# PROPERTIES OF ACTIVATED CARBON PREPARED FROM BARLEY HUSK OF BEER PROCESS RESIDUE

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## Introduction

Barley husk of beer brewing byproduct is called as brewer's spent grain. It consists of the residue of malt and barley grain which remains in the mash kettle after the mashing and lautering process. In detail it consists of barley husks, pericarp and fragments of endosperm [1]. The utilization of brewer's grain is raw material of low grade animal food and making compost. The dry base brewer's grain consists of about 43% of carbon and 3% of ash component. The brewer's grain have about 3wt.% of low ash content and have advantage in preparing adsorbent with high specific surface area comparing with high ash containing rice husk.

In this paper adsorbents were prepared from brewer's grain by carbonization and physical activation in steam atmosphere. 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 raw brewer's grains emitted from beer brewing process of Cass Beer in Korea have about 70% of water content. It was dried at 120°C and 30% of raw grain in weight was remained. The dried grain was carbonized at 700°C in 30 minute and activated at 700~900°C in steam atmosphere. Saturated steam was supplied with 2.04cm/sec of linear velocity against specimen under standard condition base and it is calculated into 8.01cm/sec under 800°C atmosphere base.

Supplied steam concentration had optimized in the previous test that the minimum steam amount was determined of no additional surface area increase with additional steam supplied. The surface area and pore properties of obtained adsorbents were analyzed with BET method, t-plot method and BJH method by $N_2$ adsorption at 77K with physisorption analyzer (Micromeritics, ASAP2020).

## Results and Discussion

To determine carbonization condition dried brewer's grain was analyzed with thermogravimetric and differential thermal analysis and result is shown in Fig.1. Thermal decomposition actively occured at 200~600°C and about 38~40% of carbonized residue remained until 700°C heat treatment. By this result brewer's grain was carbonized at 700°C in $N_2$ atmosphere and 51% residue remained. 11~13% difference comes from sample amount difference between 10mg(TGA) and 100g(Carbonization). When sample amount becomes larger, relatively larger amount of tar decomposed from grain also can be carbonized and remains as additional carbon residue.

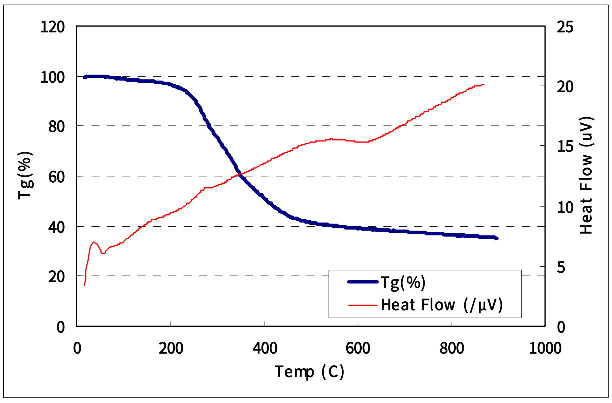



**Fig. 1** TGA-DTA curves of dried brewer's grain (5°C/min, Ar atmosphere)

**Table 1. Preparation Result of Brewer's Grain-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-30min | 94.3 | 153 | 6 (3.9%) | 147 |
| 750°C-30min | 58.5 | 387 | 2 (0.5%) | 385 |
| 750°C-60min | 77.0 | 456 | 9 (2.0%) | 447 |
| 750°C-90min | 76.1 | 608 | 14 (2.3%) | 594 |
| 800°C-30min | 63.2 | 554 | 20 (3.6%) | 534 |
| 800°C-60min | 54.3 | 1032 | 112 (10.9%) | 920 |
| 800°C-90min | 44.8 | 870 | 158 (18.2%) | 712 |
| 850°C-30min | 48.2 | 872 | 99 (11.4%) | 773 |
| 850°C-60min | 26.3 | 1408 | 482 (34.2%) | 926 |
| 900°C-30min | 22.5 | 700 | 289 (41.3%) | 411 |
| 900°C-60min | 28.1 | 931 | 293 (31.5%) | 638 |

The surface and pore properties of prepared carbonaceous adsorbents with respect to heat treatment conditions are shown in Table 1. The surface area of prepared adsorbents from brewer's grain ranged in 153~1408 $m^2$/g and yield from carbonized grain to activated adsorbents ranged in 18~84% in weight. The external surface areas of adsorbents were relatively high until 41.3%, especially adsorbents activated at high temperature, comparing with commercial coconut based activated carbons. Changes of mesopore area with respect to activation conditions are shown in Fig.2. This is assumed that the original structure of barley husk contains many capillaries and after the carbonization this structure basically maintains during activation. And when carbonized grains were activated at higher temperature pore size expands or several pores unify into single mesopore forms. Generally pore size distribution of adsorbent activated by physical activation in steam depends upon microstructure of raw material, it is assumed that microstructure of brewer's grain can be relatively easily formed mesopore than coconut shell can. These are expected good performance when they apply for liquid phase adsorption process.

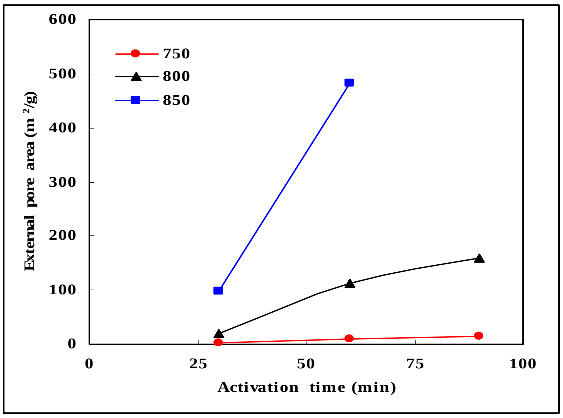
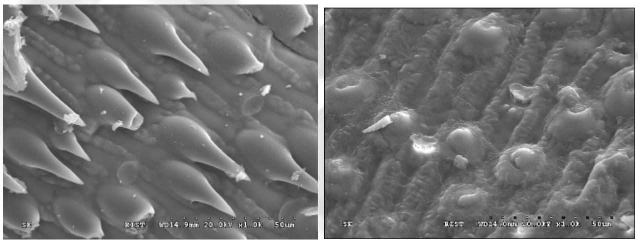



**Fig.2** Changes of mesopore area with respect to activation conditions.



(a) carbonized brewer's grain

(b) activated brewer's grain

**Fig.3** Morphology of brewer's grain based adsorbents

Fig.3 shows scanning electron microscopy morphology of brewer's grain based adsorbents and can be found microstructure of original barley husk could be maintained until activation process finished.

Fig.4 and Fig.5 show adsorption isotherm and pore size distributions analyzed by BJH(Barrett-Joyner-Halendar) plot from $N_2$ desorption isotherm of adsorbents. Isotherms in Fig.4 of adsorbents show mainly type-1 porous material with having micropores but desorption isotherms show hysteresis based on mesopore such as ink bottle shape. This result is well coincide with result of pore size distribution displayed in Fig.5.

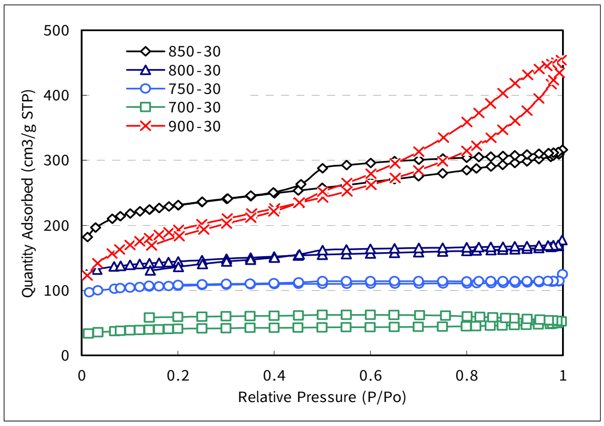



**Fig.4** Adsorption isotherms of adsorbents with respect to activation conditions

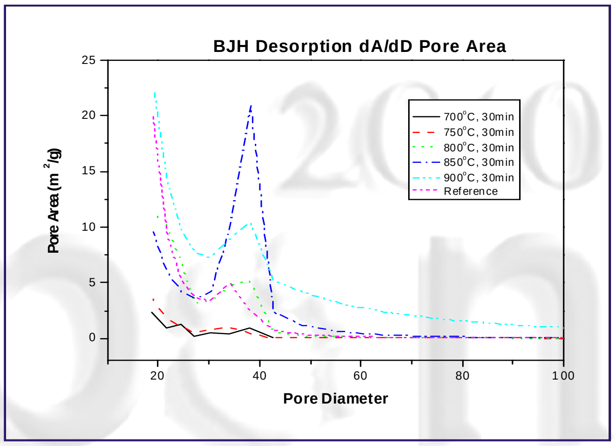



**Fig.5** Pore size distributions of adsorbents with respect to activation conditions

## Conclusions

Adsorbents were prepared from brewer's grain of beer production process waste. It was carbonized at 700°C in $N_2$ atmosphere and activated by further activation at 700~900°C in steam atmosphere. The specific surface areas of prepared adsorbents were ranged in 153~1408m$^2$/g. The barley husk have low ash content of about 3wt.% and have advantage in preparing adsorbent with high specific surface area comparing with high ash content of rice husk.

The microstructure of brewer's grain can be easily formed mesopore relatively than coconut shell and prepared adsorbents are expected good performance when they apply for liquid phase adsorption process.

## References


[1] G. Beldman, J. Hennekam, A. G. J. Voragen (18 Feb 2004). Enzymatic hydrolysis of beer brewers' spent grain and the influence of pretreatments. 30. Biotechnology and Bioengineering. pp. 668-671. Retrieved 21 March 2010.