can be found in the composition of solvent solubles (see Fig. 1).

Actually, lignin as well as cellulose in different lignocellulosic materials may have different chemical composition. As is known [84, 85], the polymerization degree of glucose monomers linked with glucoside bonds in the cellulose of bark has been estimated as 2800–3300 and that of xylanes in hemicellulose 150–250. Lignin is an amorphous heterogenic polymer consisting of propylphenyl monomers connected via C–O–C and C–C bonds. The lignin in bark composition is more heterogeneous than that in wood. Of bark lignin 30–50% was found to be similar to that of wood, but the rest did not dissolve in 72% H_2SO_4 and was characterized by high contents of carboxyl and low methoxyl groups [85]. The composition of functional groups in lignin monomers does not vary only in conformity with the parent system from which lignin is separated. Bark and

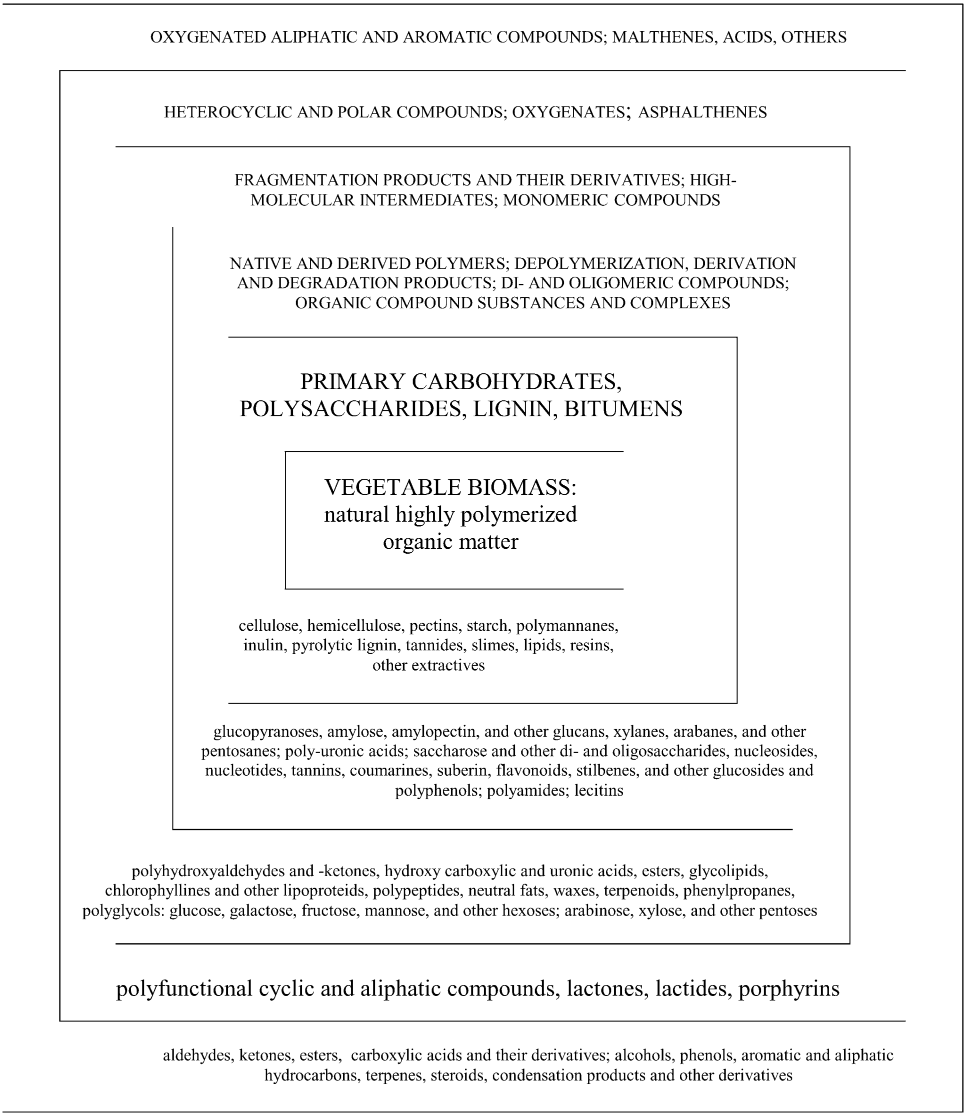

Fig. 1. Solvent soluble fragments from BM decomposition formed in different stages of TCL.

wood, needles and leaves, softwood and hardwood, both coniferous and broad-leaf trees between themselves, even individual species liable to environmental impacts or of different biological age, can differ in the lignin concentration and composition [86].

BM-derived primary liquids like initial BM also contain large amounts of oxygen but as a result of thorough upgrading most of the oxygen can be removed (Table 3).

Table 3. Ultimate analysis of liquids

Wood- or bark-derived liquids	Concentration, wt.%				Molar ratio[a]	
	C	H	N+S	O (by difference)	H/C	O/C
Wood-derived oils:						
Wood fast pyrolysis oil [87]	55.3–63.5	5.2–7.0	0.07–0.44	29.1–39.4	1.12–1.32	0.34–0.53
Acacia slow pyrolysis oil [88]	58.8	6.9	0.6	33.7	1.41	0.43
Eycalyptus slow pyrolysis oil [88]	63.9	7.8	0.6	27.7	1.46	0.32
Sawdust fast pyrolysis oil [89]	60.4	6.9	0.9	31.8	1.37	0.39
Sawdust fast pyrolysis oil upgraded [89]	87.7	8.9	0.4	3.0	1.22	0.03
Oaken BM solvolytical liquefaction oil fraction 200–280 °C [71]	82.2	9.3	5.9	2.6	1.36	0.02
Sawdust solvolytical liquefaction oil followed by catalytical upgrading [72][b]:						
Heavy fraction	84.9	8.3	0.7[b]	6.1	1.17	0.05
Light fraction	86.2	8.1	1.7[b]	4.0	1.13	0.04
Upgraded oil	86.9	9.8	0.9[b]	2.4	1.35	0.04
Bark-derived slow pyrolysis liquids:						
Bio-oil from barks (*Pinus brutia* Ten.) [82]	63.9	7.6	0.1	28.4	1.43	0.33
Bio-oil from pine bark [88]	63.3	7.2	0.8	28.7	1.36	0.34

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[a] Calculated by the authors.
[b] (N + S) by difference.

Fuels and other chemicals from BM

Different oxygen-containing chemicals have been separated from LPs and LP as total product has been successfully used as boiler fuel with heating value of 25–30 MJ/kg. Chemical fractionation of different LPs has shown them to be almost exclusively made up of oxygenated compounds. The aliphatic fraction accounts for <1 wt.% of the LP only. The aromatic, phenolic, and aromatic oxygenated compounds and polar fractions of the LP make up ca 15, 62, and 9 wt.%, respectively [82].

LPs have typically water contents of 15–35 wt.%, fast pyrolysis oils are characterized by higher and slow-pyrolysis oils by lower water contents [87]. Being mostly emulsions LPs do not form separate layers of water and oil, and the water is a constitutional part of the single-phase chemical solution. Thus water cannot be removed by conventional methods like distillation.

Primary LPs generally contain, besides water, considerable amounts of acetic and formic acids, methanol, furfurylalcohol, levoglucosan, levoglucosenone, acetone, dihydroxyacetone, hydroxyacetaldehyde, furfural, acetoine, and phenolic pyrolytic liquid [6, 90, 91]. Using mild extraction methods groups of compounds such as tannins [92, 93], sugars [94], resins and carboxylic acids [95], waxes [96], and flobafenes [91] can be obtained. The above-listed as well as other chemicals separated from LPs such as various polyphenols, glyco- and glycerylaldehydes, esters, and others can be used in the manufacturing of drugs, odourants, glues, and plasticizers [90, 91].

Investigation of the composition of the functional groups of LPs showed all types of functionalities to be present: acids, sugars, alcohols, ketones, aldehydes, phenols and their derivatives, furanes, lactones, acetates, ethers, but mostly mixed oxygenates. More than 300 compounds have been identified as fragments of the basic polymers of BM, which make up only 40% to 50% of the identity revealed until now. The phenolic fraction (often above 50 wt.% of total liquid) consists of relatively small amounts of phenol, eugenol, cresols, xylenols, and guaiacols and much larger quantities of alkylated polyphenols (so-called water insoluble pyrolytic lignin) [87]. Basically, the recovery of pure compounds from the complex liquid is technically feasible, but economically still not very attractive because of high costs of the recovery of chemicals and their low concentration in the liquids.

Production of BM energy is technically feasible but still more costly than the use of fossil fuels unless associated with disposal or pollution control [97–101]. Though BM conversion by pyrolysis has many environmental and economic advantages over fossil fuels, oil shale, coal, and natural crude production dominate because costs are kept lower by various means, including government protection. However, the Shell hydrothermal upgrading (HTU) process offers biocrude production for about 25 $/bbl oil equivalent [70]. At present the natural crude prices in the world market surpass 60 $/bbl, so the time has arrived to pay special attention to renewable resources.

Recently methods based on the utilization of various BM mixtures including those with coals as feed for thermochemical co-liquefaction have been developed with the aim to elevate the economic profitability of BM processing and to lessen the environmental pollution caused by processing codes [102–105].

One should always remember that the earth’s natural BM replacement represents an energy supply of around 3000 EJ (3×10^{21} J) a year, of which under 2% is currently used as fuel. In 2000 the bulk of BM energy was produced from wood and wood wastes (64%), followed by municipal solid wastes (24%), agricultural wastes (5%), and landfill gases (5%) [6].

DEVELOPMENTS ON BM THERMOCHEMICAL CONVERSION IN ESTONIA

Estonia has both fossil and renewable BM resources. Besides kukersite oil shale, which has been industrially burnt and liquefied for electricity and shale oil production for more than eighty years already, the energetic potential of other local resources should be taken into account. The most abundant resources in Estonia regarded as alterantive energy sources are Dictyonema argillite, peat, and forest wastes, and continuously accumulating polymeric wastes (rubber, plastics). In limited quantities easily cultivable renewables such as an energy crop (*Salix*), reed (*Phragmites communis*), and reed-mace (*Typha*) are available. Investigations on BM thermochemical conversion, concentrated on liquefaction, were initiated in Estonia by the Department of Oil Shale Technology, Tallinn University of Technology (TUT), in 2001 and since then are being carried out in parallel to researches on oil shale liquefaction. Both directions are closely connected as renewable and fossil BM (lignocellulosic and kerogeneous high-molecular organics) can be liquefied and analysed by using similar methods and apparatus. All the above-mentioned materials are under study in Tallinn Oil Shale Research Laboratory at TUT with various liquefaction methods used. Below liquefaction of forest-originating materials, which include woody sawdust, bark, and needles from forestry and wood processing activities is discussed. Such material is widely available from forest cleanings, as wood and logging residues, and from wood processing enterprises. Our investigations serve as basic research, aimed at working out fundamentals for modifying existing oil shale processing technologies for effective liquefaction of both fossil and renewable fuels to produce substitutes to natural crude petroleum.

As it is known, industrial utilization of kukersite oil shale in Estonia using the present technologies is limited by the EU till 2016. This means that during the period of transition the environmentally harmful oil shale processing technologies have to be replaced with modern ones. That is why intensive investigations are indispensable to find out the best possible solutions in the following areas:

- varying raw materials as feed for liquefaction;
- working out the fundamentals for co-processing fossil fuels with renewables (and wastes);
- elevating the proportion of organics in the liquefaction feed and increasing oil yield;
- increasing the assortment of products and modification of the oil composition obtained;
- decreasing environmental pollution.

Below the results obtained in the liquefaction of coniferous forest waste biomass (FWB) are presented. This type of BM is the most widely available BM species in Estonia. Liquefaction was carried out under the conditions similar to those used in the pyrolysis, hydrogenation, and thermal dissolution of oil shales. The aim was to obtain initial data for designing and developing fundamentals of co-liquefaction processes of domestic fossil and renewable feedstocks.

Materials

Processing of forest trees gives various wastes. The root system makes up 10–40%, stem 55–80%, and crown (branches with leaves or needles) 5–25% of the mass of a growing tree. Bark forms 10–20% of the stem or about 10% of the whole tree. The proportion of tree parts is influenced by its species, age, growing conditions, number of branches, etc.

About a half of the Estonian territory (2.25 million hectares) is covered with forest. Softwood is up to now preferably used. As a result of steady and intensive use the share of coniferous trees, pine and spruce, has decreased from 70% at the beginning of the 20th century to 52% at present. Still, conifers make up more than a half of the total forest resource.

Samples of FWB from recently felled coniferous trees were individually ground using the desintegrator technology (Desi-11, productivity 20 kg/h). As a result particles of 0.04–0.1 mm size were obtained.

As examples of unused forest residues the following materials were selected and individually liquefied: pine (*Pinus sylvestris*) sawdust and bark and spruce (*Picea abies*) sprays (needles with twigs). In practical applications wood, crushwood, bark, needles, leaves, cones, or other kinds of FWB are scarcely ever assorted before liquefaction, combustion, or gasification but are used as a blend the composition of which is seldom uniform. Liquefaction of BM species separately enables to elucidate specific and common features and variation limits in liquefaction as a basis for predicting the behaviour of mixed BM.

All the initial samples, which consisted of pine sawdust, pine bark, and spruce needles, were practically concentrates of organic matter, their mineral ash concentration (A_d) being only 0.4–3.5%. The dry organic matter ($100 - A_d$) made up 96.5–99.6 wt.%. The moisture content (W_a) fluctuated between 8 and 9 wt.% depending on storing conditions. Any BM sample like sawdust can intensively absorb atmospheric moisture and needs drying before being submitted to liquefaction. In aqueous liquefaction processes, however, drying is not necessary as part of technological water can be replaced on account of the water the sample includes. The C, H, N, and O concentrations of the initial samples were respectively 50.4–52.2, 6.3–6.5, 0.2–1.1, and 41.0–42.1 wt.%. The molar ratio H/C was 1.45–1.52 and O/C 0.59–0.63.

Methods

Liquefaction methods

TCL methods at fixed experimental conditions described in Table 4 were used for the liquefaction of tree ingredients.

Table 4. Operating conditions

Method	Reactor	Temperature, °C	Duration, h	Pressure, MPa			Weight, g	
				Initial	Working	Residual	Sample	Solvent/ Co–Mo catalyst
Semicoking	Fischer assay	Up to 525	1.5	0.1				
Water conversion	Autoclave	380	4	0.1	Up to 40	0.1–1	60	180/–
Hydrogenation	Autoclave		4	6.5	Up to 40	Up to 6.5	60	–/6

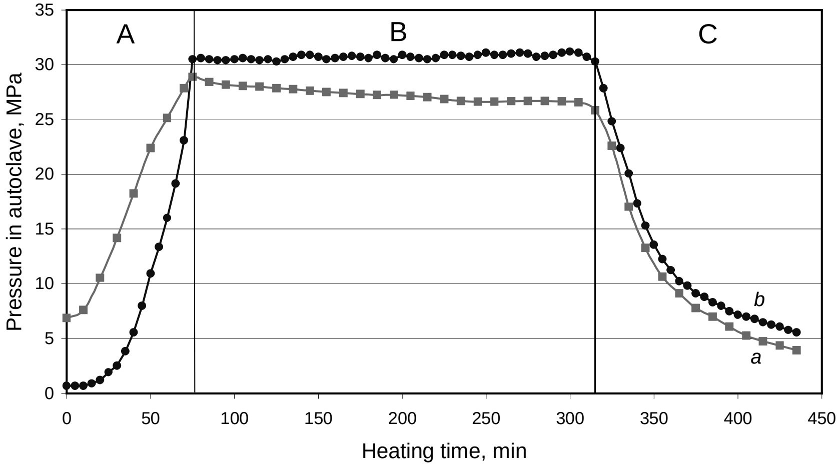

Fig. 2. Pressure versus conversion time: A – temperature rise from ambient to 380 °C, 75 min; B – temperature constant, 240 min; C – temperature drop from 380 °C back to ambient, 120 min. *a* – hydrogenation, *b* – water conversion.

The pressure vs. time diagram in Fig. 2 represents FWB hydrogenation and water conversion generally. The respective curves for sawdust, bark, and needles individually differ in the fluctuating amplitude by ±5% only.

Extraction methods

Liquid yield obtained in pyrolysis is usually determined as the weight of condensable volatile matter and that obtained in water conversion or hydrogenation as the weight of soluble matter in a certain solvent.

As LPs are of hydrophilic character and shale oils lipophilic, their solubility in conventional solvents is different. As is known [106], thermobitumen and shale oil formed as a result of its decomposition are both almost totally soluble in benzene and practically insoluble in water while the solubility of LPs from BM, 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 composition should be obtained. That is why the following extraction schemes, depicted in Figs 3 and 4, were worked out. According to these schemes the yield of LP was determined as the total weight of solvent solubles, summarizing respectively the weights of soluble matter in solvents of different polarity – in water, benzene, and acetone. Basing on solution principles enables to adequately compare the liquefaction potential of all kinds of renewable and fossil fuels when semicoking, water conversion, or hydrogenation are used as TCL methods.

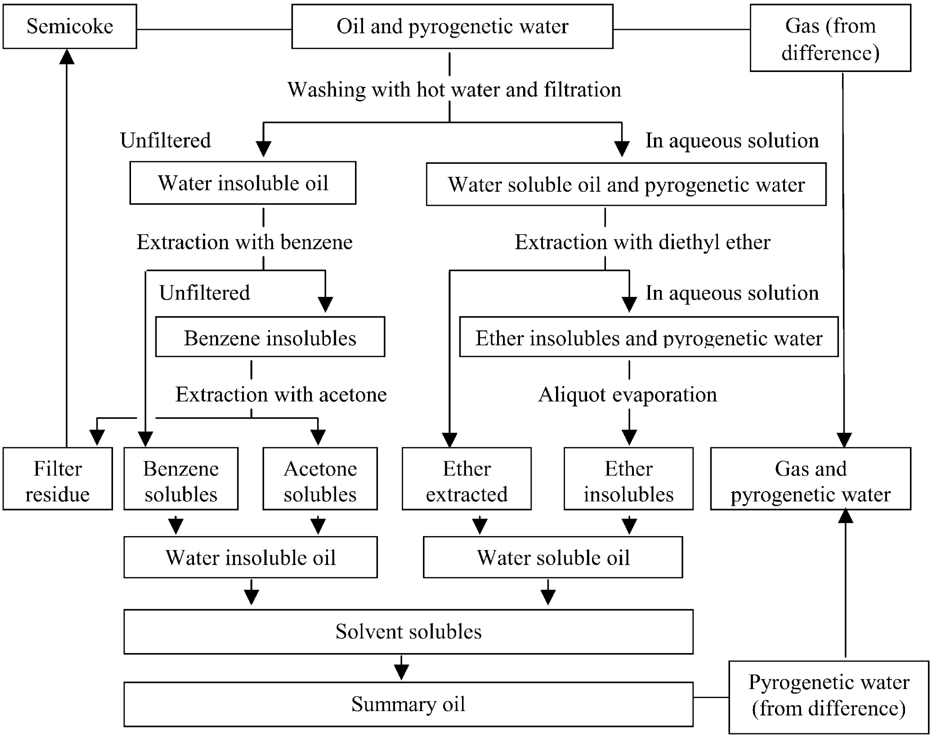

Fig. 3. Separation scheme for solid, liquid, and gaseous products obtained as a result of semicoking.

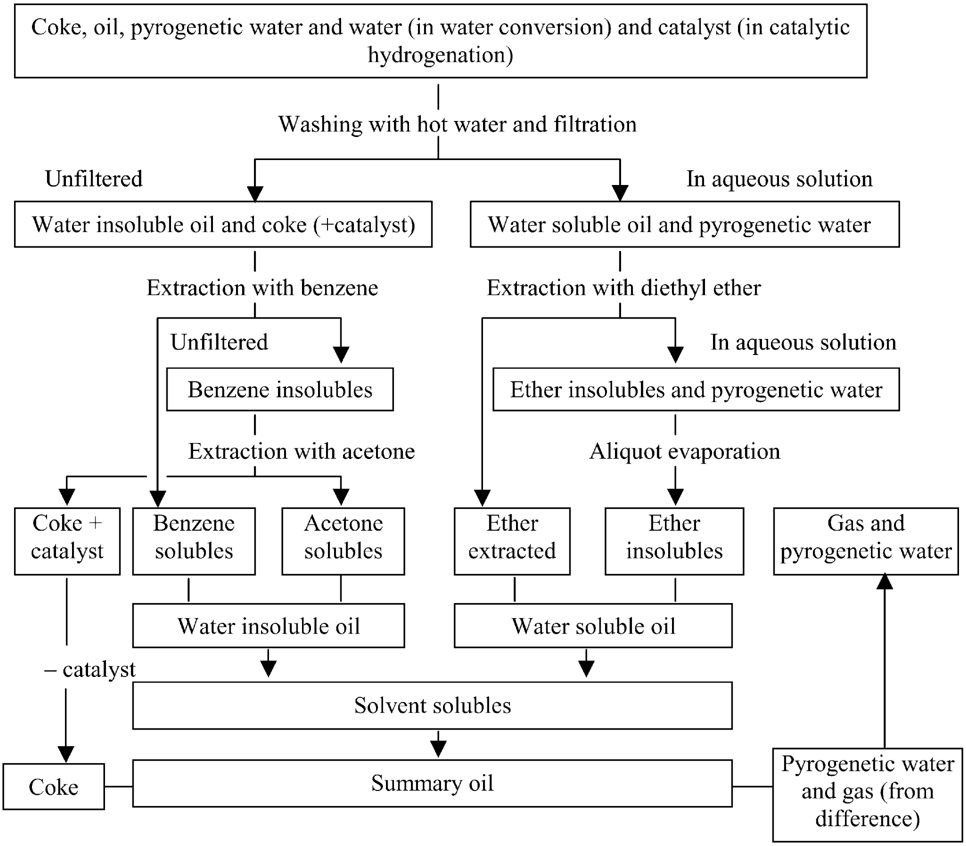

Fig. 4. Separation scheme for solid, liquid, and gaseous products obtained as a result of water conversion and catalytical hydrogenation.

Analytical methods

Chemical composition of water soluble, benzene soluble, and acetone soluble fractions was investigated using ultimate analysis and chromatographic and spectroscopic techniques. Ultimate analysis was performed with an Elementar Vario EL analyzer and infrared spectra were taken on an Interspec 2020 spectrometer. The chemical group composition of liquid samples was determined by preparative thin-layer chromatography (TLC). Plates of 24 × 24 cm coated with a 2 mm silica gel (60 µm) layer were used. Samples (500 mg) were analysed with *n*-hexane as the eluent. TLC fractions were analysed by gas chromatography using Chrom-5 apparatus in packed columns (4% E-301 on Chromaton N AW HMDS) with temperature programming. Individual composition of gaseous compounds was also analysed by gas chromatography in packed columns (molecular sieves, sepharon) under isothermal conditions.

Results and discussion

Yields of liquefaction products

The maximum and minimum yields of liquid, gaseous, and solid products obtained from sawdust, bark, and needles as solvent solubles, volatiles, and insoluble non-volatile residue by using semicoking, water conversion, and hydrogenation methods are presented in Table 5.

Table 5 shows that gas formation is the absolutely dominating process despite which method or feed was used. The proportion of non-condensable gas and water amounts on average to 50 wt.% among BM TCL products being slightly less in semicoking with the Fischer assay and slightly more in autoclavic extraction and hydrogenation, 45–46 and 47–54 wt.%, respectively. The remaining 50% of products consist of liquid (solubles) and solid (insolubles) matter in weight percentages ratio of approximately 20 : 30. However, sawdust hydrogenation yielded 8 wt.% for summary LP and bark hydrogenation 41 wt.% for solid residue as exceptional minimum and maximum values. These values differ considerably from the rest. Water has often been included into LP composition in investigations dealing with BM liquefaction. In the destruction practice of fossil fuels, on the contrary, water is seldom included into the liquid balance. We added water to gas yield wittingly, because oxygen is released as a result of intensive deoxygenation via both gas and water. As Table 5 reveals the weight proportions of gaseous, liquid, and solid conversion products of BM are rather similar although quite different methods, process variables, and feed composition were used.

As a rule, minimum and maximum yields of liquid fractions and summary LP in Table 5 were fixed when pine sawdust or spruce needles as feedstock were individually liquefied. Pine bark showed values between the maximum and minimum but very seldom close to these. In catalytical hydrogenation and water conversion needles gave the highest and sawdust the lowest liquid yield, but in semicoking just vice versa. These regularities can be of great importance in industrial-scale TCL of mixed woody materials such as logging-cuts and

Table 5. Yield of liquefaction products, wt.% (dry basis)

Product	Method		
	Semicoking	Water conversion	Catalytical hydrogenation
Liquid:			
Water solubles	8–16	6–9	1–2
Benzene solubles	7–9	6–16	5–18
Acetone solubles	1–2	3–4	2–5
Summary LP, oil as solvent soluble	16–26	16–27	8–22
Gas + reaction water	45–46	47–52	47–54
Solid residue	29–39	26–32	32–41

woodworking remnants, containing wood, bark, needles, and other tree-derived BM species in different, often in occasional quantities. Basing on the data in Table 5 one can deduce that for keeping LP in specification limits and to avoid large deviations in the liquid yield, any proportion of bark can be used in the blend but the quantities of wood and needles should be equal to roughly compensate for the minimizing influence of the former and the maximizing influence of the latter. Thus, the ratio 50 : 20 : 30 describes the disproportion regularity between the gas, liquid, and solid phases of FWB converted in this work at conditions optimum for oil shales. This regularity is approximately valid for individual FWB but much better when wood, bark, and needles are blended.

Comparison with the results obtained in kukersite oil shale TCL [107] with the same methods and under equal conditions reveals that in BM TCL considerably lower yields of liquid and higher yields of gas were obtained. Obviously, the conditions used as optimum ones for kukersite are too severe for BM. Possibilities of achieving high yields of oxygen-rich LP from BM demonstrated before were not of interest in our strivings. As it was stated before, the present work aims at obtaining liquids as partially upgraded already, characterized by a moderate oxygen content like shale oil.

Table 5 demonstrates that the lowest yields of total solubles were obtained in hydrogenation using molecular hydrogen. The result belongs to the predicted ones because in the case of long-term hydrogenation deeper deoxygenation occurs involving further decomposition and gas formation from the liquid formed. In water conversion the water probably has some preserving effect avoiding perceivable decomposition of the liquid once formed and, also, equilibrium between reaction products is achieved earlier than after 4 h. Semicoking differs from other processes used by continuous evacuation of gaseous and liquid products in the vapour phase and their rapid condensation.

Composition studies

The chemical composition of TCL products depends on the composition of the initial BM sample submitted to liquefaction and on the conditions of TCL. Opportunities to modify the chemical composition of TCL products by altering TCL conditions were studied.

Elements

The elemental composition of sawdust, bark, and needles under study in this work as initial feedstocks of BM was very similar. In Table 6 the elemental composition of LPs from pine bark with averaged C, H, and O concentrations is presented.

As can be seen the LP obtained in bark hydrogenation and kukersite semicoking oil are rather similar.

Table 6. Ultimate analysis of oils obtained from pine bark by using different TCL methods

Object/Method	Concentration, wt.%					Molar ratio			
	C	H	N	O[a]	S	H/C	N/C	O/C	S/C
LP/Semicoking	67.7	7.8	0.6	23.8	0.1	1.38	0.008	0.23	0.0005
LP/Water conversion	73.2	7.6	0.5	18.5	0.2	1.25	0.006	0.19	0.001
LP/Catalytical hydrogenation	81.5	8.5	0.5	9.4	0.1	1.25	0.005	0.09	0.0005
Kukersite semi-coking oil [108]	81–84	9.5–10.5	0.1–0.2	6–8	0.6–0.8	1.47	0.002	0.07	0.004

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[a] By difference.

Functional groups

The composition of functional groups of solvent soluble matter was investigated using infrared spectroscopic (IRS) methods. Infrared spectra of different LP fractions are presented in Fig. 5. The spectra of TCL products soluble in water, benzene, and acetone are clearly distinguishable. Visible absorptions are quantitatively rather than qualitatively distinguished and differences in the composition of spectra depend more on the method used than on the initial material liquefied.

Various oxygen functionalities occurring in abundance are the most characteristic in the composition of 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 in 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. Formation of intermolecular hydrogen bonds between polar compounds such as ethers, ketones, or amides, preferable multi-substituted nature of derivatives, and abundance of oxygen functionalities cause 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}. As it 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 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. 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 absorbtions (3020, 3050, 860, 815, 760 cm^{-1}) are visible. Benzene nucleus manifests itself at 1600 and 1500–1515 cm^{-1}.

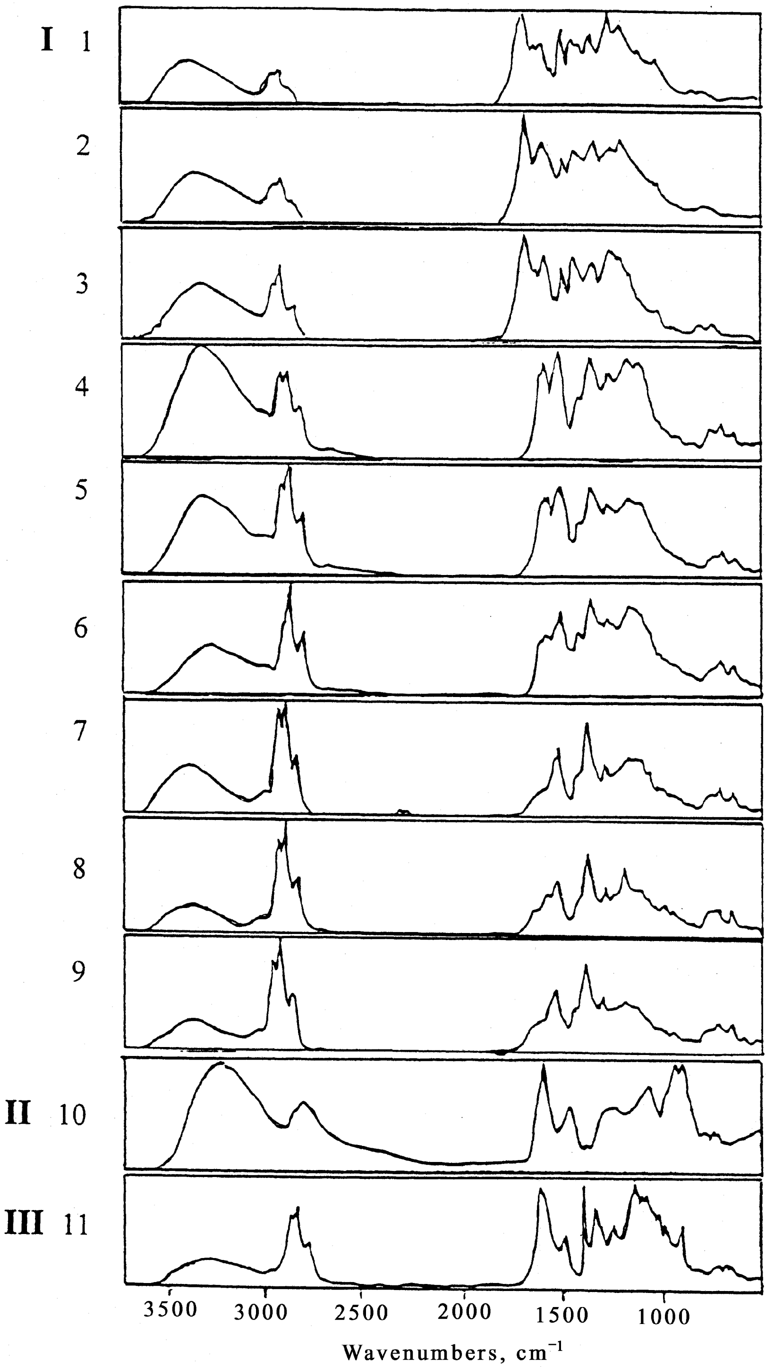

Fig. 5. Infrared spectra of acetone soluble (**I**), water soluble (**II**), and benzene soluble (**III**) fractions obtained in semicoking (1–3), water conversion (4–6 and 10), and hydrogenation (7–9 and 11) of sawdust (1, 4, 7, 10, 11), bark (2, 5, 8), and needles (3, 6, 9).

Absorptions at 1170 and 1145 cm^{-1} typical of isopropyl groups derived from lignin decomposition are more visible in semicoking liquids, while mono-, sesqui-, and polyterpenes manifest themselves at 2800–3000 and 800–840 cm^{-1} conspicuously in bark- and needle-derived liquids. Mono- and triterpenes such as 2-pinene, limonene, and suberine can be expected to be present. It is known that fossilized isoprenoids can survive severe processing conditions. In pyrolytical transformations of oil shales at inert and even at reductive conditions isoprenoids C_{19}–C_{21} are even dominating over respective *n*-alkanes in the composition of liquids obtained [109–111]. Cyclic hydrocarbons and their derivatives manifest themselves by adsorption at around 3040 and 1462–1452 cm^{-1}, more or less intensively, in all fractions.

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 work 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 remnats 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 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 consecutive 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, Fig. 5 demonstrates that 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.

As to the chemical composition of the solvent soluble fractions, we can suppose the following. Water solubles are represented by polar hydrophilic compounds, probably of different alcohols, carboxylic acids, aldehydes, sugars, phenols, and other oxygeneous compounds. As it was mentioned above, lower oxygeneous homologues such as methanol, formic and acetic acids, formaldehyde and acetaldehyde, acetone, and several simple ketoaldehydes were formed in abundance as a result of pyrolytical decomposition of BM in inert media, including semicoking. In water conversion and hydrogenation under the conditions used in this work those compounds were not rapidly evacuated from the hot reaction zone. Being in close contact with other decomposition fragments and influenced by high temperature and pressure for a long time they can initiate different reactions, including chemical incorporation, reductive decomposition, synthesis gas reactions and others. Lipophilic oily compounds such as hydrocarbons, water insoluble phenols, as well as asphalthenes are concentrated into benzene solubles. The group composition of these was determined later. Acetone soluble matter is presented 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. [79] 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.

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, letcitinic and other phospholipidic, tioketonic, tioalcoholic, tioureatic, 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 Fig. 5.

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.

Specifying water solubles as chemicals and acetone solubles as transition compounds, the goal of our investigations includes maximizing the yield of benzene solubles and minimizing that of acetone solubles. Our interest was 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 futher developing processes of co-liquefaction of Estonian oil shale and BM to obtain chemically modified syncrude and valuable phenolic compounds. Investigating the composition of the monophenolic compounds in slow pyrolysis oil of Siberian larch at different temperatures Chuprova & Levin [112] found that the proportion of the most valuable dihydroxyphenols among other ones was highest at 500 °C. In the presence of high-pressurized solvents or gases the temperature can be lowered in the range from 350 (beginning of kukersite kerogen bituminization) to 450 °C (thermobitumen decomposition).

Compound groups

The group composition of benzene soluble compounds separated by TLC is presented in Table 7. The yields of respective compounds were limited by minimum and maximum yields obtained in the TCL of sawdust, bark, and needles.

In benzene fractions high polar compounds prevail. Their proportion in all hydrogenized fractions is practically equal to that of neutral oxygen ones. Outstandingly high contents of polar compounds were registered in the composition of semicoking as well as water conversion benzene soluble extracts, respectively 58–77 and 64–71 wt.%, while that in hydrogenate was only 22–34 wt.%. Neutral oxygen compounds are another dominating class of compounds. Their percentage is considerably lower than that of high polar compounds but never lower than that of any hydrocarbonaceous fractions obtained. The concentration of the most valuable constituents of motor fuels – aromatic, alicyclic, and aliphatic hydrocarbons – is variable depending on both the method and the feedstock used. Though Table 7 includes a benzene fraction poor in hydrocarbons (2% in the semicoking of pine sawdust), other experiments yielded sometimes more hydrocarbons. The higher the content of hydrocarbons, the closer the product to natural

Table 7. Group composition of benzene soluble compounds

TLC fraction separated	Yield, wt.%			
	Semicoking	Water conversion	Catalytical hydrogenation	Kukersite semicoking [113]
High polar compounds (oxygeneous, other heteroatomics, and asphalthenes)	58–77	64–71	22–34	23
Neutral oxygen compounds	9–36	13–17	25–32	34
Polycyclic aromatic hydrocarbons	3–6	8	16–25	17
Monocyclic aromatic hydrocarbons	1–4	3	3–5	8
Non-aromatic hydrocarbons	2–9	4–8	8–24	18

petroleum. Hydrogenates stand out as having a particularly high concentration of hydrocarbons. Table 7 shows that the total yield of hydrocarbons was 34–39 wt.% (sawdust and needles), but in bark hydrogenation it amounted even to 54 wt.%. Compared with kukersite shale oil the hydrogenates obtained are characterized by a similar group composition and, in some cases, even by a higher hydrocarbon content. It is obvious that the primary extracts obtained as only partially deoxygenated and not totally decomposed urgently need additional deoxygenation and decomposition as secondary upgrading (hydrogenation). Co-upgrading of LP derived from BM with shale oil or with any heavy fraction of shale oil can open up new prospects.

Individual composition of hydrocarbons

The individual composition of TLC hydrocarbon fractions was analysed by gas chromatography. Chromatograms of non-aromatic hydrocarbons are presented in Fig. 6. It is obvious that the outstanding peaks in all chromatograms belong to *n*-alkanes C_{14}–C_{26}, those of alicyclic hydrocarbons being suppressed. Semicoking yields considerable amounts of *n*-alkenes, their concentration is close to the adjacent saturated homologues (chromatogram (a) in Fig. 6). The chromatogram of non-aromatic hydrocarbons obtained in semicoking is the most representative of the composition of different types of hydrocarbons. Smaller peaks visible belong to isomeric and cyclic alkanes and alkenes, terpenes, and steroids.

Among aromatic compounds lower benzene alkylsubstituted derivatives, naphthalene, methyl- and dimethylnaphthalenes, diphenyl, acenaphthene, fluorene, phenanthrene, and anthracene were identified.

Although there are lines of peaks among aromatic compounds, we could not identify several peaks in high concentration. These may belong to different derivatives of mono- and bicyclic aromatic hydrocarbons, but also to alicyclic compounds. In [114] it is demonstrated that in group composition determination with TLC homologous series of alicyclic and aromatic–alicyclic (hybrid) compounds were identified between aliphatic and polycyclic aromatic hydrocarbons. In any case, these compounds were separated as hydrocarbonaceous ones. The benzene solubles from different hydrogenation and water conversion experiments are quite comparable with kukersite retort oil containing in several cases even more hydrocarbons, their content amounting to 50–54 wt.% of the total extract. Similarities in the group composition and differences in the individual compounds in groups make it attractive to develop processes of co-upgrading bio- and shale oils to modify and improve compounded oil qualities.

Gas analysis

Gas, which made up about a half in the yield of autoclavic processing and one fifth in semicoking of BM, was submitted to further chromatographic analysis to determine its composition.

The main gaseous compound formed was carbon dioxide, its share being as high as 60–75% of the total gas amount in both water conversion and semicoking

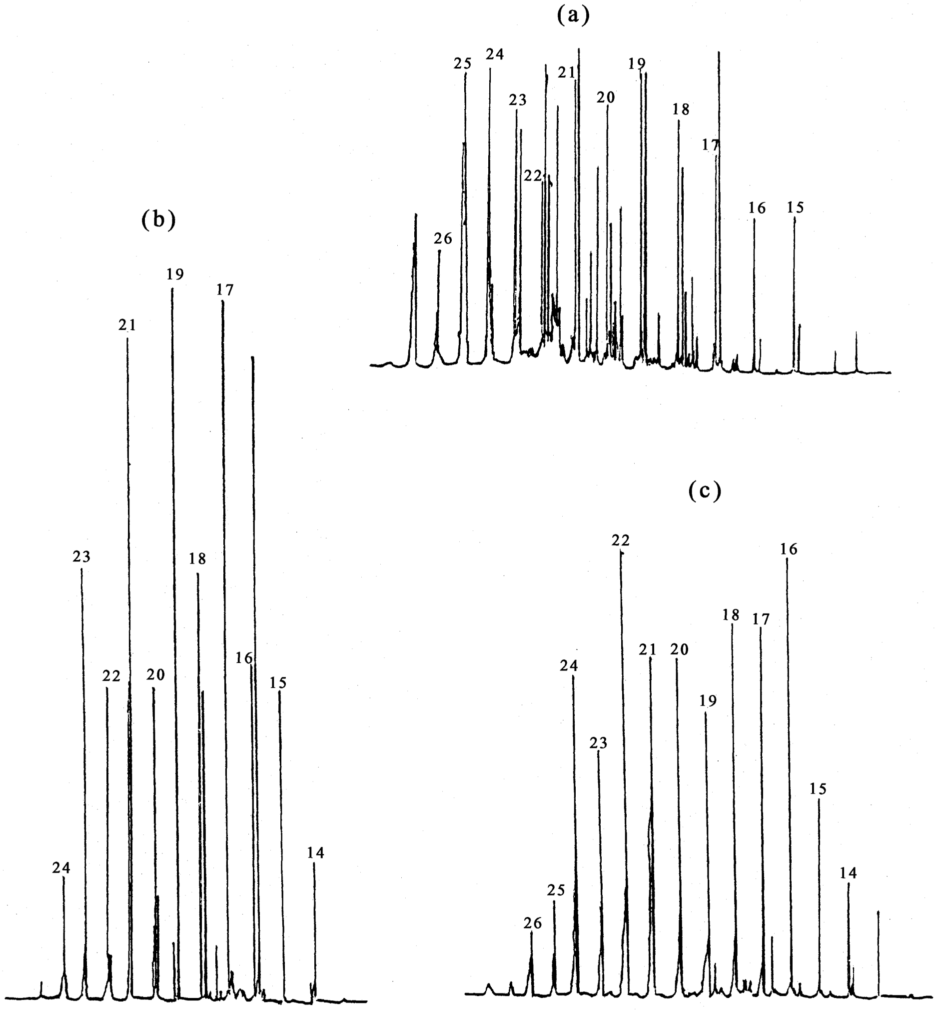

Fig. 6. Chromatograms of non-aromatic hydrocarbons obtained in pine bark semicoking (a), water conversion (b), and hydrogenation (c). The numbers 14–26 show the number of carbon atoms in the *n*-alkane molecule.

(Table 8). Hydrogenation gas, which contains large amounts of unreacted hydrogen, was characterized by a lower carbon dioxide content (27–49 vol.%). Still, the share of carbon dioxide in BM-derived gas was close to the values obtained by other methods. Semicoking yielded a considerable amount of carbon mono-oxide (especially from bark and needles). The methane percentage was high enough (6–13 vol.% in hydrogenation and even 23 vol.% in the case water conversion of needles), that of other gaseous hydrocarbons was significantly lower. The share of residual hydrogen after hydrogenation (23%) showed that as compared with other feedstocks bark consumed more hydrogen.

Table 8. Gas composition

Gas identified	Concentration in total gas, vol.%		
	Semicoking	Water conversion	Catalytical hydrogenation
Carbon dioxide	62–74	57–75	27–49
Carbon oxide	15–26	1–5	0–1
Hydrogen	1–2	1–4	32–44
Hydrogen sulphide	0–1	1–2	1–2
Methane	5–8	11–23	6–13
Alkanes C_2–C_4	1–3	9–12	6–16
Alkenes C_2–C_4	0–2	0–1	0

CONCLUSIONS

Biomass, a diversified resource in its colossal majority permanently regenerated directly or indirectly by plant growth, is generally of lignocellulosic nature. Unused BM and remainders of BM 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 BM 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 BM as a feedstock attractive.

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

Conversion processing of BM leads to the formation of fuels with a higher energy density than the original. Oxygen-containing chemicals can be separated as well. Pyrolysis, hydrogenation, and sub- or supercritical extraction are the methods often used in BM thermal and thermochemical liquefaction. Operating at temperatures within 300–550 °C with and without hydrogen, with water and other solvents and catalyst additions LPs can be obtained in various yields and chemical compositions. Both BM and liquids derived from it are characterized by as high as up to 50 wt.% oxygen content. Due to large amounts of oxygenated compounds present, the BM-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 BM-derived liquids compared with those originating from fossil fuels. Pyrolysis yields considerable amounts of a highly oxygenated liquid, which can be used as light and heavy fuel oil as well as refinery feed as the excessive oxygen can be removed via hydroprocessing. As a result of effective reductive deoxygenation the yield of upgraded LP decreases proportionally with the decreasing oxygen concentration, which can be diminished to the level meeting transportation fuel specifications.

Investigations initiated in Estonia focus on working out the fundamentals of individual and co-processing of BM 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 LPs close to shale-derived syncrude quality.

It is obvious that deoxygenation, a strongly desired process, occurred intensively in spite of which TCL process or feedstock under investigation was used though the oxygen concentration was reduced insufficiently – only by half. To further 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.

The yields of LPs obtained in this work seem to be small compared with those obtained in flash pyrolysis. Actually considerably more deoxygenated liquids were obtained in this work and theoretically calculated hydrocarbonaceous potential of BM initially containing 40–50 wt.% oxygen, after its removal as CO_2 (totally deoxygenated liquid), is less than 30–35 wt.% – due to other cracking and coke formation processes, 20–25% can be attainable. Total deoxygenation is hardly ever achieved. Further investigations are being carried out to obtain the above-mentioned level and product, which could be characterized as being in between nonconventional petroleum and natural crude.

Additional hydrocracking to upgrade BM-derived liquids alone and together with shale oil heavy fractions are also on the agenda.

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Biomassi termokeemiline vedeldamine: maailmapraktika ja hiljutised uuringud Eestis

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On esitatud ülevaade biomassi termilise ja termokeemilise konversiooni alastest töödest nii globaalses kui lokaalses lõikes ja Eestis viimastel aastatel alustatud uurimistöö praktilistest tulemustest selles valdkonnas.

On antud andmed paljude lignotselluloosset tüüpi biomassi erimite keemilisest koostisest ja vedeldamispotentsiaalist, kusjuures põhitähelepanu on pööratud erinevat sorti metsamaterjalile. Põhiliste kasutatud konversioonimeetoditena on välja toodud pürolüüs, hüdrogeenimine ja ekstraktsioon ülekuumendatud lahustitega. Konversioonitingimusi on varieeritud laias diapasoonis. On iseloomustatud konversiooniproduktide jagunemise seaduspärasusi, saagist ja keemilise koostise spetsiifikat.

Kütuste keemia ja tehnoloogia seisukohalt on biomass vaadeldav valdavalt taimset päritolu kõrgmolekulaarse ainena. Nii näiteks mahub mõistesse “biomass” mahasaetud puu tervikuna: selle osised (koor, okkad jms) – igaüks eraldi kui ka segatuna ükskõik millises kontsentratsioonis, samuti kõdunevad ja kõdunenud taimsed jäätmed. Kaustobioliitides erineva metamorfismi- ja fossilisatsiooniastmega orgaaniline aine on ka fossiilne biomass. Tööstusliku toormena klassifitseeruvad eelmainitud põlevkivide, süte, turba- ja toorbiomassina (metsa-, raie- ja puidutööstuse jäätmed või põllukultuuride mittetarbitavad jäägid). Jätkuvat teaduslikku huvi on pakkunud biomassi erimite – kuuseokaste, kookospähklikoorte, nisukõrte jpt eksootiliste ja tavapärasemate flooravormide – eraldi uurimine. Taastuv biomass, erinevalt fossiilsest biomassist, kujutab endast praktiliselt ammendamatut loodusliku tooraine ressurssi. Tohutus liigilises paljususes, koosnedes põhiosas siiski sarnastest tselluloosi, hemitselluloosi ja ligniini polümeeridest, on see kasutatav naftataolise toorõli ja naftast mittesaadavate hapnikku sisaldavate kemikaalide valmistamiseks.

Tulenevalt algmaterjali suurest hapnikusisaldusest on ka tekkinud vedelproduktid väga hapnikurikkad (kuni 50%). Kiirpürolüüsil on saadud biomassist maksimaalselt 70–80% emulsioonitüüpi õli, millest tähelepanuväärse osa moodustab õlisse emulgeerunud vesi. Deoksügeniseerimisel väheneb õli hapnikusisaldus oluliselt, vastavalt väheneb aga ka õli saagis.

Eestis on vastavasisulised uuringud käivitatud viimastel aastatel sihtfinantseeritava teadusteema raames TTÜ Põlevkivi Instituudis. Eesmärgiks on eelkõige seni toodetavale põlevkiviõlile alternatiivse naftataolise vedelprodukti saamine biomassist või biomassi ja põlevkivi koostöötlemisel, baseerudes põlevkivitööstuses kasutatavatel protsessidel ja seadmetel. Biomassi kasutuselevõtt vedeldamise toorainena võimaldaks toota traditsioonilisi põlevkiviprodukte kui ka modifitseeritud koostisega keemilisi ühendeid. Looduslikult pidevalt taastoodetava, väga väikese väävli- ja lämmastikusisaldusega biomassi kasutamisega ja tekkiva süsinikdioksiidi tagasisuunamisega fotosünteesi tsüklisse orienteeritakse olemasolev keskkonnaohtlik permanentne põlevkivitööstus ümber jäätmeväheseks jätkusuutlikuks tootmisharuks.