

On the Chemistry of Japanese Plants, II. The Composition of Fossil Wood.

By

Shigeru Komatsu and Hidenosuke Ueda.

(Received May 1, 1923)

There is no need of further discussion now as to the vegetable theory of the origin of coal.¹

The mechanism of its formation from vegetable matter, however, remains to be explained.

The present investigation, therefore, was undertaken to throw some light upon the mode of formation of coal.

K. Yasui² has stated from botanical investigation, that the fossil woods produced near Sendai and Nagoya, belonged to a species of *Sequoia*, and the same opinion regarding the original plant from which "brown lignite"—umoregi,—was formed, was reported by C. Iwasaki in his "A fundamental study of Japanese coal"³—microscopic and X-ray studies on coal.

The specimen of fossil wood from Sendai,—umoregi,—which the authors have examined, was obtained through the kindness of Professor M. Kobayashi of Tohoku Imperial University.

It was dark brown in colour, and the woody structure was perfectly preserved.

The sawdust prepared from the fossil wood, when dried, was readily reduced to powder in a disintegrator. The sawdust freshly prepared from the mass, contained much moisture; the loss in weight

¹ F. W. Clarke: The data of geochem., 1916, 738; W. A. Bone: Coal and its scientific uses, 1919, 23; D. Mendeléeff: The principles of chem., 1905, 1,368.

² Ann. Bot., 31, 10 (1907).

³ Tech. Reports. Tohoku Imp. Univ., 1, 109 (1910).

on drying at 98–100°, was 29.2% and that of an air-dried sample was 17.4%.

The air-dried sample was dried on calcium chloride dessicator in vacuo, for 3 weeks (A) and for 5 weeks (B) and was analysed with the following results, calculated on an ash-free, dry basis :

	A.	B.
C.	60.8	61.16
H.	5.9	6.02
S.	0.8	—
Ash.	2.8	2.4

The composition of the ash, obtained on incineration at about 400° in an electric oven, was as follows :

	Komatsu & Ueda.	Iwasaki.
P ₂ O ₅	0.63	—
S O ₃	35.19	—
SiO ₂	20.50	57.31
Fe ₂ O ₃	17.06	8.13
Al ₂ O ₃	18.45	21.13
MnO ₂	1.97	—
CaO	23.43	7.69
MgO	1.02	2.21
Na ₂ O, K ₂ O.	—	3.27

C. Iwasaki¹ has reported the ash-composition of the “brown lignite” (fossil wood) produced near Sendai, as seen in the table.

The results² of the ultimate analysis of wood, peat, lignite, bituminous coal and anthracite, indicate a progressive concentration in the carbon content and a gradual diminution in the oxygen and hydrogen contents. Judging from the ultimate analysis of fossil wood, bearing in mind that the successive transformation from wood to anthracite was

¹ Loc. cit.

² W. A. Bone: *Coal and its scientific uses*. 50; C. F. Cross and E. I. Bevan: *Cellulose*, 1910, 239.

attained with some numerical relations in the composition, this fossil wood seems to represent an intermediate stage like peat between wood and lignite in the formation of coal.

	C.	H.	O.	N.
wood	49-51	6.2-6.3	42-45	0.5 -0.9
peat	50-64	4.5-6.8	28-48	0.30-7.5
lignite	60-75	5.0-5.2	20-35	0.75-1.75
bituminous coal	75-90	4.5-5.5	5-15	0.75-1.75
anthracite	90-95	2.5-2.8	2.7-3.0	0.5 -1.0

As seen in the foregoing table, the ash of fossil wood contains more sulphur and less nitrogen compared with that of coal. When a plant died, the processes of decay and destruction followed; the wood, instead of being left in the open air, was buried under successive layers, either of matter like itself or else of sediments such as clay under those conditions, the action of oxygen was retarded, and the formation of earth molds was aided, i. e. incomplete oxydation of plant tissues took place, and the degradation products of plant tissues succeeded the accumulation of carbon at the expence of oxygen and hydrogen by a gradually increasing pressure and the heat generated thereby.

To find some chemical changes which took place in the constituents of wood buried under earth, the content and nature of resinous matter, carbohydrates and lignin in fossil wood were studied.

1. RESINOUS CONSTITUENT.

250 gm. air-dried sample (17.4% water) were treated with 91% alcohol in hot state, and the extract filtered from the insoluble matter was evaporated under reduced pressure and the residue heated in a steam bath to constant. This dried residue weighed 10.6 gm., which corresponded to 5.3% of the dried sample.

In another experiment, 150 gm. of the sample yielded 7 gm. resinous matter (5.6% the sample).

The resin thus obtained, was a brown amorphous substance, possessed an aromatic odour, yielding by potash fusion a phenolic compound and an acid of butyric acid odour, and the former showed bluish green coloration with ferric chloride and formed with bromine water yellow precipitate from its alcoholic solution.

The methoxy value was 0.84% measured by Zeisel's method, and the elementary composition of the resin was as follows :

C.	74.29 ;	73.72 ;	73.57	mean	73.81
H.	6.89 ;	6.60 ;	6.47	,,	6.65
Ash.	1.66 ;	1.56 ;	1.41	,,	1.54

The above mentioned analytical results of the isolated resin mass, calculated on an ash-free, dry basis, agree with those of the resinous constituents found in coal investigated by White¹.

2. CARBOHYDRATES.

A dried sample was heated with 1% HCl in a sealed-tube at 137–144° for 6 hours, and the acid-extract separated from the insoluble matter. The content of simple sugar was determined by means of Fehling's solution : it amounted to 5.1% of the sample, calculated as d-glucose.

Pentosans (furfurol yielding compounds) in the sample estimated by the Tollens and Kruger-method².

The phloroglucide, thus formed, was observed to be composed entirely of methyl furfurol phloroglucide, by the spectroscopic investigation of $N/10000$ alcoholic solution.

The cellulose-content and the preparation of a pure sample of cellulose from the fossil wood, were studied by the method first tried by Cross and Bevan and then modified by Renker.³ The purified sample was white in colour, contained no substance yielding methyl iodide by treating with hydrogen iodide solution, and gave the following results

¹ Bone: Coal and its scientific uses, 19.

² Z. angew. Chem. 40 (1896).

³ J. Soc., Chem. Ind., 28, 1269 (1910).

On the Chemistry of Japanese Plants, II. The Composition of Fossil Wood. 11

on analysis, taking it to be an ash-free, and dry substance.

$$C=44.01, \quad H=6.19, \quad \text{ash}=0.65.$$

(Theory required for $(C_6H_{10}O_5)_n$; $C=44.44$; $H=6.17$). It was also confirmed to consist of pure cellulose, yielding by acid hydrolysis d-glucose.

3. LIGNIN.

Its content in the sample was estimated by following Ost & Wilkennig and J. König¹. It was treated with 72% sulphuric acid and water, alcohol and ether successively, and the lignin-content was calculated from the loss of weight, taking the average of two experiments. The residue was analysed and the following results were obtained, the sample being taken as an ash-free, dry substance.

$$C=64.06; \quad 63.86; \quad H=5.52; \quad 5.54$$

$$\text{Ash}=0.5; \quad 0.9; \quad CH_3O=3.85$$

Lignin-content, on the other hand, in the sample, calculated indirectly from its methoxy value determined by the method of Benedikt and Bamberger² was 56.5% being 2.989 methoxy value. The methoxy value of the sample, the resinous matter having been removed by treating with alcohol, was 3.145 and consequently 59.43% was assigned for lignin-content.

The approximate analysis of the fossil wood calculated as ash-free, dried substance was as follows :-

	Water.	Ash.	Resin.	Methyl Pentosan.	Total Polysaccharide.	Lignin	Cellulose.	Total.
1.	17.18	0.994	6.09	1.87	5.44	56.50	30.07	—
2.	17.61	1.064	5.59	1.66	4.81	55.88	30.90	—
3,	—	—	5.98	—	—	—	28.30	—
Mean	17.40	1.03	5.88	1.77	5.13	56.19	29.36	96.57

On comparing the analytical results above mentioned with those

¹ Chem. Zeitung, 52. 461 (1910); Chem. u. Struktur d. Pflanzen-Zell., 1914,50.

² Monat Chem., 11. 260 (1890).

of red wood¹ (*Sequoia Sempervirens*) (A) and also of other coniferous woods (B) compiled from many analysis², disregarding the ash and water content, we have learned that in our plant by keeping under the ground, 20% cellulose, 4% other polysaccharides were destroyed, on the other hand 25% of lignin and 2% of resinous matter, were accumulated.

	(A)	(B)
Resin and fat	4.5	3
Lignin	30.2	30
Carbohydrate	8.6	10
Cellulose	52.0	50

The content of cellulose and other polysaccharides in a peat buried at 20-100 cm. below the surface, studied by H.V. Feiltzen and B. Tollens,³ being 15.20% and 12.75% respectively, shows fair agreement with our results, both fossil wood and peat being regarded as having the same relationship in the formation of coal, judging from their ultimate analysis.

Cellulose and other polysaccharides composed of plant cell-wall, and nitrogenous matter found in cell-sap are less resistant to attack of organisms and these compounds should be decomposed by organisms into methane, CO₂, water and other simple substances. On the contrary, resinous matter is most resistant to bacterial decay.⁴

This opinion harmonizes with the investigations by Katayama⁵ and others⁶ on the natural decay of pine and oak by organisms. Some of the carbohydrates and nitrogenous substances in wood were naturally destroyed in this way and the remainder would suffer incomplete oxidation or dehydration caused by pressure or heat under the earth crust, and consequently the compounds with open carbon chains which are

¹ W. H. Dore: J. Ind. Eng. Chem., **11**, 558 (1919).

² Cross and Bevan: p. 177; G. Scowalbe: p. 441; J. V. Wiesner, D. Rohstoffe Pflanzenreiches, **II**, 332 (1918).

³ Ber. D. Chem. Ges., **30**, 2571 (1897).

⁴ F. Tideswell, and R. V. Wheeler: J. Chem. Soc., **121**, 23 (1922); Clarke. p. 740. 763.

⁵ Kogyo Kwagaku Zashi, **17**, 611 (1914).

⁶ Cross and Bevan: 1910, 239.

On the Chemistry of Japanese Plants, II. The Composition of Fossil Wood. 13

permitted to maintain and manifest life in plants were transformed into substances of cyclic structure without nutritive value by losing these faculties¹.

Thus, all of the organic substances in plants their open carbon chains being closed within their molecule, forming carbon rings, enter their stabler state, or state of repose, their activity disappearing, and " la cyclisation est la mort "² is our working hypothesis in the present study.

Feb. 1923. Laboratory of Organic and Biochemistry.

¹ A. Pictet: La structure moléculaire et la vie, 1915. p. 10.

² A. Pictet. Loc. cit.