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The Infrared Spectra of Artificial Coal made from Submerged Wood at Uozu, Toyama Prefecture, Japan

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The infrared spectra of artificial coal prepared from Submerged Wood were observed and compared with those of lignin and cellulose. The artificial coalification seems to proceed in three stages, characterized by the corresponding infrared spectra, i. e., a cellulose-like spectrum, a lignin-like spectrum, and a spectrum resembling that of natural coal. The infrared spectrum of artificial coal is generally similar to that of natural coal with a little higher carbon content, suggesting that the degree of coalification is more advanced in artificial coal than in natural coal. The background absorption in the infrared spectra of artificial coal of a low coalification is weak, while that in the infrared spectra of artificial coal of a high coalification is strong.

The infrared spectra of coal have frequently been used to investigate its structure.1) The present report will deal with the mechanism of artificial coalification by observing the infrared spectra of the artificial coal prepared from Submerged Wood at Uozu, Toyama Prefecture, Japan, and by comparing these spectra with those of lignin and cellulose.

Experimental

One series of samples of artificial coal was prepared as follows. Fifty grams of the powdered sample (40—100 mesh) of the Submerged Wood was placed in a stainless steel autoclave of the shaking type (capacity; 1 l.) with 500 ml. of water. This was then heated at 150, 170, 200, 250, 260, 270, 280, 300, 325 and 350°C for 8, 24, 40 and 72 hr. under gas-steam pressure at 4, 13, 25, 50, 58, 65, 80, 105, 154 and 210 atom. (gauge pressure). The artificial coal (AC) thus obtained from the Submerged Wood was separated by filtration, washed with water, and air-dried.

Another series of samples of the artificial coal was prepared as follows. After 50 g. of the powdered sample of the Submerged Wood had been placed in a stainless steel autoclave of the rotating type (capacity; 5 l.) with 700 ml. of water, the air in the autoclave was replaced with nitrogen. Then the powdered sample in the autoclave was heated at 375 and 400°C for 8 and 40 hr. under gas-steam pressure at 210 and 270 atm. (gauge pressure). The artificial coal (AC) thus obtained was separated by filtration, then washed with water and air-dried. The conditions of artificial coalification are shown in Table I, while the elementary analysis and the yield of the artificial coal are given in Table II.

The infrared (IR) spectra of AC free from bitumen, lignins and cellulose were also measured. Powdered filter paper (No. 2) of the Toyoroshi Co., Ltd., was used as a sample of cellulose in measuring the IR spectra.

The lignin samples were prepared as follows. About 20 g. of powdered saw dust (60—100 mesh) from needle-leaved trees (Japanese red pin trees) was treated with a mixed solvent of ethyl alcohol and benzene (1 : 1) in order to extract the resinous matter and then treated with 400 ml. of concentrated hydrochloric acid (42%) and left to stand at room temperature for 24 hr., during which time it was occasionally shaken. Then the mixture was diluted with 3.6 l. of water and heated to boiling. The lignin thus obtained was filtered and thoroughly washed with hot water until the washings were free from chlorine ions. The yield was 13—16 g. of the so-called hydrochloric acid lignin, a light brownish powder.

About 100 ml. of concentrated hydrochloric acid was added to 400 ml. of waste liquor (specific gravity; 1.097 at 14°C) of sodium sulfate pulp made from pine trees and some broad-leaved trees (1 : 3), and then heated on a water bath for 1 hr. The thioalkali lignin thus precipitated was washed with hot water on a Buchner funnel until no chlorine ions were detected in the washings, and then dried at room temperature. The thioalkali lignin (30—40 g.) was thus obtained. The analytical data are listed in Table III.2)

The IR spectra of the AC, lignins and cellulose were measured on potassium bromide disks in the following way. Five milligrams of the above sample in a small glass tube was dried in a vacuum desiccator with phosphorus pentoxide at 110°C for 6 hr., and then the tube was sealed. At a constant temperature (20°C) and at a constant humidity (35%) the sealed glass tube

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1) S. Fujii, *J. Fuel Soc. Japan*, **37**, 643 (1958); **38**, 422 (1959); *Fuel*, **42**, 17, 341 (1963); The 1st Meeting of Coal Science, Tokyo, November, 1964. H. A. van Vucht, R. J. Rietveld and D. W. van Krevelen, *Fuel*, **34**, 50 (1955). D. W. van Krevelen, "Coal," pp. 363—372 (1961). J. K. Brown, *J. Chem. Soc.*, **1955**, 744. G. Bergman, G. Huck, J. Karweil and H. Luther, *Brenn. Chem.*, **38**, 193 (1957). M. M. Roy, *Fuel*, **36**, 249 (1957). W. A. Kirkby, J. R. A. Lakey and R. J. Sarjant, *Fuel*, **33**, 480 (1954). C. G. Cannon, *Nature*, **171**, 308 (1953). H. S. Rao, P. L. Gupta, F. Kaiser and A. Lahiri, *Fuel*, **41**, 417 (1962).

2) H. Tsukashima, *Bull. Fac. Eng. Toyama Univ.*, **5**, 54 (1954); **7**, 39 (1956); **8**, 22 (1957); **9**, 34 (1958); **11**, 41 (1960); **12**, 33 (1961); **13**, 41 (1962); *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **57**, 69 (1954); The 7 th, 9 th, 10 th, 11 th, 12 th, 13 th, 15 th Annual Meeting of the Chemical Society of Japan, Tokyo or Kyoto, April, 1954, 1956, 1957, 1958, 1959, 1960, 1962; Coal Utilization Technical Congress of Japan, Tokyo, November, 1959.

Table I. Artificial coalification condition

Sample	Coalification temp., °C	Coalification index	Beginning temp. of coalification, °C	Coalification time, hr.	Color
150, 8	150	1.16	14.0	8	Faint brown
150,72	150	8.31	14.0	72	Brown
170, 8	170	1.29	22.0	8	Brown
170,72	170	9.33	18.0	72	Umber
200, 8	200	1.73	18.0	8	Umber
200,32	200	5.72	12.2	32	Umber
200,40	200	6.69	12.5	40	Brownish black
200,72	200	11.30	16.0	72	Deep brownish black
250, 8	250	2.50	2.5	8	Violet black
250,72	250	15.50	3.5	72	Black
260, 8	260	2.44	17.5	8	Violet black
260,72	260	15.44	14.0	72	Black
270, 8	270	2.61	14.0	8	Black
270,72	270	16.00	15.5	72	Black
280, 8	280	2.78	13.0	8	Black
280,72	280	16.83	13.2	72	Black
300, 8	300	3.18	6.0	8	Black
325,72	325	19.93	12.0	72	Black
350,72	350	22.13	5.0	72	Black
375,40	375	13.34	24.0	40	Black
400,36	400	13.31	20.5	36	Black

Coalification velocity index 55°

Table II. Elementary analysis of AC (%, dry ash free)

Sample	C	H	O*	N	Yield
Untreated wood	52.74	6.30	40.85	0.11	
150, 8	53.63	6.03	40.32	0.02	89.37
150,72	55.56	5.85	38.55	0.04	84.33
170, 8	54.95	5.83	39.19	0.03	83.39
170,72	59.09	5.89	34.98	0.04	82.81
200, 8	59.80	6.17	33.92	0.11	79.47
200,32	65.26	5.86	28.76	0.12	71.93
200,40	66.88	5.99	26.99	0.14	69.57
200,72	70.79	5.73	23.36	0.12	66.22
250, 8	73.63	5.57	20.62	0.18	55.48
250,72	76.34	5.71	17.81	0.13	55.84
260, 8	74.90	5.77	19.16	0.17	55.99
260,72	77.54	5.64	16.65	0.17	53.36
270, 8	75.51	5.44	18.93	0.12	55.47
270,72	77.13	5.29	17.55	0.13	50.73
280, 8	74.90	5.10	19.90	0.10	53.04
280,72	77.72	4.78	17.31	0.12	46.61
300, 8	79.93	5.44	14.63		44.93
325,72	82.68	4.83	12.49		39.86
350,72	84.39	4.52	11.09		31.10
375,40	88.43	4.20	7.37		35,96
400,36	89.56	4.20	6.21		35.66

* By difference

mentioned above was broken and the sample was mixed with 500 mg. of potassium bromide which had been prepared by heating special-grade potassium bromide commercially obtained in a platinum crucible in an electric furnace at 260°C for 6 hr. and by then cooling it in a vacuum desiccator with phosphorus pentoxide; the sample was then pulverized in an agate mortar for about 20 min. Five hundred milligrams of this mixture was weighed and pressed under a 10-ton pressure for 7 min. in a vacuum. The disk obtained was 20 mm. in diameter and 0.6 mm. thick. Double-beam IR spectrophotometers (OYOKOKEN 310

TABLE III. ANALYSES OF LIGNINS (%, DRY ASH FREE)

Lignin	C	H	S	O*
Hydrochloric acid lignin	65.13	5.28	—	29.59
Thioalkali lignin	65.54	5.02	4.74	25.70

* By difference

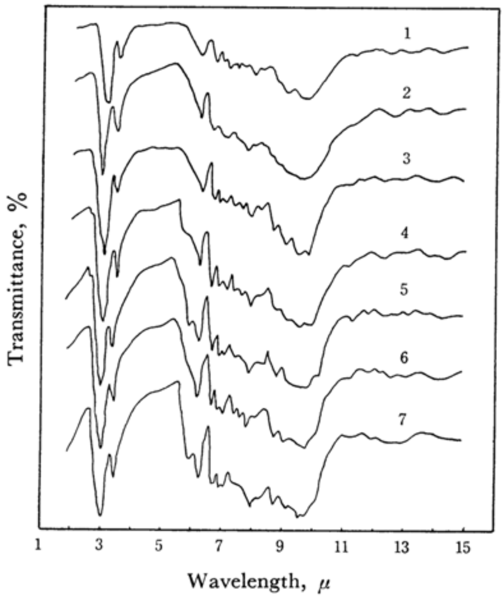

Fig. 1. IR spectra of AC.
1. Submerged wood 2. 150°C, 8 hr.
3. 150°C, 72 hr. 4. 170°C, 8 hr.
5. 170°C, 72 hr. 6. 200°C, 8 hr.
7. 200°C, 32 hr.

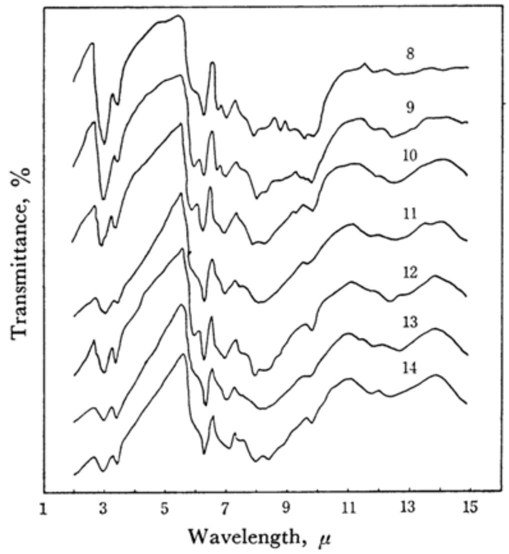

Fig. 1. (continued) IR spectra of AC.
8. 200°C, 40 hr. 9. 200°C, 72 hr.
10. 250°C, 8 hr. 11. 250°C, 72 hr.
12. 260°C, 8 hr. 13. 260°C, 72 hr.
14. 270°C, 8 hr.

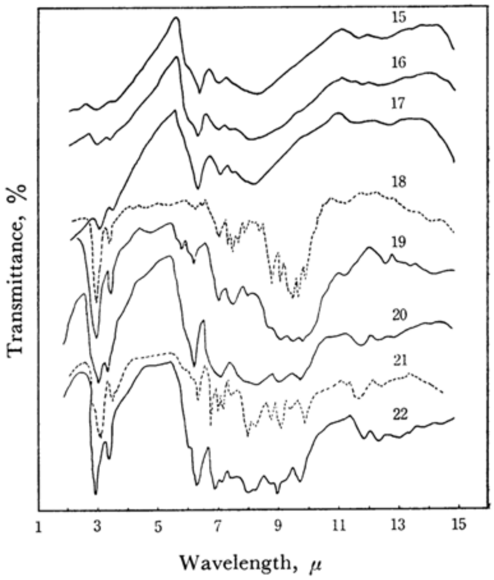

Fig. 1. (continued) IR spectra of AC.
15. 270°C, 72 hr. 16. 280°C, 8 hr.
17. 280°C, 72 hr. 18. Cell.[3] 19. Cell.
20. HCl lig. 21. Red pine lig.[7]
22. Thio lig.

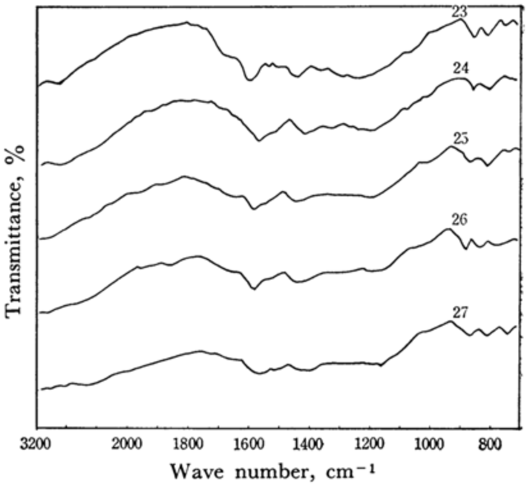

Fig. 1. (continued) IR spectra of AC.
23. 300°C, 8 hr. 24. 300°C, 72 hr.
25. 350°C, 72 hr. 26. 375°C, 40 hr.
27. 400°C, 40 hr.

type and HITACHI EPI-2 type), equipped with rock-salt prisms, were used.

Results

The IR spectra of the Submerged Wood, AC, lignins and cellulose were measured. The results are shown in Fig. 1. The IR spectra of lignin and cellulose reported by previous authors are also shown, for the purpose of comparison, in Fig. 1.

Discussion

1) There have been two explanations for the strong background absorption of the IR spectra of coal.1) One is that it is caused by the size of the particle of the sample. The other is that it is caused by the growth of graphite crystallites as the condensation of the aromatic cluster proceeds. When there is a low degree of the coalification of AC, the background absorption is weak, but it is very strong with a high degree of coalification, especially in the region from 4 μ to 6 μ, possibly because of the growth of graphite crystallites and the abundantly distributed particles of a comparatively large size. The background absorption is stronger in the spectra of AC than in that of natural coal of a similar carbon content. This might be caused by the greater refractivity of AC.

2) The IR spectrum of AC is generally similar to that of natural coal with a little higher carbon content, suggesting that the degree of coalification is more advanced in AC than in natural coal.

3) 3.03 μ (3300 cm^{-1}). The H-bonded OH group. The absorption of the H-bonded OH group increases with an advance in coalification under 200°C and decreases with an advance in coalification above 200°C. Similar results have been reported both in other kinds of AC and in natural coal.1)

4) 3.25 μ (3000—3100 cm^{-1}). The aromatic CH group. There was no absorption of the aromatic CH group in the AC spectra, but it appears in the spectra of natural coal in which the carbon content is above 80 per cent.1)

5) 3.43 μ (2800—3000 cm^{-1}). The aliphatic CH (CH$_2$, CH$_3$) group. The absorption of the aliphatic CH group appears at a medium intensity and then gradually decreases above 200°C because the aliphatic CH group in AC is broken up.

6) 5.85 μ (1700 cm^{-1}) The carbonyl and carboxyl CO group. There is no absorption of the CO group in the spectra of Submerged Wood and the AC obtained at 150°C; it appears in the spectra of the AC obtained at 200°C and increases in those of the AC obtained at 200—250°C, while it diminishes in the AC obtained above 250°C. The cellulose that contains no CO group vanishes at about 200°C. The remaining lignin that contains a CO group causes the absorption band of the CO group to appear; this gradually increases up to 250°C, possibly because of the oxidations of the lignin,4) and then decreases above 250°C, possibly because of the conversion of lignin into a coaly matter by dehydration and deoxidation.

7) 6.25 μ (1600 cm^{-1}). Aromatic C–C bond and oxygen-containing groups (H-bonded carbonyl groups). This absorption is mainly due to the C–C double bond in the aromatic structure of coal. On the other hand, it has been reported1) that the absorption intensity of this C–C vibration is enhanced by oxygen-containing groups and that the H-bonded carbonyl group is responsible for this absorption. It appears at a considerable intensity in the AC spectra and increases with an advance in the coalification of AC. In the spectra of the AC obtained above 280°C, it is weak, possibly because the background absorption has increased.1)

8) 6.64 μ (1500 cm^{-1}) The aromatic C–C bond. The absorption of the aromatic C–C bond is very strong in the spectra of lignins.1,5) In the spectra of the AC of a low coalification (obtained under 200°C), the absorption of the aromatic C–C bond at 6.64 μ is stronger than those of the aromatic C–C bond and oxygen-containing groups at 6.25 μ, but in the spectra of the AC of a high coalification (obtained at 200—250°C), the former is weaker than the latter. This shows that the oxidation of lignin in AC occurs at 200—250°C (cf. 6)).

9) 6.85, 7.00, 7.33 μ (1460, 1430, 1360 cm^{-1}). Aliphatic CH$_2$, CH$_3$, and cyclic CH$_2$ groups. The absorption intensities of aliphatic CH and cyclic CH groups decrease with an advance in the coalification.

10) 7.92, 8.30 μ (1260, 1200 cm^{-1}). The aromatic C–O (phenolic OH, aryl ether and methoxyl benzene) bond. The absorption of the aromatic C–O bond increases up to 250—260°C with an advance in the coalification and then decreases above 260°C.

11) 8.66—9.70 μ (1150—1030 cm^{-1}). The carboxyl CO group, the aliphatic ether C–O–C bond and the alcohol OH group. The absorptions of

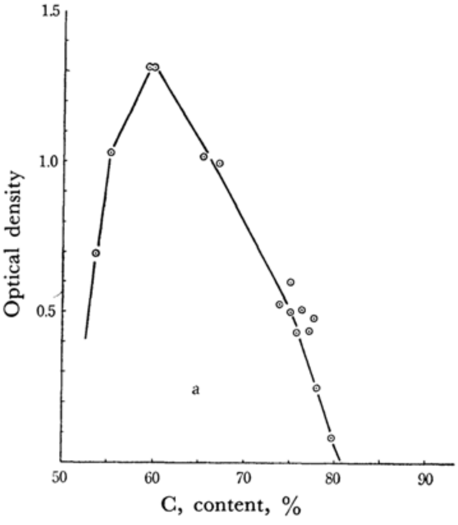

Fig. 2. Relation between carbon content and functional group optical density.
a. 3.03 μ

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3) Infrared Data Committee of Japan, "IRDC Card" (1960).

4) S. Fujii and F. Yokoyama, *J. Fuel Soc. Japan*, **38**, 98 (1959).

5) S. Fujii, ibid., **38**, 267 (1959).

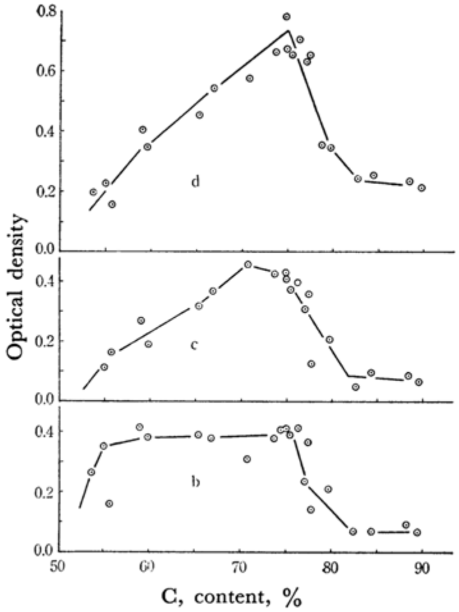

Fig. 2. (continued) Relation between carbon content and functional group optical density.
b. 3.43 μ c. 5.85 μ d. 6.25 μ

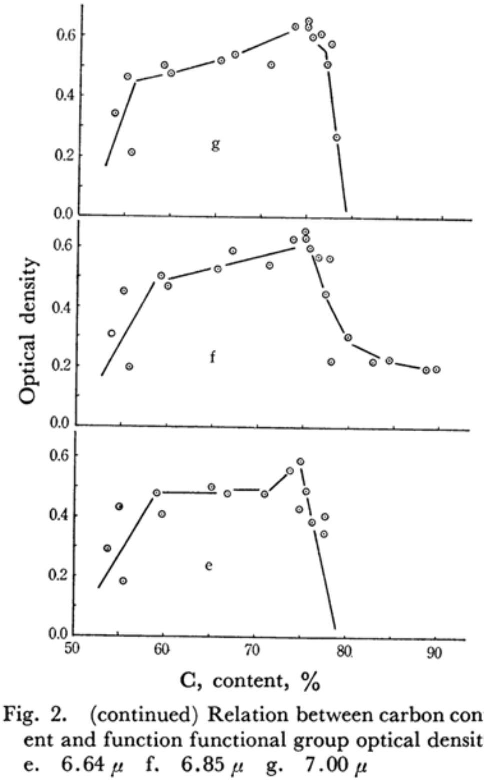

Fig. 2. (continued) Relation between carbon content and function functional group optical density.
e. 6.64 μ f. 6.85 μ g. 7.00 μ

the carboxyl CO group, the aliphatic ether C–O–C group and the alcohol OH group are very strong in the spectra of the AC obtained at 150—200°C, but they decrease in intensity in the spectra of the

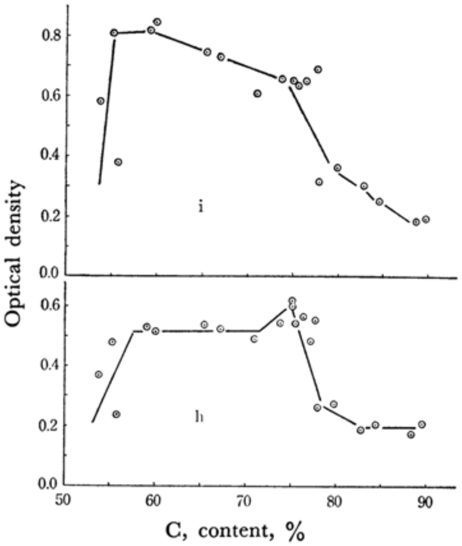

Fig. 2. (continued) Relation between carbon content and functional group optical density.
h. 7.33 μ i. 8.66 μ

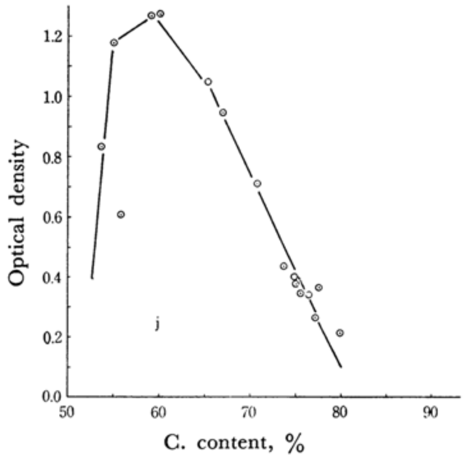

Fig. 2. (continued) Relation between carbon content and functional group optical density.
j. 9.75 μ

AC obtained above 200°C.

12) The absorption bands of the aromatic CH groups at 11—14.5 μ (690—900 cm^{-1}) do not appear clearly in the AC spectra.

13) The functional group absorptions in the IR spectrum of material of a complicated structure with a great molecular weight are difficult to discriminate because of the interference of each group with the others. In such a case, a comparison of the figures of the IR spectra of the materials is useful. For instance, the IR spectra of the AC obtained at 150—200°C are similar to that of cellulose between 5.00—6.00 μ, 7.00—7.33 μ and 9.00—9.70 μ. The IR spectra of the AC obtained at 250—260°C are similar to those of lignins between

5.00—6.00 μ, 6.25—7.92 μ and 9.00—9.70 μ. The IR srectra of the AC obtained at 270—280°C are different from those of lignins, and their absorption bands between 9.00—9.70 μ are weak.

14) The remarkable change in the IR spectra and in the results of the rational analyses of AC obtained at 200—250°C shows that a very important change in its chemical structure has occurred in this temperature range.

15) The relation between the carbon content of AC and the optical density of the bands of the functional groups is illustrated in Fig. 2.⁶⁾ The percentage transmission near 5.26 μ (1900 cm^{-1}) was chosen for the base line in calculating the optical density. In Fig. 2 there are two clearly discernible turning points at carbon percentages, about 60 and 75. Thus artificial coalification seems to proceed in three stages. In the first stage, at carbon percentages of 60 and less (coalification temperature; 150—200°C), the IR spectra of the AC are similar to that of cellulose. In the second stage, at carbon percentages from 60 to 75 (coalification temperature; 200—250°C), they are similar to those of lignins. In the third stage, at carbon percentages of 75 and more (coalification temperature; above 250°C), they are rather similar to those of natural coal. These results agree with those mentioned above (6, 13 and 14) and with those presented in a previous report by the present author.²⁾

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6) W. Funasaka and C. Yokokawa, "Coal Chemistry," Kyoritsu Shuppan, Tokyo (1960), p. 111.

7) H. Sobue and S. Fukuhara, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **61**, 1070 (1958).