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Infra-red Absorption Spectra of Products of Carbonization of Lignin

by

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This work is a continuation of our studies on coalification [1], [2]. So far, we have examined the infra-red spectra of a series of natural coals [1], and also the spectra of carbonized cellulose [2]. Since lignin is considered to be one of the substances from which most probably coal has developed, it should be interesting to follow the artificial carbonization of lignin as it appears in infra-red absorption spectra.

Experimental

3 g samples of lignin were placed in glass tubes of 26 mm diameter, heated in an electric furnace to a given temperature within the range of 125–575° (±2°C). The experimental conditions were the same as described in our previous work on carbonization of cellulose [2].

TABLE I

Results of analysis. Lignin under 15 mm Hg pressure

No	Temp. °C	Losses in weight		Analysis				Formula referred to C_{10}	$\frac{H}{C}$	$\frac{O}{C}$
		g	%	C %	H %	O %	Ash %			
1	non-carbonized	0	0	64.64	5.27	30.04	0.05	$C_{10}H_{9.8}O_{3.5}$	0.98	0.35
2	125	0.12	4.0	66.14	5.38	28.43	0.05	$C_{10}H_{9.75}O_{3.25}$	0.975	0.325
3	205	0.28	9.33	67.2	4.55	28.19	0.06	$C_{10}H_{8.12}O_{3.15}$	0.812	0.315
4	245	0.32	10.67	68.2	4.63	27.11	0.06	$C_{10}H_{8.18}O_{2.98}$	0.818	0.298
5	275	0.52	17.33	68.6	4.55	26.79	0.06	$C_{10}H_{7.97}O_{2.92}$	0.797	0.292
6	325	0.84	28.05	70.9	4.23	24.80	0.07	$C_{10}H_{7.15}O_{2.63}$	0.715	0.263
7	375	1.28	42.7	72.6	3.82	23.49	0.09	$C_{10}H_{6.31}O_{2.43}$	0.631	0.243
8	425	1.46	48.7	72.2	3.71	18.99	0.10	$C_{10}H_{5.78}O_{1.86}$	0.578	0.186
9	475	1.50	50.0	80.1	3.39	16.41	0.10	$C_{10}H_{5.08}O_{1.53}$	0.508	0.153
10	515	1.60	53.4	84.7	3.20	12.02	0.11	$C_{10}H_{4.55}O_{1.06}$	0.455	0.106
11	575	1.62	54.5	89.7	3.62	6.57	0.11	$C_{10}H_{1.85}O_{0.71}$	0 485	0.074

TABLE II

Band frequencies (cm^{-1})

Lignin under 15 mm Hg pressure												
1	non-carbonized	c. 3300 (s,b),	1695 (m),	1595 (s),	1265 (s),	1205 (m),	1140 (m),	1075 (w),	1030 (m),	970 (sh),	850 (vw),	–
2	125° C	c. 3300 (s,b),	1695 (m),	1595 (s),	1265 (s),	1205 (m),	1140 (m),	1075 (w),	1030 (m),	970 (sh),	850 (vw),	810 (sh)
3	205° C	c. 3300 (w,b),	1695 (m),	1595 (s),	1265 (s),	1205 (m).	1140 (w),	1075 (w),	1030 (w).	965 (sh),	850 (w),	810 (vw)
4	245° C	c. 3300 (vw,b),	1695 (m),	1595 (s),	1260 (m),	1205 (m),	1140 (w),	–	1030 (w),	–	850 (w),	810 (vw)
5	275° C	–	1695 (m),	1595 (s),	1260 (m),	1205 (w),	1140 (sh),	–	1030 (w),	–	850 (w),	810 (vw)
6	325° C	–	1690 (w),	1595 (s),	1260 (w),	1205 (w),	1140 (sh),	1080 (sh),	1030 (w),	–	850 (w),	810 (sh)
7	375° C	–	–	1595 (m)	1260 (sh),	1205 (w),	–	–	–	–	850 (w),	–
8	425° C	–	–	1580 (m)	1250 (sh),	–	1175 (w),	–	–	–	850 (w),	–
9	475° C	–	–	1580 (m)	1260 (vw),	–	1175 (wv),	–	–	–	850 (w),	810 (sh)
10	525° C	–	–	1580 (w)	–	–	1175 (sh),	–	–	–	860 (w),	810 (vw)
11	575° C	–	–	1570 (vw)	–	–	–	–	–	–	860 (w),	810 (sh)
Lignin under atmospheric pressure												
1	235° C	c. 3300 (m,b),	1695 (m),	1595 (s),	1265 (s),	1205 (s),	1140 (w),	1080 (w).	1030 (w),	–	850 (w),	800 (sh)
2	275° C	c. 3300 (w,b),	1695 (m),	1595 (s),	1260 (m),	1200 (m),	1140 (sh),	1080 (sh),	1030 (w),	–	850 (w),	800 (sh)
3	325° C	–	1690 (w),	1595 (s),	1260 (w),	–	1150 (w),	–	1030 (w).	–	850 (w),	800 (sh)
4	375° C	–	–	1580 (w),	1250 (vw),	1195 (vw),	1150 (sh),	–	1030 (sh),	–	850 (w),	–
5	475° C	–	–	1570 (vw),	1250 (vw),	–	1150 (vw),	–	–	–	850 (w),	800 (vw)
6	575° C	–	–	–	–	–	–	–	–	–	850 (m),	–

Legend: b – broad, m – medium, sh – shoulder, s – strong, vs – very strong, vw – very weak, w – weak.

The carbonized samples were subjected to elementary analysis and then their infra-red spectra were measured. The results of analysis are given in Table I, and the plots of losses in weight are shown in Fig. 1. In addition, the van Krevelen diagram $\frac{H}{C}$ against $\frac{O}{C}$ is presented in Fig. 3. The spectra were examined in a Hilger 800 double-beam recording spectrometer with sodium chloride optics, using Nujol mulls (ratio 50:50) of the samples as thin films. The range of the measurements was 4500—750 cm $^{-1}$. The absorption curves, given in Fig. 2, were subsequently shifted upwards in the absorption scale so as to avoid overcrowding. The band frequencies can be found in Table II.

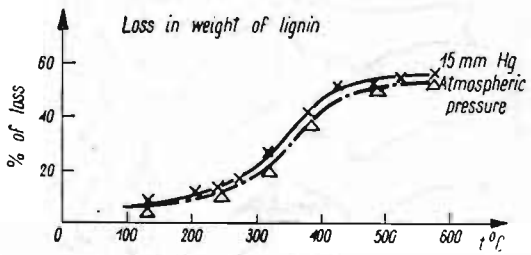

Fig. 1

Discussion

As can be seen in Fig. 1, the rate of increasing losses in the weight of the samples is highest within the range of 300—350°C. The rise of the curve is not so sharp as in the case of cellulose [2], yet it is readily observable.

It should be noted that changes in the samples start at a temperature as low as 125°C. There is only little difference between the curves for experiments under reduced pressure and for those under atmospheric pressure.

Changes in the spectra of the samples were observed throughout the whole range of temperatures used, but they were most pronounced at 275—375°C.

The broad and strong band near 3200—3300 cm^{-1} in the spectrum of non-carbonized lignin is characteristic of the O—H stretching vibration of hydrogen-bonded hydroxyl groups. Since the only strong band in the region 1300—1000 cm^{-1} was that at 1265 cm^{-1}, the hydroxyls were most probably of phenolic type. The 3300 cm^{-1} band begins to weaken at 205°C and completely merges with the background at 275°C. The strong 1265 cm^{-1} band (assigned to the C—O stretching vibration in phenolic hydroxyls and aromatic ethers) weakened at 245—325°C; only traces of it were present in the spectra at higher temperatures.

The band at 1695 cm^{-1}, of medium intensity, is assigned to the C=O stretching vibration of carbonyl groups. It disappeared from the spectra above 325°C. It is interesting to note that the same band was still present in the spectra of carbonized cellulose at much higher temperatures [2].

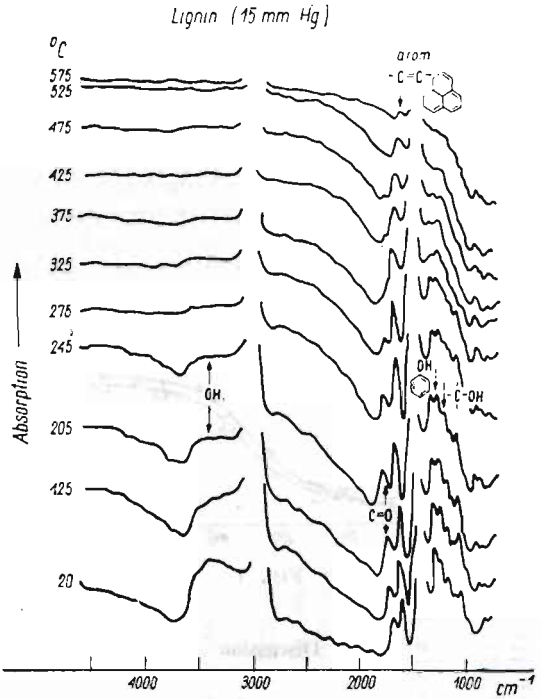
Lignin (15 mm Hg)
°C
575
525
475
425
375
325
275
245
205
125
20
Absorption
OH
arom
-C=C-
OH
-C-OH
C=O
4000
3000
2000
1000
cm⁻¹

Fig. 2

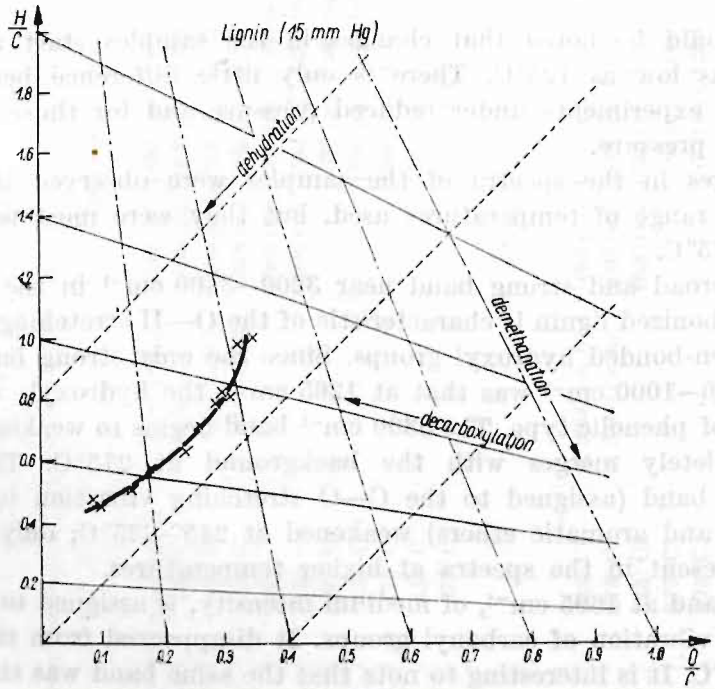
H/C
Lignin (15 mm Hg)
dehydration
demethanation
decarboxylation
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
O/C

Fig. 3

Skeletal vibrations of aromatic rings in lignin gave rise to the strong band at 1595 cm^{-1}. It remained strong up to 325°C, then weakened and underwent a shift towards lower frequencies. This shift (from 1595 to 1570 cm^{-1}) was the same as in the spectra of carbonized cellulose and in the spectra of coals arranged in order of increasing carbon content. It was most probably due to condensation of aromatic rings into larger units.

There are many weak bands in the spectrum of lignin within 1205—800 cm^{-1}. Some of them (1140, 1075 and 1030 cm^{-1}) might be attributed to various C—O stretching vibrations of alcoholic hydroxyls and aliphatic ether linkages; they disappeared at temperatures above 325°C. Those at 850 and 810 cm^{-1} should be assigned to the C—H out-of-plane vibrations in aromatic systems and they were present in all the spectra.

Conclusions

The data obtained point out that thermal carbonization of lignin begins at a temperature slightly over 200°C, yet the changes are slow up to 300°C. The process further speeds up within a narrow range of temperature (300—350°C), most of the oxygen-containing group being removed from lignin at this stage. Subsequently the carbonization slows down and most probably involves the condensation of aromatic rings.

The changes are not so rapid as during the carbonization of cellulose, nor are the losses in weight so large. This can be easily understood since unlike cellulose lignin has a highly aromatic character.

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