

Thermochemical liquefaction of reed

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Abstract. The current paper gives a survey about the use of reed biomass and reed peat for the production of liquid fuels and experimental data on the thermochemical liquefaction (semicoking at up to 520 °C, water conversion, and catalytic hydrogenation at 380 °C) of reed (*Phragmites australis* or *P. communis*). Reed is a new source of energy, for the burning of which experience is already evolving in Estonia. Liquefaction conditions have a great influence on the yield of products. In our study the highest yields of oil and oil plus coke (oil 25.7%, coke 28.5%) were obtained by using the Fischer retort. The yield of oil fractions washed successively out from pyrolytic water (in some cases also coke and catalyst) containing the reaction mixture with water (further divided to ether solubles and insolubles of water soluble oil), and benzene and acetone (water insoluble oil) as well as total oil decreases in the order: semicoking → water conversion → catalytic hydrogenation (except acetone solubles). The sharpest decrease was observed in the water soluble oil: from 15.1% to 0.7%. At the same time the proportion of the most desirable benzene solubles in total oil increased from 28.4% in the case of semicoking to 50.1% in the case of hydrogenation, which was accompanied with an increase in the carbon content in benzene solubles from 71.5% to 83.0%.

Key words: reed, *Phragmites australis*, thermochemical liquefaction, liquid fuels.

Abbreviations: A = acetone solubles of water insoluble oil, B = benzene solubles of water insoluble oil, E = ether solubles of water soluble oil, W = ether insolubles of water soluble oil, OM = organic matter.

INTRODUCTION

Reed (*Phragmites australis* or *P. communis*) is a tall perennial grass of the family Poaceae that grows in both salt and freshwater marshes, in swamps, ditches, and along shoreline around the world, and is a native species in Europe

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and North America [1]. Reed stands are common in Estonia: 26 000 ha in total according to the wetlands map compiled by the Institute of Geography, University of Tartu [2].

Thickets of reed produce 10–40 t/ha biomass per year. For example, the production of biomass of the largest wetland of North Europe – Matsalu (Estonia) – is approximately 10 t/ha per year [3, 4]. The production is the same in Sweden, where reed stands spread on about 100 000 ha [5]. In Finland the average yield of common reed is considered to be 5 t/ha per year (maximum 10–12 t) and the resource is 30 000 t/year, storage would require 3–4% of the produced energy [6].

Several strategies have been discussed to handle reed:

- it can be used as a nutrient source in agriculture (the harvested material may be chopped and spread directly on farmland or composted previously);
- harvested biomass can be used as a raw material in biogas production, and the by-product (sludge) as an organic fertilizer. The energy balance of the biogas alternative is considered to be very favourable; the profitability of the system is sensitive to changes in the price of the gas produced and in the costs of the chopping operation [5];
- liquefaction [7];
- direct use as a solid renewable fuel. It is suggested that reed may be burnt in straw boilers or as an additive in wood burning boilers [8]. The energy collected from 2/3 of the reed stands area of Estonia would be 1.98 PJ/year [8]. If Estonia fully applied the project of fertilizing the artificial wetlands (up to 300 000 ha) with polluted water, the part of reed and cattail (*Typha*) could amount up to 17% in the balance of energetic fuel [2, 9]. The biomass of reed and/or cattail from 300 000 ha of energy and/or treatment wetlands can make up about 30% of the Estonian oil shale based energy production.

In this paper (1) a review is given about the use of reed biomass and also reed peat for the production of liquid fuels and (2) experimental data on slow thermochemical liquefaction (semicoking, water conversion, and catalytic hydrogenation) of reed are presented. The work is the very first step of a wider study on the thermochemical liquefaction of wood, other renewable fuels, and/or organic wastes with oil shale for the production of liquid fuels and chemicals started in 2003. The ultimate aim of the work is to ensure an increase in the security of energy supply by expanding the use of domestic renewable energy sources. Reed is already one of the new sources of energy, and experience of burning it is accumulating in Estonia.

CHEMICAL COMPOSITION OF REED AND REED PEAT

Reed organic matter (OM) contains lignin, α -cellulose, and cellulose (27.1%, 15.5%, and 43.3%, respectively) [7]. According to another analyses routine it contains also benzene and alcohol–benzene soluble bitumen (2.4% and 7.2%, respectively, together 9.6%), in addition water soluble matter (5.0%), easily

hydrolysable matter (24.8%), cellulose (37.6%), and nonhydrolysable residue (19.6%) [10]. Similarly, reed peat contains bitumens (4.9% and 2.7%, together 7.6%), easily hydrolysable matter (20.4%), heavily hydrolysable matter (5.1%, of which cellulose makes up only 4.6%), and nonhydrolysable residue (19.5%), but also new formations typical of buried OM: humic (46.2%) and fulvic acids (1.2%) [10].

The elemental composition of reed samples taken in Estonia varies greatly: C 45–49%, H 4.9–6.8%, N 0.3–0.6% [8, 11]. A very low carbon content was determined also in a reed sample from Iraq (C 43.5%; the content of other elements: H 6.0%, N 0.5%) [12], but a higher one in reed peat (C 55.3–61.9%; others: H 5.1–6.1%, N 1.9–3.7%, O 31.1–35.2%) [10, 13–15].

The results of the determination of the elemental composition of reed depend partly on whether or to what extent the correction to moisture was made as the reed samples are hygroscopic. This may lead to a conclusion that as to carbon content reed is more similar to phytoplankton (45%) than to land plants (54%) with their carbon-rich components such as bitumens (up to 81% C) and lignin (C content 62%) [16] to which reed belongs. Thus, a more likely carbon content of the OM of reed would be 51% (oxygen content ~43%).

Roots and leaves are the most nitrogen-rich parts of reed (1.1% and 2.0%) [10]. In reed peat the content of nitrogen (up to 3.8%) [10, 14–16] is higher than in reed. The content of sulphur in reed is ~0.1%.

Thus, the componental composition of OM of reed differs from that of reed peat more than the elemental composition. Reed peat is also a suitable raw material for thermochemical liquefaction as its OM has more carbon than reed, which may compensate for its higher content of nitrogen.

THERMOCHEMICAL LIQUEFACTION

Thermochemical liquefaction of reed is poorly studied. The progress achieved in its liquefaction is based mostly on investigations first done with wood, afterwards with peat, including reed peat and peat-forming plants. Coke and the accompanying by-products were manufactured from reed and similar aquatic plants by converting the raw material into briquets by mechanical means and subjecting the briquets to destructive distillation [17]. Waeser [18] suggested liquefaction of reed instead of peat. Several investigations dealing with thermochemical liquefaction of peat have been reported by Russian scientists. These show that the retorting of pulverized reed in a current of inert gases increases the yield of tar and decreases the yield of gas [19], though the yield of tar is only half as large as for wood [20]. An investigation to carbonize reed was carried out in a Fischer-Schrader retort at 400 °C giving (in %): coke 35.1, pyrolytic water 35.1, tar 5.9, and gas 19.4 with a loss of 4.5 [21]. Continuous thermochemical conversion of reed in a flash pyrolysis system at 450–800 °C revealed that C₂H₆ is favoured at the expense of C₂H₄ in the presence of K₂CO₃ [12]. Thermolysis of reed peat [14] and the mechanism of tar formation during thermal decomposition

of peat (including reed peat) and lignin in steam at 100–450 °C were also studied [15].

EXPERIMENTS AND DISCUSSION

Conditions of thermochemical liquefaction in our experiments are given in Table 1. The separation and calculation of semicoking, water conversion, and (catalytic) hydrogenation products of reed (moisture content 7.2%, ash yield 3.0%, OM 97%) were carried out according to a new scheme [22] enabling to separate and compare oils yielded by different liquefaction methods from a complex mixture of reaction products rich in pyrolytic water and containing in some cases also solid products such as coke and catalyst and extra water as the reaction media and the reagent. More specifically, the new scheme was developed to separate and compare oils formed from renewable fuels with those formed from fossil fuels. The scheme takes into consideration the need to separate products obtained by co-pyrolysis of biomass and fossil fuels on the further steps of our investigations. The characterization procedure based on the fractionation of the oils on the first step with water and afterwards with organic solvents was successfully used to characterize wood and wheat straw flash pyrolysis oils [23].

Oil fractions and coke were analysed for C, H, N, and S elemental composition using an Elementar Vario EL Analyzer. Oxygen was determined by the difference. A preparative thin-layer chromatographic method using 24 × 24 cm glass plates coated with a 2 mm layer of silica gel 40 and hexane as eluent was applied for the investigation of the group composition of benzene solubles. Degradation products were analysed using two gas chromatographs: the non-aromatic fractions were analysed with an OV-101 capillary column and a FID detector and the gaseous products with two columns (molecular sieves and Apieson).

Table 1. Conditions of thermochemical liquefaction of reed

Method	Conditions		
	Temperature, °C	Time, min	Other
Semicoking in a Fischer retort	Rise to 220 220–520 520	10 60 20	Reed 22 g
Water conversion in an autoclave	Rise to 380 380 ± 10	110 240	Reed 60 g + water 180 g, initial pressure 1, end pressure 18 at
Hydrogenation in an autoclave	Rise to 380 380 ± 10	75 240	Reed 60 g + Ni–Co catalyst 6 g, H ₂ initial pressure 68, end pressure 61 at

The highest yields of liquid and liquid plus solid products were obtained by using a Fischer retort (oil 25.7%, coke 28.4%). Oil yields were considerably lower in the autoclave experiments, approximately three times in the case hydrogenation was used, the corresponding yields of coke and gas plus pyrogenetic water were higher (Table 2).

So, the yield of total oil, as well as of all its fractions (except the acetone soluble fraction), decreases in the order: semicoking → water conversion → catalytic hydrogenation. The sharpest decrease was observed for water soluble oil: from 15.1% to 0.7% (Table 2). At the same time the proportion of the most desirable product – benzene soluble oil – increases from 28.4% to 50.1% (Fig. 1). Kukersite shale oil, for example, is almost entirely soluble in benzene.

Reduction of the oxygen content is the aim of thermochemical liquefaction of all kinds of oxygen-rich materials, including renewable ones. All products of thermochemical liquefaction of reed (with rare exceptions) comprise more or much more carbon and hydrogen than reed, in half of the cases a lower percentage of nitrogen and sulphur; in all cases (except some water soluble oils) the oxygen content is much lower than in reed (Table 3).

Table 2. Yields (%) of thermochemical liquefaction products of reed, OM-based

Product	Semi-coking	Water conversion	Catalytic hydrogenation
Coke	28.5	31.7	38.7
Gas + H ₂ O	45.8	52.9	53.0
Oil total, incl.	25.7	15.4	8.3
1. Water soluble oil, incl.	15.1	5.6	0.7
ether solubles (E)	8.1	3.2	0.2
ether insolubles (W)	7.0	2.4	0.5
2. Water insoluble oil, incl.	10.7	9.7	7.7
benzene solubles (B)	7.3	6.5	4.2
acetone solubles (A)	3.4	3.2	3.5
Organic solvents soluble oil (E + B + A)	18.7	13.0	7.8

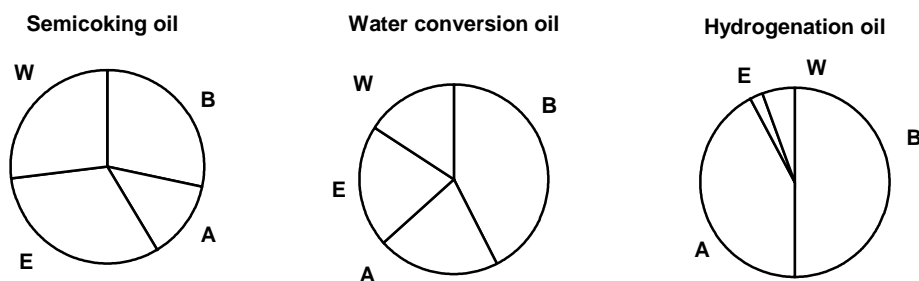


Fig. 1. Composition of total oil according to solubility, %. For abbreviations see Table 2.

Table 3. Elemental composition of dried products of thermochemical liquefaction of reed, % (E – ether solubles and W – insolubles of water soluble oil, B – benzene and A – acetone solubles of water insoluble oil, I – semicoking, II – water conversion, III – hydrogenation)

	C	H	N	S	O _{diff}
E-I	61.2	6.48	0.22	0.11	31.99
E-II	65.3	6.81	0.16	0.19	27.54
E-III	78.9	4.92	0.92	0.06	15.20
W-I	44.0	–	–	–	–
W-II	18.5	–	–	–	–
W-III	7.0	–	–	–	–
B-I	71.5	7.56	0.41	0.07	20.46
B-II	81.6	7.90	0.49	0.39	9.62
B-III	83.0	9.67	0.28	0.07	6.98
A-I	62.6	6.09	1.42	0.17	29.72
A-II	75.1	6.62	0.85	0.52	16.91
A-III	82.7	8.35	0.52	0.03	8.40
Coke-I	79.4	3.11	0.82	0.06	16.61*
Coke-II	81.4	4.88	1.00	0.19	12.53*
Coke-III	77.9	5.60	1.03	0.08	15.39*

* Including ash (Coke-I 9.9%, Coke-II 8.9%, Coke-III 7.4%).

– Not determined.

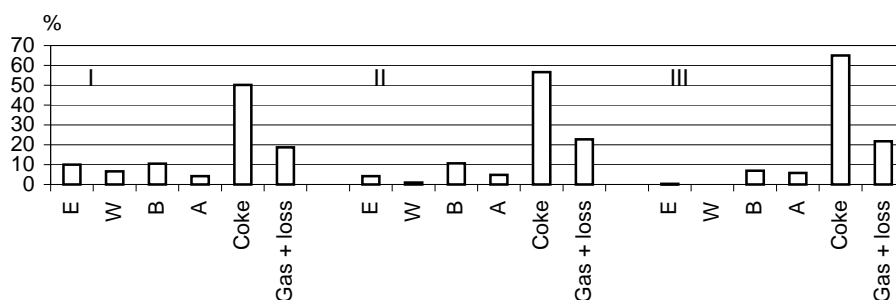


Fig. 2. Yields of thermochemical liquefaction products of reed, % carbon based (I – semicoking, II – water conversion, III – hydrogenation). For abbreviations see Table 2.

Most of the carbon of initial reed goes over to coke during processing (Fig. 2). The transition of carbon to coke rises in the direction semicoking → water conversion → hydrogenation. At the same time the transition of carbon to water soluble products decreases.

The transition of carbon to most valuable benzene solubles of water insoluble oil was almost equal in semicoking and water conversion experiments (the sum of water insoluble oils B-I + A-I 29.3% and B-II + A-II 30.9%, respectively), and surprisingly lower in the case of hydrogenation (B-III + A-III 25.4%) (Fig. 2). Biomass is a difficult material to produce liquid fuels similar to shale oil in

elemental composition (kukersite shale oil: C 83.1%, H 9.9%, S + N + O 7.0%, O/C 0.06) because it has a very high O/C value compared with that of kukersite oil shale (C 77.3%, H 9.7%, O + N + S 12.0%, O/C 0.13) (Fig. 3). Among reed oil fractions only benzene (O/C 0.07) and acetone solubles (O/C 0.08) obtained by hydrogenation and benzene solubles (O/C 0.10) obtained by water conversion reached the O/C value of shale oil.

According to thin-layer chromatography data, benzene solubles, the yields of which were equal in semicoking and water conversion experiments, varied greatly in componental composition (Fig. 4). The proportion of most polar compounds of benzene solubles decreased in the experiments in the direction: semicoking → water conversion → hydrogenation, at the same time the amount of other fractions increased.

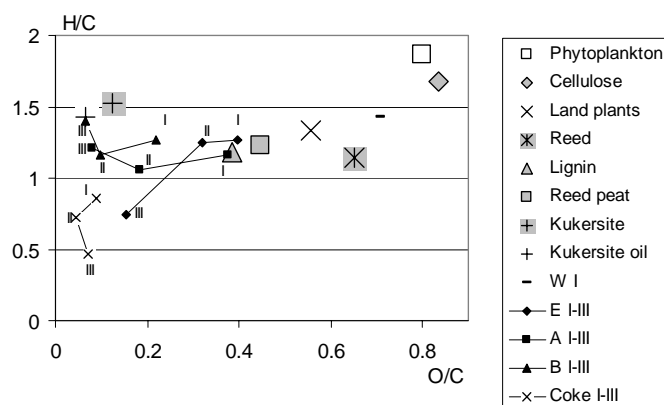


Fig. 3. H/C–O/C diagram of reed, reed peat, kukersite oil shale, and their products of thermochemical liquefaction in comparison with land plants and their components.

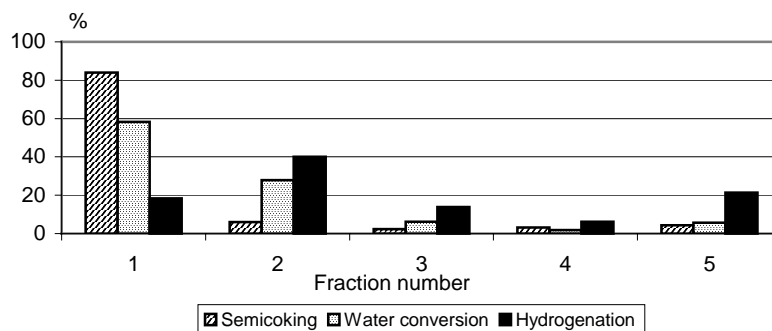


Fig. 4. Componental composition of benzene solubles by thin-layer chromatography, % (fractions: 1 – polar heterocompounds, 2 – neutral heterocompounds, 3 – polynuclear aromatic hydrocarbons, 4 – mononuclear aromatic hydrocarbons, and 5 – nonaromatic hydrocarbons).

Fraction 5 of thin-layer chromatography consisted according to gas-liquid chromatography data mostly of alkanes and alkenes, others made up 18.1% (semicoking), 1.2% (water conversion), and none (hydrogenation). In the case of thermochemical liquefaction of reed, alkanes and alkenes mostly originate from reed bitumen as the main components of reed – cellulose and lignin – do not include long chain hydrocarbons. The yield of fraction 5 from OM of reed was 0.32% (semicoking), 0.71% (water conversion), and 0.89% (hydrogenation). Alkenes prevailed slightly (55% of the sum of alkenes and alkanes) only in the semicoking experiment. They consisted mostly of homologues with an even number of carbon atoms while the composition of alkanes showed no odd–even predominance (Fig. 5I). Water conversion gave mostly alkanes (alkenes 21% of the sum of alkenes and alkanes) with odd predominance. In the hydrogenation experiment alkenes were almost completely hydrogenated to alkanes. As their yield was 2.8 times higher than the sum of alkanes and alkenes in the water conversion experiment, there must be an additional source of their formation. Most probably the source is waxes whose long chain carboxylic acids as well as long chain fatty alcohols give alkanes at hydrogenation. Also carboxylic acids of glycerides are a probable source of alkanes with strong predominance of homologues C_{16} , C_{18} , C_{24} , C_{26} , and C_{28} as we see in Fig. 5III.

The gas consisted (Fig. 6) mostly of non-combustible CO_2 (mass% 10.6, 16.9, and 11.4 of the initial reed carbon, in the semicoking, water conversion, and hydrogenation experiment, respectively). In the semicoking experiment CO yield was high too (4.8% of the reed carbon).

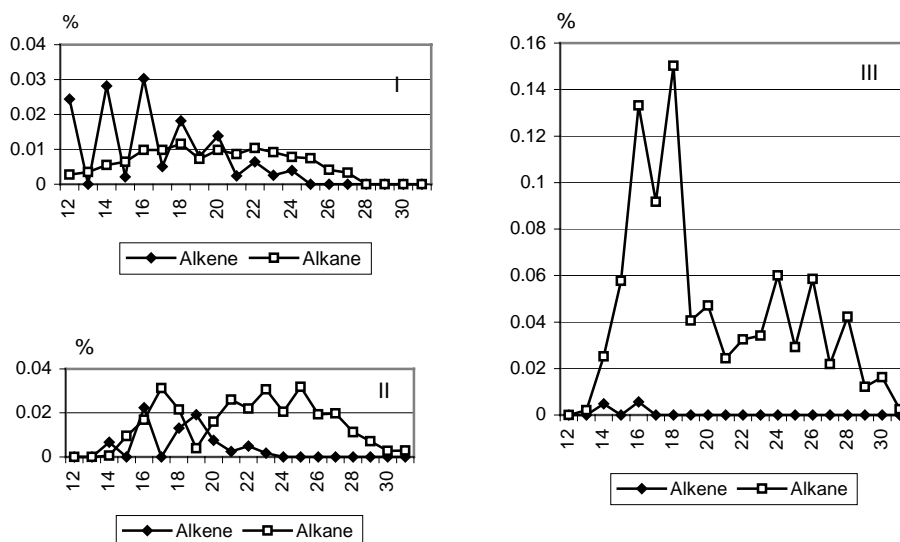


Fig. 5. Yields of alkenes and alkanes formed by thermochemical liquefaction, % from reed OM (I – semicoking, II – water conversion, III – hydrogenation).

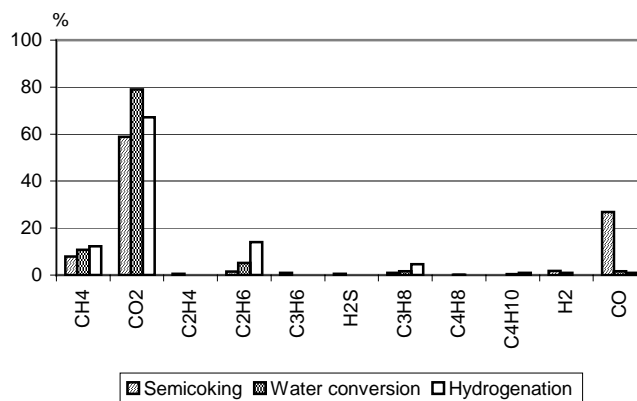


Fig. 6. Composition of gas formed by thermochemical liquefaction, vol%.

The higher percentage of methane, ethane, and propane in the hydrogenation gas than in the semicoking and water conversion gas is explained by the hydrogenation of lower water soluble compounds, which explains also the low CO content. A low CO content is characteristic of the gas formed in the water conversion experiment as well. The proportion of hydrogen in the semicoking and water conversion gas was 0.1%.

There are only a few publications on reed semicoking [21] the results of which are conditionally comparable with data obtained in this investigation.

The yields of CO, hydrogen, and gaseous hydrocarbons were also low in experiments at up to 500°C, but a sharp rise was observed when the temperature was increased to 700–800°C, especially when reed was previously impregnated with K₂CO₃ solution and dried. For example, the following mass% was obtained: CO₂ 68.1 (in our experiments: semicoking 71.2, 87.8, water conversion and hydrogenation 74.5), ethylene 0.6 (unsaturated compounds 0.4, 1.1, and 0.3), ethane plus propane 3.15 (2.4, 6.3, and 16.9), methane 3.5 (3.5, 3.3, and 4.9), CO 19.5 (20.7, 1.1, and 0.7) [12]. Gas composition, according to [21] in vol% is CO₂ 64.6 (in our experiments: 58.8, 79.0, and 67.1), unsaturated hydrocarbons 0.7 (0.6, 0.9, 0.2), CO 28.4 (26.9, 1.6 and 1.0), methane 3.5 (7.9, 10.8, 12.2 plus saturated hydrocarbons 2.5, 7.3 and 19.7), H₂ 2.8 (1.8, 1.0, n.d.).

CONCLUSIONS

The paper gives results of three slow thermochemical liquefaction methods of reed: semicoking by a standard method (Fischer retort), water conversion, and catalytic hydrogenation. It was elucidated that liquefaction conditions (Table 1) have a great influence on the yields of products (Table 2: oil, coke, gas; Fig. 2: carbon balance) as well as on their componental (Fig. 1: oil; Fig. 4: thin-layer chromatography; Fig. 6: gas) and elemental composition (Table 3).

Table 4. Comparison of yields of oil and coke from reed, peat, and wood obtained by different methods, %

	Reed			Reed [21]*	Reed peat [15]*		Estonian peats [24]*	Wood [25]*
	Semi-coking	Water conversion	Hydrogenation		Without steam	With steam		
Oil	25.7	15.4	8.3	5.9	16	17	7.6–15.6	14.0–19.9
Coke	28.4	31.7	38.7	35.1	47.3	40.8	36.2–42.4	35.0–37.8

* Semicoking.

In this investigation of reed the highest yield of the liquid product was obtained by semicoking (at 520 °C, 25.7%). This yield was much higher than that obtained in the Fischer-Schrader retort (at 400 °C, 5.9%), also higher than that obtained by semicoking reed peat (at up to 450 °C, 16–17%) or various kinds of Estonian peat samples (in a 1 m high retort, 7.6–16.6%) (Table 4). Carbonization of pine and peach wood in a metal retort at 350 °C gives respectively 11.8% and 8.1% of the so-called Stockholm tar and 8.0% and 5.9% of sodium acetate soluble material, tar and sodium acetate together 19.8% and 14.0% [25].

The hydrogenation experiment gave the highest yield of coke, which is comparable with the yields obtained from wood in semicoking experiments (Table 4). Greatest yields of oil were obtained from reed by catalytic supercritical gas extraction with methanol (38.7%) and ethanol (53.6%) [7], because part of the solvents is incorporated to oil.

This study is part of a research with an aim to obtain data for planning co-liquefaction experiments of reed and other kinds of biomass with oil shale, plastics, and other organics containing materials. The results obtained show the need to continue the investigation of semicoking of reed and other biomass as the oil shale industry uses mostly semicoking and so various apparatus and the relevant know-how are available. However, also water conversion (which gave many unexpected results as a poorly studied method) and hydrogenation are promising although the reaction conditions of our autoclave experiments were chosen as optimal to produce oil from oil shale (thus were severe for biomass). We expect that in co-liquefaction experiments liquid and gaseous products formed from reed before oil shale starts to decompose will modify shale oil, which may lead to quantitative and/or qualitative synergistic effects – greater amounts and/or better quality of products than in separate processing.

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Pilliroo termokeemiline vedeldamine

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Pilliroog (*Phragmites australis* või *P. communis*) on Eestis levinud kõrreline taim, mille kasutamine aitaks suurendada energeetika varustuskindlust. Pilliroo põletamisel on Eestis kujunemas oma kogemus. Käesolevas töös on antud ülevaade pilliroost kui vedelkütuse toormest ja esitatud termokeemilise vedeldamise (poolkoksistamine Fischeri retordis temperatuuri tõstmisega kuni 520°C, vesikonversioon ja katalüütiline hüdrogeenimine autoklaavis temperatuuril 380°C) katsetulemused. Poolkoksistamisel saadi pilliroo orgaanilise aine kohta 25,7% õli, 28,5% koksi ja 45,8% gaasi koos pürogeetilise veega, teistel meetoditel õli vähem ja koksi rohkem (vastavalt 15,4 ning 8,3 ja 31,7 ning 38,7%), kusjuures õli väärtuslikuma komponendi – benseeniekstrakti – osatähtsus suurenes 28,4-lt (poolkoksistamine) kuni 50,1%-ni (hüdrogeenimine) ja samas õli hapnikusisaldus vähenes. Katseseerial saadud tulemused on aluseks biomassi ja põlevkivi (õli on benseenis peaaegu täielikult lahustuv) koosvedeldamiskatsete kavandamisel.