

On the Formation of Coal

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Introduction

Though numerous reports on the formation of coal have been published, every one of them gives no successful explanation for the complicated characters of coal, especially for the caking property.

For the theories of the formation of coal, there had been so-called inorganic theory and organic theory, but the former was denied by the petrographic observations and the latter developed gradually. However, it was rather recent year that the question, which component of plant, cellulose or lignin, was the original material of coal, became an important subject of discussion.

In 1910 H. Potonié¹⁾, concerning with the differences between land plants and aquatic plants and the action of water and air (oxygen), classified the earlier coalification processes into four types, such as "Verwesung", "Vermoderung", "Vertorfung" and "Fäulnis". But he did not take the individual component of plant into account.

In 1920 F. Fischer and H. Schrader²⁾ asserted that the original material of coal was lignin. This famous lignin theory stands on their studies on coal chemistry.

In 1912 and 1928 F. Bergius³⁾, studying by his artificial coalification method, found that under the similar conditions cellulose, likewise to lignin, gave the coal-like products. And moreover, P. Erasmus⁴⁾ concluded that it is rather reasonable to think cellulose as the original material of coal.

This artificial coalification method have been employed by Tropsch⁵⁾, Berl, Schmidt and Koch⁶⁾, Horn and Sustmann⁷⁾, etc.

R. V. Wheeler⁸⁾ also manifested the cellulose theory, where he separated coal into three fractions, α , β and γ compounds, and concluded by the thermal decomposition experiments that α and β were cellulose origin substances and γ was bituminous substance.

The authors tried experiments on the problem of coal formation by the Bergius' artificial coalification method.

Experimental Part

I. Outline of experiments and results.

Cellulose, or another carbohydrates, lignin and other substances, considered to have relations with bitumen substances, were artificially coalified, chiefly in water medium and sometimes in alkaline or acidic medium, and the products were tested by proximate analysis and observed on their caking phenomena. The authors came to the following conclusions.

(1) Cellulose supplies comparatively large amount of bituminous substances, and it seems that this bituminous substance, produced from cellulose, is the caking component of bituminous coal.

(2) Resin, fat and wax in the original plant seem to have no participation of the caking property directly.

(3) So, from the view of the formation of coal, cellulose, in the same way of lignin, should be converted into a component of coal.

Table 1
Artificial Coalification of Cellulose No. 1
(at $300 \pm 10^\circ\text{C}$, 160 ± 10 atm., 6 hrs., excepting *marked.)

Medium	Yield (%)	Appearance of Product	Proximate Analysis (%)				Appearance of Coke
			Moist.	Volatile matter	Fixed carbon	Ash	
Cellulose	—	—	7.24	87.44	5.05	0.27	not sintering
H ₂ O	40	brown-black, powder	4.24	39.99	54.59	1.18	slightly sintering
♦* (12 hrs.)	30	♦	3.49	42.27	43.98	10.26	feebly sintering
♦* (24 hrs.)	26	♦	3.65	48.43	38.54	9.38	strongly sintering
NaOH N/100	79	dark-black, powder	2.74	43.18	51.59	2.49	not sintering
♦ N/20	24	black, powder	4.34	51.42	42.79	1.45	feebly caking
♦ N/10	14	black, powder; partly pitch-like	2.57	67.32	27.41	2.70	swelling, caking metallic lustre
♦ N/4	10	pitch-like	12.30	67.03	15.28	5.39	swelling, crust-like coke
♦ N/2	4	soft pitch-like	13.53	71.47	7.18	7.82	♦, ♦
KOH N/10	8	pitch-like	2.33	74.85	17.46	5.36	swelling, caking, metallic lustre
Ba(OH) ₂ ♦	20	soft pitch-like	10.61	68.64	5.40	15.35	swelling, crust-like coke
Ca(OH) ₂ ♦	22	♦	8.35	82.74	7.50	1.41	♦, ♦
NH ₄ OH ♦	36	brown-black, powder	2.77	50.76	41.96	4.51	strongly sintering
Na ₂ CO ₃ ♦	4	pitch-like	5.11	80.02	10.10	4.77	swelling, crust-like coke
K ₂ CO ₃ ♦	10	♦	5.98	67.90	11.07	15.05	♦, ♦
CaCO ₃ ♦	19	♦	10.43	72.52	8.94	8.11	crust-like coke
NaCl 3%	20	almost pitch-like	9.43	45.23	31.55	13.79	crust-like coke, swelling

II. Detailed description and discussion of experiments.

A. Artificial coalification of cellulose or lignin

The samples adopted as cellulose and lignin were filter-paper (made by Tôyô Roshi Co., Ltd.) and thio-alkali-lignin (obtained from the waste liquid of sodiumsulfate pulp, by the courtesy of Prof. Dr. M. Horio), respectively.

25 g of each samples were charged with 250 cc of water or other aqueous solutions of various alkalis, acids or salts, in a stainless steel autoclave (capacity

Table 2
Artificial Coalification of Cellulose No. 2
(at $300 \pm 10^\circ\text{C}$, 160 ± 10 atm., 6 hrs.)

Medium	Yield (%)	Appearance of Product	Proximate Analysis (%)				Appearance of Coke
			Moist.	Volatile matter	Fixed carbon	Ash	
Formic acid N/10	19	pitch-like	3.44	79.13	4.50	12.93	swelling, crust-like coke
Acetic acid N/100	75	dark-brown, powder	2.77	61.24	29.32	6.67	feebly caking, metallic lustre
Acetic acid N/10	24	partly pitch-like	2.86	70.14	17.92	9.08	swelling, crust-like coke
Butylic acid ♪	28	soft pitch-like	19.07	66.27	5.76	8.90	♪, ♪
Stearic acid ♪	46	gray-black, mass	2.18	71.30	5.47	21.05	crust-like coke
Oxalic acid ♪	15	almost pitch-like	2.60	72.51	11.40	13.49	swelling, crust-like coke
Succinic acid ♪	35	brown-black, powder	2.70	56.74	39.56	1.00	feebly caking
Maleic acid ♪	18	almost pitch-like	7.63	70.54	6.02	15.81	swelling, crust-like coke
Adipinic acid ♪	24	brown-black, mass	3.00	62.31	30.10	4.59	feebly caking, slightly swelling, metallic lustre
Formaldehyde ♪	44	brown-black, powder	2.59	57.97	30.13	9.31	feebly caking
Methanol ♪	67	♪, ♪	11.94	55.26	25.44	7.36	♪, ♪
Phenol ♪	19	pitch-like	10.87	71.42	8.24	9.47	crust-like, feebly swelling
Resorcine ♪	51	brown-black, powder	5.20	62.87	24.94	6.99	feebly caking
Lactic acid ♪	20	soft pitch-like	12.47	62.93	22.07	2.53	crust-like coke
Lactic acid N/100	42	black, mass	2.66	59.12	34.55	3.67	feebly caking, metallic lustre
Tartaric acid N/10	38	brown-black, powder	3.06	47.08	41.06	8.80	feebly sintering
Citric acid ♪	27	soft pitch-like	17.53	62.57	6.72	13.18	crust-like coke
Citric acid N/100	32	black, mass	3.23	55.28	37.51	3.88	feebly caking
Benzoic acid N/10	22	dark-brown, powder	3.31	62.88	27.23	6.58	♪
Phthalic acid ♪	27	partly pitch-like	9.17	69.50	6.88	14.45	crust-like coke
Salicylic acid ♪	26	soft pitch-like	9.23	77.46	5.84	7.47	♪

500 cc), heated for 6 hours at about 300°C and under corresponding pressure (about 160 atm.), and brought down to room temperature gradually. Then the products were separated, washed, dried in air, tested by proximate analysis and observed on the appearance of the coke.

The results of the cases of cellulose or lignin are summarized in Table 1, 2 and 3.

Table 3
Artificial Coalification of Lignin
(under same conditions as Table 1)

Medium	Yield (%)	Appearance of Product	Proximate Analysis (%)				Appearance of Coke
			Moist.	Volatile matter	Fixed carbon	Ash	
Lignin	—	—	2.89	58.65	36.77	1.69	feebly caking
H ₂ O	52	black, powder	4.50	31.20	62.84	1.46	slightly sintering
◇* (12 hrs.)	64	◇, ◇	7.11	34.08	57.35	1.46	not sintering
◇* (24 hrs.)	60	◇, ◇	5.25	40.40	52.97	1.38	feebly sintering
NaOH N/20	42	◇, ◇	1.93	26.45	69.56	2.06	not sintering
◇ N/4	35	◇, ◇	3.18	38.33	55.51	2.98	◇
Ca(OH) ₂ N/10	53	◇, ◇	5.20	45.44	35.55	13.81	◇
Butylic acid ◇	81	black, mass	5.76	40.84	34.96	18.44	◇
Oxalic acid ◇	56	◇, ◇	6.29	36.59	48.63	8.49	sintering

From these experiments it may be said that,

(1) Cellulose coal, produced in pure water medium, shows weak caking power, as coalification advances; but lignin coal does not.

(2) Lignin supplies larger amount of artificial coal than cellulose.

(3) Generally speaking, cellulose coal is rich in volatile matter, on the other hand, lignin coal in fixed carbon.

(4) Cellulose has a tendency to be bituminized markedly in aqueous solutions of various alkali, and depending upon the kind of alkali, may produce pitch-like substances. But the good caking coal must have a moderate amount of bitumen, while when the degree of bituminization is somewhat too vigorous, the caking property diminishes. The good caked coke of cellulose coal shows swelling and metallic lustre.

Lignin, when it is coalified under such conditions that cellulose is somewhat markedly bituminized and gives a good caking coal, scarcely supplies bituminous substance or caking component, and the coke shows neither swelling nor metallic lustre.

(5) When cellulose or lignin is coalified in aqueous solutions of various organic acids, about the same tendencies to those of the cases of alkali are recognized, and in this case, it seems that the molecular structure of the used acid has big effect on the properties of artificial coal. This fact may be considered to

be interesting on the formation and the structure of natural coal, according to the fact that there may be formed various kinds of organic acids at the earlier stage of the natural coalification. Incidentally, the authors can not find out any reports about the artificial coalification in the acidic medium.

(6) Empirically, it may be acknowledged that the necessary conditions for the formation of good coke from coal, are the properties of coal, namely, having so-called caking component, swelling component and such components which give metallic lustre and hardening power at high temperature; and now, it seems to us that the first three components, at least, are derived from cellulose:

(7) According to the differences found between cellulose coal and lignin coal, it may be reaffirmed that the assertions of Donath⁹⁾, Berl⁶⁾ etc., which manifest that the differences between bituminous and brown coal are due to the kind of original plants and not to the coalification degree, because there are some facts surmised that bituminous coal and brown coal are formed from the plants in paleozoic era, and those in mesozoic era respectively, and moreover the former are rich in cellulose and the latter in lignin comparatively.

B. Artificial coalification of some carbohydrates

Subsequently, in connection with the preceding experiments, carbohydrates, other than cellulose, were artificially coalified. Namely, these substances, such as shown in Table 4, cellulose hydrate (cellophan, viscose-sponge), cellulose ester (cellulose acetate) and soluble starch, dextrine, saccharose, glucose, agar-agar, konnyak-mannan, gum arabic. As it is clear from the results of proximate analysis in Table 4, every one of them does not give large amount of coke, and

Table 4
Proximate Analysis of Carbohydrates

Sample	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Appearance of Coke
Cellulose	7.24	87.44	5.05	0.27	not sintering
Cellophan	8.66	89.97	1.37	0.00	◇
Viscose-sponge	13.40	81.18	3.68	1.74	◇
Cellulose acetate	14.80	81.83	3.17	0.20	crust-like coke
Soluble starch	14.49	80.80	4.45	0.26	◇, shrinking
Dextrine	10.92	85.21	2.48	0.39	feebly caking
Saccharose	0.17	91.11	8.69	0.03	swelling, crust-like coke
Glucose	7.15	89.08	3.15	0.62	crust-like coke, shrinking
Agar-agar	23.65	70.05	3.68	2.62	crust-like coke
Konnyak-mannan	16.05	70.59	9.49	3.87	feebly caking
Gum arabic	16.85	68.50	12.11	2.54	feebly caking, shrinking

these cokes are non-coagulative or no more than crust-like ones, except that dextrine, konnyakmannan and gumarabic give feebly caked cokes.

The results of artificial coalification of these substances are shown in Table 5. Any one of these coals are brown-black sand or black powder and comparatively rich in fixed carbon, and some of them, namely these obtained from cellulose acetate, soluble starch, dextrine, glucose and gum arabic, show feeble caking power.

Table 5
Artificial Coalification of Carbohydrates
(under same conditions as Table 1 in pure water medium.)

Substance	Yield (%)	Appearance of Product	Proximate Analysis (%)				Appearance of Coke
			Moist.	Volatile matter	Fixed carbon	Ash	
Cellulose	40	brown-black, powder	4.24	39.99	54.59	1.18	slightly sintering
Cellophan	25	dark-brown, powder	3.07	41.27	55.05	0.61	not sintering
Viscose-sponge	31	brown-black, powder	2.87	43.21	50.98	2.94	slightly sintering
Cellulose acetate	13	black, sand	2.34	50.32	41.44	5.90	feebly caking
Soluble starch	25	⌘, ⌘	3.86	43.93	51.89	0.34	⌘
Dextrine	28	⌘, ⌘	3.89	45.04	50.78	0.29	feebly caking, shrinking
Saccharose	6	⌘, ⌘	3.50	43.97	52.28	0.25	strongly sintering
Glucose	15	⌘, ⌘	5.66	62.57	30.77	1.00	feebly caking
Agar-agar	20	⌘, ⌘	3.92	43.25	51.05	1.78	slightly sintering
Konnyakmannan	30	⌘, ⌘	3.39	51.90	42.32	2.39	strongly sintering
Gum arabic	25	⌘, ⌘	3.70	54.46	41.27	0.57	feebly caking, shrinking

As described before, cellulose coal, produced in pure water medium, had scarcely caking power, but which in aqueous solution of alkali showed comparatively strong caking power. The reason for this fact is not yet clear, but according to the latest experiments, it seems that the various decomposition products of cellulose may take parts in the formation of the so-called caking component, because some of carbohydrate coals show the caking power. These carbohydrates can not be considered to be the direct original materials of natural coal, but the preceding fact may be useful for the study of the formation of coal from cellulose. However, it is not permitted to give the full particulars of this subject, as the molecular structures of these substances are not yet successfully explained.

C. Artificial coalification of bitumen substances

Next, some of the substances which were considered to have relations with

bitumen in natural coal, were tested in the same way. The results of proximate analysis of these raw materials are shown in Table 6. Almost any one of them scarcely leaves fixed carbon as well as carbohydrates, even the substance which was coalified to comparatively higher degree, such as amber in Fuchun (Bujun)

Table 6
Proximate Analysis of Bituminous Substances

Substance	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Appearance of Coke
Cetanol	1.45	98.55	0.00	0.00	—
Stearic acid	0.57	99.34	0.00	0.09	—
Higher ketone	0.01	99.82	0.02	0.15	—
Japanese wax	0.43	99.52	0.00	0.00	—
Bee wax	0.20	99.80	0.00	0.00	—
Rosin	0.80	98.91	0.13	0.16	—
Amber	1.26	95.86	1.38	1.50	not sintering
Natural rubber	0.44	98.66	0.40	0.50	—
Polystyrene	0.06	99.31	0.16	0.47	—
Phenol resin (under acidic)	2.82	60.37	36.16	0.65	caking, black lustre
Phenol resin (under alkaline)	3.87	47.70	47.45	0.98	not sintering, black lustre

Table 7
Artificial Coalification of Bituminous Substances

Substance	Temp. (°C.)	Press. (atm.)	Yield (%)	Appearance of Product	Proximate Analysis (%)				Appearance of Coke
					Moist.	Volatile matter	Fixed carbon	Ash	
Cetanol	300	150	92	black, mass	1.88	96.66	0.38	1.08	soot-like
Stearic acid	320	◇	64	dark-black, mass	0.58	93.20	0.00	6.22	—
Higher ketone	300	100	75	◇, ◇	0.23	99.55	0.14	0.08	—
Japanese wax	◇	◇	90	◇, ◇	1.18	98.82	0.00	0.00	—
Bee wax	◇	◇	90	◇, ◇	0.48	99.52	0.00	0.00	—
Rosin	◇	150	40	brown-black, viscous liquid	24.09	69.72	0.00	6.19	—
◇	280	70	72	dark-brown, viscous liquid	5.26	94.67	0.00	0.07	—
Amber	330	150	64	black, mass	5.74	75.59	0.00	18.67	—
◇	280	70	84	brown-black, mass	1.46	96.20	1.01	1.33	soot-like
Natural rubber	320	150	40	brown-black, viscous liquid	20.27	79.73	0.00	0.00	—
Polystyrene	◇	◇	60	◇	3.33	96.10	0.40	0.17	soot-like
◇	280	70	100	white, mass	0.59	99.16	0.21	0.04	◇
Phenol resin (under acidic)	310	100	80	black, mass	3.16	53.76	42.14	0.94	caking, black, lustre
Phenol resin (under alkaline)	330	150	80	black, sand	4.22	40.22	54.68	0.88	not sintering, black lustre

(in Manchuria) (Cainozoic era, tertiary period deposit) leaves no more than about 1%. Additionally, we tested some of the higher molecular substances (natural gum, polystyrene and phenol resins). The first two leave only a little fixed carbon, but the last gives a fair amount. In these experiments it is interesting that the phenol resin which is produced under the acidic reaction shows the caking property (black, lustrous, not swelling), and on the contrary the one produced under alkaline reaction gives only black sandy coke. It may be considered that it is caused by the difference between both molecular structures, as it is believed that the former has chain structure and the latter net-work structure.

In the Table 7 the results of proximate analysis of the artificial coals obtained from these materials are summarized.

These artificial coals, in the same way of the raw materials, do not give coke, with the exception of the phenol resin; the coke of the artificial coal from phenol resin is identical to the coke of phenol resin itself.

Generally it has been believed that fat, resin or wax of plant had been bituminized during the coal formation and converted into the so-called caking component. But according to the facts that we could not obtain the good caking coal from Japanese wax, bee wax, rosin or amber, the authors ought to conclude that the bituminous materials which are formed from these substances do not partake directly in the caking property of coal.

D. Ultimate analysis and rational analysis of artificial coal

In connection with the artificial coalification processes, it seems to be very interesting that how each component changes with time. For the examinations comparatively large amount of artificial coals were produced in a large autoclave

Table 8
Ultimate Analysis and Rational Analysis of Artificial Coal

Artificial Coal	Mois- ture (%)	Ash (%)	Ultimate Analysis (%)			Rational Analysis (%)					
			C	H	O	Bitu- men	Cellu- lose	Humic acid	Lignin	Hummin	-OCH ₃
Cellulose	6.67	0.23	43.64	6.64	49.72	—	—	—	—	—	—
◇ (3 hrs.)	2.69	0.79	77.60	5.48	16.92	16.3	6.6	1.6	—	75.5	—
◇ (6 hrs.)	3.16	0.69	78.83	5.37	15.80	52.6	6.7	8.7	—	32.0	—
◇ (12 hrs.)	2.89	0.47	78.16	5.22	16.62	65.4	2.7	0.0	—	31.9	—
◇ (24 hrs.)	2.41	0.43	82.35	5.71	11.94	55.0	3.1	1.4	—	40.5	—
Lignin	12.72	1.07	65.08	4.48	30.44	—	—	—	—	—	12.88
◇ (3 hrs.)	7.67	2.08	69.53	5.19	25.28	3.9	0.3	0.0	29.2	66.6	1.86
◇ (6 hrs.)	10.03	1.67	69.62	4.36	26.02	5.1	1.1	0.1	23.6	70.1	1.18
◇ (12 hrs.)	10.45	3.18	72.67	4.30	23.03	29.6	2.1	0.1	16.2	52.0	0.75
◇ (24 hrs.)	10.53	4.31	72.76	4.08	23.16	7.7	4.3	5.7	19.3	63.0	0.50

and the artificial coals were tested by proximate, rational and ultimate analysis. The results of proximate analysis is almost same to the data in Table 1-3, so only the results of rational and ultimate analysis are summarized in Table 8.

60 g of each samples were charged with 600 cc of water into the large autoclave (capacity 1000 cc), heated at about 300°C under its corresponding pressure (about 120 atm.) for 3, 6, 12 or 24 hours respectively. Ultimate analysis was carried out in the ordinary manner and rational analysis followed to Kada's method. From these experiments it may be said that,

(1) In case of cellulose coal, with the progress of coalification, the carbon increases, hydrogen shows no considerable change and oxygen decreases.

(2) In case of lignin coal, with the progress of coalification, increase in carbon or decrease in oxygen is rather small and hydrogen decreases some extent.

The conditions of these coalification are relatively mild, hence the produced coals seem to be not the state of the so-called "Endkohle", which Bergius³⁾ pointed out. But it is interesting that cellulose coal (24 hours) consists of 82.35% carbon and 5.71% hydrogen. On the other hand lignin coal (24 hours) consists of not more than 72.76% carbon and 4.08% hydrogen.

From the above mentioned evidences it may be proved that coals made from relatively cellulose rich materials or lignin rich materials, may be fairly different in their characters; then it seems to us that Donath's theory⁹⁾ which is asserting the differences between bituminous coal and brown coal depend upon their original plants, may be reasonable.

From the results of the rational analysis, we could find following interesting facts, namely in the case of cellulose the largest amount of bitumen is formed after 12 hours coalification, and in the case of lignin, the bituminization took place most vigorously after 12 hours also, though it is considerably smaller than the case of cellulose, and moreover in both cases the amount of humin is smallest at the highest peak of the bituminization. In a word, this fact is considered as a proof which shows that there are some possibility of bitumen-formation from humus substances, especially from cellulose, and then it may be believed that this evidence offers one of the most important problems on the coal formation.

And now, as described before, bitumen which are derived from resin, fat, wax etc. in the original plants seem to take no direct participation in the caking property of coal, so the authors ought to consider bitumen, converted from cellulose, as the direct source of the caking component of coal.

Summary

The previous theories of the formation of coal have never explained satisfactorily that there are two different kinds of bituminous coal, namely one has the caking property and the other not; however, from the above described observations, the following conclusions may be obtained, because it seems that there is the possibility of the formation of the caking component only when cellulose is in the original materials.

Namely, caking coal should have been formed under such conditions, that there were still comparatively large amounts of the decomposition products of cellulose during the huminification processes and the degree of coalification was suitable; on the other hand, when cellulose was decomposed and diminished severely beyond a certain degree, sintering or non-caking coal should have been formed. In another words, Fischer's lignin theory may be able to explain only the extreme, or rather exceptional case of the coal formation, and as the general view of this subject the cellulose theory, that not only lignin but also cellulose are the important original material of natural coal, seems in any case to be reasonable.

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