Rice Hull Ash Structure and Bleaching Performance Produced by Ashing at Various Times and Temperatures

Y.Y. Chang[a], **C.I. Lin**[a,*], **and H.K. Chen**[b]

[a]Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, and [b]Department of Chemical Engineering, Hwa Hsia College of Technology and Commerce, Taipei, Taiwan 235

ABSTRACT: Surface areas, pore sizes, and bleaching efficiencies of rice hull ashes produced under different time and temperature conditions were examined. Specific surface area and average pore diameter were measured by a surface area meter. Bleaching efficiencies were calculated based on the Lovibond color indices of sesame oil before and after bleaching by rice hull ash. Experimental results indicated that specific surface area and pore size increased with increase in ashing temperature, reached a maximum, and then decreased. Specific surface area decreased while pore size enlarged with the increase in ashing time. Both surface area and pore size were observed to reach a plateau after 30 min. Bleaching efficiency increased with increasing ashing temperature, reached a maximum, and then decreased with further increase in ashing temperature. It also increased with ashing time and then reached a plateau. Bleaching efficiency remained unaffected by specific surface area when the pore diameter was less than 50 Å but varied with specific surface area when the pore diameter was larger than 50 Å.

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KEY WORDS: Bleaching efficiency, pore size, rice hull ash, sesame oil, surface area.

Activated clay has been widely used in the refining oil industry to remove color bodies and other impurities in edible oil. In recent years, rice hull adsorbents have been evaluated to replace activated clay as an adsorbent (1). Rice hull is a byproduct of the cereal industry. In Taiwan, it is normally disposed of by burning in the field, thus resulting in environmental pollution. Hence, adsorption bleaching of edible oil by rice hull adsorbents merits further investigation in order to combat environmental pollution.

Heating in an inert gas produces a charred rice hull rich in carbon. However, if rice hulls are heated in an oxidizing environment, only a trace amount of carbon is found. Ash thus produced is an amorphous silica in the form of opal CT (2) and is usually designated as rice hull ash or rice hull silica.

Rice hull ash is a good phospholipid adsorbent but ineffective for adsorbing lutein, free fatty acids, and peroxides from soy oil (1). However, it is an attractive adsorbent for Taiwan, where rice hull is plentiful and cheap.

Processing conditions of rice hull ash may affect the bleaching ability of the ash. Increasing the ashing temperature decreases the bleaching ability of the ash (3,4). Proctor and Palaniappan (3) found that the most effective ashing temperature in the range of 500–1,000°C was 500°C, but Liew *et al.* (4) observed that heat treatment of rice hull at temperatures below 300°C resulted in the most active adsorbent after acid activation. The effect of heating temperature on the pore surface area and volume in the range of 500–1,100°C was reported by Ibrahim *et al.* (5).

Heating time may also influence the bleaching efficiency of the ash. However, this topic has not yet received attention. On the other hand, the effect of heating time on the pore structure and crystal size of the rice hull was reported by Ibrahim *et al.* (5). Their data were for the interval of 180–1,440 min, while results for ashing time less than 180 min were lacking.

Research on the relation between bleaching ability and ash structure is limited, with the exception of Proctor (2), who found that the crystal form, particle fusion, and potassium content of the ash might influence the adsorption ability of soy oil components.

Most studies focus on the bleaching of soy oil/hexane miscella (1,3) or palm oil/hexane miscella (4), while any report on the adsorption of sesame oil, which is one of the edible oils in Taiwan, with rice hull adsorbent cannot be found.

To explain the relationship between the bleaching efficiency and structure, surface area, pore size, and bleaching performance of rice hull ash produced in the range of 300–1,000°C for 6–120 min were extensively studied in this investigation.

MATERIALS AND METHODS

Materials. Compressed nitrogen gas (Yuan-Ron, Taipei, Taiwan) with minimum purity of 99.999% was employed. Rice hull and sesame oil were obtained from Da-Li Co (Tainan, Taiwan) and Shin-Chen Oil Co. (Taipei, Taiwan), respectively. The activated clay was of Galleon Earth Type N_3 (Mizusawa Chemical Industries Ltd., Tokyo, Japan).

Ashing of rice hull. About 120 g of rice hull was washed four times with water and then dried in an oven at 100°C for 24 h. Ten grams of rice hull was then placed in $16 \times 4 \times 2.1$ cm deep alumina boat. A box furnace from Kinghwang VT-10 (Taipei, Taiwan) with flowing nitrogen (20 mL/s) was heated from room temperature. When the desired temperature of the furnace (300–1,000°C) was reached and had remained stable for several minutes, the boat with rice hull was placed

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*To whom correspondence should be addressed.
E-mail: cilin@ch.ntust.edu.tw

in the furnace. The flow of nitrogen gas continued during the process of ashing. When the ashing time was completed, the boat was removed from the furnace and cooled in air. The ashing time ranged from 6 to 120 min.

Determination of carbon, hydrogen, and nitrogen contents in rice hull ash. The contents of carbon, hydrogen, and nitrogen in the ash were determined by a PerkinElmer 2400-CHN elemental analyzer (PerkinElmer, Norwalk, CT).

Analysis of rice hull ash by surface area meter. Specific surface areas and average pore diameters of the rice hull and the rice hull ash were determined by a Micromeritics ASAP 2000 surface area meter (Micromeritics, Norcross, GA). The specific surface area was determined by the adsorption method of Brunauer-Emmett-Teller (BET). Average pore diameter was measured by the cumulative desorption method of Barrett-Joyner-Halenda (BJH). Adsorption and desorption isotherms of nitrogen were determined gravimetrically at liquid nitrogen temperature. Prior to the measurement, each sample was evacuated at 150°C for 2 h.

Bleaching of sesame oil. One hundred grams of sesame oil and 2 g of rice hull ash (or activated clay) were placed into a three-neck round-bottom flask. The flask was immersed into a heating mantle. The slurry of oil and ash (or clay) was stirred at 250 ± 10 rpm and heated to 120 ± 2°C in 5 ± 1 min. A stream of nitrogen was passed through the slurry to prevent it from being oxidized. Stirring was continued for another 5 min with the temperature kept in the range of 115–122°C. After that, the slurry was filtered through filter paper. A sufficient amount of filtered oil was collected for the determination of color index.

Determination of color index of sesame oil. The color indices of sesame oils before and after bleaching were measured by a Lovibond tintometer (AF 700 Model E, Salisbury, England) using a 1-in. cell. The procedure of AOCS Official Method Cc 13b-45 (6) was followed. The color index was determined immediately after the bleaching test in order to prevent the oxidation of oil in air.

Calculation of bleaching efficiency. The bleaching efficiency of rice hull ash was calculated by the following equation:

$$\mathrm{BE} = \frac{R_0 - R_1}{R_0} \times 100\% \qquad [1]$$

where R_0 = red color index of sesame oil before bleaching and R_1 = red color index of sesame oil after bleaching.

Three runs were conducted under the same experimental conditions, and the average bleaching efficiency was taken from these runs.

RESULTS AND DISCUSSION

Variation in the contents of carbon, hydrogen, and nitrogen. The contents of C, H, and N in rice hull and in rice hull ash are listed in Tables 1 and 2. Table 1 shows variations in contents with temperature while Table 2 shows variations with time. The carbon content in the ash decreased with an increase in ashing temperature or ashing time. When the temperature was above 500°C or the time was beyond 60 min, the ash contained almost no carbon. Pyrolysis may have occurred in the limited oxygen environment to produce organic volatiles that could be removed by the nitrogen flow during the longer combustion times at higher temperatures.

TABLE 1
Content of Carbon, Hydrogen, and Nitrogen of Rice Hull and Rice Hull Ash[a]

	C (%)	H (%)	N (%)
Rice hull	41.38	4.85	0.04
Rice hull ash (300°C)	43.49	1.87	
Rice hull ash (400°C)	5.03	0.96	0.27
Rice hull ash (500°C	0.34	0.31	0.00
Rice hull ash (600°C)	0.03	0.22	0.06
Rice hull ash (700°C)	0.16	0.13	0.00
Rice hull ash (800°C)	0.00	0.00	0.00
Rice hull ash (1,000°C)	0.00	0.00	0.00

[a] Rice hull was ashed at various temperatures for 60 min.

Variations in specific surface area and average pore diameter. The results of the effect of ashing temperature on surface area and average pore diameter are shown in Figure 1. The specific surface area of rice hull ash was much larger than that of rice hull (dotted line). The specific surface area and average pore diameter of rice hull ash increased with the increase in ashing temperature, reached a maximum, and then decreased. A similar trend was found by Ibrahim *et al.* (5), but the ash with maximum specific surface area was held at 700°C for 180 min.

Chakraverty *et al*. (7) reported that water in the rice hull was evaporated in the range of 50–150°C, and volatile matter was removed from the rice hull between 216–350°C, while combustion occurred at 350–690°C. The calcination process proposed by Chakraverty *et al*. (7) can be used to explain the results obtained in this study. At 300°C, only volatile matter was removed from the rice hull. Therefore, not much ash was formed. The structure of rice hull did not change too much at this temperature (8). Consequently, increases in specific surface area and pore diameter were not significant (Fig. 1). As the temperature increased, combustion occurred, which drove out more components from the rice hull and transformed most of them to ash. The departure of organic components produced the porous structure of the solid sample (8) and in-

TABLE 2
Content of Carbon, Hydrogen, and Nitrogen of Rice Hull and Rice Hull Ash[a]

	C (%)	H (%)	N (%)
Rice hull	41.38	4.85	0.04
Rice hull ash (6 min)	42.77	2.35	0.24
Rice hull ash (12 min)	17.79	1.48	0.40
Rice hull ash (18 min)	9.97	1.26	0.56
Rice hull ash (30 min)	0.32	0.35	0.00
Rice hull ash (60 min)	0.34	0.31	0.00
Rice hull ash (120 min)	0.11	0.28	0.00
Rice hull ash (180 min)	0.02	0.32	0.00

[a] Rice hull was ashed at 500°C for various durations.

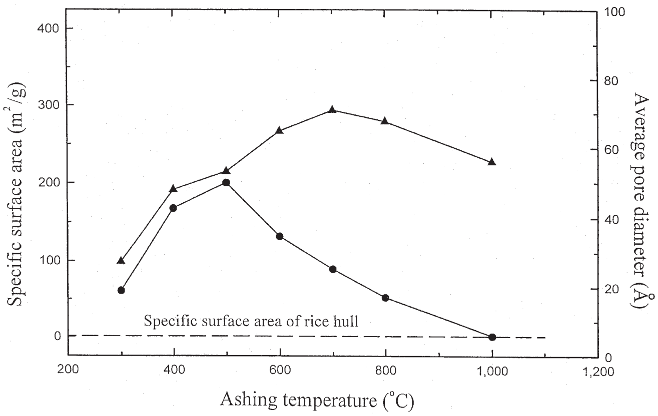

FIG. 1. Effect of ashing temperature on specific surface area and average pore diameter of rice hull ash. Rice hull was ashed for 60 min. ●, Specific surface area; ▲, average pore diameter.

creased the specific surface area as well as the average pore diameter (Fig. 1). When the temperature was increased further, combustion became more vigorous and caused the collapse of some of the structures. As a result, the specific surface area and pore size decreased (Fig. 1). When the temperature was in the range of 800–1,000°C, phase transformation occurred and a glassy structure appeared (8). Solid sample became dense again and specific surface area approached zero (Fig. 1). Proctor (2) also reported a "glassy" appearance of the ash in this temperature range due to the conversion of opal CT to opal C in the ash.

In the second series of experiments, rice hull was ashed at 500°C for 6, 12, 18, 30, 60, and 120 min. The results are shown in Figure 2. It can be seen from this figure that specific surface area decreased as the ashing time increased from 0 to 30 min and reached a plateau when the ashing time was over 30 min. Average pore diameter increased with increased ashing time and almost leveled off when the ashing time was longer than 30 min. Although Ibrahim *et al.* (5) reported the variation of surface area of the ash with ashing time, their combusting time was longer, over 180 min. Hence, comparison of this work with theirs is not appropriate.

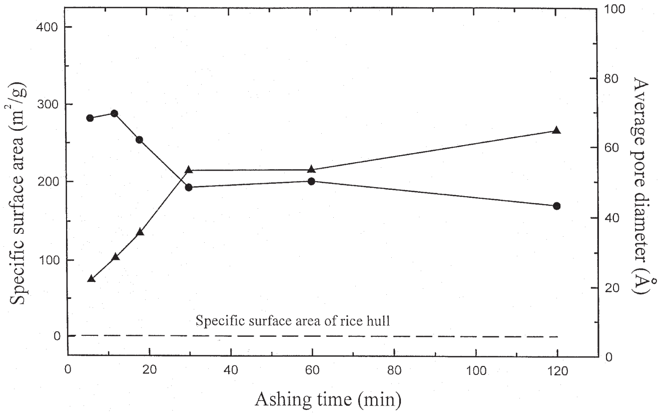

FIG. 2. Effect of ashing time on specific surface area and average pore diameter of rice hull ash. Rice hull was ashed at 500°C. For symbols see Figure 1.

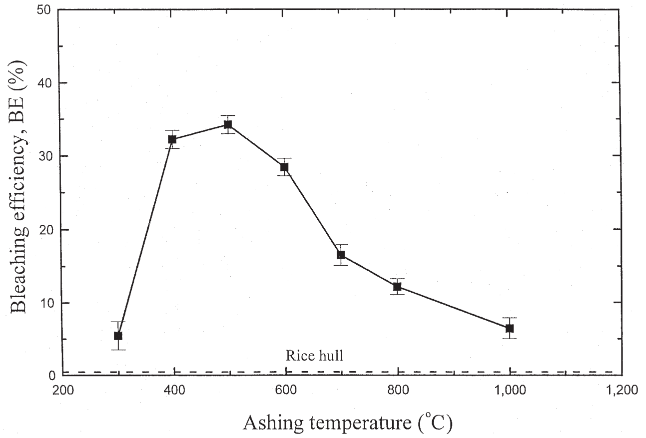

FIG. 3. Effect of ashing temperature on bleaching efficiency (see Eq. 1) of rice hull ash. Rice hull was ashed for 60 min. The range of error bars is twice the estimated standard error.

Although combustion occurred at 500°C, at short ashing times, 6 or 12 min, conversion was very low and the contents of organic matter in the sample remained high (Table 2). As the ashing time increased, the inner surface of the ash gradually became porous (8). Hence, the pore size increased (Fig. 2) and the specific surface area decreased. In addition, the mass of solid sample also decreased due to the evolving organic matter. The reduction of the former was more significant than that of the latter. The values of specific surface area and pore size were almost constant when the ashing time was longer than 30 min because ashing was almost complete at this stage.

For comparison, specific surface area of rice hull, which is almost zero, is also shown in Figures 1 and 2 by dotted lines.

Variation in bleaching efficiency. The results of bleaching efficiencies of rice hull ashes and rice hull are shown in Figures 3 and 4. As shown by the dotted lines in the figures, bleaching efficiency of rice hull is zero, which indicates that rice hull is not able to bleach sesame oil.The maximum value of bleaching efficiency obtained was 33.7% (ashing conditions: 500°C and 60 min). Although it was less than that of activated

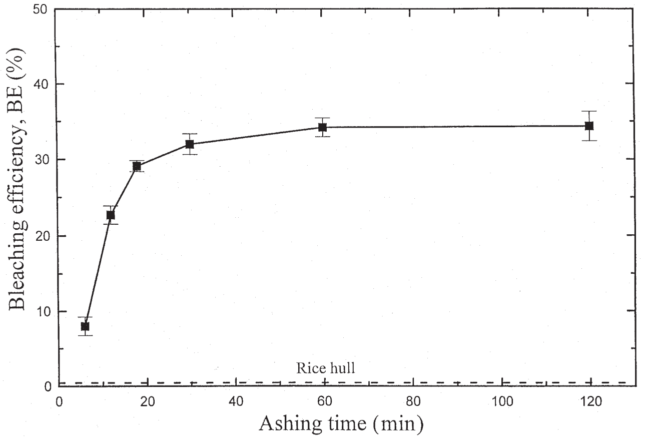

FIG. 4. Effect of ashing time on bleaching efficiency of rice hull ash. Rice hull was ashed at 500°C. For error bars, see Figure 3.

clay (52.3%), more research on better treatment of rice hull ash to obtain higher bleaching efficiency is necessary because it is beneficial from the viewpoint of environmental protection and low cost of raw material.

The effect of ashing temperature on bleaching efficiency of rice hull ash is depicted in Figure 3. Bleaching efficiency increased with the increase in temperature from 300 to 500°C. It reached a maximum of 33.7% at 500°C. Further increase in temperature decreased the bleaching efficiency. Thus, 500°C was the optimal temperature for the production of rice hull ash. Present findings confirm those of Proctor and Palaniappan (3).

Bleaching efficiency increased with ashing time up to the critical time of 30 min (Fig. 4). When the ashing time was longer than 60 min, bleaching efficiency reached a plateau. Therefore, the optimal ashing time was between 30 and 60 min.

Comparing the data in Figure 3 with those in Figure 1, we find that the relationship between bleaching efficiency and ashing temperature is similar to that of specific surface area and ashing temperature. This reveals that bleaching efficiency is closely related to specific surface area. However, comparing Figure 4 with Figure 2 suggests that bleaching efficiency is directly related only to average pore diameter. Nevertheless, it is inversely related to specific surface area. This finding is totally different from what we stated before. Figure 2 shows that pore diameter was smaller than 50 Å when ashing time was less than 30 min. Molecules of color pigments and impurities were too large to diffuse through the pore and were thus not adsorbed on the surface of the pore as the pore was small. Pore diameter controlled the bleaching efficiency, while large specific surface area had no effect on bleaching efficiency under this condition. When the pore diameter was larger than 50 Å, specific surface area controlled the bleaching efficiency. Hence, both specific surface area and bleaching efficiency remained constant even though ashing time was increased. The above reasoning may also explain the findings of Figures 1 and 3. When the pore diameter was less than 50 Å, pore diameter controlled the bleaching efficiency as temperature was less than 400°C. The increase in bleaching efficiency was due to the increase in pore diameter and not specific surface area. The increase in bleaching efficiency with the increase in specific surface area was just a coincidence. No relationship between these two terms was noticed under these ashing temperatures.

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