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Title	CARBONIZATION OF WOOD BY DEHYDRATING AGENT : Part IV. On the Properties of the Hydrated Active Charcoal (H-A Charcoal)
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Citation	北海道大學農學部 演習林研究報告, 19(1), 253-261
Issue Date	1958-03
Doc URL	<a href="https://hdl.handle.net/2115/20759">https://hdl.handle.net/2115/20759</a>
Type	departmental bulletin paper
File Information	19(1)_P253-261.pdf



# CARBONIZATION OF WOOD BY DEHYDRATING AGENT

Part IV.\*

On the Properties of the Hydrated Active  
Charcoal (H-A Charcoal)<sup>b)</sup>

By

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## Composition of hydrated active charcoal

Degree of carbonization (dehydration), percentage of losses of carbon during dehydration, content of sulphur (or SO<sub>2</sub>), and ash in the hydrated active charcoal were determined by the analysis of the elementary composition.

Samples used in this experiment were five charcoals, four of which were prepared from wood in the previous studies<sup>b)</sup>, namely, (1)1, (1)2, (1)3, (1)4, and one of them was made from pure saccharose, (A)c. The procedure of manufacture was as follows: 10 g of oven dried saw dust which was passed through 17-mesh sieve (or pure saccharose) were added to 50 g of 70 per cent sulphuric acid and stirred at 80° for one and a half hours on a water bath, then heated in an electric oven at 150° for 8 hours, washed with boiling distilled water. The results of manufacture are given in Table 1.

Table 1. Data on manufacture of hydrated active charcoal

Mark	Material (10 g)	Weight after carboni- zation (g)	% of evapo- rate during carboniza- tion (%)	pH of the last filtrate	Weight of wet product (g)	Moisture content (%)	Yield (dry product)	
							(g)	(%)
(1)1	"Todomatsu"	35.7	40.50	3.2	26.6	76.61	6.22	62.22
(1)2	"Yezomatsu"	41.3	31.37	4.0	26.5	77.33	6.01	60.08
(1)3	"Shina"	37.9	36.83	3.3	28.3	80.44	5.54	55.35
(1)4	"Nara"	38.5	35.83	4.4	27.7	78.51	5.95	59.58
(A)c	Saccharose	—	—	3.75	30.5	84.75	4.65	46.51

\* Part III was published in this Bulletin, Vol. XVIII, No. 1: 117 (1956).

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These samples were dried in the oven to absolute dryness, and analyzed by the micro-methods. The results are recorded in Table 2. The percentage of losses of carbon and degree of dehydration were calculated from the carbon content of the raw materials and the yield of the products. Content of  $\text{SO}_2$  was also obtained from the content of sulphur.

Table 2. Composition and percentage of loss of carbon and degree of dehydration

Mark	Material	In material		In hydrated active charcoal					Loss of Carbon (%)	Degree of Dehydration (%)
		C (%)	H (%)	Ash (%)	C (%)	H (%)	S (%)	$\text{SO}_2$ (%)		
(1) 1	"Todomatsu"	49.59	6.18	0.18	63.64	2.32	0.76	1.89	20.16	76.70
(1) 2	"Yezomatsu"	48.88	6.28	0.17	59.75	3.16	1.07	2.69	26.58	69.75
(1) 3	"Shina"	47.78	6.61	0.63	61.37	2.51	0.46	1.18	28.87	82.00
(1) 4	"Nara"	47.40	6.21	0.31	63.33	2.46	0.68	1.50	20.46	76.49
(A) c	Saccharose	42.10*	6.43*	—	65.73	3.60	1.92	4.92	27.10	74.23

\* Calc. for  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .

The carbon content of the hydrated active charcoals prepared from wood were 60–64 per cent (from the wood of "aotodomatsu" (fir), 63.82, "mizunara" (oak), 64.56 per cent, and 64.29 per cent from "sasa"). From these data it seems reasonable to state that in general the carbon contents of the hydrated active charcoals were about 63 per cent.

The carbon contents of the general charcoal manufactured by carbonization with thermal decomposition from wood are 91–95 per cent in "shirozumi"-charcoals, and 83–93 per cent in "kurozumi"-charcoals, while charcoals made by dry distillation have 70–90 per cent, and the general commercial active charcoal, 80–97 per cent of carbon content. Therefore, the hydrated active charcoal is a charcoal that has a low degree of carbonization with a small content of carbon. The rates of loss of carbon, which was removed as carbon dioxide or volatile and soluble matters during heating and washing, can be calculated as 20–30 per cent from the contents of carbon and the yield of the product. The quantity of the carbon lost from wood by dry-distillation is about 50 per cent at 400° (the yield of carbon is about 34 per cent), and by thermal decomposition about 50 per cent at temperatures over 600° ("shirozumi" and "kurozumi"). Compared with this differences, it may be said that the loss is much smaller in the carbonization by dehydration method than in

that by ordinary thermal decomposition methods. It is important to bear in mind this fact in the process of the dehydration reactions.

The content of hydrogen in the hydrated active charcoal was about 2.5 per cent which was almost equal to the content of the charcoal obtained by dry distillation. Therefore, the hydrated active charcoal may be said to have a low content of hydrogen even though its carbonization degree is low. The common charcoal has 1.5-3.4 per cent in "kurozumi" and in "shirozumi" 0.5-1.3 per cent of hydrogen which is removed at high temperatures over 600° in the thermal decomposition of wood, therefore in the charcoals carbonized at high temperature there is less hydrogen content than in those which are carbonized at low temperature.

The loss of hydrogen during carbonization with dehydrating agent, was calculated from the content of hydrogen and yield of charcoal. As shown in Table 2, about 70-80 per cent of hydrogen in the raw material was lost. If hydrogen was combined with oxygen as water ( $H_2O$ ) and drawn off, the percentage of loss of hydrogen may be equal to the percentage of dehydration. Hydrogen, however, may be lost not only as water but also in the form of other volatile or soluble decomposition products, the detailed study has not been achieved. Therefore, it is impossible to regard the percentage of loss of hydrogen directly as the percentage of dehydration, yet that percentage can be used as a standard for the carbonization by dehydration.

When wood is carbonized at 400°, about 80 per cent of hydrogen is lost, while about 90 and 95 per cent hydrogen are lost in case of "kurozumi"-charcoal and "shirozumi"-charcoal, respectively. In case of hydrated active charcoal the loss of hydrogen is as much as in the charcoal of dry distillation at 400°. However, from the ratio of carbon to hydrogen contents the loss of hydrogen of the hydrated active charcoal is higher than that of the charcoal made by dry distillation. As described below, the methoxyl groups that exist in wood were split off during the process of manufacture of the hydrated active charcoal, and also in the other decomposition products the carbon and hydrogen were changed into volatile and soluble matters.

The content of  $SO_3$  estimated by sulphur determination was about 1.2-2.7 per cent (average 1.52 per cent) in the hydrated active charcoal, while  $SO_3$  content in the charcoal from saccharose was as much as 4.92 per cent and nearly 5 per cent. It is very interesting to study what types of binding exist between  $SO_3$  and the charcoal constituents, and whether there is chemical combination or only mechanical adsorption.

The ash content of the hydrated active charcoal was about 0.2–0.6 per cent. This content is lower than that of general wood charcoals which are prepared by thermal decomposition. Ash contents are about 2.1, 1.8 and 1.3–1.4 per cent in “shirozumi”, “kurozumi” and dry distillation charcoal, respectively. Therefore it seems presumable that the ash in wood has been removed during the process of preparation.

According to the hydrated active charcoal made from filter paper by MIZUNO and KATO<sup>2)</sup> it was reported that the content of hydrogen and oxygen was 26 per cent as a ratio of H<sub>2</sub>O, and the SO<sub>3</sub> content was 3.0 per cent.

In the present experiment, the hydrated active charcoal made from saccharose had about 32 per cent of hydrogen and oxygen as H<sub>2</sub>O (oxygen content was calculated from the remainder of the contents of carbon, hydrogen, sulphur and ash); while in case of the hydrated active charcoal from wood, the content of hydrogen and oxygen did not exist in a ratio of H<sub>2</sub>O, but oxygen was contained more than the ratio of H<sub>2</sub>O (e.g. H:O = 1:1).

The empirical formula of the hydrated active charcoal made from saccharose was obtained from the percentage of carbon, hydrogen, oxygen and sulphur content as C<sub>90</sub>(H<sub>2</sub>O)<sub>30</sub>S. If the sulphur was quite omitted the contents of carbon, hydrogen and oxygen were assumed to be C<sub>8</sub>(H<sub>2</sub>O).

In order to compare the yields with the composition of the charcoals made under various conditions, the hydrated active charcoals were prepared from the wood of “shirakaba” (*Betula platyphylla*, birch) with sulphuric acids of 98, 70, 40, 15 and 1 per cent, at the temperatures of 120° and 150°, for the period of 8 hours, and the other conditions were the same as previously described<sup>1)</sup>. The yields of these charcoals are given in Table 3 and the results of analysis for carbon and hydrogen contents are recorded in Table 4.

Table 3. Yields of charcoals under various conditions

Temp.	Time	Concentration of H <sub>2</sub> SO <sub>4</sub>				
		98 %	70 %	40 %	15 %	1 %
120°	8 hrs	62.68%	57.63%	54.45%	57.80%	81.10%
150°	8 hrs	52.93	53.88	48.20	48.75	71.40

Table 4. C and H content of H-A charcoals under various conditions.

Temp.	Time		Concentration of H <sub>2</sub> SO <sub>4</sub>				
			98 %	70 %	40 %	15 %	1 %
120°	8 hrs	C	62.87%	66.00%	65.25%	59.64%	53.70%
		H	2.53	3.24	3.53	4.77	5.61
150°	8 hrs	C	63.59	63.30	—	64.06	55.75
		H	1.72	2.46	—	2.27	4.77

Raw material ("shirakaba" wood): C, 48.91%; H 6.34%.

From these results the losses of carbon and hydrogen were calculated as shown in the following Table 5.

Table 5. Losses of C and H during preparation

	Temp.	Time	Concentration of H <sub>2</sub> SO <sub>4</sub>				
			98 %	70 %	40 %	15 %	1 %
C	120°	8 hrs	19.41%	22.23%	29.40%	29.52%	10.96%
	150°	8 hrs	31.18	30.27	—	36.83	18.61
H	120°	8 hrs	74.59	70.59	69.21	55.83	27.09
	150°	8 hrs	85.41	78.76	—	82.47	45.42

The losses of carbon and hydrogen at 150° were much more than at 120° in each concentration of sulphuric acid. The order of loss of carbon by the concentration of acid at 120° was 15, 40, 70, 98, and 1 per cent, and loss of hydrogen was parallel to the concentration of acid. At 150° the order of loss of carbon was 15, 98, 70 and 1 per cent, and that of hydrogen was 98, 15, 70 and 1 per cent. It may be noteworthy that at the concentrations of 15 per cent and 40 per cent, the losses of carbon were much severer than at the concentration of 98 per cent, and these facts may have some significance in respect to the reaction. The charcoals that were made with low concentration had little adsorptive power.

#### Specific gravity of hydrated active charcoal

The specific gravity of the hydrated active charcoals which had been made from "todomatsu" (fir) and "nara" (oak) wood were about 1.6, the data are recorded in Table 6.

The method of determination was as follows: five or six grams of the sample were placed in a beaker, distilled water added and heated

on a wire gauze for 3 hours. After being allowed to stand 60 hours, this was decanted and the precipitated charcoal was well mixed, then transferred into 50 mℓ specific gravity measuring bottle and filled with distilled water. After being allowed to stand at 15° for 30 minutes, the bottle was fitted with stopper and the water overflowed was wiped off with a filter paper, then the water meniscus was lowered by dipping the bottle into cold water. The bottle was weighed after wiping well the outside of it (A). Then the charcoal in the bottle was filtered with a weighed filter paper, and weighed after being dried in the oven (B). The weight of the bottle containing only pure water was taken marked as (C). The specific gravity (S) is calculated from the following equation:

$$S = \frac{B}{C+B-A}$$

Table 6. Specific gravity of H-A charcoal

	Specific gravity		
	I	II	Average
"Todomatsu"-(fir)	1.573	1.580	1.577
"Mizunara"-(oak)	1.641	1.631	1.636

From these results the specific gravity of this charcoal is seen to be similar to that of "kurozumi"-charcoal of about 1.6 and this value is higher than that of dry distillation charcoal of about 1.4, and lower than that of "shirozumi"-charcoal of about 1.8. Therefore it may be said that this hydrated active charcoal has a high specific gravity even though it has a low degree of carbonization.

#### X-ray diagram of hydrated active charcoal

X-ray diagram (Fig. 1) of the hydrated active charcoal which had been made from "nara" wood was examined by DEBYE-SCHERRER's method. The conditions of photographing were as follows:

Cu K<sub>α</sub> ray, at 35 Kv., 10 mA. Time of exposure: 5 hours.

Radius of camera: 30.02 mm.

Sample was dried and well ground in an agate mortar, and affixed to a silk thread with collodion to about 1 mm thickness.

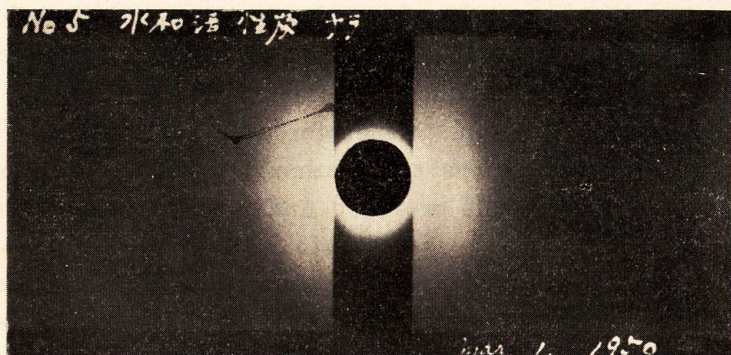


Fig.1. X-ray diagram of hydrated active charcoal

In this photograph, the exponent of face (002) appears, and (100) does not appear. According to this result it seems that the product of the carbonization by dehydration has little tendency to take a crystalline structure.

#### Methoxyl groups of hydrated active charcoals

The methoxyl group of wood is almost derived from lignin\*. For determination of lignin of wood, concentrated sulphuric acid is often used to hydrolyze the carbohydrate components and then the mixture is diluted with water and refluxed.

In common procedures of this lignin determination, 72 per cent sulphuric acid is used with the amount of 10~40 times the weight of extractive-free wood sample, stirring occasionally at room temperature for 4~16 hours, then diluting it with water to a concentration of 3 per cent acid and finally refluxing for 2~4 hours. In the treatment with concentrated sulphuric acid a part of the lignin was dissolved and again precipitated during refluxing, and the lignin was left behind as insoluble precipitates.

By this method of analysis sulphuric acid lignin is obtained. In the sulphuric acid lignin the methoxyl group is still left. However, the quantity of the methoxyl in isolated lignin is always smaller than that in the same wood because of the influence of the constituents of wood except lignin, and also of the fact that some methoxyl groups of the lignin may be lost in the isolation process.

Even at room temperature it seems that a part of the methoxyl

\* After M. H. O'DWYER, a part of the methoxyl groups in the wood is contained in hemicellulose. Chem. and Ind., 51, 968 (1932).

groups may be split away with the concentrated sulphuric acid. Since the conditions for preparation of the hydrated active charcoal are severer than those of lignin determination, there must occur splitting away of the methoxyl groups. Therefore, the authors have tried to determine in which conditions the methoxyl groups is left behind in the hydrated active charcoals prepared under various conditions.

“Shirakaba” (birch) wood was used for raw material, concentrations of sulphuric acid were 98, 70, 40, 15, 5, and 1 per cent, and the amount of acid was 5 times that of the material weight. Pretreated at 80° for an hour, then heated at 120° for 8, 14, and 24 hours and at 150° for 4 and 8 hours respectively. In order to detect the methoxyl, it was observed whether the precipitates of silver iodide were obtained by ZEISEL's method. The results are given in Table 7.

Table 7. Methoxyl group in H-A charcoal made under various conditions

Temp.	Time	Concentration of H <sub>2</sub> SO <sub>4</sub>					
		98 %	70 %	40 %	15 %	5 %	1 %
120°	8 hrs	—	+	+	+	+	+
	14 hrs	—	+	+	+	+	+
	24 hrs	—	+	+	+	+	+
150°	4 hrs	—	—	—	+	+	+
	8 hrs	—	—	—	+	+	+

The methoxyl group was split away when both the concentration of sulphuric acid and the temperature of dehydration were high. At 120° the methoxyl group was detected except the use of 98 per cent sulphuric acid, but at 150° it was split away already at the concentrations higher than 40 per cent in each time of heating.

### Summary

Some experiments were made on the chemical composition, specific gravity, X-ray diagram, and methoxyl groups of the hydrated active charcoals (H-A charcoals) which had been prepared from wood and saccharose.

The approximate content of carbon, hydrogen, sulphur, and ash of the H-A charcoal made from wood was as follows:

C: 63%, H: 2.5%, S: 0.5–1.1%, Ash: 0.2–0.6%,

and that from saccharose was as follows:

C: 66%, H: 3.6%, S: 1.9%.

From these figures, it may be said that the H-A charcoal has a lower degree of carbonization than the ordinary wood charcoal. But the H-A charcoal has a comparatively high specific gravity as about 1.6.

According to the result of studies by X-ray, it seems that the H-A charcoal has little tendency to take a crystalline structure.

Methoxyl groups of the wood were split away when it was treated with sulphuric acid of high concentration and high temperature in the preparation process of the H-A charcoal.

## 摘 要

木材および蔗糖を硫酸と加熱して脱水炭化して造つた水和活性炭について、化学組成、比重、X線解析、メトオキシル基の存否等を調べた結果、水和活性炭の炭素含有量は約63%であつて、白炭、黒炭、乾溜炭および市販の活性炭に較べて炭化度が低く、炭素の損失が少ない。水素含有量は約2.5%であつて、炭化度の低い割合に少なく、脱水によつて失われるほかに分解等によつて揮発性または可溶性の物質として失われるものと考えられる。硫黄含有量は木材から造つたものは約0.5~1.1%であるが、蔗糖から造つたものは約1.9%であつた。灰分含有量は約0.2~0.6%であつて、他の製法の木炭に比して低く、製造過程中に溶出されるものと考えられる。

蔗糖から造つた水和活性炭の実験式は大略  $C_{90}(H_2O)_{30}S$  に相当し、硫黄を除外して考えるとその組成は  $C_3(H_2O)$  に相当し、水素と酸素は  $H_2O$  の割合になつているが、木材から造つたものでは酸素が多く  $H_2O$  の割合になつていない。

また硫酸濃度と炭化温度を変えて造つたカバ材からの水和活性炭について、その収量、炭素および水素の含有量、損失量について少しく検討を試みた。

水和活性炭の比重は大体1.6程度であつて、炭化度の低い割合には大きい値を示している。

またX線解析の結果からみると水和活性炭は、はつきりした結晶構造を持つていない。

なお水和活性炭のメトオキシル基の存否について定性的の試験を行つた結果、加熱温度が120°の場合には硫酸濃度が70%以下、150°の場合には硫酸濃度が15%以下の場合に残存し、それ以上の硫酸濃度に於いては共に離脱することが認められた。

## Literature Cited

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