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Investigation on the pyrolysis products from animal bone

B. PUREVSUREN, B. AVID*,‡, J. NARANGEREL, T. GERELMAA, YA. DAVAAJAV
Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar-51, Mongolia
E-mail: avid-budeebazar@aist.go.jp

Activated carbon can be produced from virtually any carbonaceous precursor, both naturally occurring and synthetic. Process economics normally depend on the availability and suitability of low-cost feedstocks. Common examples of commercial carbon feedstocks are materials of botanical origin (e.g., wood, coconut shells, fruit stones and casein) and degraded or coalified plant matter (e.g., peat, lignite and all ranks of coal) [1–5]. Bone chars have been traditionally used to decolorize impure sugar solutions in the refining process for many years [6]. Bone char is an efficient adsorbent also for removal of toxic heavy metals such as cadmium, copper and zinc from industrial wastewater [7, 8] and adsorption of organic acid dyes from aqueous effluent solutions of a carpet printing plant [9].

Mongolia does not have industrial applications for bone except for a small amount of bone exported to other countries. Every year in Mongolia a large number of house animals die due to extreme winter conditions in the countryside. Animal residues are predominantly low-cost agricultural feedstock with little or no alternative application apart from their possible use as a fuel for energy generation. Therefore, their utilization as precursors for activated carbons has the additional advantage of providing a way for their disposal. Their importance arises also from various aspects such as utilization of tar and gas as an energy source.

In this paper, we report our study on the pyrolysis of waste bone and some properties of the bone char characterized by using TPD, FT-IR and adsorption of cadmium ion from solution.

Cattle animal bone was crushed into pieces of 3–6 mm size and rinsed three times with deionized water, boiled at least 3 times in distilled water for 4 h to remove fat and finally, dried at 105 °C overnight and allowed to cool in a desiccator. Elemental composition of bone, char and tar were determined by micro analytical methods.

Pyrolysis of bone was performed in a laboratory vertical cylindrical retort with volume of 2.5 dm^3, which was heated externally by an electric furnace. A programmable temperature controller measured the temperatures of the furnace and retort. The retort was connected with a collection vessel for the condensation of liquid product (tar and pyrolysis water) through an air-cooled iron tube and water-cooled laboratory glass condenser. The non-condensable gases after the water-cooled condenser were removed from the system through a small bore glass tube. The pyrolysis experiments were carried out at 500–600 °C temperature and the heating rate was 20 K min^{-1}. The yields of pyrolysis products including solid residue (bone char), tar and pyrolysis water were determined by weighing, and the yield of gases by differences.

The chemical compositions of the tar were determined by methods described in [10]; brief descriptions are given below. First, the tar was extracted with hot benzene and filtered. The yield of precipitation is free carbon. Then to the filtered solution was added a 5% $NaHCO_3$ and neutralized with 10% H_2SO_4, then the solution was extracted by using diethylether to give yield of organic acid. A 5% NaOH solution was used for phenol extraction. The remaining part of the solution was in the form of asphaltenes. There were intermediate precipitations in each separation and all were collected to give preasphaltenes. Tar fractions with different boiling temperature ranges were obtained using an atmospheric distillation method.

A Thermal Science STA1500 thermogravimetric analyzer (TGA) was used to do temperature programmed desorption (TPD) analysis of bone char. It connects with a VG Quadruple 300 AMU mass spectrometer by a heated stainless steel capillary lined with deactivated fused silica. About 5 mg of bone char was put into a sample bucket sealed in an oven and was not heated until the sample mass displayed became stable. The temperature programmer controlled furnace heating from room temperature to 1200 °C at rate of 15 K min^{-1} in argon gas of flow rate 50×10^{-6} m^3 min^{-1}. The gases evolved from the bone char were sampled and analyzed through a gas sample probe and a heated stainless steel capillary leading into the mass spectrometer. When the furnace temperature reached 1200 °C, sample heating was stopped. The sample was cooled to room temperature in argon. Typical m/z values of 28, 30, 44 and 46 were detected.

To measure the adsorption of metal ions in solution, the following procedure was used. About 0.1 g of bone char was doped into 50×10^{-6} m^3 of solution having the known initial concentration (0–2 mM) containing metal ions Pb, Cd and Hg. Adsorption experiments were conducted at 25 °C for 48 h. A Unicam 701 inductively coupled plasma (ICP) atomic emission spectrometer was employed to determine the concentration of stock

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*Author to whom all correspondence should be addressed.

‡*Current address:* National Institute of Advanced Industrial Science and Technology (AIST), Research Institute for Energy Utilization, Advanced Fuel Research Group, 16-1 Onogawa, Tsukuba 305-8569, Japan.

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TABLE I The basic characteristics of bone and other organic materials

No	Sample	Moisture (wt%)	Ash wt%, dry base	Volatile matter wt%, daf[a]	Ultimate analysis, wt%, daf C	H	S + N + O, by diff.[b]	H/C
1	Bone	4.1	64.7	76.2	32.9	8.0	59.1	2.92
2	Casein	8.7	4.7	82.1	52.5	7.1	40.4	1.62
3	Oil shale	5.9	61.1	90.9	66.1	10.2	21.6	1.85
4	Brown coal	6.8	10.9	48.3	66.9	5.2	27.9	0.93

[a] dry ash free.
[b] by difference.

solution and the equilibrium concentration of metal ions in solutions after adsorption. The metal ions adsorbed on bone char were calculated as follows:

$$M_A = (C_O - C_E) \times V/W_C$$

where C_O and C_E refer to initial and equilibrium concentration of metal ions in solution individually; V is the volume of solution. For all experiments, the volume V is equal to 50×10^{-6} m^3; W_C, the mass of the bone char sample; M_A, the amount of metal ions adsorbed by the char.

The FT-IR spectra for the chars were obtained on a Nicolet 20-PC FTIR spectrophotometer with CsI optics and a DTGS detector. The KBr disc contained 0.5% finely ground char sample.

The basic characteristics of bone and other organic raw materials investigated are given in Table I.

Because of the high content of inorganic elements such as calcium and phosphorus, the bone is very rich in mineral matter. Table I shows that the content of heteroatoms in bone is much higher than in other organic materials, meanwhile the carbon content is lower. The H/C ratio of bone is substantially higher than for the other materials.

The pyrolysis product distribution of bone is compared with those from the other organic materials in Fig. 1. In the case of bone, the yield of tar is a little bit lower than in coal, but in general, the pyrolysis distribution behavior is similar to that for coal. As shown in Fig. 1, from the highest yield of tar from casein it could be concluded that the casein contains relatively low molecular compounds than the other organic materials studied here. The proximate and ultimate analyses of bone char and tar have been performed and the results are given in Table II. The hydrogen content of bone char decreased drastically in comparison with the hydrogen contained in initial bone. In the case of carbon and heteroatoms, their contents in char are decreased a

TABLE II The proximate and ultimate analysis of char and tar of bone pyrolysis

No	Specifications	Bone char	Bone tar
1	Carbon (C), wt%, as analyzed	8.4	73.3
2	Hydrogen (H), wt%, as analyzed	0.5	10.1
3	Nitrogen (N), wt%, as analyzed	1.1	11.3
4	Oxygen (O) wt% (by diff.)	5.1	5.3
5	H/C atomic ratio	0.71	1.65
6	Ash, wt%, as analyzed	84.8	–
7	Volatile matter, wt%, daf	7.7	–

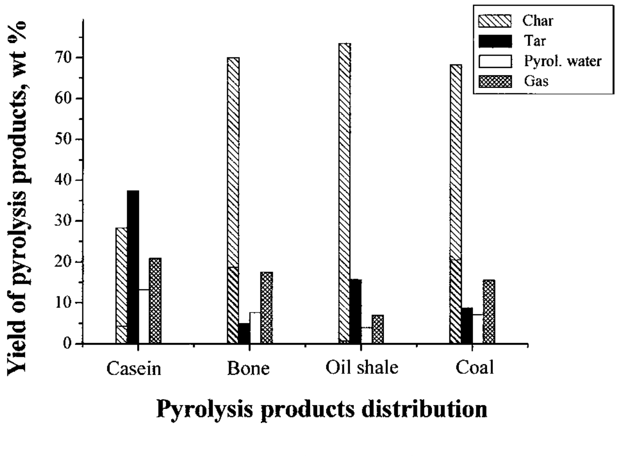

Figure 1 The pyrolysis products distribution of bone and other organic materials.

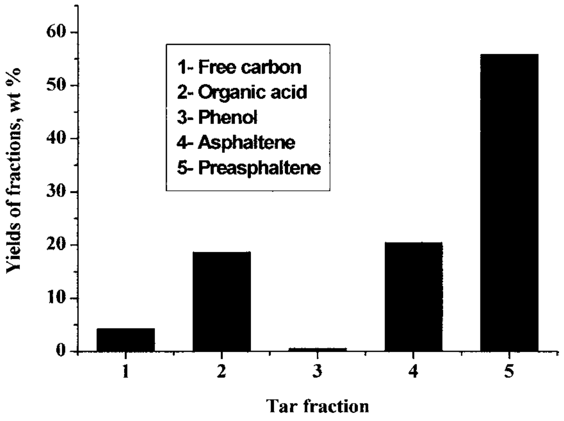

Figure 2 The chemical composition of pyrolysis tar.

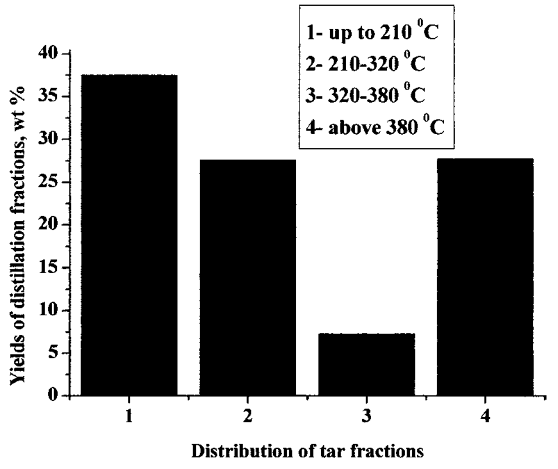

Figure 3 Air distillation of tar.

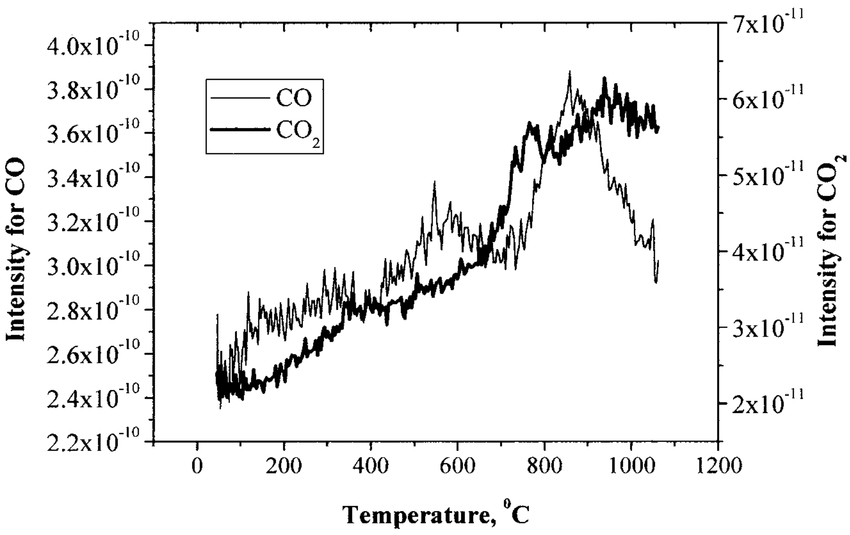

Figure 4 CO and CO_2 evolution profiles of the TPD.

little in comparison with initial bone. The bone pyrolysis tar is a viscous liquid with black-brown color. The tar was analyzed for a group of organic compounds and the results are shown in Fig. 2. It shows that the tar contains a high amount of preasphaltenes. The contents of organic acids and asphaltenes are about 20%. The bone pyrolysis tar was separated by an atmospheric distillation into several liquid fractions with different boiling ranges and a bitumen-like hard residue. The yields of these products are shown in Fig. 3. Fig. 3 shows that the major part of the tar was distilled at 210 °C; 210–320 °C and 320–380 °C boiling temperature intervals. Because of a lack information about the structure, composition and properties of the bone tar, it is necessary to investigate the tar in more detail in the future.

The temperature programmed desorption (TPD) profiles of CO and CO_2 evolution for bone char are shown in Fig. 4. The data reveal thermal stability and give an indication of what types of groups were present on the surface from their decomposition products. The CO_2 evolution shows that there are two sharp peaks, which were observed after 700 and 800 °C, and it is proposed that the char contains mainly lactone-lactole and phenol groups corresponding to desorption with range 370–700 °C. The second peak corresponds to the decomposition of calcium carbonate.

The adsorption isotherm of Cd^{2+} ion on bone char was shown in Fig. 5. The adsorption capacities drastically enhanced as the initial concentration of Cd^{2+} solution increased, i.e., maximum capacity in this condition is around 0.43 mmole Cd per g bone char. Although, bone char consists of mainly minerals, it showed relatively good adsorption properties for Cd^{2+}.

The results of our preliminary experiments on using bone char as a filtering material for used car oils show that it has relatively good cleaning properties [11].

The FT-IR spectrum for bone char is presented in Fig. 6. The broad bands observed at 1640 and 3440 cm^{-1} indicate adsorbed H_2O in the char. Broad bands appearing at wave number values 875 and 1470 cm^{-1} are indicative of the carbonate. Bands located around 1040 cm^{-1} and at 607 and 560 are coincident with phosphate group absorption.

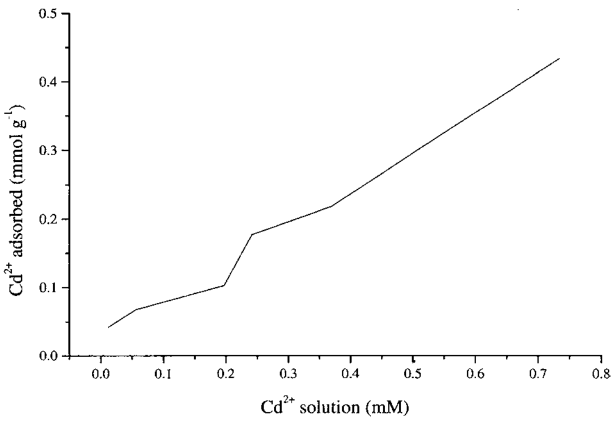

Figure 5 Adsorption isotherm of Cd^{2+} on bone char.

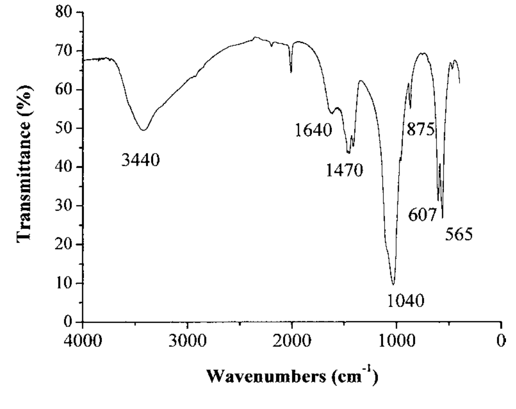

Figure 6 FT-IR of the bone char.

In conclusion, the pyrolysis of cattle bone has been carried out under optimal pyrolysis conditions and a bone char obtained with good adsorption properties. The pyrolysis products distribution of bone was compared with other organic materials. The main content of bone tar were organic acids (18.6%), asphaltanes (20.5%) and preasphaltanes (55.9%). The surface properties of the bone char were characterized by TPD and FT-IR. The adsorption isotherm of Cd^{2+} ion shows that the maximum capacity is 0.43 mmole Cd per g bone char.

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