PREPARATION OF PULP WASTE BASED ADSORBENTS AND THEIR PROPERTIES

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Introduction

Black liquor is produced as a by-product from the kraft process when digesting wood into paper pulp removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers with sodium-based alkali compounds such as sodium hydroxide and sodium sulfide.[1] Dry base black liquor contains ca. 35% of alkali compounds and 65% of lignin-based organics. Most pulp mills have used black liquor as an energy source by burning in recovery boilers. In this paper taking note of sodium compounds having a role of chemical activation agent, carbonaceous adsorbents were prepared from black liquor by simple heat treatment process. Black liquor was dried and solid black liquor was chemically activated by heat treated in inert atmosphere with including activation agents of sodium compounds. The pore properties of prepared adsorbents were evaluated with isothermal nitrogen adsorption and relationship between preparation conditions and pore properties was also considered.

Experimental

The precursor black liquor was obtained from Murim P&P which is the only pulp production company in Korea. The pristine black liquor was dried in 120°C and about 45% solid residue remained. Solid residue was reduced to 5~10mm granules and dried granules were further heat treated at 700~900°C in inert atmosphere. After heat treatment, residues were washed with purified water to remove sodium components and dried.

The surface areas and pore properties of obtained adsorbents were analyzed with BET method, t-plot method and BJH(Barrett-Joyner-Halendar) method by N_2 adsorption and desorption at 77K with physisorption analyzer (Micromeritics, ASAP2020).

Results and Discussion

The composition of black liquor is shown in Table 1 and the surface and pore properties of prepared carbonaceous adsorbents with respect to heat treatment conditions are shown in Table 2. The yield from organic portion of solid black liquor to chemical agent removed adsorbent ranged in 10~20wt.% and became reduced with BET surface area increased. The surface areas ranged between 718~1591m^2/g due to chemical activation mechanism with Na_2CO_3 and Na_2SO_4 components and heat treatment in inert atmosphere.

Normally the ideal chemical activation mechanism does not involve carbon loss because sodium atoms are intercalated into carbon lattice and expanded lattice can be worked as pore, but in this activation process pore could be formed with this chemical activation and also formed by carbon burn-out of CO or CO_2 generation with 35% of oxygen containing in black liquor.

Table 1. Components of Black Liquor

Components			wt.%
Main Components	Inorganic (35%)	Na_2CO_3	60-75
		Na_2SO_4	25-35
		Other	Little
	Organic (65%)	Lignin	65-70
		Others	30-35
Elemental Analysis		Na	19.7
		C	33.7
		H	3.6
		S	1.5
		O	35.0
		K	1.4
		Cl	4.8
		N	0.3

Table 2. Preparation Result of Black Liquor-based Adsorbents with respect to Heat-treatment Conditions.

Heat-treatment condition	Yield (%)	BET surface area (m^2/g)	External area (m^2/g)	Micropore area (m^2/g)
700°C - 10min	20.2	718	2 (0.3%)	716
700°C - 30min	20.0	910	3 (0.3%)	907
750°C - 10min	16.6	778	8 (1.0%)	770
750°C - 30min	19.8	944	1 (0.1%)	943
800°C - 10min	17.9	808	9 (1.1%)	799
800°C - 30min	16.9	861	15 (1.7%)	846
800°C - 50min	16.0	1394	45 (3.2%)	1349
850°C - 10min	14.5	1216	25 (2.1%)	1191
850°C - 20min	14.2	1282	54 (4.2%)	1228
850°C - 30min	15.2	1306	57 (4.4%)	1249
850°C - 40min	13.7	1311	56 (4.3%)	1255
850°C - 50min	13.6	1591	100 (6.3%)	1491
900°C - 10min	12.2	1373	88(6.4%)	1285
900°C - 20min	10.4	1279	132(10.3%)	1147
900°C - 30min	10.1	1111	113(10.2%)	998

The changes of surface area with respect to heat treatment temperature and time are displayed in Fig.1. In this figure increasing heat treatment temperature and time, BET surface area increased until 850°C but when temperature exceeds 900°C surface area decreasing with heat treatment time. This result is assumed that activation temperature becomes higher, pore size expands or several pores unify into single mesopore and as the result surface area per weight reduces.

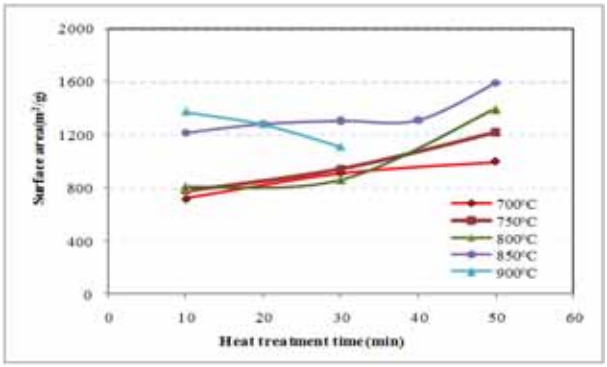
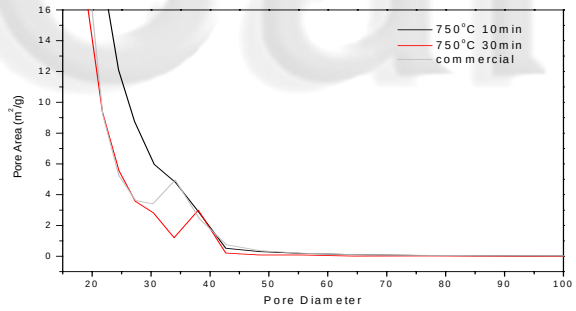


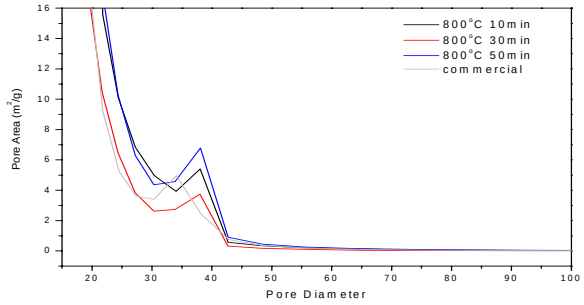
Fig. 1 Surface areas of black liquor based adsorbents with respect to heat treatment temperature and time

Fig.2 shows pore size distributions analyzed by BJH plot from N_2 desorption isotherms of black liquor based adsorbents. The mesopore areas ranged between 2~5nm in diameter increased with increasing heat treatment temperature and time. This result is well coincide with result of surface area in Fig.1.

Fig.3 shows morphologies of 700°C and 900°C activated adsorbents by observing scanning electron microscope.



(a)



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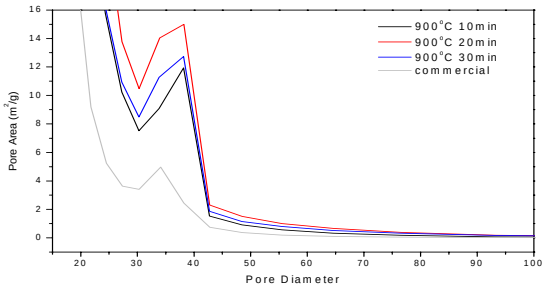
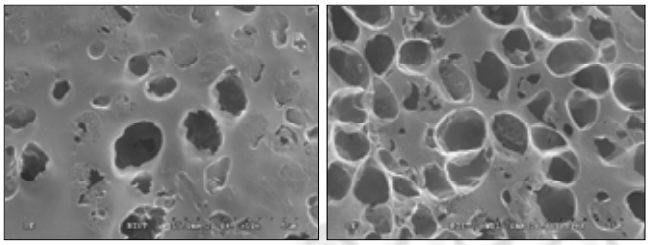


(c)

Fig. 2 Pore size distributions of black liquor based adsorbents. (a) 700°C activated, (b) 800°C activated, (c) 900°C activated



(a) (b)

Fig. 3 Morphology of black liquor based adsorbents.(a) 700°C activated, (b) 900°C activated

Conclusions

The carbonaceous adsorbents were prepared from black liquor of kraft process by-product. Black liquor was chemically activated by heat treatment in inert atmosphere with chemical activation agents of including sodium based components and they have high surface area until 1591m^2/g. Pore size distributions of black liquor based adsorbents mainly consist of micropores based on chemical activation mechanism of lattice expansion. But when heat treatment temperature exceeded 900°C pore size expanded and several pores unified into single mesopore and as the result mesopores were developed and surface areas per weight decreased.

References

[1] Stenius, Per, ed (2000). "2". Forest Products Chemistry. Papermaking Science and Technology. 3. Helsinki, Finland: Fapet OY. pp. 62–78. ISBN 952-5216-03-9.