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Infra-red Absorption Spectra of Products of Carbonization of Cellulose

by

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There are two theories concerning the origin of natural coal [1]. That of Bergius [2] suggests that cellulose is the primary substance in the coalification process; the other maintains that coal has been formed due to some action of temperature and pressure on lignin (Fischer and Schrader [3]). The latter view is not generally prevailing.

In one of our earlier papers [5] we noted that the infra-red spectrum of a relatively young brown coal showed a group of bands characteristic of cellulose, unlike the spectra of older coals. The work now presented is an attempt of following the process of artificial carbonization of cellulose by examining the absorption spectra of the products of carbonisation.

Experiments were made with cotton linters (98% α-cellulose) and wood cellulose (96% α-cellulose), so as to eliminate accidental errors and to make sure of a general character of the changes. Since the process of thermal decomposition was carried out in a slow flow of nitrogen under reduced or atmospheric pressure, the volatile products were removed and a clearer picture of carbonization could be obtained; also eventual pressure effect might be traced. The process run under higher pressure, i. e. in conditions more resembling those of natural coalification, will be the subject of further investigation.

Experimental

Three series of experiments were made: two with cotton linters (under 15 mm Hg and atmospheric pressure) and one with wood cellulose (under 15 mm Hg pressure). 4 g samples of the substance were placed in a glass tube of 26 mm in diameter, heated in an electric furnace to a definite temperature with ±2°C deviations. Nitrogen was slowly drawn through the tube in order to avoid combustion of the sample, and to remove the volatile products of decomposition. Inside the tube either atmospheric or

15 mm Hg pressure was maintained. The heating of the samples was continued at a constant temperature until no further decomposition could be detected, i. e. no more gaseous products were evolved and (in a special series of experiments) a constant weight of the samples was attained. Two hours were sufficient to obtain this stage. Each series of experiments involved heating the samples at different temperatures within the range of 205–575°C.

Thereafter, elementary analysis of each sample was performed. The results are given in Tables I and II. The losses in the weight of the samples are plotted against the temperature in Fig. 1, the van Krevelen diagram $\frac{H}{C}$ against $\frac{O}{C}$ is shown in Fig. 3.

The infra-red spectra of the carbonized samples were measured in a Hilger 800 double-beam recording spectrometer with sodium chloride optics. Nujol mulls (ratio 50:50) of the samples were used as thin films. The range of measurement was 4500–750 cm^{-1}. The spectra are given in Fig. 2; the curves are subsequently shifted up in the absorption scale to avoid overcrowding. The band frequencies are listed in Tables III and IV.

Discussion

There is a considerable increase of losses in the weight of both cotton linters and wood cellulose near 300°C (Fig. 1). The rise of the curve, slightly more pronounced for the experiments under reduced pressure, is very sharp in each case. The van Krevelen diagram (Fig. 3) shows that there is a large decrease of the atomic ratios $\frac{H}{C}$ and $\frac{O}{C}$ when passing through a narrow range of temperature about 300°C. The direction of the curve suggests that dehydration of the samples should occur. These facts point out that some essential changes in the structure of cellulose must take place after a certain critical temperature has been reached. A more detailed picture of the changes can be obtained from the infra-red spectra.

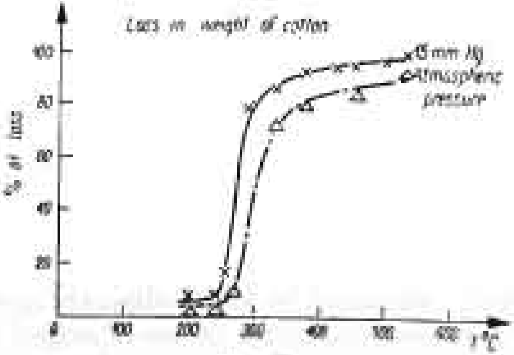

Fig. 1

Since the results of the infra-red analysis are nearly identical for all the series of experiments, the discussion continued below involves them as a whole.

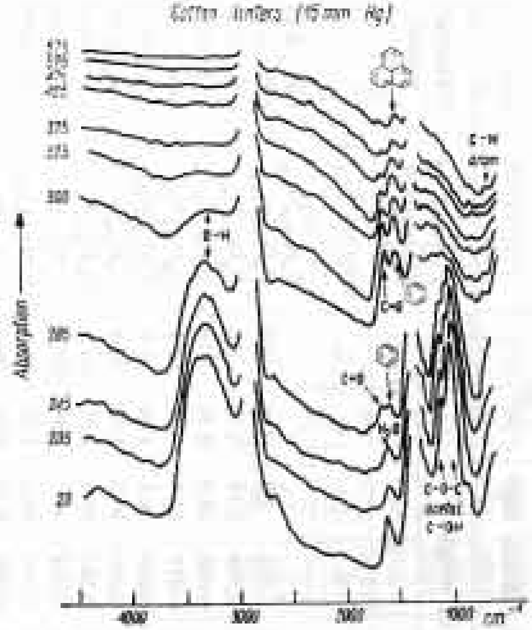
Cotton linters (15 mm Hg)
475
385
425
400
375
350
300
285
245
235
20
Absorption
C-H
C-H arom
C=O
C=O
C-O-C acetal C-OH
4000
3000
2000
1000
cm⁻¹

Fig. 2

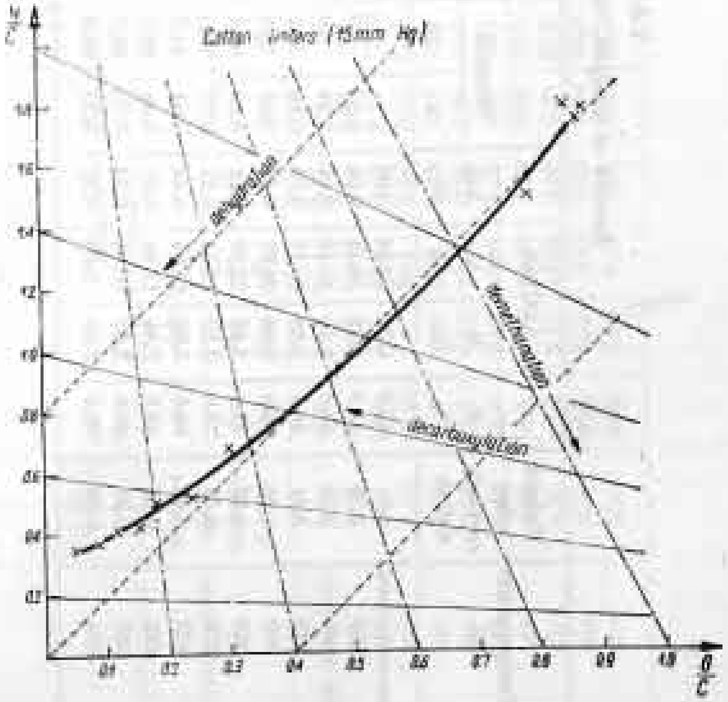
H/C
Cotton linters (15 mm Hg)
dehydration
decarboxylation
decarbonylation
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
O/C

Fig. 3

TABLE I

Results of analysis. Cotton linters (15 mm Hg)

No	Temperature °C	Weight after carbonisation	Analysis				Losses in weight								Formula of carbonized substance referred to C_6	Atomic ratios	
			C %	H %	O %	Ash %	General		C		H		O			$\frac{H}{C}$	$\frac{O}{C}$
							g	%	g	%	g	%	g	%			
1	non-carbonized	4.0	43.0	6.32	50.64	0.04	—	—	—	—	—	—	—	—	$C_6H_{10.63}O_{5.31}$	1.77	0.88
2	205	3.76	43.5	6.32	50.14	0.04	0.24	6.0	0.08	4.6	0.015	5.9	0.14	6.9	$C_6H_{10.4}O_{5.2}$	1.73	0.87
3	245	3.76	44.0	6.50	49.16	0.04	0.24	6.0	0.07	4.0	0.008	3.13	0.17	8.4	$C_6H_{10.7}O_{5.1}$	1.78	0.85
4	275	3.34	46.1	5.68	48.17	0.05	0.66	16.5	0.18	10.5	0.063	24.8	0.42	20.8	$C_6H_{8.9}O_{4.7}$	1.49	0.78
5	300	0.95	69.0	3.86	26.97	0.17	3.05	76.3	1.06	61.7	0.216	85.4	1.77	86.4	$C_6H_{4.08}O_{1.8}$	0.68	0.297
6	325	0.72	73.4	3.42	22.96	0.22	3.28	82.1	1.19	69.1	0.228	90.1	1.86	91.8	$C_6H_{3.36}O_{1.4}$	0.56	0.237
7	375	0.43	78.6	3.30	17.33	0.37	3.57	89.0	1.38	80.0	0.229	90.3	1.95	96.4	$C_6H_{3.00}O_{1.02}$	0.50	0.17
8	425	0.46	80.6	3.02	15.94	0.44	3.64	91.0	1.43	83.0	0.242	95.6	1.97	97.4	$C_6H_{2.52}O_{0.89}$	0.42	0.148
9	475	0.32	83.8	2.84	12.86	0.50	3.68	92.0	1.45	84.1	0.244	96.2	1.98	97.8	$C_6H_{2.46}O_{0.69}$	0.41	0.115
10	525	0.30	86.8	2.63	10.04	0.53	3.70	92.5	1.46	84.8	0.245	96.5	1.99	98.0	$C_6H_{2.22}O_{0.54}$	0.37	0.09
11	575	0.28	90.8	2.55	6.08	0.57	3.72	93.0	1.47	85.2	0.246	97.0	2.01	99.0	$C_6H_{2.04}O_{0.30}$	0.34	0.05

TABLE II

Results of analysis. Wood cellulose (15 mm Hg)

No	Temperature °C	Weight after carbonization	Analysis				Losses in weight								Formula of carbonized substance referred to C_6	Atomic ratios	
			C	H	O	Ash	General		C		H		O				
			%	%	%	%	g	%	g	%	g	%	g	%		$\frac{H}{C}$	$\frac{O}{C}$
1	non-carbonized	4.0	43.5	6.15	50.21	0.14	—	—	—	—	—	—	—	—	$C_6H_{10.2}O_{5.16}$	1.70	0.86
2	205	3.76	43.3	6.22	50.33	0.15	0.24	6.0	0.11	6.32	0.012	4.9	0.12	5.97	$C_6H_{10.3}O_{5.22}$	1.72	0.87
3	245	3.71	43.9	6.35	49.6	0.15	0.29	7.25	0.11	6.32	0.011	4.5	0.17	8.71	$C_6H_{10.4}O_{5.1}$	1.74	0.85
4	275	3.50	44.25	5.5	50.1	0.16	0.50	12.5	0.19	10.9	0.054	22.0	0.23	11.7	$C_6H_{8.95}O_{5.13}$	1.49	0.86
5	300	1.05	60.8	4.09	34.6	0.53	2.95	73.5	1.10	63.2	0.203	83.0	1.65	82.1	$C_6H_{4.86}O_{2.55}$	0.81	0.425
6	325	0.74	72.2	4.08	22.95	0.76	3.26	81.5	1.21	69.0	0.216	88.0	1.84	92.0	$C_6H_{4.09}O_{1.43}$	0.68	0.24
7	375	0.42	75.2	3.50	19.97	1.33	3.58	89.5	1.43	82.2	0.231	94.0	1.93	96.0	$C_6H_{3.36}O_{1.2}$	0.56	0.20
8	425	0.32	78.8	3.44	16.01	1.75	3.68	92.5	1.49	85.5	0.235	95.5	1.96	97.5	$C_6H_{3.18}O_{0.91}$	0.515	0.15
9	475	0.31	81.4	3.21	13.58	1.81	3.69	92.5	1.49	85.5	0.236	96.0	1.97	98.0	$C_6H_{2.84}O_{0.75}$	0.475	0.125
10	525	0.32	86.6	3.12	8.53	1.75	3.68	92.5	1.46	83.8	0.236	96.0	1.988	99.0	$C_6H_{2.58}O_{0.44}$	0.43	0.07
11	575	0.31	89.0	2.86	6.33	1.81	3.69	92.5	1.46	83.8	0.237	96.0	1.995	99.3	$C_6H_{2.33}O_{0.37}$	0.385	0.06

TA

Band

Cotton linters under

1	non-carbonized	c. 3300 (vs,b),		1640 (m),		1270 (sh),
2	205° C	c. 3300 (vs,b),		1635 (w),		1280 (sh),
3	245° C	c. 3300 (s,b),		1635 (w),		1270 (sh),
4	300° C	c. 3300 (w,b),	1695 (m),		1600 (w)	1280 (vw)
5	375° C	c. 3300 (vw,b)	1695 (s),		1595 (m)	1280 (vw)
6	375° C	c. 3300 (vw,b),	1695 (w),		1580 (m),	1280 (vw)
7	425° C		1690 (w),		1580 (m),	1280 (vw),
8	475° C		1690 (vw),		1575 (w)	
9	525° C		1690 (vw),		1570 (w)	
10	575° C		1690 (vw)		1570 (w)	

Cottons linters under

1	245° C	c. 3300 (vs,b)		1640 (w)		1280 (w),
2	275° C	c. 3300 (vs,b)	1690 (w),	1630 (m),		1280 (w),
3	325° C	c. 3300 (vw,b),	1690 (s),	1595 (m),		1280 (vw),
4	375° C		1690 (s),	1590 (s),		1280 (vw),
5	475° C		1690 (vw),	1580 (w),		1280 (vw)
6	575° C			1580 (w)		

TA

Band

Wood cellulose under

1	non-carbonized	c. 3250 (vs,b),		1640 (m),		1280 (sh),	
2	205° C	c. 3250 (vs,b),		1640 (m),		1280 (w),	
3	245° C	c. 3250 (vs,b),	1695 (sh),	1640 (w),		1280 (vw),	1240 (w),
4	275° C	c. 3250 (vs,b),	1695 (w),	1640 (w),		1280 (vw),	1240 (w),
5	300° C	c. 3250 (s,b),	1695 (s),		1600 (m),	1280 (vw),	1240 (w),
6	325° C	c. 3250 (w,b),	1695 (s),		1600 (s),	1280 (vw),	
7	375° C	c. 3350 (vw,b),	1695 (s),		1600 (s),	1280 (vw),	
8	425° C		1695 (m),		1600 (s),	1280 (vw),	
9	475° C		1695 (w),		1595 (s),	1280 (vw),	
10	575° C		1690 (vw),		1580 (m),		
11	575° C		1690 (vw)		1570 (w)		

Legend: b – broad, m – medium, sh – shoulder, s – strong, vs – very strong, BLE III

frequencies (cm^{-1})

15 mm Hg pressure

1195 (sh),	1155 (s),	1105 (sh),	1050 (vs),	1025 (sh),		895 (w),	
1195 (sh),	1155 (s),	1105 (s),	1050 (vs),	1025 (sh),		895 (sh),	
1195 (sh),	1155 (s),	1105 (s),	1050 (vs),	1025 (s),		895 (sh)	
	1155 (vw),	1105 (vw),	1050 (vw),			895 (vw),	790 (vw)
	1155 (sh),	1105 (sh),	1050 (sh),	1025 (sh)	945 (sh),	870 (vw)	
	1155 (sh),		1050 (sh),		950 (sh),	880 (vw),	795 (vw)
	1155 (sh)					870 (vw)	
	1155 (sh)					860 (vw),	800 (vw)
						870 (w),	800 (vw)
						870 (w)	

atmospheric pressure

1200 (w),	1155 (s),	1105 (s),	1050 (vs),	1030 (vs),	1000 (sh),	900 (sh)	
1200 (sh),	1155 (s),	1105 (s),	1050 (vs),	1030 (vs),	1000 (sh),	910 (sh)	
1200 (vw),	1155 (sh),		1045 (sh)				
1200 (sh),	1155 (sh)					880 (vw)	
	1155 (vw)				950 (vw),	880 (vw),	805 (vw)
					960 (vw),	880 (w),	805 (vw)

BLE IV

frequencies (cm^{-1})

15 mm Hg pressure

1200 (w),	1155 (s),	1100 (sh),	1050 (vs),	1030 (sh),	1000 (sh),	900 (w),	
1200 (sh),	1155 (s),	1105 (s),	1050 (vs),	1030 (sh),		900 (w),	
1200 (sh),	115 (s),	1105 (s),	1050 (vs),	1030 (sh),		900 (w),	
1200 (sh),	1155 (s),	1105 (s),	1050 (vs),	1030 (sh),		900 (vw)	
1200 (w),	1155 (w),		1050 (s),	1030 (sh),		905 (sh),	880 (sh)
1200 (sh),	1155 (sh),		1050 (sh),		960 (sh),		880 (sh)
1200 (sh),	1155 (sh),				960 (sh),		880 (vw)
	1155 (sh),				960 (sh),		880 (vw) 800 (vw)
	1155 (sh),				960 (sh),		880 (vw), 800 (vw)
	1155 (sh),						880 (w) 800 (sh)
	1155 (sh),				960 (sh),		880 (w), 800 (sh)

vw—very weak, w—weak

The spectra of the samples decomposed below 300°C do not differ greatly from each other and are much the same as the spectrum of non-carbonized cellulose. The strong and broad band near 3300 cm^{-1} is characteristic of hydrogen-bonded hydroxyl groups, and the group of strong bands: 1155 cm^{-1}, 1105 cm^{-1}, 1050 cm^{-1}, 1025 cm^{-1} and 900 cm^{-1} is most probably due to C—OH and C—O—C vibrations of hydroxyl groups and acetal type linkages in cellulose [4]. These bands remain almost unchanged at temperature up to 300° C. The only characteristic change in this range of temperature is observed with the band at 1640—1635 cm^{-1}, which gradually weakens and finally disappears above 275° C. As it was shown by some of us [4], the band should be attributed to the O—H deformation vibration of the water bound in carbohydrates. It is an interesting fact that such water should still be present in cellulose at the temperature as high as 275° C, even under reduced pressure.

Essential changes in the spectra occur on passing the temperature of 300°C. The hydroxyl band at 3300 cm^{-1} rapidly weakens, and so does the group of bands between 1155 and 900 cm^{-1}. Only traces of them can be observed at higher temperatures and even these disappear above 400°C. The band at 1635 cm^{-1} (that due to the bound water) is no more present at 300° C, but two other bands, 1695 and 1600 cm^{-1}, appear in this region. The former is characteristic of the C=O stretching vibration of carbonyl groups. It is observed in the spectra throughout the whole range of 300—575° C, its maximum intensity falling at 320—370° C. The latter band (1600 cm^{-1}) should be assigned to the skeletal vibrations of aromatic rings. Its intensity reaches maximum at c. 370° C and then decreases, but the band is still observable at the highest temperature used. The frequency of the band gradually shifts from 1600 cm^{-1} at 300° C to 1570 cm^{-1} at 575° C. Similar behaviour of this band is noted in the spectra of natural coals, going from brown coal to anthracite [5]. The other bands that appear in the spectra of the samples decomposed at above 300°C are those at 880—870 and 805—800 cm^{-1}. They can be assigned to the aromatic C—H out-of-plane vibrations. Finally, it should be noted that the background level in the spectra rapidly rises in the region of 300—330° C and then slowly goes up until an overall shape of absorption like that in the spectrum of anthracite is obtained.

Conclusions

It is evident from the spectra that the change of the structure of cellulose leading eventually to the formation of coal-like substance begins at 300° C. Below this temperature only the bound water is removed from cellulose: the basic aliphatic structure remains intact under these conditions. Rapid changes start at somewhat below 300° C. The process is formally dehydration (see the van Krevelen diagram on Fig. 3), but the spectra show that it is a quick aromatization of the former aliphatic structure. This intermediate stage ends at 330°C, and then only slow changes take place with increasing temperature. It can be deduced from the absorption curves, which approach ever closer to the infra-red spectrum of graphite as the temperature is raised, that condensation of aromatic rings into larger systems is the main process at temperatures 330—575°C.

So far no particular conclusions can be drawn on the possible pressure effects, but we hope that a series of experiments carried out under higher pressure will solve the problem. Such experiments will be undertaken in the near future.

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