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THE USABILITY OF THERMOGRAVIMETRY IN FUEL RESEARCH

PART VI: ON THE KINETICS OF THE PYROLYSIS OF THE PEAT IN THE STOCKPILES WITH AND WITHOUT THE SELF-HEATING TENDENCY.

TERMOGRAVIMETRIAN KÄYTTÖMAHDOLLISUUDET POLTTOAINETUTKIMUKSESSA
OSA VI: KUUMAN JA KYLMÄN AUMAN TURPEEN PYROLYYSIN KINETIIKASTA

The prediction of the self-heating tendency of peat at different peat bogs and at different places of the production sites is of important help when the peat production is planned and executed. If it would be possible to predict the self-heating tendency already from the field samples, a lot of expenses could be saved during the production and the peat storages were under control.

We have investigated peat samples taken from two stockpiles at Läyniönsuo production sited located in Hankasalmi, Middle-Finland. The other stockpile, abbreviated A1, was so-called hot stockpile while the other, appreviated B1 was cold stockpile. The samples were taken from the top and from the sides of the stockpiles from the depth of 0.5 and 1.0 m as calculated from the surface points. The methods of investigation were thermogravimetric analysis and infrared spectroscopy. We have previously noted that if an exact area from the thermogram around the T_s-temperature is chosen, the combustion and pyrolysis of peat can be handled with sufficient accruacy according to the first order kinetics.

In this way the kinetic quantities of the reactions of different fuels and peat species can be made mutually comparable (Tummavuori et al. 1978, parts I and II).

The activitation energies have been calculated with two different methods (Broido 1969, Horowitz 1963).

$$\ln\ln (1/y) = -\ \frac{E^*}{RT} + \text{const.} \tag{1}$$

$$\ln\ln (1/y) = \frac{E^*\Theta}{RT_s^2} + \text{const.} \tag{2}$$

The pre-exponential factor A has been evaluated from the equation (Horowitz, 1963):

$$A = \frac{q \times E^*}{RT_s^* \times e^{-E^*/RT_s}} \tag{3}$$

The rate constants are computed using the Arrhenius equation

$$k = Ae^{-E^*/RT} \tag{4}$$

The notations of the equation are explained previously (Tummavuori et al. 1978, part II). The experimental part of thermogravimetry was carried out as described previously (Tummavuori et al. 1978, part II). The infrared spectrometer was Perkin-Elmer model. The powdered peat samples were diluted with potassium bromide. (E. Merck A. G. Uvasol) to 1 weight percent.

Tables 1 and 2 present the calculated thermodynamic quantities. In nitrogen

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Table 1. The initial (T_o), inflection point (T_s) and end point (T_f) temepratures (K) and the values of the kinetic quantities of the reaction of the samples under investigation (* kJ·mol^{-1}) in nitrogen gas. A is the hot stockpile and B is the could stockpile.

Taulukko 1. Pyrolyysin alkupisteen (T_{o}), reaktion käännepisteen (T_s) ja loppupisteen lämpötilat (K) ja reaktion kineettiset suureet typpiatmosfäärissä. Näyte A on kuumenevan auman ja B on kylmän auman näyte.

Sample	Volatile matter %	T_0	T_s	T_f	E* Eq. (1)	Log A Eq. (3)	R^2	E* Eq. (2)	Log A Eq. (3)	r^2
A from the top surface	69.7	434	625	747	41	0.763	0.997	39	0.620	0.990
from the top 0,5 m deep	66.1	429	629	747	38	0.502	0.996	38	0.473	0.997
from the top 1,0 m deep	68.7	424	633	748	39	0.562	0.996	39	0.520	0.996
from the side surface	67.3	434	633	752	41	0.715	0.997	40	0.614	0.994
from the side 0,5 m deep	65.4	429	637	749	39	0.507	0.995	39	0.502	0.997
from the side 1,0 m deep	65.6	432	638	779	40	0.621	0.995	40	0.580	0.997
B from the top surface	73.7	434	571	616	72	4.31	0.995	73	4.36	0.997
from the top 0,5 m deep	74.5	430	573	617	74	4.39	0.990	74	4.47	0.995
from the top 1,0 m deep	74.0	459	575	621	74	4.46	0.991	75	4.47	0.992
from the side surface	73.8	433	567	613	72	4.36	0.990	73	4.41	0.994
from the side 0,5 m deep	73.6	439	574	621	72	4.24	0.994	72	4.27	0.996
from the side 1,0 m deep	73.3	436	560	606	70	4.18	0.993	70	4.22	0.996

Table 2. The initial (T_o), enflection point (T_s) and end point (T_f) temperatures (K) and the values of the kinetic qunaties of the reaction of the samples under investigation (E* kJ mol^{-1}) in mixed gas. (80 % nitrogen and 20 %) A is the hot stockpile and B is the cold stockpile.

Taulukko 2. Pyrolyysin alkupisteen (T_o)$_l$ reaktion käännepisteen (T_s) ja loppupisteen lämpötilat ja reaktion kineettiset suureet seoskaasussa. (20 % O_2 ja 80 % N_2). Näyte A on kuumenevan auman ja B on kylmän auman näyte.

Sample	T_0	T_s	T_f	E* Eq(1)	log A Eq(3)	r^2	E* Eq(2)	log A Eq(3)	r^2	Ash %
A from the top surface	430	542	554	158	13.31	0.936	160	13.53	0.939	4.7
from the top 0.5 m deep	426	545	559	163	13.66	0.956	163	13.66	0.956	6.3
from the top 1.0 m deep	431	552	563	181	15.20	0.956	180	15.17	0.958	5.7
from the side surface	441	536	554	161	13.73	0.965	158	13.51	0.964	5.5
from the side 0.5 m deep	419	541	552	166	14.16	0.949	168	14.32	0.0952	5.4
from the side 1.0 m deep	429	540	553	156	13.19	0.985	157	13.25	0.987	7.6
B from the top surface	437	568	591	125	9.45	0.991	126	9.51	0.994	2.3
from the top 0.5 m deep	439	551	569	128	10.07	0.981	129	10.22	0.985	2.2
from the top 1.0 m deep	429	544	571	115	8.96	0.994	116	9.03	0.996	0.9
from the side surface	427	553	572	127	9.97	0.970	129	10.18	0.975	2.4
from the side 0.5 m deep	435	549	573	97	7.08	0.973	97	7.12	0.976	2.5
from the side 1.0 m deep	425	540	565	104	7.94	0.978	106	8.12	0.984	2.4

atmosphere the stockpile B1 (cold) is significantly more reactive than the stockpile A1 (hot). The T_o temperatures are equal at each stockpiles but both T_s- and T_f-temperatures are lower at stockpile A1 than at stockpile B1. The activation energy at stockpile B1 is about 40 % larger, the pre-exponential factor about 6.0·10' times and the amount of volatile matter about 6 % larger than in the stockpile A1. In mixed gas atmosphere there is no difference between the stockpiles with respect of T_o, T_s and T_f temperatures. In mixed gas, however, the stockpile A1 is more reactive than B1. The activation energy in the stockpile A1 is about 26 % and the pre-exponential factor about 3.0·10^4 times larger than in the stockpile B1. The ash content in the stockpile A1 is about 4 % larger than B1 which is due to the self-heating occurred.

Figure 1 depicts the -1n k as a function 1/T. The lines represent the samples taken from the top of the stockpile. The figure well illustrates the difference in reactivity between the stockpiles. In the stockpile A1 the differences in reaction reates in nitrogen and in mixes gas are markedly large as compared with the stockpile B1.

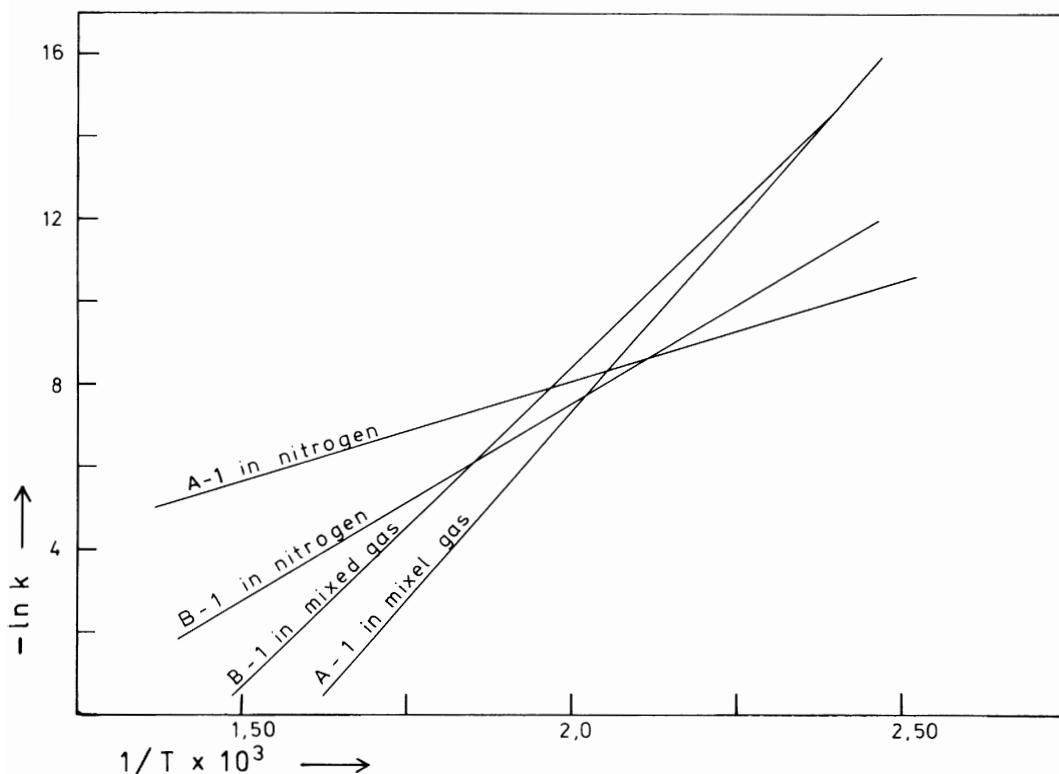Figure 2 shows the IR spectra of the

Fig. 1. The -lnk versus l/T of the top surface samples of the stockpiles A and B.

Kuva 1. Reaktion -lnk = f(l/T) kuuman auman (A) ja kylmän (B) auman huipun pintanäytteistä sekä typpi että seoskaasussa.

samples taken from the top surface and from the depth of 1 meter on the top of the stockpiles. If we compare the spectra of the same stockpile, there is practically no difference between the surface sample and the sample from 1 meter deep. Comparing the surface sample with the sample from the depth of 1 meter shows that in the stockpile A1 these samples exhibit a distinguishable resolution with the double peaks at wavenumbers 1627 cm^{-1} and 1712 cm^{-1} and diminishing of the absorption at 1070 cm^{-1}. The corresponding changes in the spectra of the similar samples from the stockpile B1 are also obsurable but weakly. The comparison of corresponding samples from different stockpiles shows clear mutual differences. The wavenumbers 1627 cm^{-1} and 1712 cm^{-1} of the samples from the stockpile A1 are changed to 1631 cm^{-1} and 1729 cm^{-1} in the corresponding samples from the stockpile B1.

The absorption of the samples from B1 at this region are distient and equal by the intensity but clearly weakly than the corresponding absorption of the samples from A1. Further, the absorption at 1729 cm^{-1} is remarkably weaker than the absorption at 1631 cm^{-1}. Also, the absorption of the samples from B1 at 1070 cm^{-1} is much stronger than the corresponding absorption of the samples from A1 at this region.

These relationships in the absorptions show that the amount of hydrolyzable matter in the "hot" stockpile diminishes while the carbonization proceeds. Perhaps the most widely used thermoanalytical method in the self-heating investigations has undoubtely been the DTA. These investigations deal with the effect of various organica materials on the self-heating process. The investigations stress the effect of the presence of easily hydrolyzable
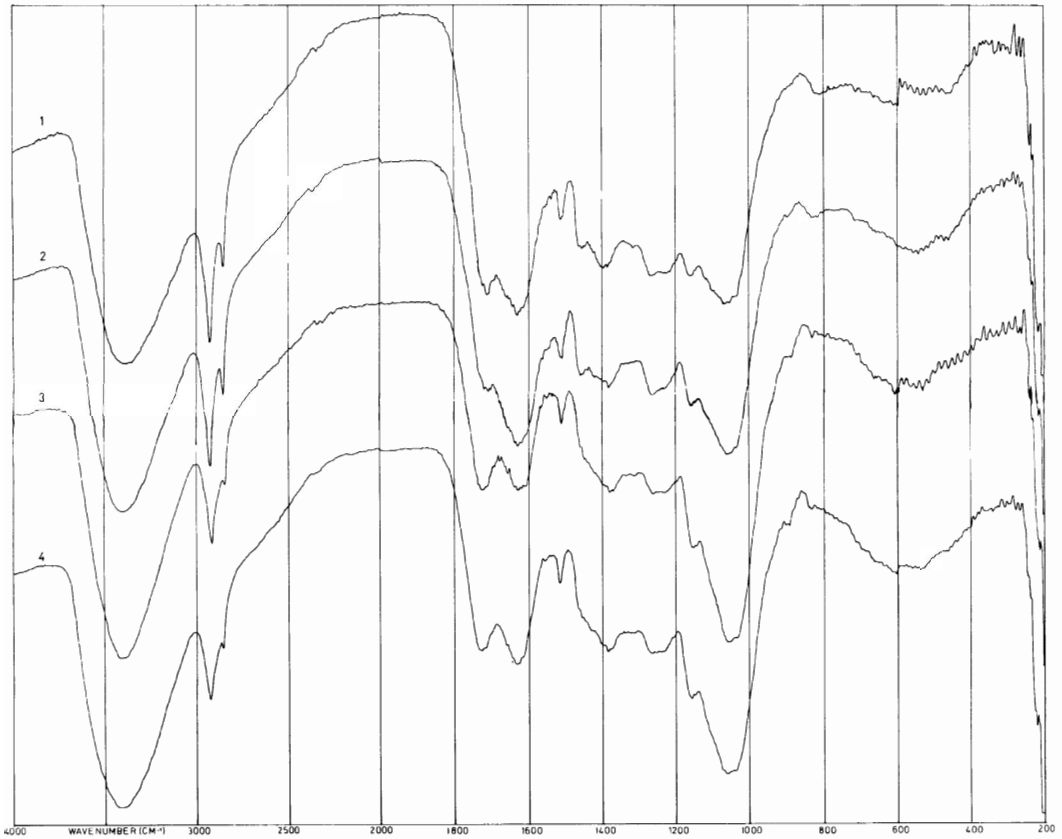
Fig. 2. The IR spectra of the samples taken from the top surface and from the depth of 1 meter (on the top) of the stockpiles A (1 and 2) and B (3 and 4).

Kuva 2. Aumojen huipulta ja yhden metrin syvyydestä otettujen näytteiden infrapunaspektrit. (1 ja 2 auma A ja 3 ja 4 auma B)

material on the self-heating tendency Furthermore, the ocalic acid gielding during the self-heating reactions plays an important role in the total process. (Faljusin 1974, 1976), Pankrator 1977).

Our results devised from the IR spectra also confirm the impression of the important role of the hydrolyzable material in the selfheating process.

In inspection of the results shows that both the kinetic quantities and IR spectra distinquish the differences between the hot and cold stockpile. At at most concrete way this can be seen in the rate constant. The difference in the rate constants of the stockpile A1 are noticeably larger than in the corresponding reactions in different atmospheres of the stockpile B1. Since these preliminary studies show that the kinetic quantities together with IR data can

be used to determine the rate of the self-heating as well as the status of the process, the classification of the stockpiles according to their self-heating properties might be possible to establish.

Further, in the preliminary experiments we have found correlation between the field samples and the samples taken from the stockpile collected from that field. If this correlation really exits and can be reliably established, then the prediction of the self-heating tendency and rate can be made before the stockpile is collected. The advantage of the methods used in the analysis is their simpliness, they do not reguire the tedious chemical analyses from peat. The results presented reguire, of course, a plenty of additional experiments before they reliably can be adopted to the practice in the peat production.

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YHTEENVETO:

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Olemme tutkineet termogravimetristen suureiden merkitystä määritettäessä kuuman auman (A) ja kylmän auman (B) välisiä eroja.

Totesimme, että reaktiokineettiset suureet poikkeavat huomattavasti toisistaan, mikä voidaan varsin selvästi todeta kuvasta 1., josta ilmenee kuuman auman reaktioiden nopeuksien huomattava ero eri kaasuatmosfääreissä tapahtuvissa reaktioissa.

Infrapunaspektroskopia paljastaa myös sen tunnetun asian, että hydrolysoituvien aineiden määrä vaikuttaa huomattavasti aumojen itsepalamiseen.

Näitä alustavia tutkimuksia on tarkoitus jatkaa ensi tuotantokautena siten, että pystyisimme suoraan kenttänäytteestä ennustamaan auman itsepalamisominaisuuksia. Myöskin tältä alueelta tehdyt alustavat kokeet ovat olleet rohkaisevia.