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CO-LIQUEFACTION OF KUKERSITE OIL SHALE AND PINE WOOD IN SUPERCRITICAL WATER

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Samples of kukersite oil shale and pine wood and their mixtures were liquefied with water in supercritical state in an autoclave. Chosen conditions (380 ºC, 4 h) give synergy to desired direction in all feed compositions: yields of solid residue and gas with pyrogenetic water were lower 1.7–2.0 and 1.4–2.0 times, respectively, while the yield of the most expected component of oil – benzene solubles was – 1.5–1.9 times higher than additive yields. Rise in co-liquefaction oil yields (y) resulted completely from the rise in the yield of the polar components and depended on the share of wood in feed (x) according to equation $y = -0.0089x^2 + 0.6626x + 34.846$ *(*R^2 *0.97).*

Introduction

High price of petrol rouses interest in shale oil, wood and wind energy in Estonia. Estonia is rich in oil shale and also in renewable fuels such as wood and peat. The use of domestic fuels means, in the first place, their direct combustion to produce heat and/or power. Shale oil is the only considerable liquid fuel produced from local natural resources since 1921 in Estonia [1, 2]. The main positive sides of the large-scale use of oil shale are the security of supply for the state energy sector and the relative price independence from the world market. The negative sides are great environmental damage due to mining and use of oil shale and low calorific value of oil shale [3, 4].

The transportation of renewable solid fuels in large quantities over any appreciable distance, just like in the case of oil shale, is expensive. Energy density of bio-oil is, for example, ten times higher than that of biomass [4].

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Calorific value of kukersite shale oil is four times higher than that of oil shale. Bio-oil substitutes for fuel oils in combustion systems or engines for heat and electricity generation. Specifications for upgraded by hydrogenation bio-oil are close to those of petroleum-derived fuel oils enabling it to be used in vehicles powered by diesel engines [5**,** 6].

Co-liquefaction of oil shale and wood in supercritical water is one of the possibilities to solve the problem. The need to investigate thermochemical liquefaction of solid renewable fuels together with oil shale was argued at the fourth conference "Investigation and Usage of Renewable Energy Sources" for the first time in 2002 [7]. Since then there have been no publications on that matter. So, this paper is the very first study on the possibilities to process oil shale together with a renewable fuel (wood waste) for production of liquid fuel. No work has been done on co-liquefaction of oil shale and renewable fuels in supercritical water. Yet, there are some papers, for example, on co-liquefaction of kukersite oil shale with plastics and tyres [8, 9], oil shales with lignites [10], and also kukersite with dictyonema oil shale [11]. Some papers deal with co-liquefaction of coals with cellulose. Co-liquefaction, depending on reaction conditions, leads to higher production of gas [12], or liquid products [13], or water soluble products [14].

Oil shale

Some studies have been conducted with kukersite oil shale in super- and supracritical water to produce oil and gas [1, 15–19] or in subcritical conditions to study the mechanism of petroleum formation [20, 21]. Water was also used in supercritical conditions to study some other oil shales: dictyonema [22], Green River [23], Maoming [24, 25], Göynük [26, 27], Rotem [28], Timahdit [28, 29], Beypazar [30] oil shale.

In the case of Göynük oil shale, for example, supercritical water acted not only as a solvent but reacted with oil shale organic matter (OM), it afforded higher oil yield compared with slow and fast pyrolysis, but this oil contained a high proportion of asphaltenes and polar compounds [27].

Wood and some new trends in liquefaction

Lignin was converted, in good yield, to brown viscous oil in supercritical water (Pd on C catalyst and a H_2) [31], sugi wood gave mostly water-soluble saccharides [32], more exactly oligosaccharides, glucose, fructose, methylglyoxal, glycolaldehyde, dihydroxyacetone, erythrose, levoglucosan and 5-hydroxymethyl furfural [33], most of the residue consisted of products of lignin origin [32]. Metals were recovered and/or a creosote-like mixture was generated from preserved wood by reaction in supercritical water [34]. In comparison with several other thermochemical processes such as pyrolysis, air or steam gasification, extraction with supercritical water can directly deal with wet biomass without drying [35].

Water conversion of wood in supercritical conditions is not the main trend in wood thermochemical processing. Almost all national governments of the European Union have specific programmes for development of the renewable fuel sector. Emphasis is also put on co-utilisation of biomass and waste with fossil fuels for production of liquid biofuels whatever market conditions permit [36]. A considerable effort has been made, especially in respect of fast pyrolysis of biomass, involving commercial organizations, which resulted in the construction of a number of pilot plants (for example [37]). Fast pyrolysis, Rapid Thermal Processing RTP™, was commercialized in 1989 [38].

A typical liquid fuel yield at fast pyrolysis of hardwood which contains 10–15% moisture is about 73% [38]. However, to date the “best” option has not been clearly identified, with most plants showing opportunities for further development and optimisation [6]. One of the most promising second-generation renewable fuel technologies – ligno-cellulosic processing – is already well advanced. Three pilot plants have been established in the EU: in Sweden, Spain and Denmark [39]. The biggest renewable fuel liquefaction projects operate in Canada by Pyrovac 17.5 MW_{th} [40].

The by-products of wood fast pyrolysis – char and gas – are now used to produce the energy required by the pyrolysis process [37]. Slow pyrolysis of biomass was largely used as traditional process to produce char (semi-coke), gas or oil. In new grill char plants gas and oil are burned to produce char.

We have already published some works about separate liquefaction of renewable fuels, peat and oil shales [41, 42].

Experimental

Samples of kukersite oil shale (W^a 0.6, $(CO_2)^d_{min}$ 12.8, A^d 37.2 and OM^d 50.5%) and pine sawdust without bark ingredients (W^a 9.1, A^d 0.4 and OM^d 99,6%, hereafter instead of sawdust – wood) and their mixtures were liquefied in a 0.5-L autoclave with water (feed 60 g:water 180 g) in supercritical state in conditions optimal to kukersite liquefaction [41]: rise up to the nominal temperature 380 °C 110 min, duration at that temperature 4 h, maximum pressure up to 400 at, end pressure 6–23 at.

Separation and calculation of products and preparative thin-layer chromatographic analysis were carried out as described in [43, 44]. Yields of products are given on OM basis. In supercritical water from kukersite some mineral new formations were formed, and a portion of mineral matter became soluble in water [45]. So we had to treat solid residues obtained in experiments with mineral acid to determine the exact yield of OM in process residues and the yield on feed OM basis.

The highest yields of total oil (74.6%), and of oil soluble in organic solvents (70.3%), incl. water-insoluble part (67.0%) were obtained at liquefaction of the mixture containing 75% kukersite and 25% wood on OM basis. The corresponding data for pure kukersite are 63.4, 58.7 and 55.7% and for wood – 15.9, 14.9 and 10.3% (Table 1). The yield of the most desirable product – oil soluble in benzene – was highest (63.7%), too. It is worth mentioning that 25% of kukersite in feed on OM basis, gave sharp increase in the yield of total oil (50.1%) as well as of oil soluble in organic solvents (45.3%), incl. water insoluble portion (38.3%).

The maximum yield of oil was accompanied with the minimum yield of gas and pyrogenetic water. According to thin-layer chromatography data, component composition of the fraction soluble in benzene varied slightly, but differed from that of kukersite semi-coking oil (Table 2); the most polar compounds (component 1) prevailed upon the other components, unlike those of semi-coking oil.

Table 1. **Yield of products obtained by water conversion of kukersite, wood and their mixtures**

Product	Wood in feed, % on OM basis				
	0	25	54	75	100
Solid residue	6.5	7.1	12.6	16.1	32.2
Gas and pyrogenetic water	30.1	18.3	29.9	33.8	51.9
Water-soluble oil, incl.	7.7	7.6	8.9	11.8	5.6
soluble in ether (E)	3.0	3.3	5.2	7.0	4.6
insoluble in ether (W)	4.7	4.3	3.7	4.8	1.0
Water-insoluble oil, incl. compounds	55.7	67.0	48.6	38.3	10.3
soluble in benzene (B)	53.2	63.7	39.8	33.5	6.0
soluble in acetone (A)	2.5	3.3	8.8	4.8	4.3
Oil soluble in organic solvents (E + B + A)	58.7	70.3	53.8	45.3	14.9
Total oil (E + W + B + A)	63.4	74.6	57.5	50.1	15.9

Table 2. **Component composition of benzene soluble oil by thin-layer chromatography.**

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

Compo-nent	Semi-coking oil		Water conversion oil. Wood in feed, % on OM basis				
	Kukersite [46]	Wood [42]	0	25	54	75	100
1	23*	58.0	52.9	66.6	70.6	71.9	63.9
2	34**	36.1	20.4	18.9	14	16.6	17.1
3	17	2.9	19.4	8.6	10	7.9	8.4
4	8	0.5	1.2	1.3	2.2	1.2	2.7
5	18	2.5	6.1	4.6	4.3	2.4	8

* Phenols – polar heterocompounds separated previously.

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

Data processing and discussion

Experimental and calculated data presented in Fig. 1 demonstrate very strong synergic effect of co-conversion. The yields of products or their combinations (numerical data) are compared with additive ones (straight lines) on OM basis. There are some exceptions considering water-soluble oil (E and W), acetone-soluble part of the water-insoluble oil (A), and their sum (E + W, E + W + A) – almost no synergy when the share of wood was low and, as for acetone-soluble part additionally, when the share of kukersite was low, too (Fig. 1).

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

The correlation between the share of kukersite in feed on OM basis and the yield of solid residue turned out to be very strong (R^2 0.98), it was somewhat weaker in the case of the yield of gas with pyrogenetic water (R^2 0.93) (Fig. 2).

To characterize the oil soluble in solvents

(1) the yields of fraction of benzene-soluble oil separated by thin layer chromatography were calculated, and the yields of more polar components soluble in ether and acetone were added to the yield of heterocompounds of the benzene-soluble oil (components 1 and 2) (Fig. 3, *1*),

(2) component composition of oil soluble in organic solvents was calculated (Fig. 3, *2*), and

(3) the same was calculated for wood semi-coking oil (Fig. 3).

Oil obtained by water conversion of kukersite and its mixtures with wood contain more heteroatomic compounds and are poor in nonaromatic hydrocarbons compared with kukersite semi-coking oil (Fig. 3). Heteroatomic components of water-conversion oils originate from kukersite as well as from wood, as they are main components in both cases, constituting for wood almost 92% the oil soluble in solvents (E + B + A). Wood semi-coking oil differs slightly from water-conversion oil by the yield and component composition.

The correlation between the share of wood in feed on OM basis and the yield of solvent soluble oil is very high (R^2 0.97), and the same can be said on components of polar oil (E + A + 1, R^2 0.97) (Fig. 2). The correlation between the yield of oil components 2 + 3 + 4 + 5 and the share of wood

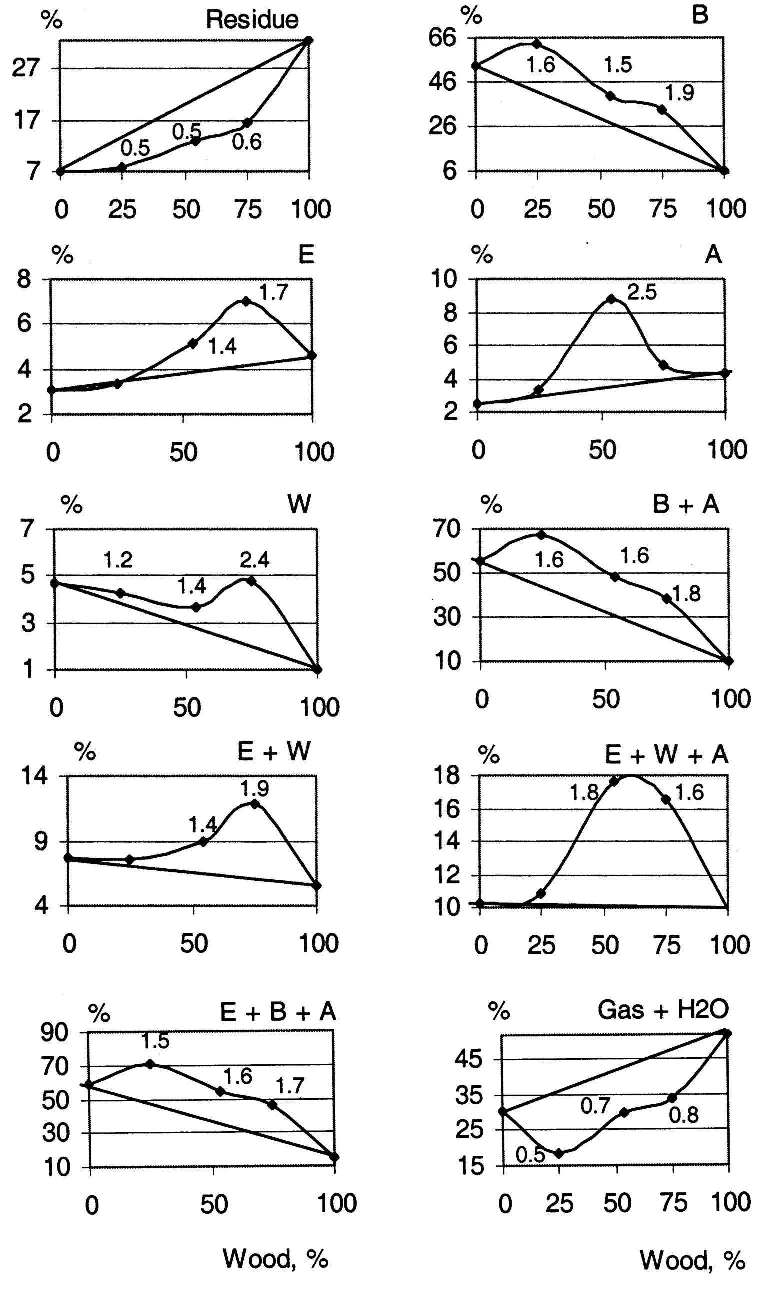

Fig. 1. Yield of products obtained by water conversion and calculated additive ones (straight lines) on OM basis, % (for abbreviations see Table 1, for numbers on the plot area see the text)

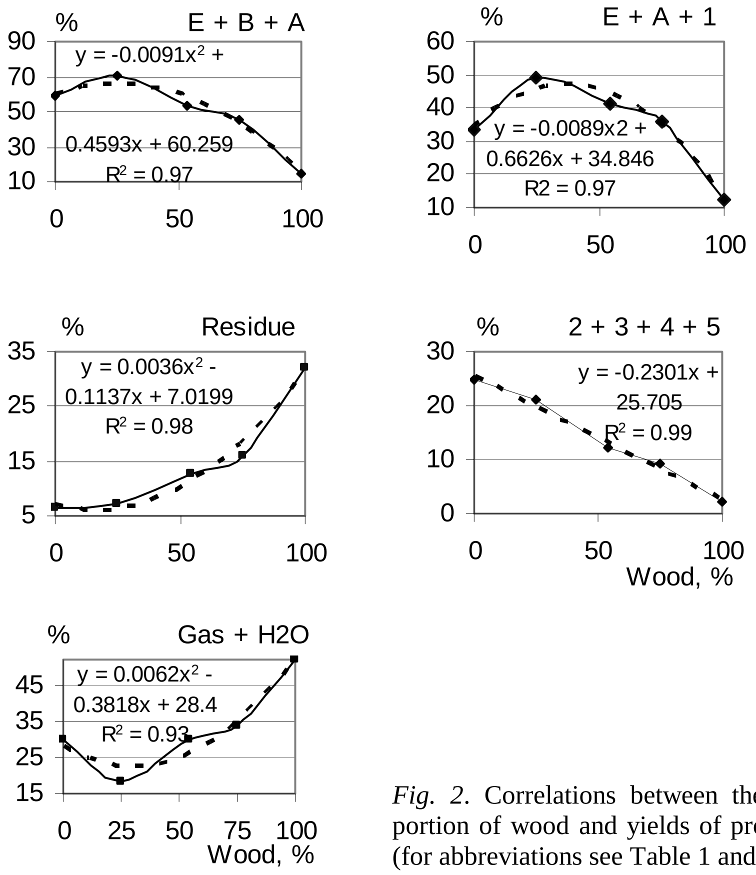

Fig. 2. Correlations between the proportion of wood and yields of products (for abbreviations see Table 1 and 2)

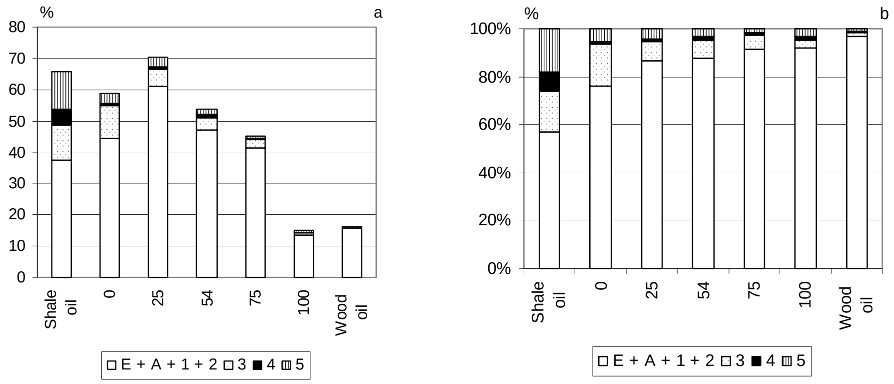

Figure 3. Yields of oil and its components soluble in organic solvents on OM basis (a) and component composition of oil soluble in organic solvents (b): E +A +1 + 2 – oil soluble in ether and acetone + heterocompounds soluble in benzene, 2–5 – components according to Table 2 in comparison with kukersite and wood semi-coking oil, % (for abbreviations see Table 1)

according to linear equation is also very high (Fig. 2, R^2 0.99, the yield decreased from 25% to 2.2%). So, the rise in oil yields in co-liquefaction experiments (y) in comparison with additive ones is caused by the rise in the yields (and the share in oil) of polar heterocompounds according to equation $y = -0.0089x^2 + 0.6626x + 34.846$ (R^2 0.97).

It was expected that in co-liquefaction experiments liquid and gaseous products formed from wood at lower temperatures will react with kukersite OM that achieves its chemical activity later at higher temperatures. We recently motivated suitability of kukersite and wood as a co-liquefaction feed [47]. Our optimism is based on the well-known property of kukersite to decompose to thermobitumen at lower temperatures (for example, as described in 48–51].

It follows from Table 3 that the period of formation of chemically active kukersite thermobitumen overlaps with the active period of decomposition of wood, not depending whether kukersite or wood is semi-coked (atmospheric pressure) or altered to thermal decomposition under pressure, including water conversion. So, the interaction between chemically active kukersite thermobitumen and products formed from wood evidently played an important role in development of quantitative synergistic effects revealed in this research. At the same time we do not underestimate the role of water in supercritical conditions to react with the feed and the products formed.

Table 3. **Decomposition of kukersite and wood depending on temperature, pressure and time**

°C	Kukersite		Wood	
	Atmospheric pressure	Under pressure	Atmospheric pressure	Under pressure
250	72 h: volatiles (V) 2% from organic matter (OM) [52]	Water:Kukersite (K) 1:2,8, 100 h, 5.9 MPa: oil 7, OM in residue (R) 86% from initial OM [21]	V 50.4% [53]. In N_2 stream 11 min: V 47.5, 58 min: V 60.8% [54]	Water:Wood 6:1, 1 h: oil 6.4, gas 6, R 43.6, other 44% [55]
300	12 h: V 2 % from OM [52]. 20 h: V 4.6% from OM [56]	Water:K 1:2,8, 24 h, 10.8 MPa: oil 35, R 62% [21]	R 33.6% [53]. 35 h: conversion 90%, 5 h ~60% [57]	Water:Wood 15:1, 30 min: oil 21–>75, R 50–>21, depending on lignin content 54–>15% [58]
350	Heating rate 50 ºC/min: oil 0% [48]. 0.6–>3.5 h: V 10–>26.7% [58]. 1 h: oil 3%, 2 h: oil 6% from potential [49]	Water:OM concentrate 2:1, 6 h, 15 MPa: oil 69.6% [18]. 6 h, 38 atm: thermobitumen (TB) 40% [50]. In water under pressure, 4 h: oil 45% (from diagram) [19]	V 55.7% [53]	8–10 kg/cm^2: V 57.5–57.9% [53]

360	1–>5 h: V 16.6–>28.9, TB 33.2–>70.0% [59]. 1 h: TB + V 20.3% [60]. 1 h: oil 6%, 2 h: oil 12% from potential [49]. 2 h: TB 9.1%, 4 h: 16% and 6 h: 30% from K [49, 51]	In water under pressure, 4 h: oil 89% (from diagram) [19]	V 57% [53]	Water:wood 0.4:1, 6 h: V 78.5%, incl. oil 8.9%; R 21.5% [61]. 23 MPa: water solubles 82.5–94.1% [62]
380	0.5 h: TB 12.4%, V 19.5% [60]. 0.5–>1 h: V 20.1–>25.4, TB 69.9–>72.8%, R 1.8% [59]. 1 h: TB 24.6%, 3 h 26.9% from K [49, 51]	Water:K 3:1, 4 h: oil 62.7 % [41]	V 58% [53]	Water:wood 0.75:1, 6 h: V 78.2%, incl. oil 10.3%; R 21.8% [61]

Conclusions

1. For the first time oil shale was co-processed with a renewable fuel – pine wood.
2. Chosen conditions (380 °C, 4 h) gave synergic effect at every feed composition affecting the process in the desired direction: the yields of solid residue and gas with pyrogenetic water were reduced by 1.7–2.0 and 1.4–2.0 times, respectively, while the yield of the most expected component of oil – benzene-soluble part was 1.5–1.9 times higher than additive yields.
3. Water-conversion oils from kukersite and wood mixture were richer in heterocompounds, incl. polar ones, than the oils obtained at their separate semi-coking.
4. The rise in the yields of co-liquefaction oil (y) was completely caused by the rise in the yield of polar components, depending on the share of wood in feed (x) according to equation $y = -0.0089x^2 + 0.6626x + 34.846$ (R^2 0.97).
5. Synchronous chemical activity of kukersite thermobitumen and wood volatiles, and reactivity of water in supercritical conditions play an important role in quantitative and qualitative synergistic effects revealed in this research.
6. It is recommended to add suitable components (polymers, tyres etc.) to kukersite-wood mixture before processing to rise the share of nonpolar components in the oil obtained.

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