Utilization of beer lees waste for the production of activated carbons: The influence of protein fractions on the activation reaction and surface properties

Hiroyuki Wakizaka a, Hajime Miyake a, Yutaka Kawahara b,c,⁎

a North Eastern Industrial Research Center of Shiga Prefecture, 27-39 Misayamatomachi, Nagahama, Shiga 526-0024, Japan
b Division of Environmental Engineering Science, Gunma University, 1-5-1, Tenjin-cho, Kiryu 376-8510, Japan
c The Center for Fiber & Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

ARTICLE INFO

Article history:
Received 17 November 2015
Received in revised form 18 February 2016
Accepted 23 March 2016
Available online 31 March 2016

Keywords:
Beer lees
Carbonization
Activated carbon

ABSTRACT

Activated carbons (ACs) were produced by carbonizing and activating beer lees waste, and the influence of protein fractions on the activation reaction order and surface properties of the resultant ACs was investigated. In the untreated control sample, the activation reaction could be regarded as first order. Conversely, the reaction system changed to zero order when the protein fractions were reduced by treatment with an alkali. In addition, the AC produced from the beer lees with reduced protein fractions showed a BET surface area of 1390 m²/g, which was approximately 1.4 times greater than that of AC from the untreated control beer lees. The tar fractions obtained from proteins in beer lees through dry-distillation at 280 °C or below were transformed into charcoals with somewhat densely packed carbon layers. This appeared to make the charcoal less reactive to CO₂ and limited the adsorption capacity of the resultant AC.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Activated carbon (AC) is utilized in various industrial fields. Global demand for AC was 650,000 metric tons in 2007 and has increased 5% annually through 2015 [1].

Pitch and coke, the heavy fractions of petroleum and coal, respectively, are the two major starting materials used in AC production. Their carbonization behavior and resulting carbon properties have been extensively studied. However, these carbon resources are not sustainable because of their limited reserves and the rising price of oil. Moreover, these materials are hazardous from the viewpoint of pollution via heavy metal contamination or particulate matter generation [2–4].

Woody biomass rich in cellulosic compounds is often used as a starting material, particularly in the production of AC destined for drinking water control systems. Coconut shells are one of the most promising materials for this purpose and have been used worldwide. However, due to the limited availability of coconut shells, there is an incentive to find sustainable alternative resources for manufacturing AC.

As an alternative to traditional feedstock materials (fossil fuels, coconut shells), we have previously proposed alternative materials such as coffee lees [5], triacetylcellulose waste [6], and oak woods [7] to produce AC.

To establish the mass production of AC from biomass, it is important to secure resources from the viewpoint of supply chain costs. In the case of woody biomass, it can be difficult to secure a consistent supply of waste wood chips from lumber mills because these facilities are typically scattered throughout mountainous areas, thus raising transportation and agglomeration costs. In contrast, the beer industry already has an established transportation network in place, thus assuring a consistent supply of beer lees waste without incurring extra costs for transportation and agglomeration.

As for the waste management of beer lees waste, the anaerobic (oxygen-free) digestion process producing biogas energy and manure for agricultural use is applicable [8]. Another potential application for beer lees wastes their compounds as nutritional supplements for industrial fermentation processes [9]. From the viewpoint of potential AC manufacturing resources, beer lees waste is promising due to its composition; beer lees are primarily composed of malt husks, which contain 16.8–25.4% cellulose, 21.8–28.4% hemicellulose, 11.9–27.8% lignin, 3.4–4.6% ash and 15.2–24.2% proteins [10]. Beer lees are rich in cellulosic compounds that can be transformed into carbon through a polycondensation reaction. Unlike woody biomass, however, beer lees contain protein fractions, which may modify the obtained carbon structure and then will limit the adsorption capacity of AC [11]. Therefore, it is important to clarify the carbonization behavior of the protein...
fractions to ensure an effective reaction with activation gases and create porous structures with significant adsorption capacity.

This study focused on two types of protein-based carbons: one from the tar fractions obtained by the dry-distillation of beer lees at 280 °C or below and the other from glutein, which is a major component of the protein fractions in beer lees. The potential of beer lees waste as a starting material for the production of AC was examined.

2. Experimental

2.1. Materials

Beer lees waste (hereafter denoted as BW) was supplied by the Shiga works of the Kirin Brewery Co., Ltd. (Tokyo, Japan). Protein fractions in the beer lees were reduced by boiling in an aqueous solution of 2.5 wt.% NaOH for 30 min. After this treatment, the sample was filtered off, neutralized, rinsed thoroughly with distilled water, and air-dried. Then, the beer lees sample with reduced protein fractions was obtained (hereafter denoted as L-BW). The gases derived from the dry-distillation of the beer lees at 280 °C or below, corresponding to the early stage of thermal decomposition of the beer lees, were condensed into tar (hereafter denoted as BW-Tar). Laboratory-grade glutein from the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) was used without further purification.

2.2. Laboratory-scale carbonization and activation

To implement carbonization, the sample was heated using an electronic furnace (FUR-122, Advantec, Tokyo) to 800 °C at a heating rate of 10 °C/min, kept at 800 °C for 15 min, and allowed to cool to room temperature under N2 gas flowing at 1 L/min. The yield of charcoal, Yc (%), was defined as the relative mass of charcoal, Mc, against the mass of the starting sample, M0, and was calculated using the following equation:

\[ Y_c = \frac{M_c}{M_0} \times 100. \] (1)

To engage activation, 0.5 g of charcoal was initially heated using an electronic furnace (FUR-122, Advantec, Tokyo) to 950 °C at a heating rate of 10 °C/min under N2 gas flowing at 1 L/min; then the gas was changed to CO2. The activation lasted for 30 min. The yield of AC, Ya (%), was defined as the relative mass of AC, Wa, against the mass of the starting sample, W0, and was calculated using the following equation:

\[ Y_a = \frac{W_a}{W_0} \times 100. \] (2)

2.3. Measurements

The BW-Tar showed stickiness at room temperature while other samples were solid. Thus the viscosity of BW-Tar was measured by applying a shear rate of 10 S\(^{-1}\) at room temperature using a rheometer (AR-1000, TA Instrument, New Castle, US).

A thermogravimetric analysis (TG) was performed using a TGA8120 (Rigaku Co., Akishima, Japan) on a 10-mg sample at a heating rate of 10 °C/min until reaching 800 °C under N2 gas flowing at 50 mL/min. TG measurements were also made on charcoal samples to estimate their activation reaction kinetics against CO2. The charcoal sample was heated to 950 °C under N2 gas flowing, kept at 950 °C, and then the TG curve was recorded under CO2 gas flowing at 20 mL/min.

The elemental compositions of C, H and N were measured using an organic elemental analyzer (MT-6, Yanako Bunseki Kogyou Co, Tokyo, Japan).

Fourier transformation infrared (FT-IR) spectra were obtained by means of a spectrophotometer (FTIR-8300, Shimadzu Co., Kyoto, Japan). The pyrolytic product originating from BW-Tar was measured using a pyrolytic gas chromatograph equipped with a mass analyzer (GC/MS QP-5050 A, Shimadzu Co., Kyoto, Japan). Pyrolytic gases from a sample thermally decomposed at 550 °C were separated by heating the column (diameter, 0.25 mm; thickness, 0.25 μm; length, 30 m) at 15 °C/min from 50 to 300 °C; the column was then kept at 300 °C for 5 min. The pyrolytic gases were analyzed while heating the column at 230 °C.

The N2 gas adsorption capacity was determined using an adsorption measurement instrument (AUTOSORB-I-C/VP, Yuasa-Ionics Co., Osaka, Japan). The surface area (S, m\(^2\)/g) was determined using the Brunauer-Emmett-Teller (BET) plot [12]. The volume (V, mL/g) was determined from the amount of N2 adsorbed at a relative pressure of 0.99. The mean pore diameter (D, nm) was calculated by assuming that the pores were uniformly nonintersecting cylindrical capillaries by using the following equation:

\[ D = \frac{4000V}{S}. \] (3)

3. Results and discussion

The tar (BW-Tar) obtained by the dry-distillation of BW was liquid at room temperature and showed a viscosity of 5.7 Pa·s. The FT-IR spectra for BW-Tar are shown in Fig. 1. A broad peak with two shoulders in the range of 3200 to 3400 cm\(^{-1}\) and sharp peaks at 2800–3000 cm\(^{-1}\) can be assigned to O–H stretching and C–H stretching, respectively. The peaks at 1650, 1230 cm\(^{-1}\), and the shoulder at 1540 cm\(^{-1}\) represent the spectra of amide I (C = O stretching), amide III, and amide II (combination of C–N stretching and N–H bending), respectively, which suggests that BW-Tar was fairly rich in protein derivatives.

The GC/MS spectra for BW-Tar and the chemical structures of the compounds corresponding to the numbered peaks in the GC/MS chart are shown in Fig. 2. The phenolic compounds are likely derived from tyrosine (Tyr) residues in the protein fractions [13–15]. Phenolic compounds can also be obtained from the lignin fractions in the beer lees waste (BW) through thermal decomposition [10]. However, the thermal decomposition of lignin fractions normally occurs above 300 °C [16]. BW-Tar in this study were prepared by the dry-distillation of BW at 280 °C or below. Thus, it is likely that the phenolic compounds in Fig. 2 were derived from Tyr residues in the protein fractions. However, the indole derivatives in Fig. 2 were likely to be isolated from pyrolysis products (Trp), which is not contained in glutein, a major component of the protein fractions [13–15]. Therefore, the indole derivatives were obtained from the protein fractions of BW exclusive of glutein. The protein content was measured at approximately 30–40% of the total protein fractions in BW [13–15].

TG measurements were made on BW, L-BW, BW-Tar, and glutein (see Fig. 3). The thermal decomposition of BW began abruptly when the temperature exceeded 250 °C. However, the thermal decomposition temperature of L-BW was approximately 30 °C higher. The reduction of protein fractions effectively raised the thermal decomposition
temperature of the beer lees waste to the level of woody biomass [17]. However, the TG curve of the glutein almost overlapped with that of BW, whereas the glutein increased the charcoal yield by approximately 5%. It appears that the thermal decomposition of cellulosic compounds in the beer lees was initiated by the thermolysis heat of the glutein. When the TG curves are compared between BW-Tar and glutein, it can be seen that BW-Tar was virtually vaporized and/or decomposed before the glutein began to decompose due to the dry-distillation treatment used in preparing the tar sample. The elemental composition data for the charcoals produced at 800 °C are summarized in Table 1. In examining the difference in N content derived from the protein fractions of starting sample, it can be seen that alkali rinsing reduced the protein content of beer lees to less than half of its initial level (compare BW and L-BW in Table 1). As for BW-Tar and glutein, N contents were within a similar range of approximately 10%, even though the respective TG curves were quite different (see Fig. 3).

The TG curves for various charcoal samples activated at 950 °C under CO2 gas flow are shown in Fig. 4. The activation reaction with CO2 can be expressed as follows:

\[ C + CO_2 \rightarrow 2CO_\text{fl} \]  

(4)

When the TG curves are compared between BW-based charcoal and L-BW-based one, the former curve decreased exponentially, whereas the latter decreased almost proportionally and rapidly with increased activation time. The apparent reaction rate can be expressed by the following equations [18,19]:

\[ -\frac{dW}{dt} = K \]  

(5)

\[ -\frac{dW}{dt} = K'W \]  

(6)

where \( W \) is the mass of the charcoal, \( t \) is the activation time, and \( K \) or \( K' \) is the reaction rate constant.

When the activation reactions are classified using these equations, the BW-based charcoal, which showed a somewhat exponential decrease in the TG curve, follows Eq. (6); the L-BW-based charcoal, which showed a monotonic decrease, follows Eq. (5). Accordingly, the former can be classified as a first-order reaction and the latter a zero-order reaction. As for the charcoal sample from BW-Tar, the TG curve decreased exponentially and slowly, indicating a lower reactivity to CO2 and a first-order reaction. Conversely, the TG curve of glutein-based charcoal decreased almost as rapidly as the charcoal from L-BW fractions, indicating a zero-order reaction. At the same reaction order, the larger the reaction constant becomes, the faster the activation reaction proceeds. In a case of AC production, a zero-order reaction means that a number of activation reaction sites are kept constant throughout an activation process, while a first-order reaction means a decrease in a number of reaction sites as activation proceeds [19]. The reaction order and constant calculated from each TG curve in Fig. 4 are summarized in Table 2.

It is well known that the composition of the starting material and the chemical structure of each component affect the carbon structure. A carbonaceous material with a significant graphitization degree (P1) tends to transform into a charcoal with a graphite-like structure [20–23]. P1 is defined as the probability of finding a carbon layer pair that achieves a graphitic ordering in a solid state [21]. In the case of pure graphite, P1 equals one. Such a densely packed graphite-like structure, however, is not suitable for the production of AC because the diffusion of activation gases such as water vapor or CO2 into carbonaceous materials is inhibited, and the AC will display limited adsorption capacity. As for chemical compositions, BW-Tar was rich in aromatic compounds (see Fig. 2). Moreover, BW-Tar contained Trp, which demonstrates good graphitizing ability [24]. Therefore, BW-Tar could form more densely packed carbon structures that are less reactive with CO2.

The surface properties of the ACs are listed in Table 2. The yield of AC was greatest for BW-Tar-based charcoal due to its peculiar densely packed structure, which also suppressed the development of the BET surface area. The BET surface area of AC obtained from BW-Tar-based charcoal was no more than 334 m2/g, which is much smaller than the value of commercial AC [7]. It also can be seen that the reduction of protein fractions was effective in modifying the beer lees waste to a starting material suitable for AC production, with BET surface areas exceeding
In addition, the AC produced from L-BW-based charcoal showed a first order. Conversely, the reaction system was changed to zero order when the protein fractions were reduced through treatment with an alkali. In addition, the AC produced from L-BW-based charcoal showed a BET surface area of 1390 m²/g, which was approximately 1.4 times greater than that of AC from BW-based charcoal. On the other hand, BW-Tar sample was transformed into charcoals with somewhat densely packed carbon layers, which appeared to make the charcoal less reactive to CO₂ and limited the adsorption capacity of the resultant AC.

Table 2
Surface properties of ACs activated in CO₂ at 950 °C for 30 min.

<table>
<thead>
<tr>
<th>Starting sample</th>
<th>Reaction Order</th>
<th>Rate constant (s⁻¹)</th>
<th>Yield (%)</th>
<th>BET area (m²/g)</th>
<th>Pore volume (mL/g)</th>
<th>Mean pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW</td>
<td>1</td>
<td>0.00011</td>
<td>40.4</td>
<td>972</td>
<td>0.77</td>
<td>3.18</td>
</tr>
<tr>
<td>L-BW</td>
<td>0</td>
<td>0.00004</td>
<td>42.0</td>
<td>1390</td>
<td>0.67</td>
<td>1.92</td>
</tr>
<tr>
<td>BW-Tar</td>
<td>1</td>
<td>0.00006</td>
<td>70.8</td>
<td>334</td>
<td>0.14</td>
<td>1.69</td>
</tr>
<tr>
<td>Glutein</td>
<td>0</td>
<td>0.00004</td>
<td>60.8</td>
<td>533</td>
<td>0.23</td>
<td>1.73</td>
</tr>
</tbody>
</table>

1000 m²/g, which is comparable to woody biomass [7] (compare BW and L-BW in Table 2).

4. Conclusions

ACs were produced by carbonizing and activating beer lees waste, and the influence of protein fractions on the activation reaction order and surface properties of the resultant ACs was investigated. As for the untreated control sample, the activation reaction could be regarded as first order. Conversely, the reaction system was changed to zero order when the protein fractions were reduced through treatment with an alkali. In addition, the AC produced from L-BW-based charcoal showed a BET surface area of 1390 m²/g, which was approximately 1.4 times greater than that of AC from BW-based charcoal. On the other hand, BW-Tar sample was transformed into charcoals with somewhat densely packed carbon layers, which appeared to make the charcoal less reactive to CO₂ and limited the adsorption capacity of the resultant AC.

References