The Manufacture of Ion-exchange Substance from Wood Charcoal

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from Wood Charcoal[3],[4]

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Abstract

Since the operating conditions in an industrial practice are becoming more and more severe, the marked tendency to require both the higher resistance to attack by chemical reagents and the higher thermal stability for an ion-exchange substances are seen over a wide range of industrial applications. In order to serve the present purpose the ion-exchange substance from wood charcoal has been presented. This present investigation was undertaken to discuss the conditions of preparing the cation exchanger from charcoal by treating with sulfuric acid.

1. Introduction

In recent years, since the major chemical engineering use of ion-exchange operations is in a manner supplementary or complementary to other unit operations, operating conditions become more and more severe. Consequently a marked tendency to require the higher exchange capacity, the thermal stability and on the other hand being highly resistant to the action of chemical reagents, are seen over a wide range of applications. The present inorganic exchangers, in exchange capacity, the present resinous exchangers in both thermal stability and the resistance to the chemical reagents, are not always meet these reqirement.

This present investigation was undertaken to discuss the conditions of preparing the ion-exchange substance from charcoal and some properties of this product[1],[2].

2. The mauufacture of ion-exchange substance from wood charcoals by treatment with sulfuric acid

In order to elucidate the conditions of preparing the ion-exchange substance from charcoal, the crushed charcoal was sulfonated with conc. sulfuric acid at 100, 150 and 210°C, and the exchange capacity of the products have been measured. The results show that charcoals can be converted into cation exchangers by sulfonation. Sulfonic acid groups are introduced and additional carboxylic acid groups are formed by oxidation[3]~[5].

2-1 Properties of wood charcoal

The property of materials used is given in Table 1.

The experimental procedure of each item in Table 1 is as follows. A cylindrical piece of charcoal is divided into four parts at the center and a square of 1 cm³ is cut from a part as a test piece. Water content is estimated by drying

Table 1. The property of material used

Raw wood		Degree of carbonization	Apparent density a b	Water content %	Adsorbed water (in air) %	Adsorbed water (in water) %
Oak		bright color	1.21 0.65	2.52	1.42	7.76
Quercus glandulifera		"	0.88 0.49	10.45	11.34	40.21
" (Iwate)		black color	0.66 0.36	10.63	10.63	67.41
Sophora japonica	1	"	0.59 0.35	8.60	8.69	52.87
Quercus serrata	1	"	0.52 0.44	7.79	8.35	55.11
" glandulifera	1	"	0.46 0.36	10.53	10.46	109.98
Chestnut	1	"	0.40 0.24	9.65	10.63	32.50
White birch	1	"	0.38 0.22	9.54	9.62	103.16
Acacia	2	"	0.37 0.25	6.14	9.32	104.19
Oak	1	"	— 0.33	7.47	—	—
"	2	"	0.54 0.33	5.76	7.47	61.03
"	3	"	0.51 0.31	7.36	8.41	116.45
Bamboo	1	"	— 0.20	7.55	—	—
Bamboo grass	1	"	— 0.23	6.09	—	—
Maple (Acer)	1	"	— 0.32	8.03	—	—

this sample at 105°C until constant weight is reached. The amount of adsorbed moisture is measured by keeping this dried sample for 24 hours within a desiccator which is maintaining at relative humidity of 100%. The amount of adsorbed water is possible to estimate by immersing this dried sample in the water for 24 hours. The apparent density (a) for a square sample described above, the apparent density (b) for the granules of 10–20 mesh, are estimated respectively.

2-2 Experimental method

Place 10 g of the crushed charcoal and 40 ml of conc. H_2SO_4 in a 100 ml flask which is kept a constant temperature within a thermostat, while maintaining in this manner at a certain temperature (± 2°C) for a given hour. The carbon suspension should be kept throughly stirred while it is being reacted. Throughly wash the resulting product with the desalted water. Then this product is placed in a tube (15 by 250 mm) and a 0.1 per cent solution of NaOH may be introduced onto this carbon bed excessively. After the excess NaOH is washed from the bed, the large amount of 4% HCl solution may be passed through. Again wash the resulting exchange substance of H-type with the desalted water throughly until Cl ion in the supernatant liquid does not detect.

2-2-1 The salt-splitting capacity

The presence of the $-SO_3H$ group imparts the property to an exchanger of splitting a NaCl solution with formation of HCl. A measure of the amount of HCl formed by a given amount of exchanger would therefore be a measurement of its theoretical capacity and of the number of $-SO_3H$ groups.

About 5 g of the weighed sample is placed in a tube. The volume is

determined on the tube, approximately 400 ml of 4% NaCl solution is then introduced onto the bed and allowed to flow downward at a rate of SV 3-4. The effluent is collected and titrated with the 0.1N NaOH solution using methyl red- methylene blue mixed indicator. The exchanger is then regenrated with 4% HCl solution and the procedure repeated until the NaCl value checks. The salt-splitting capacity is calculated from the titer either on a weight basis or volume basis.

2-2-2 The total exchange capacity

A measure of the amount of NaOH consumed by a given amount of exchanger would be a measurement of its theoretical capacity and of the number of $-SO_3H$, $-COOH$ and $-OH$ groups.

Place 100 ml of 0.1N NaOH solution in a flask, add about 1.2 g of a weighed sample being tested. Stir it sometimes and allow it to stand for above 48 hours. Remove 20 ml of the supernatant liquid with a pipette and titrate with the 0.1N HCl using methyl red indicator. The total exchange capacity is calculated from the titer either on a weight basis or volume basis.

2-2-3 The weak-acid exchange capacity

It is calculated from the difference between the total exchange capacity and the salt-splitting capacity.

A) *Exchange capacity based on COOH group*

In addition to $-SO_3H$ groups, this cation exchanger have $-COOH$ and $-OH$ groups. Although these may not split NaCl, they will split a salt of a weaker acid. Exchange capacity based on $-COOH$ group is estimated on careful comparison for the following two methods.

A-1 *Acetate value by means of batch operation*

After the NaCl value of the exchanger has been determined, the excess NaCl may be washed from the carbon and dried. Place 100 ml of 0.5N $Ca(CH_3COO)_2$ in a flask and add about 0.5 g of a weighed sample being tested. Stir it sometimes and allow it to stand for 24 hours. Remove 20 ml of the supernatant liquid with a pipette and titrate with 0.1N NaOH using phenolphthalein indicator.

A-2 *Phosphate value by means of percolation operation*

After the NaCl value has beed determined, the excess NaCl may be washed with the desalted water and a 2 per cent solution of $Na_2HPO_4 \cdot 12H_2O$ introduced onto the bed at the rate of 1 drop per sec. The effluent is titrated in 50 ml portions to a phenolphthalein endpoint. The total volume of NaOH is used in determining the phosphate value.

$-COOH$ group of Amberlite IRC-50 and $-COOH$ group of the sample C are estimated by means of the two procedures respectively as given in Table 4. Since agreement between these quantities is reasonable, phosphate value by means of percolation operation is adopted in this experiments.

Table 2. Comparison of measuring procedure of exchange
capacity due to COOH group

Sample	Procedure	Liquor	Wt. (g)	Exchange capacity (meq/g)
C	Batch	$Ca(CH_3COO)_2$	0.5	2.3
	Percolation	Na_2HPO_4	3.0	2.18
Amberlite IRC–50	Batch	$Ca(CH_3COO)_2$	0.5	5.0
		Na_2HPO_4	0.5	4.8
	Percolation		3.0	5.0

B) *Exchange capacity based on OH group*

In addition to the NaCl and Na_2HPO_4 values, a third value may be obtained which is due to the weak phenolic hydroxyl group. For this procedure a measured volume of sodium phenolate is passed over the sample being tested and titrated with acid to a phenolphtalein end point. A blank is run on an equal volume of sodium phenolate and the difference in titration is used in determining the phenolate value. However, since this titration did not show the clear end point, place 80 m*l* of the filtrate in a beaker and titrated with 0.1N HCl using the procedure of the conductimetric titration.

2-3 Result and its consideration

2-3-1 Exchange capacity due to sorts of wood charcoal

The carbonized material is crushed to the range of 10–24 mesh and this granule is treated with conc. H_2SO_4 at 210°C for 3 hours. The results are shown in Table 3.

Table 3. Exchange capacity of exchanger produced from charcoal

Name of wood		Degree of carbonization	Salt splitting (meq/g)	Weak-acid (meq/g)	Total (meq/g)
Oak		Bright color	0.07	0.13	0.20
Quercus glandulifera		"	0.23	0.25	0.58
"	(Iwate)	Black color	0.75	1.55	2.30
Sophora japonica		1 "	0.76	1.55	2.31
Quercus serrata		1 "	0.55	1.53	2.08
Quercus glandulifera		1 "	0.96	1.62	2.58
Chestnut		1 "	0.58	1.74	2.32
White birch		1 "	0.85	1.46	2.31
Acacia		2 "	0.70	3.08	3.78
Oak		1 "	0.93	1.52	2.45
"		2 "	0.98	1.90	2.88
"		3 "	1.08	4.37	5.45
Bamboo		1 "	0.51	1.92	2.43
Bamboo grass		1 "	0.60	1.55	2.15
Maple (Acer)		1 "	0.78	1.91	2.69

Both the salt-splitting capacity and the weak acid exchange capacity are estimated to be the smaller value for the charcoal carbonized at the higher temperature, so-called white charcoals. Assuming that the degree of carbonization is the same, it is found that there is the difference of exchange capacity due to the sorts for the charcoal carbonized at the lower temperature, so-called black charcoals. Namely, relatively speaking the charcoal of bamboo, chestnut, quercus serrata and bamboo grass is inferior to that of quercus glandulifera and oak in exchange capacity. In general, provided that the degree of carbonization is the same, in proportion to the adsorbed amount of water, it may be sulfonated more easily. Significant effects of the degree of carbonization on the exchange capacity are noticed for the same sort of wood. For example, in a case of the charcoal of oak corresponding to the degree of carbonization 1, 2 and 3 that is shown in Table 3, in spite of the fact that the salt-splitting capacity is approximately the same, the weak acid exchange capacity is reversely proportional to the degree of carbonization. Treating the granule of the lower degree of carbonization with conc. H_2SO_4, the liquor becomes dark as tars. Therefore in practice, the degree of carbonization should be selected according to the purpose.

The size of the crystallites is influenced by the temperature of carbonization and, to some extent, by the composition and structure of the raw material. During pyrolysis, the original organic substance may be split into fragments which regroup to form the thermostable aromatic structure existing in the hexagon. It is also possible that suitable nuclei initiate a transformation in which the hexagonal lattice grows gradually at the expense of the original substance. The transformation is seldom complete and residual hydrocarbon chains and rings remain. The so-called white charcoal is the more thermostable and the less reactive crystallite. Accordingly the exchange capacity of resulting products is extremely low. On the basis of these data, it seem reasonable to assume that
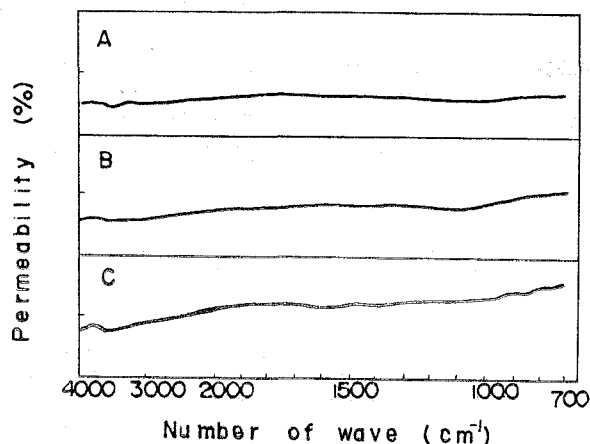

Fig. 1. Infrared absorption spectrum of charcoal
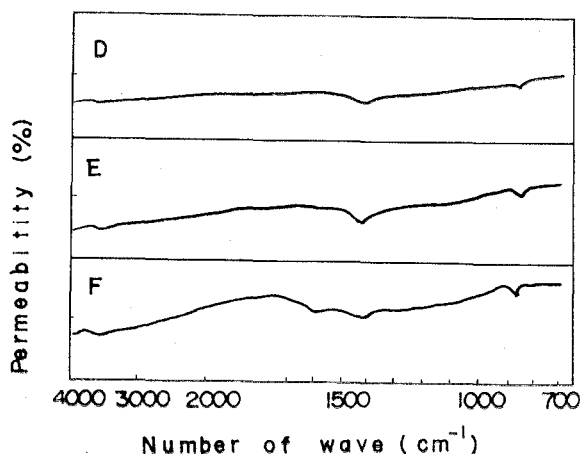A: Oak (white)   B: Bamboo   C: Maple

Fig. 2. Infrared absorption spectrum of charcoal
D: Oak (black-1) E: Oak (black-2) F: Oak (black-3)

the resulting aromatic hydrocarbons are sulfonated and residual hydrocarbon chains are oxidized. Qualitatively speaking, according to the infrared absorption spectrum of charcoal as given in Fig. 1 and 2, charcoals having the absorption spectrum near 7.3 and 11.75 μ that are supposed to show the structure described above are more reactive and these observations are in good agreement regarding to the degree of carbonization.

2-3-2 The size and the exchange capacity

Relation between the size and the exchange capacity is given in Table 4 for the charcoal of maple.

No significant effects of the size on the exchange capacity are noticed at the temperature of 100–150°C for the size above 24 mesh, however the effects being greater at the temperature of 210°C and at the size below 24 mesh.

Table 4. Effects of the size on the exchange capacity

Size (mesh)	Temperature (°C)	Time (hr)	Salt-splitting (meq/g)	Weak acid (meq/g)	Total (meq/g)
8~10	100	3	0.34	0.48	0.82
10~24	100	3	0.37	0.48	0.85
24~60	100	3	0.55	0.55	1.10
8~10	150	3	0.74	0.90	1.64
10~24	150	3	0.75	0.90	1.65
24~60	150	3	0.83	0.92	1.75
8~10	210	3	0.81	2.18	2.99
10~24	210	3	0.87	2.32	3.19
24~60	210	3	1.00	2.62	3.62

2-3-3 Effects of treating time and reaction temperature on the exchange capacity

Relations between the treating time and the exchange capacity at a given temperature (100, 150 and 210°C) using the glass tube of 2 cm in diameter are estimated respectively, as given in Fig 3. In this case, the crushed charcoal (maple) of 24–60 mesh is used.
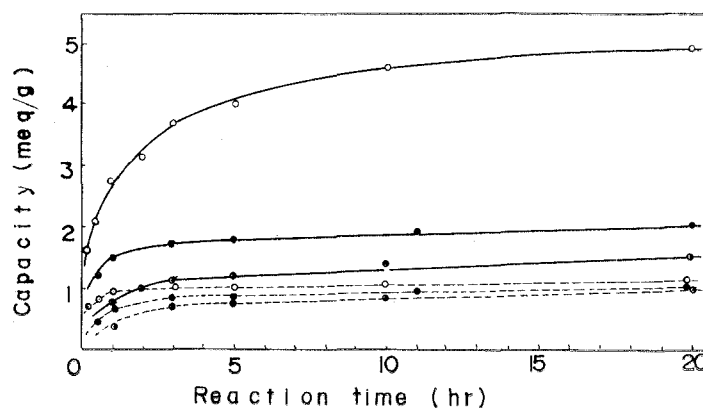

Fig. 3. Effects of reaction time on capacity
— : Overall capacity ···· : Salt-splitting capacity
○ : Reaction temp. 210°C ● : 150°C ◑ : 100°C

The salt-splitting value is reached a finite one (1 meq/g) after 2 hours at the temperature of 210°C. However the overall exchange capacity increases with the lapse of time. In another word, the sulfonation reaction is finished within several hours, however the oxidation reaction is progressed and weak
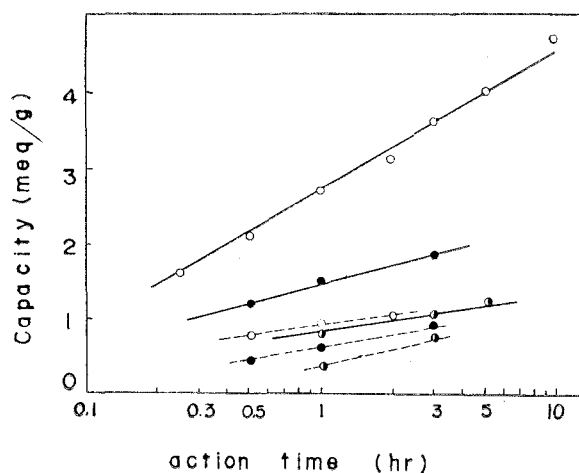

Fig. 4. Effects of reaction time on exchange capacity
— : Overall capacity ···· : Salt-splitting capacity
○ : Reaction temp. 210°C ● : 150°C ◑ : 100°C

acid groups increase with the lapse of time. The following equation is derived from the relations that are shown in Fig 4,

$$Q = k \log t + C$$

where Q: exchange capacity, t: reaction time, k and C: constant.

Relation between the reaction temperature and the exchange capacity is given in Fig 5. The reaction temperature is not significantly affected on the salt-splitting capacity within the range used in this experiment. However the weak acid capacity suddenly increase near 150°C.
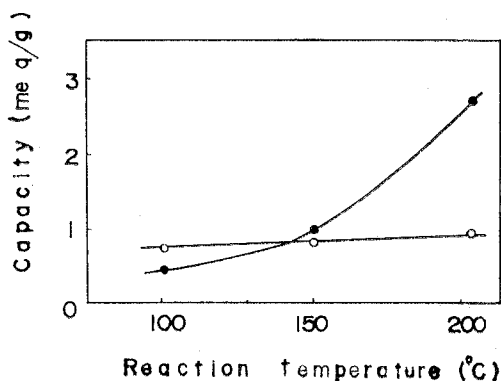

Fig. 5. Effects of reaction temperature on exchange capacity
Reaction time 3 hr
● : Weak acid capacity
○ : Salt-splitting capacity

3. Conclusion

In order to eluciate the conditions of preparing the ion-exchange substance from charcoal, the crushed charcoal was sulfonated with concentrated sulfuric acid at 100, 150 and 210°C, and the exchange capacity of the products have been measured. The results show that charcoals can be converted into cation exchangers by sulfonation. Sulfonic acid groups are introduced and additional carboxylic acid groups are formed by oxidation.

It was confirmed that carboxyl group content of the solid product increased along with the decrease in the degree of wood carbonization, but the sulfonic acid group content increased little. Under these conditions, the salt-splitting capacity reached a certain constant value within several hours, but weak acid exchange capacity increased as the reaction time and temperature increased, where the effect of temperature being particularly large.

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