

# On the Formation of Humic Substance from Cellulose

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## I. Introduction

We have previously discussed<sup>1)</sup> about the formation of coal on the basis of the artificial coalification method of F. Bergius, and have concluded that cellulose, like lignin, is an important material for the formation of coal, and it is conceivable that a substance originating from cellulose is the caking constituent of coal.

In order to support our theory, we shall discuss on the experimental results and opinion of F. Fischer which he holds as the basis of his lignin theory.

F. Fischer is of the opinion that cellulose, compared with lignin, is biochemically very unstable, and that, it has easily decomposed at the early stage of coalification, and lignin alone has become the original substance of coal. To support the above statement, F. Fischer and his collaborators studied the natural peat layer<sup>2)</sup> and found that the content of methoxyl-group became greater as the layer became deeper, and, at the same time, the quantity of the substance insoluble in HCl (the substance which did not receive hydrolysis) became greater. They concluded that this phenomena show the trend in which cellulose decomposes and lignin increases relatively. Further, they compared in their laboratory<sup>3)</sup> the resistance of cellulose and lignin against aerobic fungi and recognized the fact that, while cellulose was readily decomposed, lignin existed in stable condition. Still further<sup>4)</sup>, they based their lignin theory on the fact that the natural coal, humic acid, etc., like lignin, had aromatic structure as their basic framework, but it was very difficult to obtain the substance which has aromatic structure from cellulose.

The fact that, when vegetable undergo natural decay, cellulose is decomposed more easily than lignin and the latter is enriched, is recognized not only by the studies of F. Fischer, but also by the studies of E. Rose and M. W. Lisse<sup>5)</sup>, and also of W. Fuchs and J. Sebelien<sup>6)</sup>. However, the analytical method which was employed in these studies consisted of hydrolysis of cellulose with a quite highly

concentrated inorganic acid, and then the quantity of lignin was measured by the Cross-Bevan method, but it is quite doubtful whether cellulose and/or its derivatives had been completely separated from lignin and/or its derivatives. P. Erasmus<sup>7)</sup> holds an opinion that cellulose or carbohydrates, when transformed a little, may not receive any hydrolysis by acid; and L. H. Hawley and E. E. Harris<sup>8)</sup> have reported as obtaining lignin-like-substance by heating cellulose at about 130°C for a considerable length of time, therefore, it is conceivable that there is a possibility of determining cellulose and lignin together in the rational analysis of decayed wood or peat. Although it is generally accepted today that the aromatic structure is the basic structure of coal and that it is condensed to a considerably high degree, it will not obstruct the possibility of cellulose-originating-substances to be present in coal. It has been pointed out by E. Berl<sup>9)</sup> that it can be considered that artificial coal obtained from cellulose has aromatic structure. And also, H. E. Blaydon, J. Gibson and H. L. Riley<sup>10)</sup> have said that, from the X-ray studies, it was possible to think that bitumen originated from cellulose.

We have carried out, in support of our cellulose theory, the following experiments by clarifying the fact that cellulose, in the coalification process, changes into a substance which can be mistaken for lignin and this substance transforms into humin or bitumen, which has aromatic structure, and also pointing out the fact that the supposition of cellulose being completely decomposed at the early stage of natural coalification is carried a bit too far.

## II. Experiments and Results

The filter paper for qualitative analysis, manufactured by the Toyo Filter Paper Co., was used as the specimen of cellulose. 25 g (as dry material) of the specimen, together with 250 cc. of various medium, was put into an auto-clave of 500 cc. capacity (\*denotes 20 g, 200 cc.) and was subjected to artificial coalification under the desired conditions, after completion of the reaction, it was left to cool itself to room temperature and was then filtered. The artificial coal was then water-washed and air-dried, and the washing water and filtrate were put together and used immediately for the following test.

The ultimate analysis of the filter paper used as the cellulose specimen is shown in Table 1.

Table 2 shows the conditions of artificial coalification and the results of rational analysis of the artificial coal. In the table, C, AC, and SC stand for cellulose being subjected to artificial coalification in water, in N/10-NaOH and in N/10 - oxalic acid, respectively. For example, AC<sub>200</sub><sup>6</sup> shows that the cellulose was subjected to artificial coalification in N/10-NaOH at 200°C for 6 hours.

Table 1. Ultimate Analysis of Filter Paper (%)

Moisture	Ash	Dry-Ash-Free Basis		
		Carbon	Hydrogen	Oxygen
6.68	0.26	44.18	6.27	49.55

Table 2. Artificial Coalification of Cellulose under Mild Condition

	pH	Yield (%)	Gas (cc)	Pressure (atm)		Rational Analysis (%)				
						Bitumen	Cellulose	Humic acid	Lignin	Humin
C <sub>170</sub> <sup>48</sup>	4.0	76.6	300	11	13	17.3	75.4	0.8	6.5	0.0
C <sub>200</sub> <sup>6</sup>	3.4	71.8	260	17	19	4.7	84.3	1.2	6.7	3.1
C <sub>200</sub> <sup>48</sup>	3.8	26.9	900	17	40	23.8	20.4	6.6	41.9	7.3
C <sub>240</sub> <sup>0.5</sup>	3.0	52.2	570	41	49	15.0	72.3	0.4	8.8	3.5
C <sub>240</sub> <sup>3</sup>	2.6	37.7	1310	41	60	30.5	12.8	0.0	43.8	12.9
C <sub>260</sub> <sup>0.5</sup>	—	41.7	—	60	61	27.0	23.1	0.0	47.6	2.3
C <sub>260</sub> <sup>3</sup>	3.2	37.7	1550	60	81	37.5	9.8	0.0	29.9	23.2
O <sub>260</sub> <sup>6</sup>	—	33.2	2000	59	75	34.8	4.4	0.0	50.7	10.1
C <sub>300</sub> <sup>0.5</sup>	3.2	33.9	1400	109	110	35.2	1.0	0.0	36.3	27.5
C <sub>300</sub> <sup>3</sup>	3.8	35.3	1320	110	110	43.6	0.0	0.0	33.2	23.2
C <sub>300</sub> <sup>6</sup>	3.8	28.2	2020	110	120	47.9	0.0	0.0	27.1	25.0
AC <sub>200</sub> <sup>6</sup>	4.4	77.7	210	8	10	—	—	—	—	—
AC <sub>240</sub> <sup>0.5</sup>	—	—	430	40	41	—	—	—	—	—
AC <sub>240</sub> <sup>3</sup>	4.0	30.3	1550	43	70	56.6	13.9	0.5	28.2	0.8
AC <sub>260</sub> <sup>3</sup>	4.0	23.8	2650	70	98	75.6	1.7	0.1	21.2	1.4
AC <sub>300</sub> <sup>0.5</sup>	4.2	23.2	1600	110	134	72.9	8.6	0.0	12.6	5.9
SC <sub>240</sub> <sup>3</sup>	2.8	34.3	1600	53	74	34.2	0.0	0.5	28.2	37.1

The pH value was determined, by using pH testing paper, after diluting the medium to 500 cc. after completion of the artificial coalification. The yield is shown on dry base and the pressure at the desired temperature and the pressure at completion of the artificial coalification are shown. The rational analysis was carried out in the usual method, and bitumen, cellulose, humic acid, lignin and humin are shown by weight per cent of the dry substance.

The pH value indicated acidic in every case, and it is of interest to note, that, though the artificial coal obtained under the condition of AC<sub>200</sub><sup>6</sup> seemed ostensibly like the original filter paper undergoing no transformation, it showed

a value of 4.4. It has been known that bituminisation occurs to a great extent when coalification of cellulose is carried out in an alkaline medium. For instance, E. Berl<sup>11)</sup> says that when coalification takes place in a condition of at  $\text{pH} > 7.0$ , the formation of caking constituent can be considered and this acceleration of bituminisation is generally considered to be the effect of the pH. R. A. Mott<sup>12)</sup> also says that the degree of coalification depends on the alkalinity. However, referring to the results of these experiments on artificial coalification, the medium easily becomes acidic at the early stage of coalification, and, as already mentioned<sup>1)</sup>, the bituminisation occurs to a great extent when NaCl or CaCO<sub>3</sub> exists, but on the contrary no special bituminisation could be observed in the NH<sub>4</sub>OH solution compared with the case of NaOH or KOH. Taking these into consideration, it could be considered that the coalification is affected not by the pH, but by the catalytic action of alkaline metal or alkaline earth metal.

The colour of the artificial coal becomes darker as the conditions become severer (the product is in the form of powder at conditions C and SC), and it is whitish brown at C<sub>170</sub><sup>48</sup> and C<sub>200</sub><sup>6</sup>, but becomes darker and is brown or dark black under the other conditions. As mentioned above, the cellulose shows little or no affect at AC<sub>200</sub><sup>6</sup>, but the bituminisation is quite great and pitch is formed in case of other members of the AC series.

The rational analysis shows that, as the conditions of coalification become severer, the quantity of cellulose decreases and that of bitumen and lignin increase, and huminification gradually takes place; and it seems that humin is formed through lignin.

The following should be noted, however, to avoid misunderstanding: that the lignin mentioned above does not undergo hydrolysis with 78% H<sub>2</sub>SO<sub>4</sub> but is dissolved by the Cross-Bevan method, and that it is not the so-called natural lignin, but is a substance which is classified as lignin in rational analysis. Therefore, a substance resembling lignin is formed from cellulose at a temperature below 200°C, and it is conceivable that through this substance humin and bitumen are formed. In our previous report<sup>1)</sup>, this lignin-like-substance was included in the fraction of humin according to the classification of rational analysis.

The medium of artificial coalification generally has a light yellow colour, apparently dissolves carbon dioxide in a supersaturated state; it is acidic in nature in all cases, as mentioned above, and possesses a particular smell. Every diluted solution of these mediums reduces Fehling's reagent, and is positive to Schiff's reaction. Volatile acid is generated when distilled after addition of H<sub>2</sub>SO<sub>4</sub>. When these liquid is left exposed to the air, the colour gradually darkens and in 24 hours it usually becomes intransparent dark black and precipitates a black

insoluble substances. It was noted by E. Berl<sup>13)</sup>, but we carried out the following observation for the purpose of clarifying this point. A representative medium was sealed in an Erlenmeyer flask equipped with a mercury manometer, the temperature and pressure were measured over a long period of time, and the volume of gas sealed in was calculated. The process of change in volume is as shown in Fig. 1. The composition of gas at the point where its volume becomes constant, are as shown in Table 3, and it is clear that oxygen has decreased and a large quantity of CO<sub>2</sub> existed. In the figure, the increase of volume of gas at the

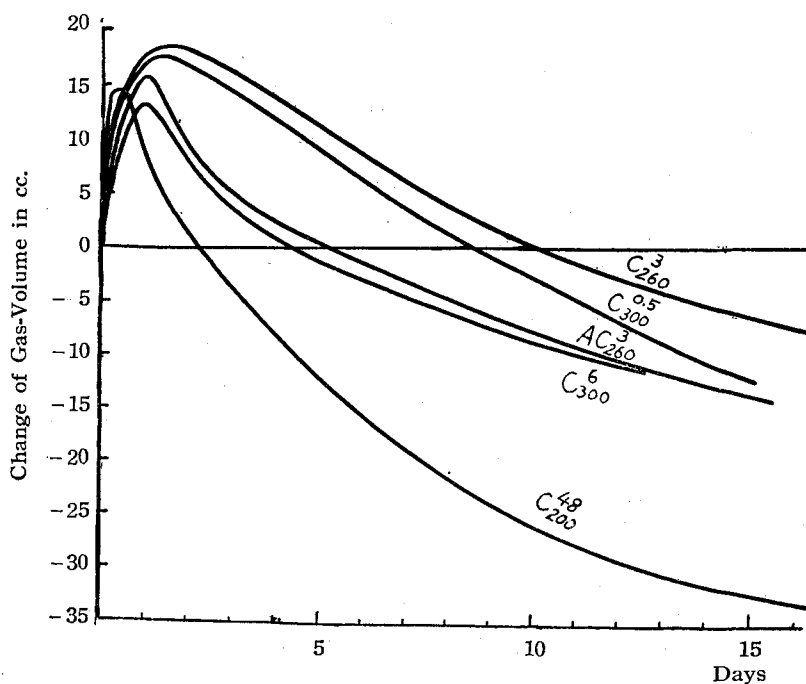


Fig. 1. Oxygen Absorption by Medium.

Table 3. Analysis of Gas at the End of Oxygen Absorption

	Composition of Gas (%)			Reduced Volume (cc)
	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	
AC <sup>6</sup> <sub>200</sub>	4.5	12.5	83.0	55
C <sup>3</sup> <sub>260</sub>	9.9	7.5	82.6	45
AC <sup>3</sup> <sub>260</sub>	13.7	6.5	79.8	55
C <sup>0.5</sup> <sub>300</sub>	13.8	9.1	77.1	61
C <sup>6</sup> <sub>300</sub>	6.5	13.1	80.4	32

early stage is noted and it is considered due to the fact that the  $\text{CO}_2$ , which is dissolved in the medium in a super-saturated state, is liberated and then  $\text{O}_2$  is absorbed. Thus gradually resulting in decrease of the gas volume and a state of equilibrium is reached at the end. The reducing ability for Fehling's reagent, when pursued by the Bertrand method, will be as shown in Fig. 2. The number

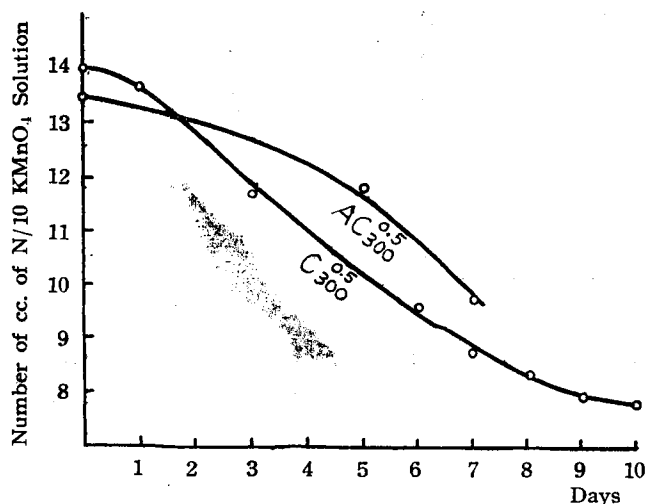


Fig. 2.  
Change of Reducing Power  
of Medium

of cc. of N/10- $\text{KMnO}_4$  solution, equivalent to the  $\text{Cu}_2\text{O}$  produced, was taken as the equivalent for the reducing ability, and 25 cc. of the medium diluted to 500 cc. was used as sample. Hence, it can be understood that the intermediate product dissolved in the medium contains aldehyde group, and this substance absorbs  $\text{O}_2$ , and forms the insoluble substance by polymerisation or condensation.

This substance is soluble in dilute alkaline solution and in alcohol, and precipitates in the form of humic acid from alkaline solution by  $\text{HCl}$ . The result of ultimate analysis of this substance is shown in Table 4, and it possesses the characteristics which are very much similar to those of hymatomelanic acid.

A yellow oily substance is obtained when the medium is extracted with ether. The reducing power of the medium against Fehling's reagent, before and after extraction, is measured and the equivalent quantity of N/10- $\text{KMnO}_4$  is shown by the number of cc. in Table 5. Almost all the extracts seem to be the cause of the reduction power. As glucose is insoluble in ether, it can be considered that no glucose exists in the medium. The ether solution of the extract is positive to the Schiff's reaction and precipitates hydrazone from the water solution by reacting with 2-4-dinitrophenylhydrazine. This extract is very unstable, and, when left in the air, it quickly polymerizes and turns into a brown resinic sub-

Table 4.

Ultimate Analysis of Humic acid-like  
Substance (%)

	C	H	O
C <sup>48</sup> <sub>200</sub>	62.40	4.47	33.13
C <sup>6</sup> <sub>300</sub>	64.86	4.32	30.82

Table 5.

Reducing Power of Medium before and  
after Extraction  
(Number of cc of N/10-KMnO<sub>4</sub> Solution)

	before	after
C <sup>48</sup> <sub>200</sub>	16.8	7.5
C <sup>0.5</sup> <sub>300</sub>	14.1	—
C <sup>3</sup> <sub>300</sub>	16.5	1.3
C <sup>6</sup> <sub>300</sub>	12.1	1.4
AC <sup>0.5</sup> <sub>300</sub>	13.5	—
SC <sup>3</sup> <sub>240</sub>	15.0	—

Table 6. Analysis of Gas Generated at Artificial Coalification from Gellulose (Vol. %)

	CO <sub>2</sub>	CmHn	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
C <sup>48</sup> <sub>170</sub>	24.9	0.0	5.3	2.3	15.8	4.0	47.7
C <sup>6</sup> <sub>200</sub>	30.0	0.2	2.8	6.6	4.3	0.3	55.8
C <sup>48</sup> <sub>200</sub>	42.0	0.0	1.5	6.2	29.4	4.1	16.8
C <sup>0.5</sup> <sub>240</sub>	67.8	0.6	0.3	8.4	0.0	—	—
C <sup>3</sup> <sub>240</sub>	77.8	1.2	0.2	7.8	1.8	0.6	10.6
C <sup>3</sup> <sub>260</sub>	62.3	0.8	0.1	8.8	4.0	2.2	21.8
C <sup>0.5</sup> <sub>300</sub>	67.2	1.8	0.1	8.8	8.1	2.1	11.9
C <sup>3</sup> <sub>300</sub>	65.8	1.2	0.3	10.2	6.8	2.3	13.4
C <sup>6</sup> <sub>300</sub>	78.3	1.7	0.1	2.8	6.3	3.0	7.8
AC <sup>6</sup> <sub>200</sub>	12.3	0.0	4.6	6.0	—	—	—
AC <sup>0.5</sup> <sub>240</sub>	60.4	0.3	0.4	15.6	—	—	—
AC <sup>3</sup> <sub>240</sub>	62.3	0.8	0.3	22.5	4.5	0.3	9.3
AC <sup>3</sup> <sub>260</sub>	88.3	0.7	0.1	5.7	4.5	0.3	0.4
AC <sup>0.5</sup> <sub>300</sub>	84.9	1.5	0.3	2.6	3.9	0.8	6.0
SC <sup>3</sup> <sub>240</sub>	68.4	0.9	0.1	16.8	4.3	0.8	8.7

tance which is insoluble in water. It is necessary to carry out further study on this substance, but it seems to contain a substance which possesses the aldehyde group.

The result of analysis of the gas which was generated at artificial coalification is shown in Table 6. The major substance of the gas produced is CO<sub>2</sub>, and a certain amount of CO also exists. It is interesting to note that a large quantity

of CO can be found in the case of AC when bituminisation occurs to a great extent. The nitrogen which appears in the table is the nitrogen which already existed in the air that filled the space in the auto-clave.

It has already been mentioned that cellulose coal has aromatic structure. Six species of cellulose coal which we had prepared were oxidized with an alkaline  $\text{KMnO}_4$  solution according to W. A. Bone's method<sup>14)</sup>, and the oxidized products are shown by the carbon balance method in Table 7. That is, 5 g of the coal sample was taken, 4 g of KOH and 200 cc. of water (or at this ratio) were added, the temperature was gradually raised, at about 60°C, 3.5%  $\text{KMnO}_4$  solution was added, drop by drop, and the reaction was carried out at the boiling point. After completion of the reaction, the excess  $\text{KMnO}_4$  was reduced with  $\text{Na}_2\text{S}_2\text{O}_3$ -solution, filtered, and  $\text{MnO}_2$  was thoroughly washed, the washing water was added to the filtrate. A portion of it was taken and the quantities of  $\text{CO}_2$ , volatile acid and oxalic acid were determined respectively. The major portion of it was evaporated till dry, then extracted with ether, acetone and ethyl alcohol, the extracts were put together and was regarded as crude benzenoid. It was then dissolved in water,  $\text{NH}_4\text{Cl}$  was added, and then it was cooled to precipitate the ammonium salt, and then the amount of mellitic acid was calculated from this quantity. Furthermore, the precipitate was dissolved in water, copper acetate was added, then light greenish blue precipitate was obtained. This substance can be regarded as the copper salt of mellitic acid<sup>15)</sup>. This substance was heated and converted into  $\text{CuO}$ , then weighed and the content of Cu was determined.

Table 7. Carbon Distribution among Acids Formed by Alkaline  $\text{KMnO}_4$  Oxidation of Various Coals

Coals	$\text{KMnO}_4$ added (g) per Coal (g)	Duration (hrs.)	Carbonic acid (%)	Acetic acid (%)	Oxalic acid (%)	Benzene carboxylic acid	
						Mellitic acid (%)	Others (%)
Lignite	7.8	8	60.9	5.3	15.3	—	18.5
Sub. Bituminous Coal	9.6	6	42.6	9.4	17.1	3.2	27.7
Sub. Bituminous Coal	8.4	6	41.6	7.5	9.8	5.4	35.7
Bituminous Coal	7.7	20	31.7	9.8	10.2	7.5	40.8
Anthracite	9.2	24	35.4	13.6	3.4	21.6	26.0
Artificial Coals							
Cellulose (4 hrs.)	8.9	6	49.5	14.4	8.6	2.2	25.3
" (6 hrs.)	8.7	8	42.8	9.1	11.1	2.5	34.5
" (9 hrs.)	8.2	6	48.0	12.4	7.2	2.8	29.6
" (12 hrs.)	8.7	7	40.5	10.8	11.4	3.1	34.2
" (24 hrs.)	8.9	6	35.0	11.7	6.4	2.7	44.2
" (32 hrs.)	8.8	10	32.4	9.8	11.6	2.5	43.7



The values of 36.7 and 35.4% for CuO were obtained. The theoretical value of CuO obtained from copper mellitate is 36.2%.

As apparent from Table 7, benzenoid was obtained from each of the cellulose coal and, though in a small quantity, the existence of mellitic acid was recognized. Therefore, though the aromatic character increases with the coalification time of the cellulose coal, it can be said that cellulose coal has aromatic structure of rather a low degree of condensation, when the quantity of mellitic acid produced is brought into consideration. It is difficult to describe the mechanism of aromatization of cellulose, but as has been already mentioned, it is not impossible to entertain the assumption, as it can be considered that aldehyde group exists in the intermediate product.

The following points are clarified by the above-mentioned experiments:-

1) A substance similar to lignin is easily produced from cellulose, and it can be assumed that this substance transforms into humic substance and bituminous substance.

2) A very active intermediate product, which has aldehyde group, exists in the transformation process of cellulose, and this substance, with the existence of oxygen, produces a substance similar to humic acid.

3) Cellulose coal has aromatic structure, though it is considered to be of a low degree of condensation.

Therefore, cellulose transforms easily under a rather mild conditions, and produces a substance which is determined as lignin by the rational analysis and this substance, after receiving further coalification, turns into humin or bitumen, which has aromatic structure.

When these facts are compared with the basis of the lignin theory of F. Fischer and his collaborators, the experimental facts and views shown by them cannot be considered as the necessary conditions—and certainly not the sufficient condition—for the theory that cellulose is not, and lignin only is, the basic material of coal.

Considering from the experimental results which the authors described above, it is considered more appropriate to assume that cellulose is as important as lignin for the formation of coal: and furthermore, it is considered that the quality of coal depends on the degree of decay which the original vegetables undergo at the early stage of coalification, that is to say, on the ratio of the remaining quantity of cellulose and lignin.

### III. Summary

The authors have pointed out in this report, that when cellulose receives

artificial coalification by the Bergius method under a rather mild condition, a substance which can be analysed quantitatively as lignin in the process of the rational analysis, is produced from cellulose at a temperature of 200°C or below, and this type of cellulose-originating-substance is contained in the substance shown as lignin in the rational analysis of natural decayed wood or peat. On the other hand, we have clarified that when artificial coal obtained from cellulose is oxidized with an alkaline  $\text{KMnO}_4$  solution, the mellitic acid is obtained, which goes to show that cellulose coal contains aromatic structure. We present both of these arguments to support the cellulose theory.

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