Suo 38 (5): 105—110, 1987

MARTTI AHO

PYROLYSIS OF PEAT

TURPEEN PYROLYYSISTÄ

Aho, M. 1987: Pyrolysis of peat. (Tiivistelmä: Turpeen pyrolyysistä.) — Suo 38: 105—110, Helsinki.

The release of nitrogen and sulphur compounds in peat pyrolysis was investigated between 300 and 700 °C. Seven peats with different nitrogen and sulphur contents (N: 0.8—2.9 %, S: 0.08—0.24 %) were studied. The pyrolysis was studied indirectly by following the elemental composition and the structure of the char residue. The tars of one peat sample were trapped.

The greatest portion of the sulphur-containing compounds pyrolysed below 500 °C. Nitrogen-containing compounds pyrolysed in a larger temperature range. One group of peats contained easily pyrolysable and the other group weakly pyrolysable nitrogen compounds. This suggests that the behaviour of fuel nitrogen in combustion will be difficult to predict because pyrolysis compounds may react further to corresponding oxides. The nitrogen content may be high in the tar in which case the tarry intermediates may also increase the amount of NO in flue gases. Infrared spectroscopy provided information about the decomposition of the main compounds in peat, like carbohydrates and long chained hydrocarbons during charring complementary to the information provided by elemental analyses.

Keywords: pyrolysis, peat, air pollution.

M. Aho, Technical Research Centre of Finland,
Domestic Fuel Laboratory,
P.O. BOX 221,
SF-40101 Jyväskylä,
Finland.

INTRODUCTION

Pyrolysis is an important stage in peat combustion, although the three stages of drying, pyrolysis and char burning extensively overlap in a true burning process. This study deals with the release of the nitrogen- and sulphur containing compounds and the structure of the char residue formed during peat pyrolysis between 300 and 700 °C. A part of the nitrogen and sulphur compounds react further in oxidizing conditions to the corresponding oxides, which cause the acidification of the atmospheric water. The degree of conversion of peat nitrogen to NO varies between 2—10 % in fixed bed combustion. If a single fuel particle is removed from the bed and burned alone the conversion can be even five times higher (Aho 1987a, b).

The pyrolysis was followed by analysing the residue from an isothermal thermogravimetric run in nitrogen atmosphere with elemental analyzers and an infrared spectrophotometer. Despite the simplicity of the methods, they provided valuable information about the pyrolysis phenomenon. More thorough analyses could be made with PY-MS, TG-MS or TG-FTIR combinations (Herod et al. 1985, Szekely et al. 1980, Carangelo et al. 1987). (The cited publications concern the pyrolysis of coal.)

EXPERIMENTAL

The peats studied represent the main peat types in the mires of Southern and Central Finland (*Sphagnum* and *Carex* peats). *Carex* peats were collected at Haapavesi (Piipsanneva) and *Sphagnum* peats at Leivonmäki (Kailasuo).

The contents of major elements (C, H, N and S) in the original and charred peats were determined with a Leco CHN-600 elemental analyzer, a Carlo-Erba 1108 elemental analyser and a Leco SC-132 sulphur analyser. Oxygen content was calculated as follows:

$$0(\%)=100—(C+H+N+S+ash)\% \qquad (1)$$

Ash content and volatiles were analysed according to DIN norms (VTT 8420-80 and VTT 8421-80, respectively). Peat types were partly analysed at the Department of Peatland

Forestry, University of Helsinki, and partly at the Technical Research Centre of Finland. The degree of humification was analysed by von Post's method. Table 1 shows the results for the peat samples.

Table 1. The botanical and chemical composition of the peat samples. S = Sphagnum, C = Carex, Er = Eriophorum, L = Woody =, H = degree of humification, von Post method.

Taulukko 1. Analysoitujen turpeiden kasvinjäännös- ja kemiallinen koostumus. S = rahkaturvetekijä, C = saraturvetekijä, Er = tupasvillaturvetekijä, L = puuturvetekijä, H = maatumisaste von Postin menetelmällä määritettynä.

Peat type *Turvelaji* %	H	Volatiles *Haihtuvat* %	Ash *Tuhka* %	C %	H %	N %	S %	O
S (85 %) S)	2	72.4	1.2	52.6	6.3	1.0	0.09	38.8
S (80 % S)	4	69.4	3.5	57.4	6.6	1.5	0.13	30.9
ErS (50 % S)	6	65.4	3.0	53.4	6.1	0.8	0.08	36.6
LS (55 % S)	8	63.2	5.0	55.3	5.3	1.2	0.24	33.0
SC (45 % C)	6	67.6	7.1	51.3	6.1	2.9	0.15	32.5
C (80 % C)	5	66.7	5.2	55.0	6.1	2.0	0.15	31.6
S'-	4	69.0	3.5	58.0	5.9	1.6		

The extreme peats (S H2 and LS H8) were very different from each other and the nitrogen content in the SC peat sample exceeded the upper limit of nitrogen concentration in Finnish peat reported in the literature (Seppälä et al. 1980).

The samples were pyrolysed in nitrogen atmosphere at constant temperature at intervals of 100 °C between 300 and 700 °C, using a thermobalance system (Fig. 1). The sample size was 1 g and the nitrogen flow rate 0.67 dm^3/s. The samples were dried and powdered.

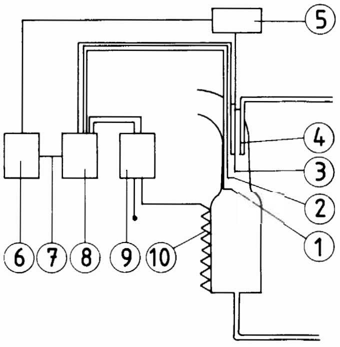
The residues of S and N in the char were calculated using the formulas

$$S^* (\%) = \frac{S \cdot m}{S_0 \cdot m_0}, \quad N^* (\%) = \frac{N \cdot m}{N_0 \cdot m_0} \qquad (2)$$

where,

m	is the weight of the sample at temperature T
m_0	is the initial weight of the sample
S, N	is the concentration of the element at temperature T
S_0, N_0	is the initial concentration of the element

The chars of the LS H8 peat were studied more carefully with Vapo's Perkin-Elmer 983 infrared spectrophotometer, and the tars formed in the pyrolysis of single sods of S H4 peat in 35 % moisture content were collected in a cold trap cooled with liquid nitrogen for elemental analysis. Sods (ø 30 × 30 mm) weighing about 15 g each were placed in an open-bottomed metal cylinder equipped with a steel pipe leading to the trap. The temperature range in the experiments on tar trapping was reduced to 300—500 °C, with a temperature interval of 50 °C, because the vigour of the pyrolysis made it difficult to collect tars at temperatures greater than 500 °C.



Codes

1, 2 = thermocouples
3 = sample
4 = gas sampling tube
5 = balance sartorius 1265 MP
6 = computer HP 9845
7 = HP-IP way
8 = Data-logger HP 3497
9 = power regulator
10 = resistance (3 kW)

Figure 1. Schematic diagram of the thermobalance system.

Kuva 1. Termovaakalaitteiston kaaviokuva.

Infrared spectra provide qualitative data on the structure of peat (Tummavuori et al. 1982). The method has also been used to study the changes in coal char during thermal treatment (Chen et al. 1985). In spite of the extremely complicated chemical structure of peat the origin of several of the absorption peaks is known. The OH group absorbs at 3400 cm^{-1}, groups typical of long-chained hydrocarbons ($-CH_2$; $-CH_3$) absorb at 2930 and 2860 cm^{-1}, the carboxyl group (COOH) absorbs at 1710 cm^{-1} and C = C and C = 0 bonds absorb at 1600 cm^{-1}. The signal at 1050 cm^{-1} is mainly due to the C-O-bond of carbohydrates (Adhikari et al. 1973, 1978, Chen et al. 1985).

RESULTS AND DISCUSSION

The thermogravimetric curves of the peats obtained in isothermal experiments in nitrogen atmosphere are shown in Figure 2.

The curves of the S H2 peat (72.4 % volatiles), ErS H6 peat (65.4 % volatiles) and LS H8 peat (63.2 % volatiles) diverge at temperatures > 500 °C. At 700 °C the

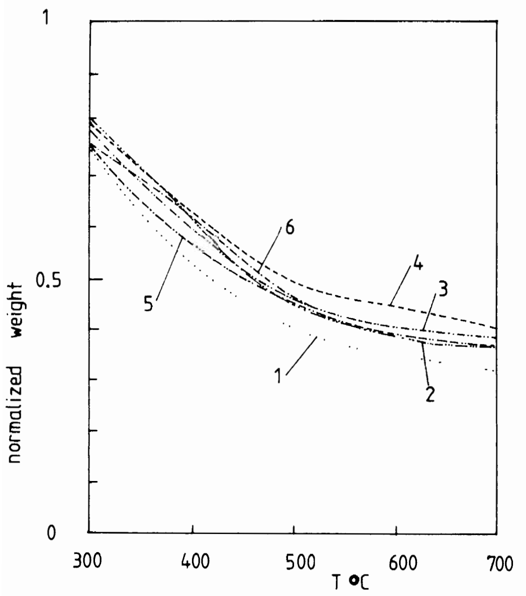


Figure 2. Normalized weights of the samples after pyrolysis between 300 and 700 °C. Codes: 1=S H2-peat, 2=S H4-peat, 3=ErS H6-peat, 4=LS H8-peat, 5=SC H6-peat, 6=C H5-peat.

Kuva 2. Näytteiden normalisoitu paino pyrolyysin jälkeen lämpötilavälillä 300—700 °C. Merkit: 1=S H2-turve, 2=S H4-turve, 3=ErS H6-turve, 4=LS H8-turve, 5=SC H6-turve, 6=C H5-turve.

weight of the char residue was 31—40 % of the original peat.

Figure 3 shows the amounts of N and S in the char after pyrolysis.

If the ErS H6 peat with low sulphur content is excluded, the evolution of sulphur compounds is maximum between 300 and 400 °C. Typically about 50 % of S has pyrolysed at 400 °C. Above 500 °C the pyrolysis of sulphur compounds is very weak and the char contains 22—37 % of the initial sulphur content at 700 °C.

The peats could be divided into two groups on the basis of the behaviour of nitrogen compounds during pyrolysis. In one group most of the nitrogen compounds pyrolysed after 600 °C and their weight concentration in the char increased strongly between 300 and 600 °C. In the other group nitrogen compounds pyrolysed strongly between 300 and 600 °C and the nitrogen content in the char remains roughly constant or increases slightly with temperature. The pyrolysis behaviour of nitrogen compounds was not dependent on the botanical composition of peat. The interesting step in the future could be to follow the amounts of different nitrogen compounds in pyrolysis gases using TG-MS or TG-FTIR combinations.

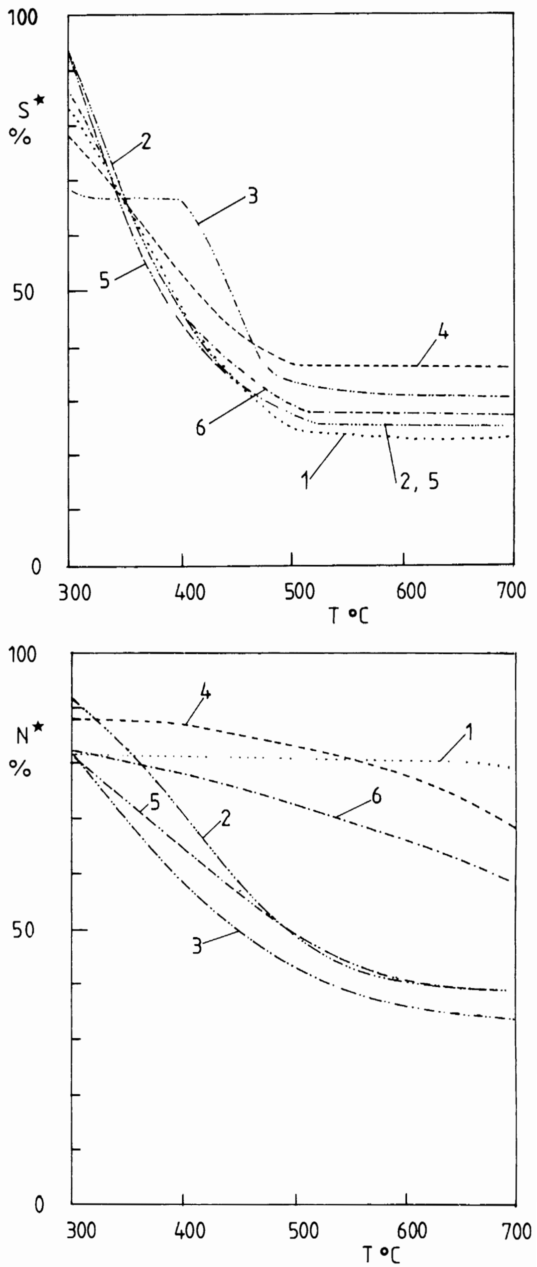


Figure 3. The relative amounts of S and N in solid phase after pyrolysis. Codes as in Figure 2 and formula 2.

Kuva 3. Rikin ja typen suhteelliset määrät kiinteässä faasissa pyrolyysin jälkeen. Merkinnät ovat kuvassa 1 ja kaavassa 2.

Rensfelt and co-workers (1978) studied the elemental composition of the solid residue of peat and wood after pyrolysis but only one figure dealing the pyrolysis of one type of peat was shown. So this study completes those results.

To confirm that the mass concentration of the nitrogen-containing compounds may be high in the pyrolysis products of peats of high nitrogen content and high nitrogen reactivity, the tars of pyrolysis of S' H4 peat were collected in a cold trap cooled with liquid nitrogen. S' H4 peat strongly resembled S H4 peat (see Table 1) and its nitrogen compounds were easily pyrolysed in the studied temperature range (300—500 °C). Figure 4 shows the nitrogen concentrations in tar and char after pyrolysis. It was not possible to study the composition of the gas phase because of the large number of releasing compounds.

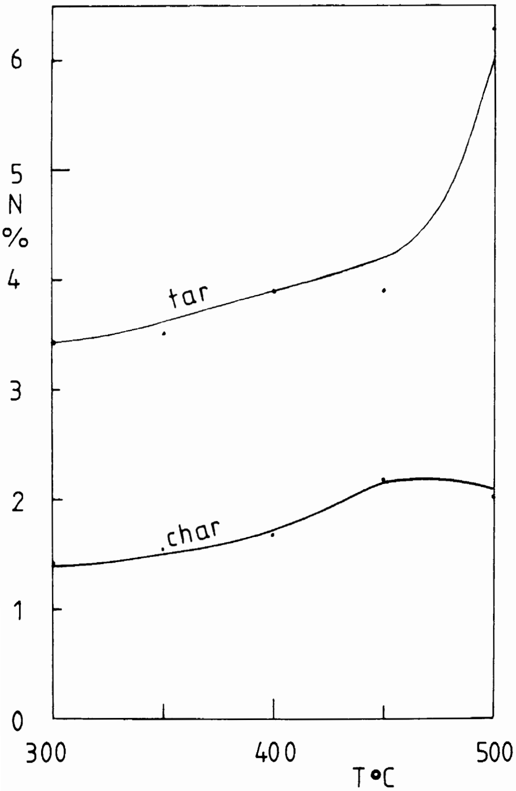


Figure 4. The weight concentration of nitrogen in char and tar in peat pyrolysis. Sample=S' H4-peat sod. Moisture content=35 %.

Kuva 4. Typen konsentraatio hiiltojäännöksessä (char) ja tervassa (tar) turpeen pyrolysoituessa. Näyte: S' H4-pala. Kosteuspitoisuus 35 %.

Nitrogen compounds concentrate in tar (the nitrogen content increases up to 6 %). This means that the emissions of NO might increase during peat burning if the tar concentration became high during some period of the combustion. To confirm this the tendency of tar nitrogen to convert to NO would need to be measured. This has not been done yet. The conversion of peat nitrogen varies in grate combustion between 5 and 10 % and in gasification combustion between 10 and 20 %, where prominent tar formation is possible (Vesterinen 1986). In grate combustion it is possible to reduce the conversion level to 2—5 % which would reduce the total emissions of NO (Aho 1987a).

The changes in the structure of the char were studied by elemental analysis and infrared spectroscopy.

Figure 5 shows the infrared spectra of LC H8 peat char during pyrolysis in the temperature range 300—700 °C. Figure 6 shows the elemental composition of the char in the same temperature range. The amount of H and O decrease strongly in that range. The infrared spectra are not exactly quantitative (a constant amount of peat per cm^{2}) because increasing scattering in the samples charred at higher temperatures necessitated a reduction in the sample/KBr ratio (Solomon et al. 1987). However, conclusions can be drawn from the signal intensities in the spectra.

The absorption signal at 1050 cm^{-1} practically vanished between 300 and 400 °C, which means that the greatest part of the carbohydrates pyrolysed below 400 °C. This together with the weakening signals at 2930 and 2860 cm^{-1} indicating the disappearance of long-chain hydrocarbons, explains the reduction in the H and O contents in the char between 300 and 500 °C. The absorptions due to -OH and C = 0 groups also weaken continually between 300 and 500 °C, but the signal of the COOH group is still strong at 400 °C. The spectrum of the sample charred at 700 °C strongly resembles that of coal, where the C = C signal at 1600 cm^{-1} is often of highest intensity (Chen et al. 1985).

CONCLUSIONS

Our relatively simple analytical methods provided valuable information on peat pyrolysis. The relative amount of sulphur decreases in approximately the same way in the solid residues of the studied peats during pyrolysis (one exception). Nitrogen-containing compounds behave more irregularly, and on that basis the peats can be divided into two groups: one containing easily pyrolysable

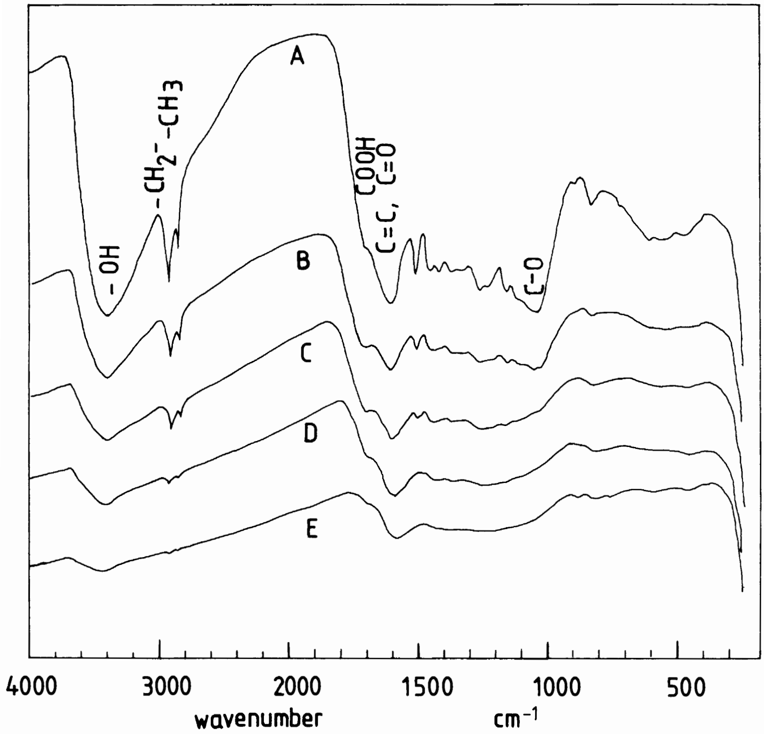


Figure 5. The infrared spectra of chars of LS H8 peat after pyrolysis at different temperatures.
A=untreated sample,
B=charred at 300 °C,
C=charred at 400 °C,
D=charred at 500 °C,
E=charred at 700 °C.

LS-H8-turpeen hiiltojäännöksen infrapunaspektrit eri lämpötiloissa pyrolysoinnin jälkeen. A=käsittelemätön näyte,
B=hiilolämpötila 300 °C,
C=hiilolämpötila 400 °C,
D=hiilolämpötila 500 °C,
E = hiilolämpötila 700 °C.

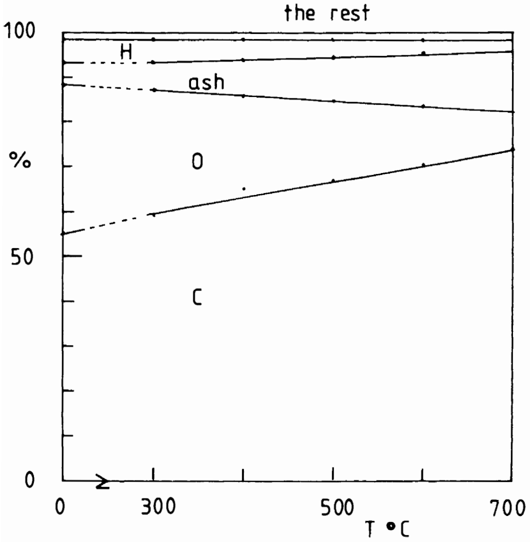


Figure 6. The elemental composition of the char residue as a function of charring temperature. Sample=LS H8 peat.

Kuva 6. Hiiltojäännöksen pääalkuaineiden suhteelliset pitoisuudet hiilolämpötilan funktiona. Näyte=LS H8-turve.

nitrogen and the other weakly pyrolysable nitrogen. No interaction between the botanical composition of peat and the releasing tendency of nitrogen compounds was found. The results explain the difficulty in predicting the conversion level of fuel nitrogen to nitrogen oxides in peat combustion. If the peat contains easily pyrolysable nitrogen, nitrogen compounds concentrate in the tar (the N content may rise to > 5 %). This in turn may increase the levels of nitrogen oxides in combustion, where tar is an abundant intermediate. The nitrogen content in one of our peat samples exceeded the highest value published for nitrogen concentration.

The effect of the releasing tencency of nitrogen compounds to the NO-emissions should be studied with many peat samples to find out its importance on NO-conversion. It will give more information than the analysis of nitrogen contents alone.

Infrared spectroscopy provided information on the structure of the char which complements the information obtained from ordinary elemental analysis. The reasons for the decreasing oxygen and hydrogen contents in the char as a function of increasing pyrolysis temperature were found.

REFERENCES

Adhikari, M. & Chakrabarti, G. 1973: Infrared spectra of natural and microbially synthesized humic acids. — J. Indian Chem. Soc. 1: 394—396.

Adhikari, M., Mandal, B. & Mukherjec, T. 1978: Studies on physico-chemical properties of natural, synthetic and microbial humic acids. — Proc. Indian Nat. Sci. Acad. 44 A: 202—210.

Aho, M. 1987a: Decrease of the emissions of nitrogen oxides in peat combustion. — Proceedings of the Swedish Flame Days, Studsvik 8—9. 8. 1987. 14 p.

Aho, M. 1987b: Pyrolysis and combustion of peat and wood as single particles and as a layer. — Journal of Analytical and Applied Pyrolysis 11: 149—169.

Carangelo, R., Solomon, P. & Gerson, J. 1987: Application of TG-FTIR to study hydrocarbon structure and kinetics. — Fuel 66: 960—967.

Chen, P., Yang, P. & Griffits, P. 1985: Effect of preheating on chemical structures and infrared spectra of Yanzhou coal. — Fuel 64: 307—312.

Herod, A. & Smith, C. 1985: Release of oxygen and sulphur compound from coal. — Fuel 64: 281—283.

Rensfelt, E., Blomkvist, G. & Liinanki, L. 1978: Basic gasification studies for development of biomass medium — BTU gasification. — Symposium papers, Energy from biomass and wastes. Washington D.C. 14—18. 8. 1978: 465—495.

Seppälä, R., Äijälä, M. & Asplund, D. 1980: Jyrsinturpeen käsittely ja polttotekniikka Suomessa, Irlannissa ja Neuvostoliitossa. — Technical Research Centre of Finland, Research Reports 63. 379 pp. + app. 91 pp. Abstract in English.

Solomon, P. R., Carangelo, R. M. & Best, P. E. 1987: Analysis of particle emittance, composition, size and temperature by FT-IR emission/transmission spectroscopy. — Fuel 66: 897—908.

Szekely, T., Till, T. & Varhegyi, G. 1980: Characterization of fossil fuels by computer aided thermobalance-mass spectrometer system. — 6th International Conference on Thermal Analysis. Bayreuth, West Germany: 365—370.

Tummavuori, J., Kuusela, P., Nyrönen, T. & Lehtovaara, J. 1982: Predicting the self-heating tendency of milled peat. An application of IR-spectroscopy. — Proceedings of the International Symposium of the IPS Commissions IV and II. Minsk, USSR: 523—531.

Vesterinen, R. 1986: Emissions of wood and peat fired heating plants. (Tiivistelmä: Puuta ja turvetta käyttävien lämpölaitosten päästöt.) — Suo 37: 11—18.

TIIVISTELMÄ:

TURPEEN PYROLYYSISTÄ

Työssä tutkittiin typpi- ja rikkipitoisten yhdisteiden syntyä turpeen pyrolyysin aikana lämpötilavälillä 300—700 °C. Lisäksi analysoitiin yhden turvenäytteen pyrolyysissä syntynyttä tervaa ja toisen näytteen pyrolyysijäännöstä tarkemmin. Työvälineet olivat termovaaka, alkuaineanalysaattori ja infrapunaspektrometri. Pyrolyysi on tärkeä palamisen välivaihe ja siinä syntyvät yhdisteet ovat tärkeitä välituotteita poltossa. Rikki- ja typpiyhdisteet muodostavat happamia oksideja, jotka happamoittavat edelleen ympäristöä. Turpeen rikistä yleensä yli puolet muodostaa SO_2:ta. Turpeen typen reaktioaste NO:ksi on 5—20 % polttotavasta riippuen.

Turvenäytteet edustivat Etelä- ja Keski-Suomen pääturvetyyppejä: rahka- ja saraturvetta. Näytteiden rikin ja typen pitoisuudet vaihtelivat suuresti (N: 0,8—2,9 %, S: 0,08—0,24 %). Korkein typpipitoisuus ylitti aikaisemmin kirjallisuudessa mainitun ylärajan (2,5 % N).

Typpi- ja rikkiyhdisteiden syntymistä tutkittiin epäsuorasti analysoimalla näiden alkuaineiden määrät eri lämpötiloissa hiilletyistä jäännöksistä. Suora, mahdollisimman täydellinen määritys kaasusta vaatisi termovaakaan kytketyn massaspektrometrin.

Suurin osa turpeen rikkiyhdisteistä pyrolysoitui alle 500 °C:n lämpötilassa. Typpiyhdisteiden pyrolysoituminen riippui voimakkaasti näytteestä siten, että osa turpeista sisälsi helposti pyrolysoituvia typpiyhdisteitä (pääosa pyrolysoitui alle 500 °C:n lämpötilassa), ja osa vaikeasti pyrolysoituvia typpiyhdisteitä. Tämä tekee hankalaksi ennustaa turpeen typen muuntumista NO:ksi poltossa.

Jos turpeen typpiyhdisteet pyrolysoituvat helposti, typen pitoisuus saattaa nousta tervassa korkeaksi (> 5 %). Tämä saattaa olla syynä sellaisten polttotapojen kohonneisiin NO-pitoisuuksiin, joissa tervaa syntyy helposti välituotteena.

Infrapunaspektroskopia antoi lisätietoa niistä pyrolyysijäännöksen kemiallisen rakenteen muutoksista, jotka pienentävät vedyn ja hapen suhteellisia määriä jäännöksessä hiiltolämpötilan noustessa. Tällaisia muutoksia ovat hiilihydraattien, vahojen ja hartsien hajoaminen.

Received 22. IX. 1987
Approved 25. XI. 1987