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A biochar from casein and its properties

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A biochar was prepared by pyrolysis of casein. A helium and mercury porosimeter were used to measure the true and apparent densities of the chars respectively, elemental and IR analysis were used to characterize the chemical composition of char. A SEM was used to observe the char surfaces in order to verify the presence of porosity. The biochar has 9.02% of nitrogen, content of porosity is 20%. The experimental results show that it is possible to prepare chars with relatively high porosity from casein for the further preparation of activated carbon.

1. Introduction

It is well known that activated carbons can be prepared from a variety of raw materials. The most frequently used precursors are hard coal, brown coal, wood, coconut shells, fruit stones, polymer wastes and etc. [1–6]. It has been extensively proved that any cheap material with high carbon content can be used as raw material for the production of active carbon. These raw materials are well suited for activated carbon manufacture, if their pyrolytic transformation into porous char produce in economically justifiable yield. The most important adsorbent properties are adsorption capacity, hardness, and compactness [2]. Thermal degradation properties of casein have been reported in [7, 8] that casein is easy to pyrolize and obtained a solid char is characterizing with comparatively higher yield-28.0% and a compact material with high developed visible porous structure.

An addition, it is very interesting that biochars obtained from the selected nitrogen-enriched precursors had considerable effective surface areas and displayed good sulfur removal. Nitrogen-enriched carbons can be formed from raw materials with high content of nitrogen e.g., from biological materials or from materials with lower content of nitrogen by using the chemical treatment with ammonia or its derivatives [9]. For this reason we have chosen casein as a biological material with high content of nitrogen (13.4%) for the producing of activated carbon [7].

The aim of the present paper was to characterize the properties of biochar of casein. For characterization, helium and mercury porosimeter were used to measure the true and apparent densities of the chars respectively, elemental and IR analysis were used to characterize the chemical composition of char. A SEM was used to observe the char surfaces in order to verify the presence of porosity.

2. Experimental

Casein of cow milk was used in this study as a nitrogen-enriched raw material for the obtaining of activated carbon. A char (biochar) of casein was obtained by pyrolysis of casein in a stainless steel retort, placed in a electric furnace at a heating rate of 20°C min^{-1} up to 600°C and held 2–3 hrs until the finishing of the formed condensed liquid product. Details of the overall experimental setup and results of carbonization have been reported elsewhere [8]. The elemental analysis of biochar and starting casein were performed according to ASTM standard test methods using a CHV-600 analyzer of Leco Corporation. The biochar was powdered and dried at 80°C in oven for 4 hrs and directly kept it for a hour under vacuum. A helium and mercury porosimeter (Accupas 1330, Micromeritics) apparatus were used to measure the true and apparent densities of the chars respectively and the total pore volume of biochar was calculated on the basis of measurement of true and apparent densities.

The porosity ($\in$) of the sample of casein biochar was calculated by the following formula using the apparent and true densities:

$$\in = (1 - g_a/g_t) \times 100\% \qquad (1)$$

where g_a-apparent density, g_t-true density.

The pore size distribution of biochar was measured by mercury porosimeter model ASAP 2010. The samples for taking IR spectra were prepared in the form of

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TABLE I Proximate and ultimate analysis data of casein and it's biochar

No.	Indices	Casein	Biochar
1	C, %	52.49	60.68
2	H, %	7.14	0.70
3	N, %	15.75	9.02
4	O, (by diff.)	24.62	29.60
5	H/C atomic ratio	1.63	0.138
6	O/C atomic ratio	0.35	0.37
7	Ash A^a, %	8.72	14.50
8	Moisture W^a, %	4.72	4.56
9	Volatile matter, % (on dry matter)	78.25	11.24
10	Porosity, %	–	20

a thin films pressed between the plates of KBr. Spectra were recorded between 4000 and 500 cm^{-1} using a Nicolet 750/1600 FT-IR spectrometer. For SEM studies the samples were mounted in carbon-tabs and examined with a HITACHI S 3500 N by different acceleration voltages, depended on the roughness and conductivity of the specimen surface. The magnification of the SEM was selected as ×50, 100, 200 and 1000 in this study.

3. Results and discussion

The results of proximate and ultimate analysis of casein and it's biochar are given in Table I.

Table I shows that content of C and O in biochar increased, but content of H and N decreased in comparison with elemental dates of pure casein. These changes of elemental content depends from the carbonization process in which decomposed mostly parts of casein macromolecule with aliphatic structure and formation of biochar accompanied with cyclization or aromatization of the molecular structure of hard residue. An indication of aromatization process is the drastically decreasing of H/C ratio.

During pyrolysis and carbonization process the O/C ratio remained almost the same value. It means that O in casein had been taken part in formation of surface functional groups (–OH, >C=O, –COOH, –CO–O–CO–) of biochar. It is very interesting that nitrogen content of biochar is high, proximately 9.0%. This indicates that during pyrolysis and carbonization process nitrogen not only took part in emission of NO_x and NH_3, but also mostly in formation of aromatization process.

The biochar (casein char) was examined by Fourier transform-infrared (FT-IR) spectroscopy. This analysis tool has frequently been used in investigations of surface chemistry of chars and activated carbons [10] as it provides valuable information on the chemical nature and the concentration of the surface functional groups. The FTIR spectra of biochar is presented in Fig. 1.

Various bonds in the spectra representing due to OH (at 3427 cm^{-1}) aliphatic (2924 cm^{-1}), C=O carboxyl group (1630 cm^{-1}), aromatic ring (1432 cm^{-1}), etheric C–O–C group (1159 cm^{-1}), aromatic C–H (615 cm^{-1}, 500 cm^{-1}) were identified. The results of FTIR and elemental analysis show that the biochar of casein has a complex carbonized polymer material with high aromatic structure attached carbonyl and hydroxyl surface groups.

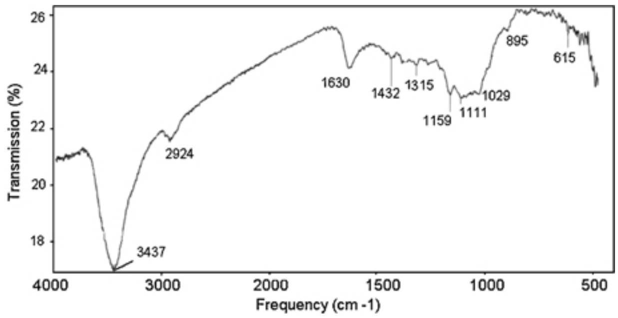


Figure 1 FTIR spectra of biochar of casein.

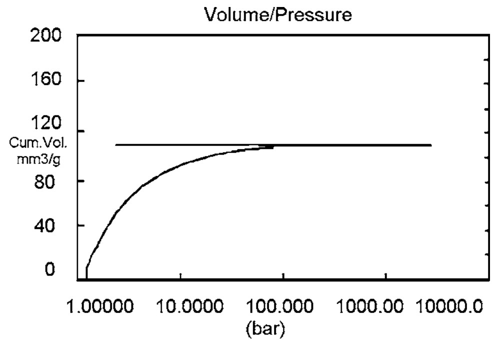


Figure 2 Relationship between volume and pressure (bar).

The pore size distribution of casein biochar by porosimetry is shown in Figs 2 and 3.

Carbonized sample of casein biochar was characterized by measuring the bulk density and the porosity (%) was calculated by formula (1) using the apparent ($g_a = 1.5567$ g/cm^3) and true ($g_t = 2.894$ g/cm^3) densities:

$$\in = (1 - g_a/g_t) \times 100 = 20\%$$

From Fig. 2 cumulative volume was found ~112.6 mm^3/g and from Fig. 3 was measured the porosity of biochar ~20%, which is the same as calculated by above mentioned equation. It shows that this results is comparable, with the porosity of char obtained at 700°C (retention time 3 h) and 800°C (2 h) from oil palm [4].

Pore sizes are classified in this study in accordance to the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC) [6], that is,

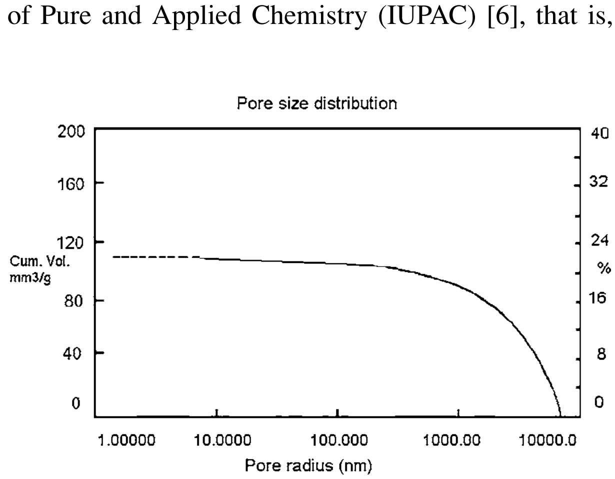
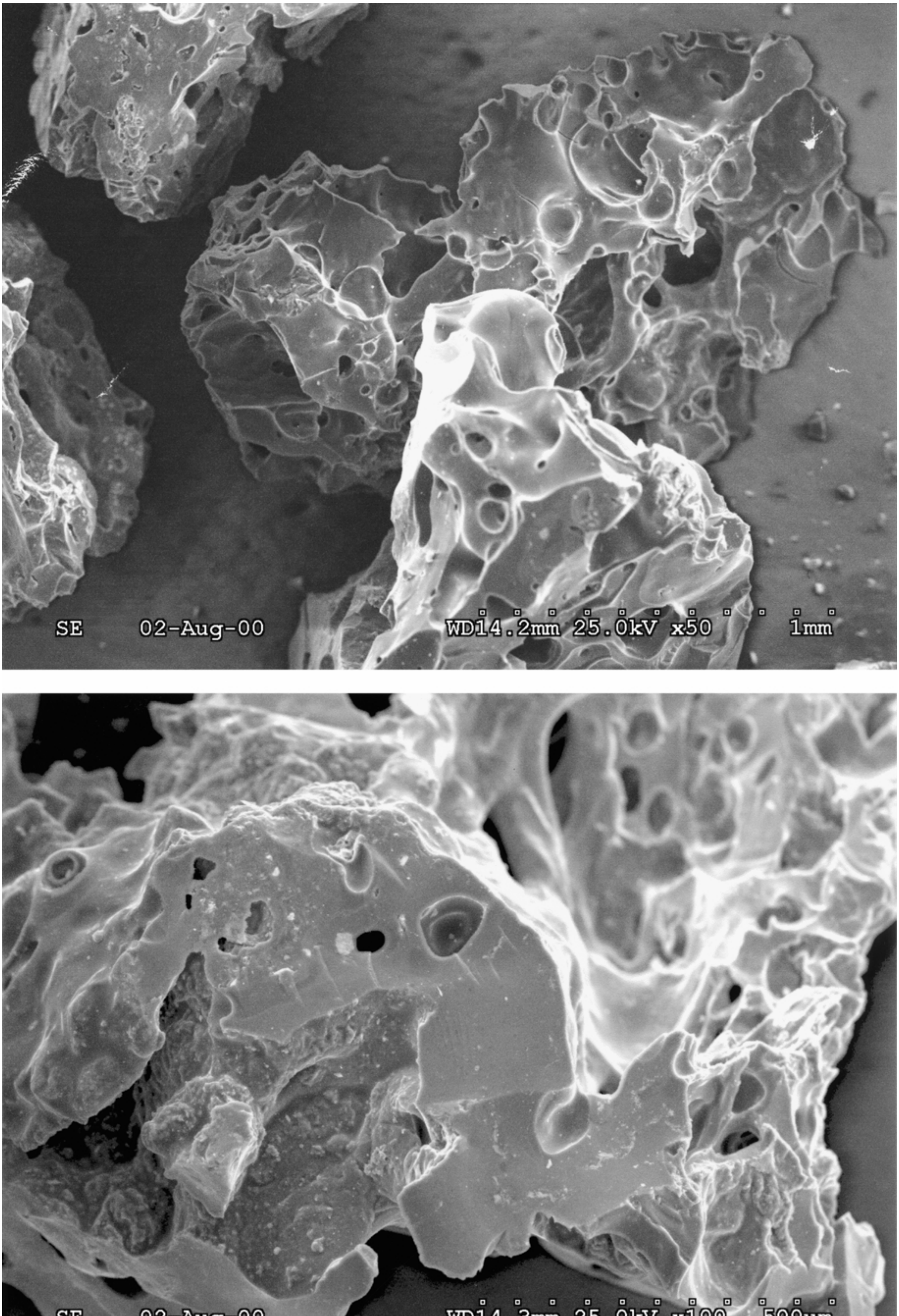
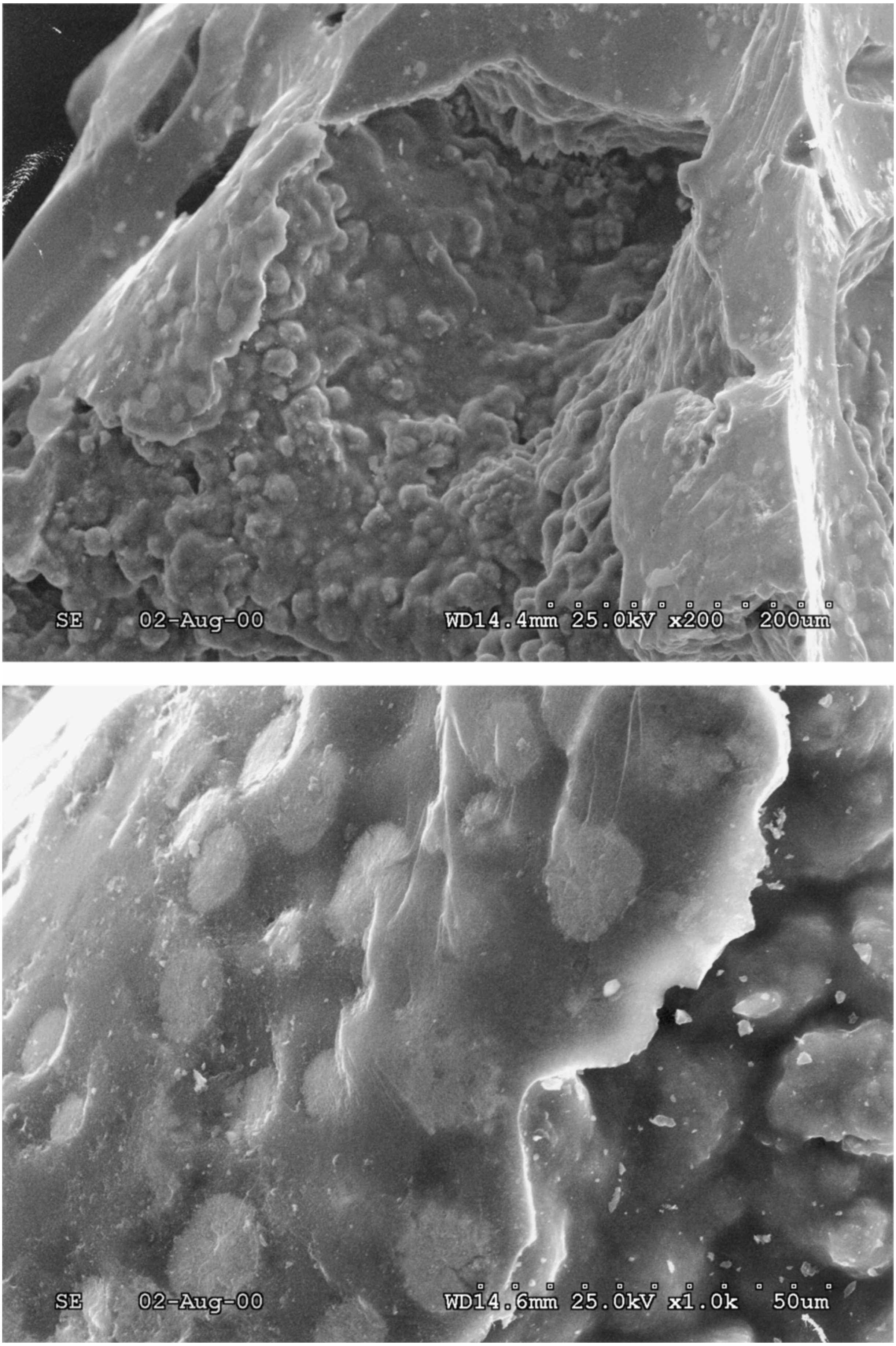


Figure 3 Pore size distribution of casein biochar.



(a)

Figure 4 SEM images of casein biochar: (a) Biochar particle with porous structure and (b) Biochar particle with filled in by volatile matter. (*Continued*)



(b)

Figure 4 (*Continued*).

micropores (<2 nm diameter), mesopores (2–50 nm diameter) and macropores (>50 nm diameter).

Each type of pore plays an essential role for the adsorption property of porous materials. According to this classification of pore size the biochar of casein is characterizing with mostly meso (3.7 < Ø < 41.7 nm) and macro pores (Ø > 88.04–6811.04 nm) pores (Fig. 3).

As mentioned above the biochar is not activated, but it has a visible porous material with meso and macro pores. The adsorption of methylene blue by the macro pores of casein biochar was determined as 28 mg/g of biochar.

SEM analysis of powdered sample of casein biochar also indicates the porous structure (Fig. 4a), but some pores are covered (filled in) by volatile matters (Fig. 4b), which are could not leave during pyrolysis fully. So the porosity of biochar will be increased, after the activation in other to obtain the activated carbon. A detailed activation investigation and SEM study are needed to comment further on actual structure of biochar.

4. Conclusions

1. First time biochar with higher content of nitrogen was obtained by pyrolysis of casein and determined elemental composition and technical specifications.

2. The porous structure of casein biochar was characterized by mercury porosimeter and SEM analysis and confirmed that casein biochar has mostly meso and macro pores.

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