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Pyrolysis of peat: Product yield and characterization

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Abstract−Pyrolysis of peat obtained from Yeniçağa, Bolu, Turkey was conducted in a fixed-bed tube furnace under various conditions, and variations in the structure of the char, tar and gas products were examined. The chars produced were studied by proximate and ultimate analyses. The maximum tar yield of 20.41% was obtained at a heating rate of 20 °C/min, a temperature of 450 °C, a sweeping gas flow rate of 100 ml/min and a 0.5-2.0 mm size range. The chemical composition of the tar was examined by elemental analysis, FTIR spectroscopy, ^{1}H-NMR spectroscopy and column chromatography. The chemical composition of the tar with dense aliphatic structure was established to be $CH_{1.22}O_{0.25}N_{0.02}$. The composition of the gases obtained at a heating rate of 20 °C/min for the 0.5-2.0 mm size range was examined by gas chromatography.

Key words: Peat, Pyrolysis, Pyrolysis Temperature, Heating Rate, Sweeping Gas, Particle Size, Tar, Char, Gas

INTRODUCTION

One of the thermochemical technologies employed to convert biomass into solid, liquid and gas products for use as an energy source is pyrolysis [1-4]. When biomass is pyrolyzed the volatile products consist of a condensable portion comprising tars and an aqueous liquid, and a noncondensable portion comprising the pyrolysis gases [5].

Peat is formed largely from inhibited decomposition of various plant materials in the waterlogged environment of marshes, bogs and swamps [6,7]. Peat occurring in Yeniçağa is used as manure to help flowers, vegetables and fungi to grow [8]. Char, a solid product obtained from pyrolysis of peat, is used as a chemical reducing agent, an adsorbent, and a catalyst support. It is also used, due to its electrical properties, as anode in electrochemical applications as well as a bonding agent in rubber production and in producing pigment and lubricants. The gas product can be used as a fuel. The liquid product, tar, can be used as a liquid fuel, a lubricant, a solvent and pitch [5].

Many studies have been carried out on pyrolysis of peat and the composition of the gaseous products [9-14] and variations in the structure of the liquid products [13-22] were examined.

In this study, peat obtained from the Yeniçağa township of Bolu, Turkey was pyrolyzed and the effect of pyrolysis temperature, heating rate, sweeping gas flow rate and particle size on the pyrolysis was investigated as well as the structure of the solid products. Moreover, an investigation was carried out on the structure of the gaseous products obtained at the heating rate of 20 °C/min and on the tar produced with the highest recovery.

EXPERIMENTAL

1. Material

The sample was obtained from Yeniçağa, Bolu, Turkey. The samples were air-dried, ground and divided into four different groups (below 0.5 mm, 0.5-1.0 mm, 1.0-2.0 mm, above 2.0 mm). Table 1 gives the results of the proximate and ultimate analyses conducted in accordance with ASTM.

2. Pyrolysis Method

The pyrolysis experiments were carried out in a tubular fixed-bed tube furnace. The diagram of the process is given in Fig. 1. The peat used in the pyrolysis experiments conducted for the purpose of observing the effect of heating rate was of size 0.5-2.0 mm. Approximately 50 g of the sample was introduced into the furnace and nitrogen was fed in to the system at a flow rate of 200 ml/min for 30 minutes. The pyrolysis tests were carried out at varying final temperatures of 350 °C, 450 °C, 550 °C and 650 °C at heating rates of 5 °C/min and 20 °C/min. The sample was kept at these temperatures for 1 hour. The liquid and aqueous phases collected in the traps were separated with dichloromethane by means of a separating funnel. The liquid product was removed from the dichloromethane in a rotating evaporator. The yields of liquid and solid products were calculated on the basis of weight and the gas yield by difference. The results were expressed on a dry free basis.

The tests conducted to establish the effect of the sweeping gas flow rate and the peat particle size on pyrolysis were conducted at a heating rate of 20 °C/min and temperature of 450 °C, which were the pyrolysis conditions that gave the highest tar yields. The sweeping gas flow rate varied between 50 ml/min, 100 ml/min, 200 ml/min and 400 ml/min and the particle sizes were in the range of below 0.5 mm, 0.5-1.0 mm, 1.0-2.0 mm, above 2.0 mm.

3. Characterization

The results of the proximate and ultimate analyses of the chars obtained from the pyrolysis tests, during which pyrolysis temperature, heating rate, sweeping gas flow rate and particle size varied, are shown in Tables 2 and 3.

The composition of the gas obtained from the pyrolysis tests performed at a heating rate of 20 °C/min was determined by using HP 5890A Series II Gas Chromatography. The results are given in Table 4.

The chemical composition of the tar was investigated which was

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Table 1. Proximate and ultimate analyses of peat (0.5-2.0 mm size range)

Ash[a]	Volatile matter[a]	Fixed carbon[a]	C[b]	H[b]	N[b]	S[b]	O[b,c]	H/C (molar)	O/C (molar)	Mj/kg[b]
6.51	69.15	24.34	56.38	5.98	1.43	0.52	35.69	1.27	0.47	22.39

[a]df %
[b]daf %
[c]O=100−(C+H+N+S)

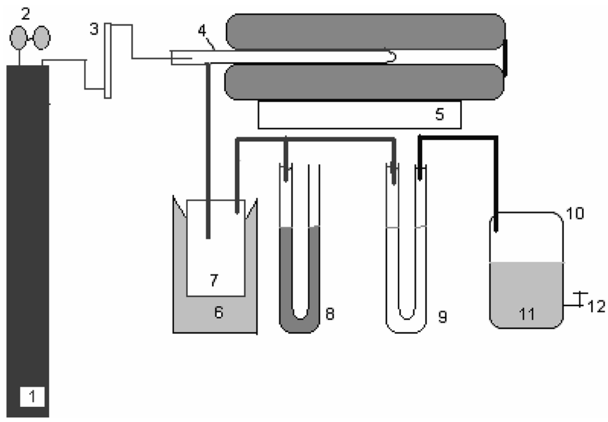

Fig. 1. Schematic diagram of experimental apparatus.

1. Nitrogen tube
2. Regulator
3. Flowmeter
4. Quartz tube
5. Tube furnace
6. Water iced bath
7. Tar collector
8. Manometer
9. Filter for removing water
10. Gas collector
11. Water
12. Valve

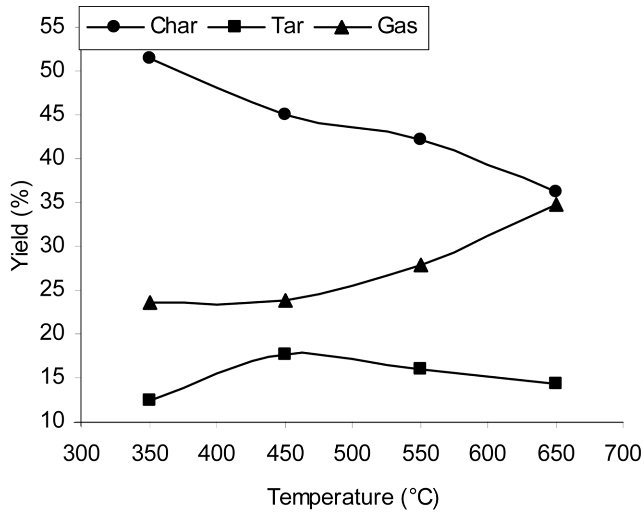

Fig. 2. The effect of the heating rate of 5 °C/min on pyrolysis products.

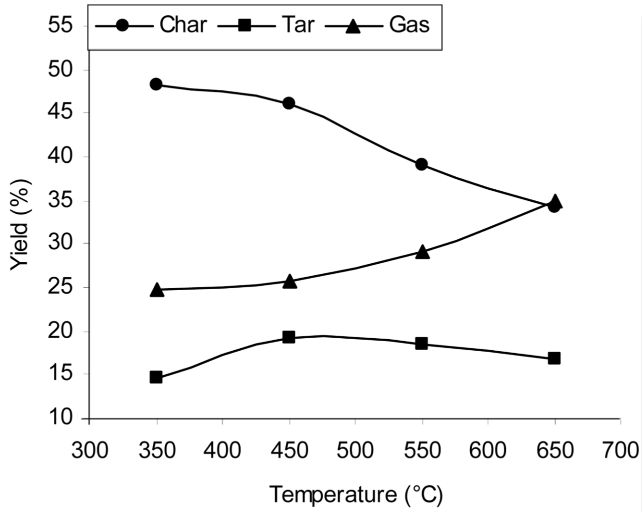

Fig. 3. The effect of the heating rate 20 °C/min on pyrolysis products.

obtained at a heating rate of 20 °C/min, a temperature of 450 °C, a sweeping gas flow rate 100 ml/min and a 0.5-2.0 mm size range. The ^{1}H-NMR spectrum of the tar was obtained by means of BRUKER ARX 250 in a solution of $CDCl_3$ or CCl_4 taking $SiMe_4$ as a reference. The FTIR spectrum was obtained with a Jasco FTIR/300E instrument. The tar was kept in n-pentane and separated into soluble and insoluble fractions. The n-pentane soluble material was further separated into subfractions by using column chromatography [23-25]. The silica gel (70-230 mesh) employed in column chromatography was kept at 170 °C for 2 hours. The column was separated into aliphatic, aromatic and polar aromatic subfractions, using n-pentane, toluene and methanol, respectively. Each fraction was dried and weighed. The n-pentane subfraction was analyzed by using HP 5890A Series II Gas Chromatography.

RESULTS AND DISCUSSION

1. Product Yields

Fig. 2 shows variation in relation pyrolysis temperature of the product yields obtained from pyrolysis performed at heating rate of 5 °C/min. The char yield decreased from 51.44% to 36.19% with the increasing pyrolysis temperature. The tar yield, which was 12.33% at a pyrolysis temperature of 350 °C, reached its maximum value of 17.72% as the temperature was increased to 450 °C. Above this temperature, it exhibited a downward trend. As for the gas yield, it increased from 23.66% to 34.67% as the pyrolysis temperature was increased from 350 °C to 650 °C.

Fig. 3 gives variation in the yields of products obtained from pyrolysis at a heating rate of 20 °C/min at temperatures varying from 350 °C to 650 °C. With the increasing pyrolysis temperature, there was some decrease in the char yield, whereas the tar and gas yields increased. Apart from the results of the experiments carried out at the heating rate of 5 °C/min, char yields were obtained lower at the heating rate 20 °C/min. The heating rate affects the speed at which the volatiles leave the peat [26]. The peat structure undergoes faster disintegration at high heating rates, which means that the char yield is lower [27,28]. Low heating rates result in higher char yields [29]. As the pyrolysis temperature increased, the char yield, which was 48.25% at 350 °C, dropped to 34.15% at 650 °C. The tar yield is maximal at 450 °C with 19.29%. Above this temperature, it displayed a downward trend as was the case at other heating rates. The gas yield reached its maximum value of 34.97% at pyrolysis temperature of 650 °C. As opposed to the heating rate of 5 °C/min, during the pyrolysis tests conducted at a heating rate of 20 °C/min, the char yield increased by about 3%, whereas there was an increase of 2.5% in the tar yield.

Decomposition intensified in the 450-550 °C temperature range, which yielded more tar compared to other temperatures. Lignin and bitumen occurring in the peat structure decompose and as a result enormous amounts of tar and gas are released [6]. The maximum gas yield was achieved at 650 °C at which the tar yield started to decrease.

In the experiments conducted at two different heating rates, the highest tar yield was obtained at a heating rate of 20 °C/min and at pyrolysis temperature of 450 °C. Therefore, the tests which aimed at investigating the effect of the sweeping gas flow rate and the peat size on pyrolysis were carried out at temperature of 450 °C at a heating rate of 20 °C/min.

Fig. 4 gives variations in relation to the sweeping gas flow rate in the pyrolysis product yields obtained. Increasing the sweeping gas flow rate resulted in yielding less char and gas compared to the experiments conducted at two different heating rates. The char yield decreased with increasing sweeping gas flow rate. As to the gas yield, a maximum yield of 20.41% was achieved at a flow rate of 100 ml/min. The sweeping gas affects the removal of the steam phase formed during the pyrolysis [30,31]. While the gas yield displayed a downward trend at a heating rate of up to 400 ml/min, it increased at this rate.

Fig. 5 gives the effect of the peat size on pyrolysis products. As the size increased, so did the char and gas yield. However, there was decrease in the tar yield. The decrease in the tar yield regards the mass- and heat-transfer restrictions of the different sizes [1]. The

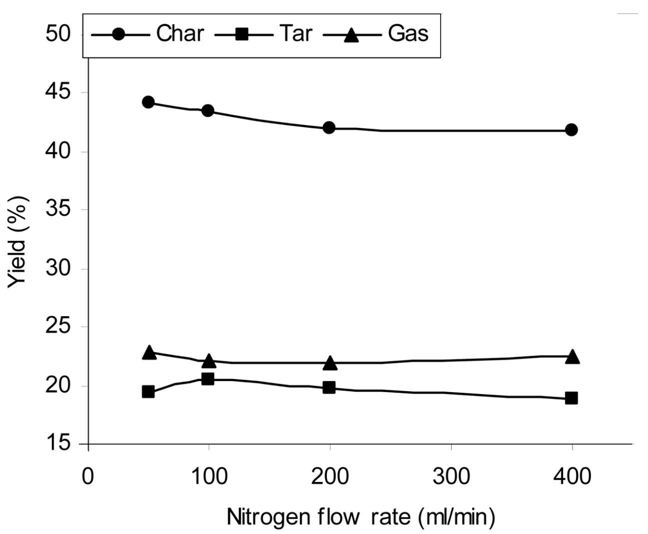

Fig. 4. The effect of pyrolysis products on the nitrogen flow rate.

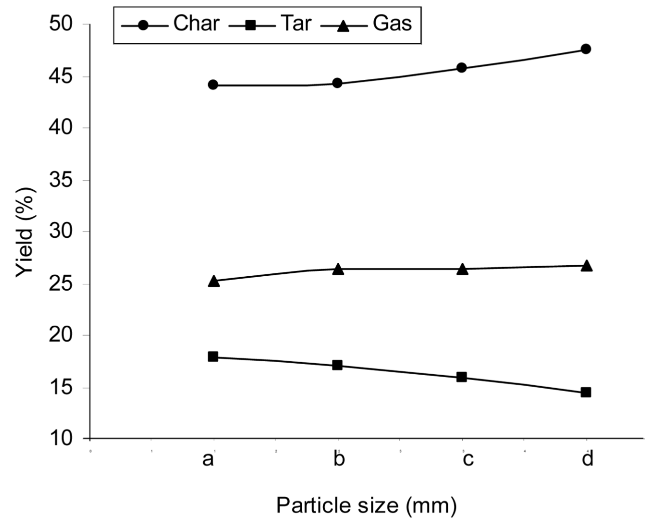

Fig. 5. The effect of the peat size on pyrolysis products: a. below 0.5 mm, b. 0.5-1.0 mm, c. 1.0-2.0 mm, d. above 2.0 mm.

Table 2. The proximate and ultimate analyses of the chars obtained from pyrolysis conducted at varying heating rates (df, %)

	5 °C/min				20 °C/min			
	350 °C	450 °C	550 °C	650 °C	350 °C	450 °C	550 °C	650 °C
Ash[a]	10.88	11.74	12.57	13.34	10.35	11.85	13.54	14.33
Volatile matter[a]	33.67	27.05	18.49	15.21	35.26	28.14	19.16	17.08
Fixed carbon[a]	55.45	61.21	68.94	71.45	54.39	60.01	67.30	68.59
C[b]	76.30	80.19	85.30	91.04	77.80	80.93	84.50	92.45
H[b]	3.85	3.18	2.99	2.65	3.71	3.20	2.87	2.51
N[b]	1.23	1.21	1.15	1.15	1.22	1.21	1.18	1.14
S[b]	0.31	0.35	0.37	0.36	0.32	0.33	0.37	0.37
O[b,c]	18.31	15.07	10.19	4.80	16.95	14.33	11.08	3.53
H/C (molar)	0.60	0.48	0.42	0.35	0.57	0.47	0.41	0.33
O/C (molar)	0.18	0.14	0.09	0.04	0.16	0.13	0.10	0.03

[a]df %
[b]daf %
[c]O=100−(C+H+N+S)

Table 3. The results of proximate and ultimate analyses of the chars obtained from pyrolysis of peat with varying sizes and at varying sweeping gas flow rates: Pyrolysis temperature: 450 °C, heating rate: 20 °C/min (df, %)

	N_2 flow rate (ml/min)				Size (mm)			
	50	100	200	400	Below 0.5	0.5-1.0	1.0-2.0	Above 2.0
Ash[a]	11.28	11.47	11.56	11.58	9.43	8.62	7.99	6.75
Volatile matter[a]	26.11	26.04	26.86	26.75	35.96	35.92	35.94	33.88
Fixed carbon[a]	62.61	62.49	61.58	61.67	54.61	55.46	56.07	59.37
C[b]	81.03	81.51	80.91	81.11	78.12	79.03	77.98	80.42
H[b]	3.11	3.13	2.99	3.03	3.10	3.11	3.11	3.13
N[b]	1.19	1.20	1.20	1.21	1.20	1.20	1.21	1.20
S[b]	0.33	0.32	0.31	0.33	0.35	0.33	0.34	0.31
O[b,c]	14.34	13.84	14.59	14.32	17.23	16.33	17.36	14.94
H/C (molar)	0.46	0.46	0.44	0.45	0.48	0.47	0.48	0.47
O/C (molar)	0.13	0.12	0.13	0.13	0.16	0.15	0.16	0.14

[a]df %
[b]daf %
[c]O=100−(C+H+N+S)

larger the size, the more difficult the transfer of heat and mass. That is to say, release of volatiles get slower.

It was established that the tar yield obtained at pyrolysis temperature of 450 °C at heating rate of 20 °C/min was 19.29%, the char yield 46.04% and the gas yield 25.72%. According to the results of the experiments conducted for different size groups under the same pyrolysis conditions, the tar yield decreased by 1.5% to 4.5%. For the greatest size group, the char yield increased by 1.5%. While the gas yield obtained from the pyrolysis for the smallest size decreased by 0.5%, the pyrolysis for other sizes yielded more gas.

2. Characterization of the Products

2-1. Char

The results regarding the chars obtained from the pyrolysis tests, which involved varying pyrolysis temperature, heating rate, sweeping gas flow rate and peat size, are given in Table 2 and 3. Apart from, the liquid and gas products obtained through the pyrolysis of peat, char is also an important product that can be utilized economically [6]. Chars are used as a domestic fuel, fuel for power generation, agricultural fertilizer, adsorbent, decolorizing agent and catalyst support. Char is rich in carbon, light and highly porous [5]. At both heating rates, as the pyrolysis temperature increases, so does the ash value of chars as opposed to a decrease in the volatile matter.

The chars obtained from pyrolysis at two different heating rates at the same temperature have similar amounts of ash and volatile matter (Table 2). The volatile matter content of the chars obtained at the heating rate of 5 °C/min decrease from 33.67% to 15.21% as the pyrolysis temperature increases. The volatile matter of the chars obtained at the heating rate of 20 °C/min decreases from 35.26% to 17.08% with the increasing pyrolysis temperature. Their carbon content increases from 76.30% to 91.04% at the heating rate of 5 °C/min and from 77.80% to 92.45% at 20 °C/min with the increasing pyrolysis temperature. The sweeping gas flow rate has no effect on the results of proximate and ultimate analyses of the chars. The particle size does not have a considerable effect on the proximate and ultimate analyses. The ash content of the char decreases only as the particle size increases (Table 3).

2-2. Gas

Table 4. Composition of the gas (vol%)

	350 °C	450 °C	550 °C	650 °C
H_2	5.11	16.56	21.17	30.03
CO	15.70	20.03	18.12	13.23
CO_2	30.11	40.31	29.93	13.22
CH_4	8.91	14.65	19.04	11.71
C_mH_n	2.30	5.50	3.87	2.47
N_2	2.23	2.95	3.38	3.92

Table 5. Analyses results of the tar

C[a]	68.61
H[a]	6.98
N[a]	1.86
O[a,b]	22.55
H/C (molar)	1.22
O/C (molar)	0.25
Density, 15 °C (kg/m^3)	1,040
Water content	-
Viscosity, 50 °C (cSt)	42
Mj/kg	37.31

[a]%
[b]O=100−(C+H+N+S)

The composition of the gas product from pyrolysis of the peat within the size range of 0.5-2.0 mm is given in Table 4. The main constituents of the gas are carbon oxides, hydrogen and hydrocarbons [14]. Non-condensable gases obtained from the pyrolysis of peat can be used as a fuel [5].

The yield of CO_2 and CO decreases with the increasing pyrolysis temperature. CH_4 increases at up to 550 °C, whereas it decreases at 650 °C. As for C_mH_n, it increases at 350 °C to 450 °C and above this temperature, it tends to decrease.

2-3. Tar

Peat tar is a complex liquid, useful as a fuel and as a source of many organic compounds. The tar is a dark-brown to almost black, strong-smelling product which at room temperature is a semi-solid or a viscous liquid [32].

The chemical composition of the tar was examined by ultimate analysis, FTIR spectroscopy, ^{1}H-NMR spectroscopy and column chromatography. The analytical results of the tar are given in Table 5. According to the results of the ultimate analysis, the tar was established to be composed of $CH_{1.22}O_{0.25}N_{0.02}$.

The FTIR spectrum of the tar is shown in Fig. 6. The O-H stretching vibrations between 3,300 cm^{-1} and 3,400 cm^{-1} are indicative of alcohols and phenols. The peak at 3,050 cm^{-1} is stretching vibration in the aromatic ring. The bands at 2,923 cm^{-1} and 2,957 cm^{-1} indicate an aliphatic structure. The C=O stretching vibrations between 1,715 cm^{-1} and 1,640 cm^{-1} indicating the presence of carbonyl groups denote ketones, phenols, carboxylic acids or aldehydes [1,25,33]. Coexistence of O-H and C=O stretching vibrations is indicative of carboxylic acids and esters which are their derivatives [5]. The bands between 1,378 cm^{-1} and 1,465 cm^{-1} indicate the existence of alkanes. The band 1,265 cm^{-1} is indicative of the stretching vibration of ethers. The bands of 700 cm^{-1} and 900 cm^{-1} indicate single and substituted aromatic hydrogens and the existence of an aromatic ring and C=O stretching vibration denote aromatic esters [5].

Fig. 7 gives the 1H-NMR spectrum of tar. The aliphatic resonances range from 0.5 to 3.0 ppm, olefinic or phenolic resonances from 4.5 to 6.0 ppm and aromatic ones from 6.0-9.0 ppm. The data obtained from the interpretation of this spectrum are shown in Table 6. The aliphatic structure in the tar was established to be 59.73%.

The tar was fractionated into n-pentane soluble and n-pentane insoluble. n-pentane soluble was further separated by column chromatography into subfractions n-pentane, toluene and methanol. The yields of the fractions termed aliphatic, aromatic and polar aromatic were established to be 47.75%, 23.80% and 28.45%, respectively. According to the results of the column chromatography, tar contains aliphatic structure, aromatic and polar aromatic structures as well.

The GC analytical graph of the aliphatic fraction is given in Fig. 8. It was determined that the carbon distribution varied in the C_{10}-C_{27} range and it occurred abundantly in the C_{15}-C_{18} range.

CONCLUSIONS

The structure of chars was clarified by proximate and ultimate analysis and the composition of the gas by GC.

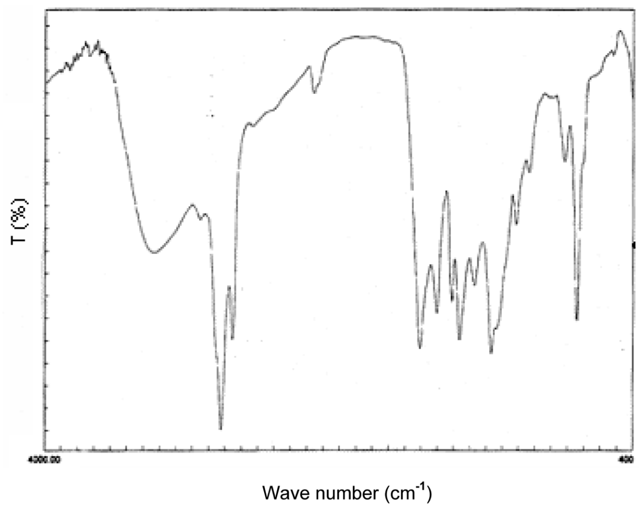

Fig. 6. FTIR spectrum of the tar.

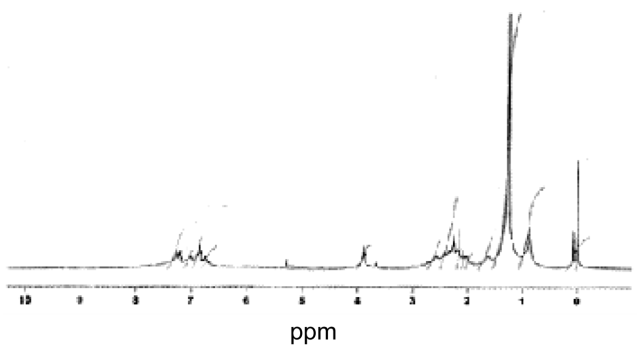

Fig. 7. ^{1}H-NMR spectrum of the tar.

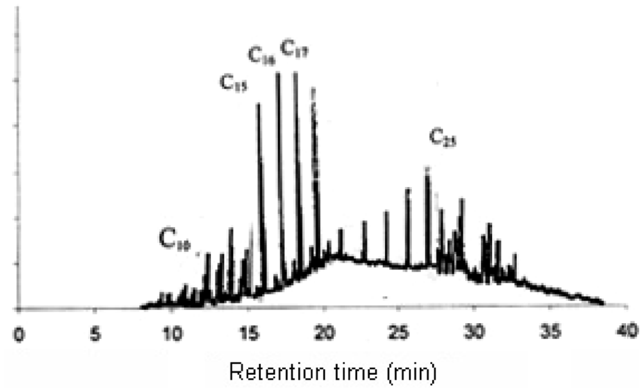

Fig. 8. GC graph of the tar.

Table 6. Definition of ^{1}H-NMR spectrum of the tar

Proton type	Chemical shift (ppm)	%
Aromatic protons	6.0-9.0	20.79
Olefinic protons or phenolic protons	4.5-6.0	2.20
CH_2 protons adjacent to two aromatic rings	3.0-4.5	4.98
CH_3, CH_2 and CH protons adjacent to an aromatic ring	2.0-3.0	23.72
α CH_3 and CH_2 protons adjacent to aromatic ring	1.5-2.0	5.56
β CH_3 and CH_2 protons adjacent to aromatic ring	1.0-1.5	31.33
CH_3, CH_2 protons adjacent to no aromatic ring and γ-CH_3 proton	0.5-1.0	11.42

It has been established that the chemical properties of the chars produced at two different heating rates and four different pyrolysis temperatures are similar. The flow rate of the sweeping gas has no definite effect on the chemical properties of the char. The chars obtained by means of the pyrolysis of peat of four varying sizes have lower ash contents than those obtained in other pyrolysis conditions.

With the increasing pyrolysis temperature, the amount of H_2, a constituent of the gas product, increases. In contrast, the other constituents exhibited no definite behavior.

The highest tar yield of 20.41% was achieved at a pyrolysis temperature of 450 °C, at a heating rate of 20 °C/min and at a sweeping gas flow rate of 100 ml/min in the 0.5-2.0 mm size range. The structure of the tar was investigated by ultimate analysis, column chromatography, FTIR spectroscopy and ^{1}H-NMR spectroscopy. It was established that the tar is composed mainly of $CH_{1.22}O_{0.25}N_{0.02}$ and consists mostly of an aliphatic structure of alkanes and alkenes.

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