THERMOCHEMICAL CO-LIQUEFACTION OF ESTONIAN KUKERSITE OIL SHALE WITH PEAT AND PINE BARK

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Abstract. *Kukersite oil shale + pine bark, kukersite oil shale + peat as well as kukersite, bark and peat individually were submitted to thermochemical liquefaction in an autoclave with and without solvent for two hours at different temperatures from 340 to 420 °C. Water and benzene as solvents were used. The influence of several factors such as temperature, solvent and its type, and oil shale-to-peat or oil shale-to-biomass ratio on the yield of liquid, gaseous and solid products was investigated. The chemical composition of the goal liquid product separated as the benzene soluble oil was characterised by using FTIR-spectroscopy and ultimate analysis apparatus. Group composition of the oil was determined by using thin-layer chromatography. In co-liquefaction experiments several synergistic effects in product yields were observed. The most important synergistic effect was noticed at co-liquefaction of the mixture oil shale with peat (10 : 4 by mass of the organic matter) at 360 °C in the medium of water in which case the yield of the liquid product was 25% higher than the sum of corresponding yields obtained at liquefaction of oil shale and peat separately in the same experimental conditions. The group composition of oils shows that various polar and high-polar oxygen compounds prevail over hydrocarbon fractions. Data on the elemental and group composition demonstrate that partial substitution of biomass or peat for oil shale leads to obtaining chemically modified shale oil.*

Keywords: kukersite, peat, biomass, co-processing, synergistic effect.

1. Introduction

The demand for liquid fuels, chemicals and other products traditionally produced from natural petroleum rapidly increases in the industrialised

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countries. At the same time, the reserve of fossil resources in Earth's crust is not inexhaustible. Availability and pumping of conventional petroleum become more laborious. These circumstances lead to drastic increase in prices and stimulate the search for feedstocks and technologies for production synthetic petroleum as an alternative to the natural one. Oil shales, hard and brown coals, biomass in its varieties, as well as industrial wastes of organic polymers represent an available feedstock of hydrocarbon crude, and their potential is being realised by developing advanced methods of destruction and liquefaction. Diversity in the assortment of source raw material for obtaining petroleum substitutes is a motive power impelling dynamic development of complex thermochemical co-liquefaction processes basing on pyrolysis or thermal dissolution methods. At present, studies on the potential of co-processing of varied feedstocks are highly topical on the world scale. Co-processing of biomass [1–16], plastic or rubber wastes [17–25] with fossil fuels (mainly with coal and petroleum residues) has sometimes demonstrated higher efficiency and led to chemically modified products compared with processing of aforenamed objects individually [1, 5, 9, 11–14, 19, 22, 24, 25]. The effect of kukersite oil shale co-processing with peat and biomass is the subject matter of this paper.

1.1. Kukersite oil shale – the main energy source in Estonia

The role of oil shale as feedstock has been and still is very important for Estonian industry. In fact, kukersite oil shale is the basis of the Estonian economy being used as a source of energy to produce electricity, heat, liquid fuels and lots of chemicals by combustion and liquefaction methods. Numerous chemicals have been separated from the shale oil obtained from the kukersite oil shale liquefaction by using semicoking technology in retorts of different configuration, and Estonia has historical experience on shale oil upgrading into motor fuels [26]. Shale oil produced may be considered a type of unconventional petroleum, and it has manifested itself as a marketable product meeting the demands of domestic and world market. The yield of oil is not high in industrial conditions. The main body of kukersite oil shale is transformed in vertical retorts to hazardous solid residue (semicoke) the latter having practically no prospective for further utilization. The residual carbon content of semicoke is as high as 10–14% [27, 28]. In more progressive solid heat carrier retorts the semicoke formed is combusted in the same process to produce some addition heat necessary for oil shale destruction. As a result of *in situ* combustion, large quantities of CO_2 are emitted into the atmosphere. Severe prescriptions and taxes on both CO_2 emission and disposal of hazardous wastes are established by EU Commission to limit environmental pollution. Taking into account the fact that yielding one barrel of oil from kukersite oil shale in industrial retorts is accompanied by formation of both 0.6 tons of hazardous waste and up to $250 \, m^3$ of CO_2, it is obvious that the semicoking technology should be

further improved or replaced by alternative ones to enhance oil yield and diminish the amounts of polluting by-products.

1.2. Alternative energy sources for oil shale

The most prospective substitutes for oil shale to generate synthetic petroleum in Estonia are peat, the resource of which is estimated as one of the biggest in Europe, and forest biomass. Both peat and wood have been directly used as solid fuels in Estonia to produce heat and electricity, but never being industrially liquefied. Oil shale is the strategic resource and can be economized by using these solid fuel types as components in liquefaction feedstock.

1.2.1. Peat

Peat as a regular natural organic resource in the world stratifying in wetlands is considered one of the important Estonian energy sources and the strategic reserve in the future. World's peat reserves are estimated at about 700,000 million tons [29]. Peatlands – bogs and fens – cover over 22% of the Estonian territory, peat resources exceeding 2400 million t [30]. Peat is the youngest and least-altered member of the fossil fuels, turning into brown coal with time. Coalification includes low-temperature biogeochemical processes from burial of plants to coal formation [31]. Peat as other ligno-cellulosic materials is characterized by high oxygen content. Besides humic substances formed as a result of humification, peat contains considerable amounts of lignin, cellulose and bitumens as typical constituents of ligno-cellulosics not maintained in the fossil organic matter [32]. Raw peat in the natural deposits is characterized by moisture content as high as 90%, that of ash being variable [33–35]. Thus, peat is a particularly appropriate feedstock for conversion in water needing no prior drying. The heating value of peat is close to that of wood and brown coal, but sulfur content is lower than that in petroleum or coal [36].

When peat is pyrolyzed, the volatile products consist of a condensable portion (tars and an aqueous liquid), and a noncondensable portion (pyrolysis gases) [37]. Char, a solid product formed at pyrolysis of peat, is, unlike semi-coke, not a hazardous useless waste but can be used as a chemical reducing agent, an adsorbent, and a catalyst support. It is also used, due to its electrical properties, as anode in electrochemical applications as well as a bonding agent in rubber production and in producing pigments and lubricants. Peat gas and tar can be used as fuel gas or liquid fuel, lubricant, solvent and pitch, respectively [38].

1.2.2. Biomass

Renewable biomass in its availability and variety represents a practically inexhaustible resource of feedstock for energetical and chemical needs. By its origin biomass is lignocellulosic matter consisting mainly of varying

amounts of three biopolymers – cellulose, hemicellulose, and lignin. Biomass is a term for all organic material that stems from plants, including trees. Biomass energy, the energy stored in plants, actually originates from solar energy through the photosynthesis process, and the energy of sunlight in plants is stored in chemical bonds [39]. In fact, oil shales are also sedimented biomass, since they are fossilized remains of higher plants and marine fauna that grew and lived hundreds of millions years ago. The chemical composition of growing biomass differs from that of fossilized biomass known as kerogen by large amounts of oxygen.

In Estonia, the term biomass is most often used when referring to forestry, including all ingredients of trees. About a half of the Estonian territory (2.25 million hectares) is covered with forest. Conifers make up more than a half of the total forest resource. Processing of forest trees yields various wastes and residues. Bark usually forms up to 20% of the trunk or about 10% of the whole tree and, as disregarded so far, can be used as biomass for liquefaction. The energy enclosed in biomass can be released either by direct combustion or converted, via thermochemical upgrading, into synthetic liquid and gaseous fuels or products of higher value for the chemical industry. Pyrolysis of biomass generates three different energy-effective products in different quantities: char, gas and oil. Varying pyrolysis conditions closer to coking, gasification or liquefaction, one of these products of market value in high yield can be obtained. So, the pyrolysis of biomass can be described as direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gaseous products. Biomass pyrolysis yield is a complex combination of the products obtained at individual pyrolysis of cellulose, hemicellulose, and lignin, each of which has its own kinetic characteristics [40]. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks. Biomass pyrolysis oils have a potential to be used as a fuel oil substitute. Combustion tests indicate that these oils burn effectively, in standard or slightly modified boilers and engines, with rates similar to those for commercial fuels [41].

1.3. Co-processing of fossil and renewable feedstocks

Oil shale, peat and biomass, being miscellaneous, by the content and chemical composition of the organic matter represent, in fact, biomass of different degree of metamorphosis, natural high-molecular matter with polymerized structure, and they can all be available sources of petroleum substitutes. Renewable lignocellulosic biomass, decaying and partly humified biomass in peat, and oil shales as kerogeneous rocks containing sedimented and fossilized biomass are, individually and in blends, convertible to hydrocarbon-rich light-middle oils, using analogous thermochemical liquefaction processes and reactors. At the same time, liquefaction regularities of blends should be investigated, as they differ significantly compared with those of individual feedstocks.

Co-processing of the kukersite oil shale with other combustible fuels to obtain petroleum substitutes is not much investigated. There are available results of kukersite co-processing with wood in supercritical water and of chlorine fixation capacity of the oil shale mineral matter in PVC and kukersite co-pyrolysis [42–48].

In this work kukersite oil shale, pine bark, peat and their mixtures were submitted to liquefaction in an autoclave with the aim to determine the effect of feedstock combination and processing conditions, including the presence of solvent, on yield and composition of the products.

2. Experimental

2.1. Initial feedstocks

Air-dried, finely powdered (less than 0.1 mm) and homogenized kukersite oil shale, peat and pine bark, characterized in Table 1, were used as the initial feedstocks. Benzene and water were used as solvents. The mixtures of kukersite with peat and kukersite with pine bark for co-pyrolysis were taken in different ratios on organic matter (OM) basis.

Table 1. Characteristics of the initial feedstocks

Proximate analysis	Kukersite	Peat	Pine bark
Moisture W^a, %	0.7	11.9	8.7
Ash content A^d, %	37.2	6.1	2.9
Carbon dioxide $(CO_2)^d_M$, %	12.8	2.0**	
Organic matter OM^d, %	50.5*	91.9***	97.1

OM content was determined on acid-treated basis

*$OM = 100 - A^d_{825^oC} - 0.625 S_p$; S_p – pyritic sulphur, %

**$(CO_2)^d_M = A^d_{550^oC} - A^d_{825^oC}$

***$OM = 100 - A^d_{550^oC}$

2.2. Liquefaction and analysis

Kukersite oil shale, peat, pine bark individually and their mixtures were submitted to the thermochemical liquefaction. Either a 4-g sample, or, in the case a solvent was used, the sample with 6 g of the solvent were charged into 20-cm³ autoclaves. The autoclaves were put into a preheated muffle oven. The liquefaction experiments were carried out at temperatures 340, 360, 390 and 420 °C with the constant residence time of two hours. The yield of liquid, gaseous and solid products obtained was determined as follows. The yield of the liquid product was calculated as a sum of benzene solubles (oil)

and reaction water. The mass of gas formed was determined by the weight loss after opening the autoclave. The share of the solid residue was determined as the mass insoluble in benzene, the latter representing the residue after filtration and containing both the mineral matter and charred input material, dried in a thermostat at 105 °C for two hours to a constant mass. The coke yield was calculated by subtracting the mass of the mineral matter from the mass of the dried solid residue.

The elemental composition of the kukersite oil shale sample, peat, pine bark and the oils generated from these individual and combined feedstocks was examined by using Elementar Vario EL analyzer.

The functional group composition of oils obtained was investigated by FTIR-spectroscopy using an Interspec 2020 FTIR-spectrometer.

The group composition of the benzene-soluble oils was determined by thin-layer chromatography using plates 24×24 cm coated with a 2-mm silica gel layer (Fluka, 40). 0.5-g oil samples were analyzed and *n*-hexane as eluent was used. Three individual groups of hydrocarbons – aliphatic, mono-aromatic and polyaromatic ones –, and two groups of oxygen compounds – neutral and high-polar oxygen compounds – were separated and their share in total oil calculated.

3. Results

3.1. Liquefaction and co-liquefaction of kukersite oil shale and peat

The yields of liquid, gaseous and solid products obtained in an autoclave after thermochemical liquefaction of oil shale, peat and their mixture without solvent are presented in Table 2.

It can be seen that gas + water yield from peat alone exceeds 5-8 times that of oil and the maximum yield of oil forms at 390 °C, a temperature 30 °C higher than the optimal conditions for oil formation from kukersite (360 °C). As for solid residue, the addition of peat to kukersite decreases its share to 30.3% at the temperature (390 °C) of maximum oil yield (35.1%), while at the same optimal temperature for oil formation from peat it amounts to 52.4%, while at the optimal temperature (360 °C) for maximum oil production from kukersite oil shale the share of solid residue is 33.4%.

Table 2. Share of pyrolysis products of oil shale, peat and their mixture without solvents, % of the total yield

	Kukersite				Peat				Kukersite + peat (OM ratio 1:1)			
Temperature, °C	340	360	390	420	340	360	390	420	340	360	390	420
Oil	15.4	56.9	51.8	38.2	6.7	7.3	9.7	5.1	12.9	15.0	35.1	16.2
Gas + water,	11.5	9.7	13.2	41.7	37.8	38.3	38.1	43.2	24.2	26.9	34.6	46.5
Solid residue	73.1	33.4	35.0	20.1	55.5	54.4	52.2	51.7	62.9	58.1	30.3	37.3

The influence of solvents on the yield of pyrolysis products from individual feedstocks and the mixture of kukersite and peat in ratio 1 : 1 on OM basis is presented in Figures 1 and 2.
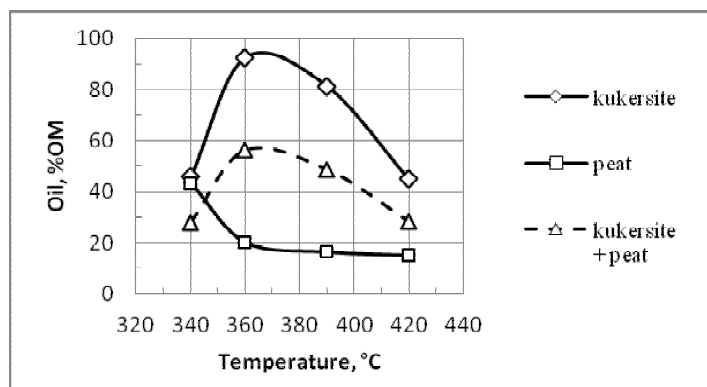

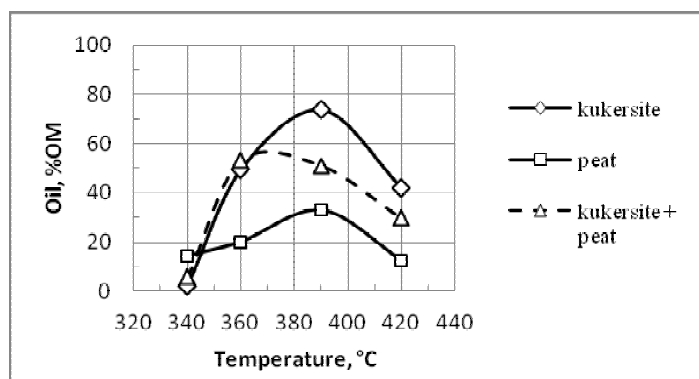Fig. 1. Oil yield *versus* temperature. Liquefaction in benzene.

Fig. 2. Oil yield *versus* temperature. Liquefaction in water.

As it can be seen from the figures, the yield of oil from peat with addition of benzene increases at 340 °C from 6.7% (Table 2) to 43.3%, but with the increasing temperature the oil yield decreases due to the presence of insoluble components in peat and formation of coke, while, as a result of using supercritical water, 33.3% of peat organic matter was transformed into an oily liquid. The addition of water to kukersite increases the oil yield in comparison with oil shale alone, but it also increases the temperature of maximum oil yield to 390 °C. The addition of benzene to kukersite has a significant influence on the oil yield giving 91%. As for the mixture, the oil yield was approximately the same at the same temperature 360 °C when

using both solvents. But due to higher price and toxity of benzene, the use of water seems to be more efficient.

Comparing different pyrolysis conditions and choosing solvent type most suitable for mixtures, it was found that addition of water at 360 °C may produce a significant synergistic effect (see Fig. 3).
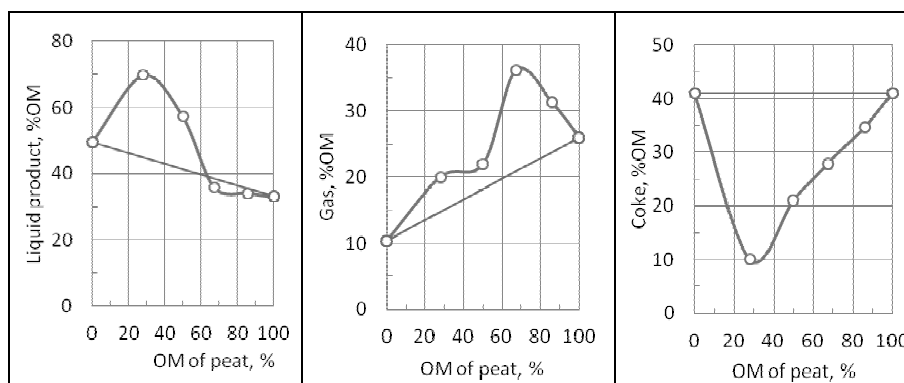

Fig. 3. The yield of liquid product, gas and coke *versus* kukersite-to-peat ratio in co-liquefaction of kukersite and peat in water medium at 360 °C.

In this case the liquid product yield from the mixture is 70% of OM, which is 24.8% more than the corresponding additive yields. The maximum gas yield obtained was 36%. Coke yield is maximum (40%) if kukersite and peat are liquefied individually. Liquefaction of the mixture decreases coke yield considerably, even four times (down to 10%).

At 340 °C a moderate synergistic effect was observed for the mixture without solvents.

3.2. Liquefaction and co-liquefaction of pine bark and kukersite oil shale

The yield of liquid, gaseous and solid products formed at thermochemical liquefaction of pine bark and oil shale + pine bark in the mixture in an autoclave without solvent are presented in Table 3.

Table 3. Share of pyrolysis products of pine bark and oil shale-pine bark mixture without solvents, % of the total yield

	Pine bark				Kukersite + pine bark (OM ratio 1:1)			
Temperature, °C	340	360	390	420	340	360	390	420
Oil	7.3	4.7	2.9	1.2	13.2	14.0	31.3	15.6
Gas + water	41.5	46.2	49.9	52.0	22.2	26.1	33.5	49.1
Solid residue	51.2	49.1	47.2	46.8	64.6	59.9	35.2	35.3

As it can be seen from the table, pine bark individually liquefied yields much more solid residue and gas + water than in oil soluble in benzene, especially at higher temperatures – the oil yield decreases from 7.3 to 1.2% with the temperature increasing from 340 to 420 °C. With the addition of oil shale the share of oil yield increases and achieves its maximum at 390 °C.

Figures 4 and 5 show the influence of added solvents on the yield of pyrolysis products from individual feedstocks and the mixture of kukersite and pine bark in ratio 1 : 1, on OM basis.
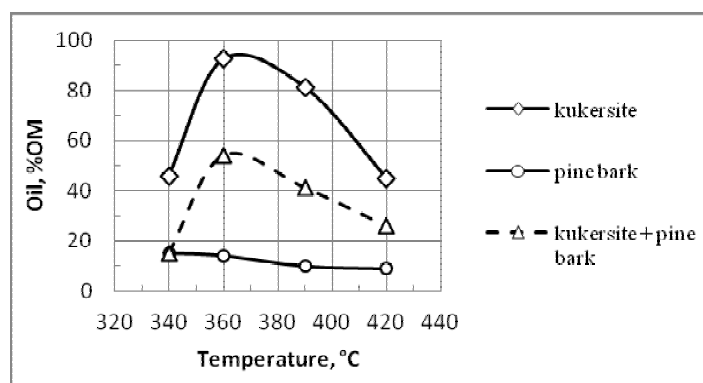

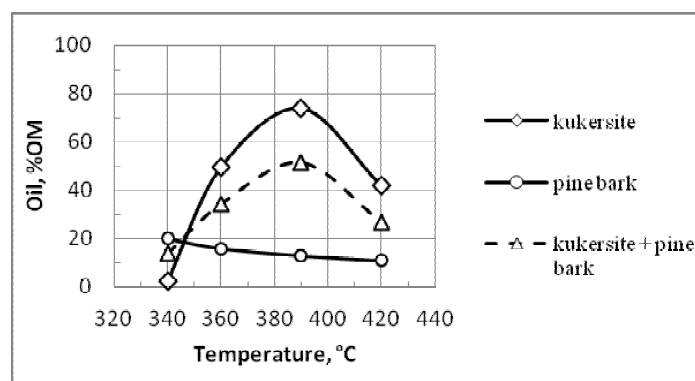Fig. 4. Oil yield *versus* temperature. Liquefaction in benzene.

Fig. 5. Oil yield *versus* temperature. Liquefaction in water.

As it can be seen, the yield of oil from pine bark is increased in the presence of solvents, benzene or water, but analogously to pine bark lique-faction alone, the quantity of oil decreases with the increasing temperature. At liquefaction of kukersite + pine bark in benzene the oil yield was increased to 52% at 360 °C, and thereafter, with increasing the temperature to 420 °C, decreased to 25%. Comparing the liquefaction of kukersite and

pine bark mixture in water and in benzene, one can see that the maximum oil yield recorded was 50%, but when using water as solvent, the maximum was achieved not at 360, but at 390 °C (see Fig. 5).
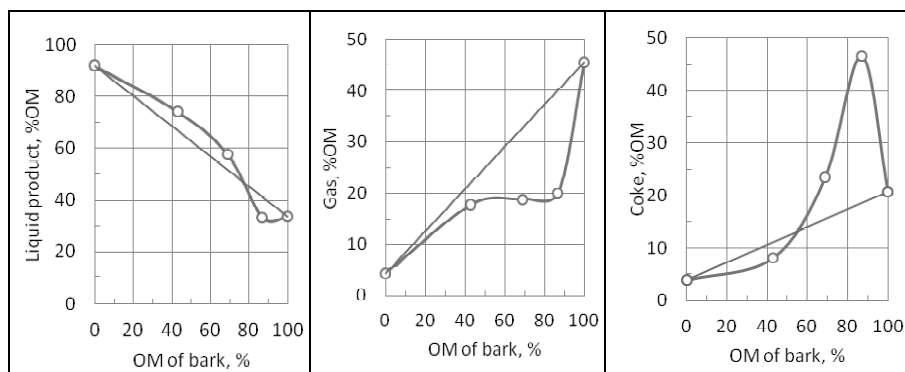

Fig. 6. The yield of liquid product, gas and coke *versus* kukersite-to-pine bark ratio at co-liquefaction of kukersite and pine bark in water medium at 390 °C.

One can see that synergism in the liquid product yield becomes evident when bark content of its mixture with kukersite is less than 80%. Gas yield at liquefaction of kukersite + pine bark was in all mixture ratios lower than that obtained at liquefaction of kukersite or bark individually. Also, it is clearly seen that the coke yield increases abruptly when bark content in the mixture exceeds 50%.

3.3. Liquefaction and co-liquefaction of kukersite oil shale, peat and pine bark: chemical composition of the products

3.3.1. Elemental composition

The results of the ultimate analysis of the initial feesdtocks and oils obtained are given in Table 4.

Table 4. Elemental analysis of the initial feedstocks and oils generated from the initial and combined feedstocks, % of organic matter

Element	Initial feedstock			Oil				
	Kuker-site	Peat	Pine bark	Kuker-site	Peat	Pine bark	Kukersite + peat (1:1)	Kukersite + pine bark (1:1)
C	78.4	57.1	52.3	82.4	75.0	76.2	78.4	78.6
H	9.3	7.2	6.3	10.1	7.3	9.0	8.7	8.8
N	0.1	2.6	0.5	0.2	0.5	0.4	1.3	0.7
S	1.3		–	0.7	0.3	0.1	1.0	1.0
O	10.9	33.1	40.9	6.6	16.9	14.3	10.6	10.9
H/C	1.426	1.514	1.449	1.472	1.169	1.419	1.333	1.345
O/C	0.104	0.435	0.590	0.060	0.169	0.141	0.101	0.104

One can see that the chemical composition of peat and pine bark biomass significantly differs from that of kukersite oil shale by lower content of carbon and hydrogen, as building blocks of hydrocarbons, and by much higher, (even 3–4 times) content of oxygen. Nevertheless, oxygen content of benzene-soluble oils is noticeably decreased amounting to 14.3–16.9% compared with 33.1–41.0% in the initial feedstocks. The most of oxygen has been transferred into gas and water.

3.4. Group composition of oils

FTIR-spectroscopic analysis was accomplished to determine the functional groups present in the benzene-soluble liquid fraction obtained at autoclaving of the following feedstocks: kukersite oil shale, kukersite oil shale blended with peat, and kukersite oil shale blended with bark.

Figure 7 shows that each of the three spectra displays absorptions at 725, 750, 1380, 1460, 2860, 2930, and 2960 cm^{-1} caused by methyl and methylene groups in aliphatic chains, and complex absorption bands at 750, 820, 880, 1020, 1080, 1600 and near 3000 cm^{-1} characteristic of aromatic compounds. Absorption at 1720 cm^{-1} refers to carbonyl groups and that at 3400 cm^{-1} is characteristic of hydroxyl groups. Absorptions in the region 1100–1250 and at 1600 cm^{-1} refer to ether groups and benzene derivatives, respectively. Also, one can see in Fig. 7 that oils obtained at thermochemical destruction of blended feedstocks – oil shale + peat and oil shale + pine bark biomass – show
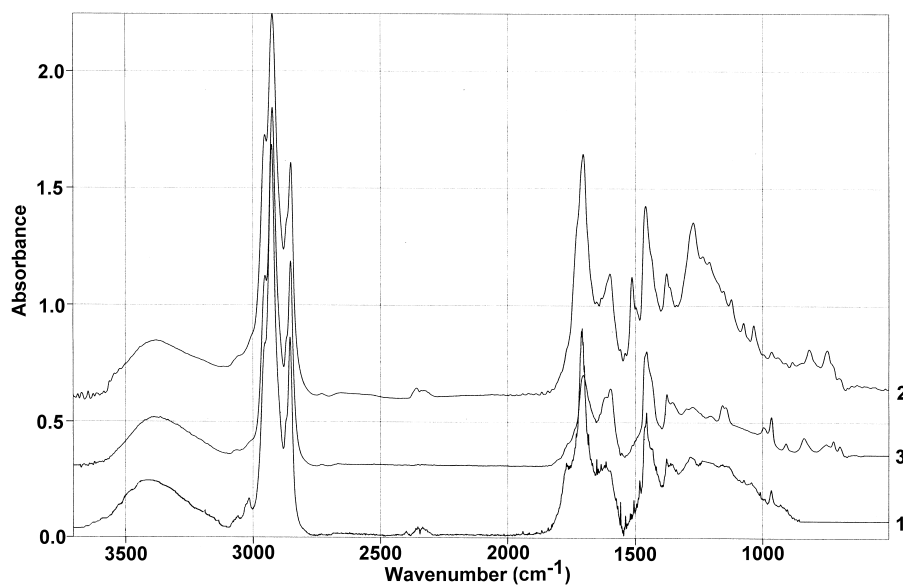

Fig. 7. FTIR-spectra of the benzene soluble oils formed at liquefaction of kukersite oil shale (1), kukersite oil shale + peat (2), and kukersite oil shale + pine bark (3) in an autoclave.

quantitative rather than qualitative differencies in the functional groups' composition compared with shale oil.

The group composition of oils determined by using thin-layer chromatography is presented in Table 5. One can see that neutral and high-polar oxygen compounds prevail, making up 75% of oils investigated. The oil obtained from kukersite differs from other two oils by lower content of monoaromatic hydrocarbons and higher share of polyaromatic hydrocarbons. To elevate hydrocarbon content of oils so as to approximate their chemical composition to that of natural petroleum, additional hydrogenation should be applied.

Table 5. Group composition of oils, %

Compounds	Kukersite	Kukersite + peat	Kukersite + pine bark
Aliphatic hydrocarbons	6.1	5.1	6.4
Monoaromatic hydrocarbons	1.2	3.4	4.1
Polyaromatic hydrocarbons	19.4	14.8	14.2
Neutral oxygen compounds	20.4	13.8	12.8
High-polar oxygen compounds	52.9	62.9	62.5

4. Conclusions

Liquefaction of both peat and pine bark biomass in the mixture with the kukersite oil shale at certain feedstock ratios leads to higher yields of liquid and gaseous products compared with liquefaction of peat and pine bark individually in the same conditions in an autoclave. Liquefaction of the individual and mixed feedstocks can be significantly accelerated in the presence of solvents. Besides, it is obvious that solvent addition decreases the temperature of the maximum oil yield from every kind of feedstock.

It was found that both solvents used increase the yield of oil from individual feedstocks as well as from their mixture in the 1 : 1 ratio studied in this work. The strongest synergistic effect was achieved by co-pyrolysis at 360 °C with water, in which case the liquid product yield from the kukersite-peat mixture is 70% of OM, which is 24.8% more than the corresponding additive yield.

It was found also that it is not rational to use mixture in which bark share is higher than 50%, because in this case oil and gas yields decrease, while coke quantity increases.

The liquid products obtained (including benzene-soluble oil) urgently need upgrading in order to be used as petroleum substitutes because of elevated oxygen content.

Compared with liquefaction of oil shale, that of oil shale mixture with peat or bark biomass generates less harmful gaseous emissions and considerably reduces the amount of solid waste used as landfill.

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