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CHEMICAL INVESTIGATION OF ESTONIAN PEAT

Viron soiden kemiallinen tutkimus

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Peat, alongside with oil shale, is one of the most important national energy resources of Estonia. Some 9836 peatlands cover 22.3 per cent of the Estonian territory. Peat resources exceed 2.37 billion tons. The chemical composition of Estonian peat was studied as early as in the 1920's. At the end of the 1930's some experiments on peat coking were carried out. Later on the chemical content of peat was studied by the Geological Survey of Estonia. An experimental plant for producing fodder yeast has been established, and attempts made to extract growth stimulators from peat. An experimental plant for the production of activated coal is under construction.

Key words: Estonia, peat chemistry, peat technology

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INTRODUCTION

The developmental history of Estonian mires has recently been described (Ilomets 1992, Zobel 1992) and utilization of peat (Valk 1988, Orru 1992, Zobel 1992). However, data about peat chemistry are very scarce. The main aim of this paper is to give some comprehensive data about chemical properties of Estonian peat, the emphasis mainly being a historical one.

ESTONIAN PEATLANDS

About 22% (1 009 101 ha) of Estonian territory is covered by peatlands (Orru 1993). According to the Geological Survey of Estonia there are some 9 836 peatlands, of which 1598 (901 648 ha) have peat resources suitable for economic use. The other 8238 (107 453 ha) peatlands are mainly thin-peated fens. Mires with an area of less than 1.0 ha have not been included in the survey. In 1981, 5 mire protection areas were established in Estonia, with a combined area of 122 189 ha (Orru 1992).

In the beginning of 1991, the total amount of Estonian peat resources was estimated at 2 374.1 mill. tons of which usable reserves made up to 1523.4 mill. tons (348 639 ha), unusable reserves 687.8 mill. tons (133 833 ha) and possibly usable reserves 162.9 mill. tons (51 879 ha). More intensive studies have been carried out on 539 peatlands, covering 749 948 ha. Of these 68.6% (514 218 ha) are minerotrophic fen peats, 22.3% (167 075 ha) ombrotrophic bog peats, 7.0% (25 369 ha) mixed bog peats and about 2.1% (16 286 ha) transitional peats (Orru 1992).

Up to now, peat in Estonia has been used for heating, litter, horticulture and as fertilizer. The total amount of peat excavated in 1992 was about 2.7 million tons of which 1.4 million tons was fuel peat, 1.1 million tons of slightly decomposed peat litter, and 0.2 million tons of slightly decomposed horticultural peat.

On the basis of certain characteristic features of mires and peat deposits, Estonia has been divided into 20 regions. Using the genetic type of peat and its degree of decomposition, the best use of a peat deposit can be prognosticated. However, a decision concerning the utilization of a particular peat deposit can only be made after a profound technical, botanical and chemical analysis, as well as an environmental impact assessment.

BASIC PROPERTIES OF PEAT

During the last fifty years the study of peat properties in Estonia has been made mainly using the former USSR State Standards. These were only based on the determination of botanical composition, moisture and ash content. For example, the moisture content of milled peat used for briquette industry should not exceed 50%, and the ash content of the dry matter of milled peat should be below 15%.

Several state standards were established for agricultural peat and peat products, according to which the acidity, ammonia absorption capacity, content of ammonium and nitrate nitrogen and exchangeable calcium, magnesium and potassium, water-soluble salts, and total content of calcium and magnesium carbonate of the peat were evaluated. The former Estonian SSR also had its own standards for peat used for horticulture, energy, compost as well as for fertilizer peat. The former Lithuanian SSR Technical Specifications set the quality requirements for semi-briquette and peat for export. The Belorussian standards fixed the quality requirements for peat used for processing wax.

One of the most important properties of peat is its degree of decomposition. In the former Soviet Union, peats were divided into three groups: poorly decomposed, R_1, 1–20% (von Post H = 0–1), moderately decomposed, R_2, 20–40% (H = 1–4) and highly decomposed, R_3, > 40% (40–70%, H = 5–10). Other basic properties of peat such as its density, water absorption capacity and calorific value have also been taken into account. These characteristics may give indirect or partial information about the chemical composition of peat but much basic data are required about the elemental composition of the mineral material (ash) fraction and organic matter of peat. Such data about Estonian peats, particularly the composition of the organic matter fraction, are very scarce.

ELEMENT CONCENTRATIONS IN PEATS

Peat used for agriculture, the chemical industry and energy should have as low ash content as possible. The ash content of compost peat may be as high as 35%. About 98–99% of peat ash consists of silicon, aluminium, iron, calcium, magnesium, sodium, phosphorus and sulphur compounds (Lishtvan et al. 1989). The first data about the ash contents of Estonian peats were based on 133 peat samples taken from various peatlands by the Estonian Experimental Chambers between 1924–1939. The average ash content was 7.2% (range 0.9–38.9%) (Avaste et al. 1947). The average ash content of 288 samples from 34 northern Estonian peatlands and of 183 samples from 21 southern Estonian peatlands were analyzed during the last decades by the Geological Survey of Estonia (Table 1). Northern Estonian peats have lower ash content than those from southern Estonian peats with corresponding degrees of decomposition: R = 4–56% and 14–66%, respectively. The most important oxides in peat ash are CaO and SiO_2, Fe_2O_3 or Al_2O_3 may be present in small amounts.

In certain cases, trace elements in Estonian peat have been analyzed by semi-quantitative spectral analysis (Table 2). Values in peat are lower than in soil. However, if the data are expressed per unit mass of mineral matter, the element concentrations of different types of peats and soils are of the same order, except for Zn, Mo, Ag, B and Sr, which were higher for peat than for soil.

ORGANIC CONSTITUENTS OF PEAT

In the course of peat formation, the organic carbon content of the plant residues increases with corresponding decrease of hydrogen and oxygen contents. There is also a certain decrease

Table 1. Concentrations of some macroelements and nitrogen in dry matter of Estonian peats (%, mean with extreme values in brackets). The mean sulphur concentration northern of Estonian peats is 0.23 (0.01–2.93%)

Taulukko 1. Muutamien tärkeiden alkuaineiden pitoisuuksia Viron eri osien soiden turpeissa (keskiarvo, %, vaihteluväli sulkeissa). Pohjois-Viron turpeiden keskimääräinen rikkipitoisuus on 0,23 (0,01–2,93%).

Mire class	Number of cores studied	Number of samples studied	Degree of decomposition	SiO_2	Fe_2O_3	Al_2O_3	CaO	F_2O_5	N
Northern Estonian mires	66	288	29 (4–56)	2.12 (0.05–33.5)	0.46 (0.02–4.57)	0.44 (0.01–3.58)	1.95 (0.12–15.5)	0.10 (0.01–1.81)	1.54 (0.47–2.97)
Fens in southern Estonian river valleys	27	107	44 (26–66)	9.55 (0.16–65.1)	2.05 (0.09–19.2)	1.50 (0.01–9.67)	3.48 (0.11–19.7)	0.24 (0.02–3.22)	1.86 (0.38–2.66)
Fens on southern Estonian moraine plains	12	46	45 (32–65)	3.57 (0.10–26.3)	1.21 (0.12–3.04)	0.87 (0.04–5.55)	4.43 (1.80–19.6)	0.13 (0.04–0.37)	2.13 (0.75–2.94)
Southern Estonian bogs	9	30	35 (14–64)	2.50 (0.09–16.3)	0.11 (0.01–0.35)	0.30 (0.05–2.40)	0.59 (0.09–2.21)	0.04 (0.01–0.12)	0.87 (0.37–1.99)

in the concentrations of nitrogen and sulphur (Table 3). Simultaneously there is a reduction in the hygroscopicity and in the concentrations of volatile substances but an increase in the calorific value of the peat.

The organic composition of Estonian peats was determined for the first time at the State Experimental Chambers between 1924–1939. Out of 27 samples that were analysed, two were subject to obvious determination errors. The organic composition of peat used in coking experiments was also determined 9 times by the Peat Section of the Institute of Natural Resources and by the Institute of Industrial Investigations between 1938–1945.

Different methods for the determination of organic groups have been established. The one elaborated by the Belorussian Peat Institute (Lishtvan et al. 1989) is perhaps the most suitable for comparing peat types. Bitumens (B) are first removed with a benzene extraction, after which water-soluble substances (WS) are extracted by heating. Next, easily hydrolysable substances (EH) are extracted by 4% HCl on a boiling water bath. The yield of humic substances (HS) is determined by repeated treatment of the peat residue with 0.1 N NaOH solution at 80°C. Humic substances are solubilised as sodium salts. By acidifying the alkaline solution with 10% HCl acid solution, humic acids (HA) are precipitated, and the yield of fulvic acids left in the solution can be calculated indirectly. To extract difficultly hydrolysable substances (cellulose-C), a 80% solution of sulphuric acid

Element	R A^d =3%	RS A^d =1%	SS A^d =5%	M A^d =7%	In Estonian soil	In litho-sphere
Ti	50	60	78	74	2300	4500
V	0.6	0.7	1.2	1.0	40	90
Cr	0.6	0.4	1.0	0.7	40	83
Mn	10	15	18	48	430	1000
Co	0.16	0.16	0.22	0.20	7.4	18
Ni	0.60	0.73	0.75	0.90	18	58
Cu	2.0	2.0	1.7	2.4	19	47
Pb	0.90	0.42	0.90	0.65	20	16
Zn	7.2	6.0	4.0	5.6	47	83
Mo	0.16	0.30	0.32	0.48	1.5	1.1
Ag	0.01	0.01	0.01	0.01	0.12	0.07
Sn	0.12	0.10	0.16	0.12	2.4	2.5
Be	0.01	0.01	0.01	0.01	1.3	3.8
B	1.2	2.0	1.8	2.4	30	12
Sr	7.5	8.0	10	15	100	340
Ba	8	17	24	30	400	650
Ga	0.15	0.12	0.28	0.18	13	19
Zr	3.0	4.0	5.2	4.8	289	170
Y	0.60	0.60	1.2	1.0	25	19
Yb	0.05	0.05	0.10	0.08	2.5	3.3
La	0.6	0.6	2.0	1.7	92	29
Ce	0.14	0.18	0.40	0.26	59	70

Table 2. Concentrations of trace elements in Estonian peats (g/t) with low ash content (medians calculated for air-dry peat with a 10 % ash content). R-raised bog; RS-raised bog mixed; SS-transitional peat, and M-fen peat, A^d – Ash content per dry matter of peat.

Taulukko 2. Alkuainepitoisuuksia (g/t) virolaisissa turpeissa, joiden tuhkapitoisuus on pieni. R-rahkaturve, M-nevaturve, RS ja SS - väliturpeita. A^d*-tuhkapitoisuus kuivamassasta. Vertailun vuoksi on taulukossa annettu alkuaineiden pitoisuudet myös Viron maaperässä ja maankuoressa.*

is used. The non-hydrolysable residue is lignin (L).

The Institute of Chemistry has made organic composition analyses from lake gyttja samples taken from Lake Lahepera, Värska, Lake Peipsi and some interglacial sapropels in order to study the initial material for oil shale formation (Palu and Veski 1982, Saarse et al. 1984). Raised-

Name	C	H	N	S	O
Peat forming plants	51.8 (49.4–53.9)	6.0 (5.5–6.5)	1.2 (0.8–1.9)	–	41.0 (38.5–43.9)
Peat in former USSR	57.5 (48.0–65.1)	5.9 (4.7–7.3)	2.1 (0.5–4.0)	0.35 (0.02–6.65)	34.3 (24.7–45.2)
Estonian peat (n =34)	57 (52.1–60.4)	5.7 (5.0–6.3)	1.8 (1.1–2.7)	0.4 (0.1–1.0)	35.1 (30.3–40.1)

Table 3. The element concentrations in organic matter of peat forming plants (Rakovskij and Pigulevskaja 1978), peats of the former USSR (Lishtvan et al. 1989) and Estonian peat deposits (Avaste 1974, Avaste et al. 1947). Values are average percentage values with extremes in brackets.

Taulukko 3. Alkuainepitoisuuksia turvetta muodostavissa kasveissa Rakovskij ja Pigulevskaja 1978), entisen Neuvostoliiton turpeissa (Lishtvan ym. 1989) ja Viron turpeissa (Avaste 1974, Avaste ym. 1947). Arvot ovat keskiarvoja (%, vaihteluväli suluissa).

bog peats have more bitumens, hydrolysable substances and cellulose than fen peats, with simultaneous smaller contents of humic acids and lignin (also Luukkanen 1984, 1988). The differences between peat group composition are primarily related to the degree of decomposition. The greatest amount of hydrolysable substances can be obtained from weakly decomposed raised-bog peats (*Sphagnum fuscum* and *S. magellanicum* peat with R = 5–10%.) A high bitumen content is characteristic for highly decomposed cotton-grass peat whereas a high content of humic substances is associated with wood and cotton-grass peats (Rakovskij and Pigulevskaja 1978).

In 1970 the Belorussian Peat Institute studied 14 Estonian, Latvian and Belorussian weakly decomposed raised-bog peat deposits for industrial purposes. The degree of decomposition of the studied peats was between 5.4–15%. The results showed that bog peats have a total content of hydrolysable substances of about 46.3–53.8% (Pidoplichko 1971).

In 1987–1989 the Peat Group of the Geological Survey of Estonia, in the course of studying the possible utilization of Estonian peat resources, took five samples to the Central Laboratory of the Production Association, “Gealtorfrazvedka” to be analysed. The results showed that peats with high bitumen as well as hydrolysable and humic substances contents can be found in Estonia (Table 4).

PEAT CHEMICAL INDUSTRY

Although the chemical composition of peat has not been throughly investigated, attempts have been made to develop a peat chemical industry for Estonia. Experimental peat coking was started in the Peat Section of the Estonian Institute of Natural Resources as early as in 1938 (Avaste 1947). The former USSR authorities planned to produce fodder yeast from raised bog peat. It was intented to build one plant in Estonia, another in Latvia, 2 in Belorussia and 8 in Russian Federation. The one in Estonia was to be the largest, with an annual production of 60 000 tons of fodder yeast (Pidoplitchko 1971). These plans were never realised, however. On the initiative of the Estonian authorities, one small fodder yeast plant was built in Estonia. However, it did not function for long.

Experiments to produce growth stimulants from peat were also made. The use of peat to clean up oil spills has been investigated in Estonia. The first attempts to elaborate original

Table 4. Chemical group composition of organic matter of Estonian peat, %. B = bitumens, WS = water-soluble substances, EH = easily hydrolysable substances, HA = humic acids, FA = fulvic acids, C = cellulose-C, L = lignin, R = degree of decomposition (%), A^d = ash concentration per dry matter of peat.

Taulukko 4. Viron soiden orgaanisen aineksen kemiallisia ryhmäkoostumuksia (%). B = bitumit, WS = vesiliukoiset yhdisteet, EH = helposti hydrolysoituvat yhdisteet, HA=humushapot, FA = fulvohapot, C = selluloosa-C, L = ligniini, R = maatumisaste (%), A^d = turpeen kuiva-aineksesta laskettu tuhkapitoisuus.

Type of peat	B	WS+EH	HA	FA	C	L
S. fuscum peat R 6%, A^d 0,68%	4.1	40.7	15.9	18.5	14.8	4.6
Same, R 11%, A^d 0.81%	4.4	35.3	19.6	21.3	12.7	5.5
Cotton-grass *Sphagnum* -peat R 30%, A^d 1.83%	6.2	28.0	32.2	18.4	9.0	5.8
Cotton-grass peat R 44%, A^d 1.33%	8.7	17.0	40.8	18.8	4.8	9.2
Transitional sedge-*Sphagnum* fen peat R 31%, A^d 1.24%	6.8	13.3	42.9	18.8	6.3	10.9

technology for producing activated coal is presently in an experimental stage.

In spite of estimation of peat resources and extraction of peat and briquette production technology, the utilization of peat in Estonia remained peripheral to Belorussia and Russia in the former Soviet Union. It is hoped that independent Estonia will now be able to pay more attention to the development of a national peat science.

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TIIVISTELMÄ

VIRON SOIDEN KEMIALLINEN TUTKIMUS

Viron alueesta (1009101 ha) on soita 22,3%. Virossa on yli 1.0 ha:n soita yhteensä 9 836. Viron turvevarat olivat vuoden 1991 alussa 2 374,1 milj. tonnia, joista teollisesti hyödynnettävissä olevia (aktiivisia) varoja oli 1 523,4 milj. tonnia.

Viron soiden kehityksen ja turpeen käytön kysymyksiä on kirjallisuudessa käsitelty perusteellisesti (Ilomets 1992, Zobel 1992, Valk 1988, Orru 1992), mutta yleiskatsaus turpeen kemiallisista tutkimuksista on puuttunut.

Ennen toista maailmansotaa määritettiin kosteuden ja polttoarvon mukana myös turpeen tuhkapitoisuus (Avaste 1947) ja turvetta muodostavan orgaanisen aineen tekijöiden koostumus (Taul. 3). Sodan jälkeen turpeen kemiallista koostumusta on pääasiallisesti tutkittu Viron Geologian Tutkimuskeskuksessa Neuvostoliiton GOST-standardien mukaan.

Viron Geologian Tutkimuskeskuksessa on määritelty 56 suosta 114 profiilin 472 turvenäytteen tärkeimpien pääravinteiden ja hivenaineiden määrät (Taul. 2). Virossa ei ole määritetty turvetta muodostavan orgaanisen aineen kemiallista ryhmäkoostumusta, kuten on tehty järvimudista (Palu ja Veski 1982) ja jääkausien välillä syntyneistä sapropeleista (Saarse ym 1984). Vuonna 1970 Valko-Venäjän Tiedeaka-

temian Turpeentutkimuslaitos tutki Latvian ja Valko-Venäjän turve-esiintymien ohella myös muutaman Viron vähän maatuneen kohosuoturpeen kelpoisuutta hydrolyysiteollisuuden raaka-aineeksi (Pidoplitsko 1971). Myöhemmin tilattiin analyyseja turvetta muodostavan orgaanisen aineen kemiallisesta ryhmäkoostumuksesta (Taul. 4). Tulokset osoittivat, että Virossa on sekä runsaasti bitumeja että myös helposti hydrolysoitavia aineita ja humushappoja sisältäviä turpeita.

Viron turpeiden kemiallisen koostumuksen tutkiminen ja muutamat yritykset juurruttaa turvekemian teknologiaa maahan ovat olleet verrattain satunnaisia. Kokeita turvekoksin valmistamiseksi tehtiin jo ennen toista maailmansotaa (Avaste 1947). Sodan jälkeen suunniteltiin Neuvostoliiton vähän maatuneiden kohosuoturve-esiintymien lähelle 12 suuren rehuhiivatehtaan rakentamista. Niistä suurimman piti tuottaman 60 000 tonnia rehuhiivaa vuodessa. Tämä suunnitelma ei toteutunut. Sittemmin rakennettiin Virossa oma-aloitteisesti pieni rehuhiivatehdas, joka pian suljettiin. Myös kasvustimulantteja yritettiin tuottaa. Jonkinverran työskennellään tällä hetkellä öljypuhdistusturpeen kehittämiseksi, sekä aktiivihiilen tuottamiseksi.

Vaikka turve on Virossa palavakiven jälkeen toinen tärkeä polttoaine, mahdollisuuksia turpeiden perusteelliseen kemialliseen tutkimukseen ei juuri ole, koska valtion tiederahoitus on jatkuvasti vähentynyt. Nykyisin täytyy ensiksi turveteollisuudessa nostaa energiaturpeen määrää, minkä vuoksi ei ole mahdollista kiinnittää tarpeeksi huomiota uusien turvekemiallisten tuotteiden valmistukseen.

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