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Pyrolysis of animal bone, characterization of the obtained char and tar and application of bone tar for crosslinking of epoxy resin

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In this investigation the technical characteristics and elemental composition of animal bones were determined and their pyrolysis, production of bone char, tar, water and gases and application of bone tar as a curing agent of epoxy resin were studied. It was found that animal bone has a higher quantity of mineral components - (A^a -63.5%) than organic matter - (V^a- 31.30%) and also has less organic carbon - (C^{daf}-32.90%) than oxygen and other elements - (O^{daf} + others - 55.9%). Pyrolysis experiments of animal bone were carried out at different heating temperatures and the yields of obtained solid (char), liquid (tar and pyrolysis water) and gas products were determined. A temperature around 600ºC was determined as the optimal heating temperature of pyrolysis and the obtained products were approximately 66.35% char, 4.33% tar, 18.02% pyrolysis water and 11.29% gas. The bone char has a higher ash content – 84.8% compared to initial bone (A^a– 63.5%) and significantly lower contents of carbon, hydrogen, nitrogen and oxygen. For tar the contents of carbon, hydrogen and nitrogen increased almost 10 times compared to char while the content of oxygen was the same in both products. The pyrolysis of the animal bone samples was carried out in a laboratory reactor. In the present work a curing agent- tar was obtained from animal bone by pyrolysis. The product contains 18.95% of pyrolysis water with 76.05% degree of curing reaction for epoxide resin ED – 20. We prepared a new curing agent for epoxide resin by mixing bone tar and diethylenetriamine at a mass ratio of 1:1 (homogeneous mixture), which has 96% degree of curing reaction.

Keywords: animal bone, bone pyrolysis, bone char and tar, application of tar as a crosslinking agent of epoxy resin.

INTRODUCTION

Animal bones are very important bio-organic source of Ca and P [1] and are also used for obtaining bone powder, glue and fat. About 40-50 thousand tons of animal bones per year are produced in Mongolia. Unfortunately, animal bone is almost considered as a waste materialin Mongolia, except the production of small amount of bone powder for export. The production of cheap animal glue was, however, closed. The same is the situation in Bulgaria, only the quantity of animal bones is smaller.

An alternative method of animal bone processing is the thermal treatment (pyrolysis) for producing bone char and tar [2]. Bone char is a cheap and effective filtering and adsorbent material after it's activation [3]. Usually pyrolysis of a mixture of animal bones and meat is carried out [4]. The first experiments of pyrolysis of pure animal bone have been carried out in a laboratory of the Mongolian Academy of Sciences and the yields of bone char, tar and gas products were determined [5, 6]. The bone char was processed by activation with preheated water steam to produce activated carbon material with porous structure [7]. In this work a more detailed investigation of the pyrolysis process was performed.

EXPERIMENTAL

The applied cattle bones were crushed into pieces of 3-6 mm size and rinsed three times with deionized water. After that the bones were boiled at least 3 times in distilled water for 4 h. to remove meat residues, fat and finally the samples were dried at 105ºC and allowed to cool in a desiccator. The analytical samples were prepared by powdering to a particle size < 0.2 mm in a steel mill. These processes are described in the Mongolian National Standards: 2719.2001 (analytical sample preparation), 656-79 (moisture content), 652-79 (ash yield), 654-79 (volatile matter yield) and 669-87 (gross calorific value). The apparatus used for elemental analysis was 5E C 2000 model CNH – analyzer. FTIR spectra were recorded on a Nicolet 20-PC FTIR spectrometer with CsI optics and DTGS detector with KBr pellets with 0.5% sample content. Thermogravimetric analyses were made with TG/DTA7200 Hitachi, Japan model equipment in

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the temperature range of 20 – 1150 ^{0}C, with heating rate of 40^{0}C/min, carrier gas nitrogen p.a. and a Pt-Rh thermocouple for temperature measurement. All pyrolysis experiments of animal bone samples were performed in a laboratory quartz retort (tube) which could contain dry air. All samples (1 g) were powdered to a particle size < 0.2 mm. The retort was placed in a horizontal electric tube furnace with a maximum heating temperature of 950^{o}C. The actual heating temperature in the tube furnace was measured by a chromel-alumel thermocouple. The pyrolysis experiments were carried out at different heating temperatures in the range of 200-700^{o}C with a constant heating rate of 20^{o}C/min. Firstly, the quartz retort with the bone sample was heated to 600^{o}C with a heating rate of 20^{o}C/min and was kept at 700^{o}C for 80 min. The retort was connected with a thermostated glass tube also heated in a tube furnace at 80^{o}C for collecting tar. This tube was connected with an air-cooled glass vessel for collecting pyrolysis water. The glass vessel for pyrolysis water was also connected with a thin glass tube for collecting non-condensable gases. The yields of pyrolysis products including solid residue (coal char), tar (condensed liquid product) and pyrolysis water (condensed liquid product) were determined by weighing and the yield of gases was determined by difference as the average value of 3 replicates.

The preparative-scale pyrolysis experiments of animal bone samples were performed in a laboratory vertical cylindrical retort made of stainless steel which could contain 1000 g. of sample. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 950^{o}C. The actual heating temperature was measured using achromel-alumel thermocouple immersed in the bone bed, equipped with a potentiometer for temperature control. The retort was connected with an air-cooled iron tube, a water-cooled laboratory glass condenser and a collection vessel for the condensate of liquid products (tar and pyrolysis water). The non-condensable gases after the water-cooled condenser left the system through a thin glass tube. The experiments were carried out a tatemperature of 900^{o}C at a heating rate of 20 ^{o}Cmin^{-1}. The yields of products including solid residue (char), tar and pyrolysis water were determined by weighing and the yield of gases - by difference.

Method for separation of tar and pyrolysis water

The liquid condensed products of bone pyrolysis consist of tar and pyrolysis water. They form two immiscible layers which can be easily separated by means of a separatory glass funnel. The upper layer is tar (a viscous liquid) with black-brown color and unpleasant smell. The bottom layer is pyrolysis water (not viscous liquid) with bad smell and brown color. The final cleaning of tar from pyrolysis water residues takes place by mixing with thermally treated $CaCl_2$ and separating (filtering or centrifuging). The mass ratio of tar and pyrolysis water is approximately 1:4.

The pyrolysis water can be concentrated by vacuum distillation. The distillation starts at 45 ^{o}C by foaming and forming colorless water drops and continues until 85 ^{o}C. In our experiments 63% concentrated pyrolysis water with black-brown color and some precipitates, 27% colorless distilled water and 14% uncondensed gas was obtained.

Method for curing of epoxy resin with tar and concentrated pyrolysis water

A sample of 1.0 g. of technical grade epoxy resin ED-20,made in Russia, was mixed with 15-20% tar or 20-25% concentrated pyrolysis water in a small glass vessel to form a homogeneous mixture. When this mixture was kept for 24 h. at room temperature, no curing of the epoxy resin took place. Therefore, this mixture was transferred to a small glass vessel and was kept for 2h. in an oven at 120^{o}C. In this case there was curing of the epoxy resin resulting in a hard glassy product. The cured epoxy resin was powdered in a steel mill and 1.0 g. of the sample was packed in a pre-weighed filter paper and was extracted with technical grade acetone, product of Merck on a Soxhlet apparatus. After finishing the extraction, the sample and filter paper were dried at 105 ^{o}C in an oven until constant weight and the fraction insoluble in acetone (gel fraction or degree of curing reaction of epoxy resin in %) was determined. The accuracy of weighing was 0.0001 g. To increase the curing ability of bone tar, a homogeneous mixture of bone tar and technical grade diethylenetriamine, CAS N 111-40-0, product of DOW, was made by mixing the liquids (mass ratio 1:1) in a glass vessel. Diethylenetriamine (DETA) is a standard curing agent of epoxy resin.

RESULTS AND DISCUSSION

The average results of the pyrolysis of animal bones are given in tables 1 and 2.

Animal bone is a bio-organic material characterized with a higher mineral content such as 63,35% ash and for this reason has comparatively

Table 1. Analytical results for the pyrolysis of animal bone samples

№	Sample	Moisture, %, W^a	Ash, %		Volatile matter, %		Caloric value,
			A^a	A^d	V^a	V^{daf}	Q^{daf}, ккal/kg
1.	Animal bone	5.68	63.35	67.17	31.30	86.06	3604

daf = dry, a = ash-free;

Table 2. Results of the analysis of animal bones.

№	Sample	C^{daf},%	H^{daf},%	N^{daf},%	H/C	O^{daf} + others %
1.	Animal bone	32.90	8.00	3.20	2.91	55.90

$(N+O)^{daf}$- by difference

Table 3. Yield of pyrolysis products at different heating temperatures of animal bone samples.

№	Heating temperature, T°C	Time of heating, min.	Char, %	Condensed liquid products, %		Uncondensed gas, %
				Tar	Pyrolysis water	
1.	200	80	93.20	1.30	2.98	2.52
2.	300	80	83.02	2.63	7.53	6.82
3.	400	80	75.12	4.84	13.10	6.94
4.	500	80	70.86	6.55	13.27	9.32
5.	600	80	69.71	7.21	12.57	10.51
6.	700	80	68.60	7.20	12.10	12.00

Table 4. Yield of pyrolysis products in a large-scale retort at 600°C

№	Char, %	Condensed liquid products, %		Uncondensed gas, %
		Tar	Pyrolysis water	
1.	67.25	4.31	17.60	10.84
2.	65.89	4.45	18.66	11.00
3.	65.92	4.24	17.80	12.04
4.	66.35	4.33	18.02	11.29

Table 5. Elemental composition of the bone pyrolysis char and tar and main technical specifications.

№	Elemental composition and specifications	Char	Tar
1.	Carbon (C), wt %,	8.4	73.3
2.	Hydrogen (H), wt %	0.5	10.1
3.	Nitrogen (N), wt %	1.1	11.3
4.	Oxygen (O), wt % (by difference)	5.1	5.3
5.	H/C atomic ratio	0.71	1.65
6.	Ash, wt %	84.8	-
7.	Volatile matter, wt % (daf)	7.7	-
8.	Caloric value, kcal/kg	560.33	-

Table 6. Conditions of curing tests and determined degree of curing reaction of epoxide resin with bone pyrolysis tar and pyrolysis water

№	Samples: Epoxy resin(ER), Tar (T), Pyrolysis Water(PW), Diethylenetriamine (DETA)	Added amount of curing agent, %	Weight of cured sample for extraction in acetone, g	Weight of cured sample after extraction in acetone, g	Acetone soluble fraction,%	Acetone insoluble fraction(degree of curing reaction),%
1	ER+T	15.00	1.2626	0.2393	81.05	18.95
2	ER+PW	20.00	0.6477	0.4077	37.05	62.95
3	ER +PW	60.00	0.7243	0.5509	23.94	76.05
4	ER+PW(concentrated)	20.00	0.9952	0.7282	26.81	73.12
5	ER+(T+DETA)(50:50wt.%)	15.00	1.0231	0.9812	4.00	96.00

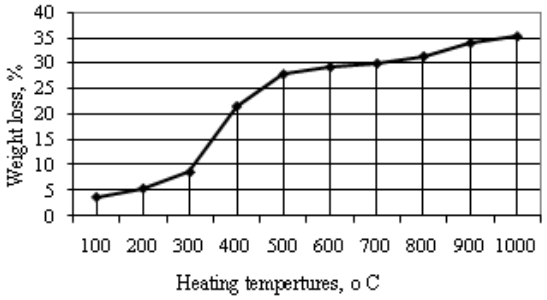

Fig.1. Results of the thermogravimetric analysis of animal bone.

lower volatile organic matters and caloric value. The elemental composition of bone (Table 2) shows that the contents of organic C,H and N are lower and the contents of O and other elements are higher, which is an evidence for the higher mineral content of animal bone (Table 1).

The results of the thermogravimetric analysis of animal bone are shown in Figure 1.

The heating of the bone sample at temperatures in the range of 25-1000 ºC in nitrogen atmosphere shows that the thermal decomposition of bone ends with a 35% weight loss and 65% hard residue at 1000 ºC (Figure 1). The TG curve in Figure 1 consists of different temperature intervals (steps) such as 25-200ºC; 200-500ºC; 500-700ºC; 700-1000ºC. In the first step (25-200ºC) the weight lost is due to the release of some absorbed gas and moisture from the bone sample. In the second step (200-500ºC) intensive thermal decomposition of the organic matter of the bone samples starts forming liquid (tar and pyrolysis water) and gas products. In the third step (500-700ºC) the weight loss strongly decreases, which is an indication for ending thermal decomposition and starting carbonization of the bone sample. In the fourth step (700-1000ºC) the weight loss lowly increases, which is related with the release of gas, e.g., CO_2, H_2, P_2O_5 from the mineral bone contents.

The further experiments focused on the pyrolysis of the bone samples at different heating temperatures in a standard quartz retort and the yields of obtained hard residue (char), condensed liquid (tar and pyrolysis water) and gas products after pyrolysis were determined (Table 3).

Table 3 shows that the yield of char decreases and the yields of tar, pyrolysis water, gas lowly increase by increasing the heating temperature. The yields of pyrolysis products are comparatively higher in the temperature range of 500-700 ºC, which is the optimal heating temperature. The results of the thermogravimetric analysis (Figure 1) and the results of the pyrolysis experiments (Table 3) are very similar and confirm each other. 600ºC was chosen as the optimal heating temperature and the further experiments of pyrolysis were carried out in a large-scale retort at this temperature for collecting more char and tar for their characterization. The yields of pyrolysis products in the large-scale retort (for 3 replicate experiments) are shown in Table 4.

The FT-IR spectrum of bone char is shown in Fig. 2.

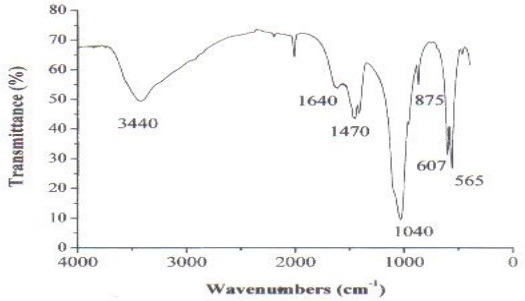

Fig. 2. FT-IR spectrum of bone char

The FT-IR spectrum of bone char in Figure 2 shows that the bands observed at 1640 and 3440 cm^{-1} indicate adsorbed H_2O in the char. The bands appearing at 875 and 1470 cm^{-1} are indicative of carbonate. Bands located around 1040, 607 and 560 cm^{-1} are related with phosphate group absorption. The FT-IR spectrum of bone tar is presented in Figure 3.

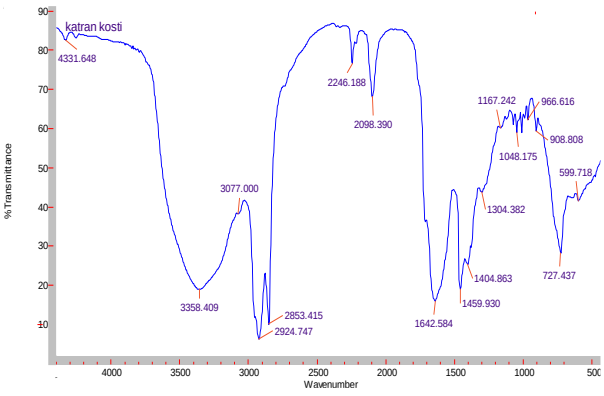

Fig. 3. FT-IR spectrum of bone tar

The FT-IR spectrum of bone tar in Figure 3 shows weak absorption bands for H of aromatic -CH group at 1000-1300,700-800 cm^{-1} and strong bands for H of aliphatic $-CH_3$, $-CH_2$ and -CH groups at 2853-2924 cm^{-1} and also for H of -OH and -NH, $-NH_2$ groups at 3358 cm^{-1}. There are strong bands at 1400-1642cm^{-1} for skeletal vibrations of >C=O groups in ketones, aldehydes, esters and quinines. Therefore the bone tar is a multicomponent mixture mainly consisting of organic substances with aliphatic chains and aromatic structures with oxygen and nitrogen functionalities.

The separated bone tar and pyrolysis water were tested as curing agents for epoxide resin, because the oxygen and nitrogen functionalities in them can react with the epoxy ring of the resin. Epoxy resin, tar and pyrolysis water are soluble in acetone. In case of curing reactions between them, the product should not be soluble in acetone, because of crosslinking reactions between the epoxide chain molecules. The primary results obtained and the conditions of curing reactions are presented in Table 6.

The data in Table 6 show that T and PW both display some curing ability for ER, but the curing ability of PW is over 3.3 times higher than that of T. By increasing the amount of PW 3 times, the degree of curing increased to 76.05%, but such large amount of the curing agent is not suitable. Therefore, as mentioned in the experimental part, the PW was concentrated and used as a curing agent. In this case almost the same result was achieved (73.12%) compared with that of unconcentrated PW (76.05%). This result shows that T and PW originate from the bio-organic material – bone, containing 3.2% N. Therefore T and PW have a certain amount of oxygen (-OH; -COOH) and nitrogen (-NH; $-NH_2$; -CN) functionalities, H atoms from which are able to react with the epoxy groups of ER in crosslinking reactions. PW has more functionalities than T.

To increase the curing ability of bone tar a homogeneous mixture of tar and diethylenetriamine was prepared at a mass ratio of 1:1; the determined degree of curing reaction was 96%. The results of this experiment show that this is a reasonable way for increasing the curing ability of bone tar for epoxy resin (Table 6).

In our previous work a curing agent (casein tar from milk casein, having higher nitrogen content (15.75%) than bone (3.2%)), has been obtained with 94.00-96.00% degree of curing reaction for ER [9]. In our present work a curing agent with 18.95% (T) and 76.05% (PW) degree of curing reaction for ER was obtained from animal bones by pyrolysis. The lower degree of curing reaction of bone T and PW in comparison with that of milk casein is due to the lower content of N in bones.

CONCLUSIONS

1. For the first time the technical characteristics and elemental composition of pure animal bones were determined. Animal bones contain a larger amount of mineral components (A^a-63.5%) than organic matter (V^a-31.30%) and also have less organic carbon (C^{daf}-32.90%) than oxygen and other elements (O^{daf} + others -55.9%).

2. Heating of bone samples in the temperature range of 25-1000 ºC in nitrogen atmosphere shows that the thermal decomposition ends with 35% weight loss and 65% hard residue. The TG curve consists of different temperature intervals (steps) such as 25-200ºC; 200-500ºC; 500-700ºC and 700-1000ºC. In the first step (25-200ºC) the weight loss is due to the release of absorbed gas and moisture from the bone samples. In the second step (200-500ºC) intensive thermal decomposition of the organic matter of the bone sample starts, forming liquid (tar and pyrolysis water) and gas products. In the third step (500-700ºC) the weight loss strongly decreases, which is an indication for ending thermal decomposition and starting carbonization of the bone sample. In the fourth step (700-1000ºC) the weight loss slowly increases, which is related with the release of gas, e.g., CO_2, H_2, P_2O_5 from the mineral content of the bone.

3. The bone char has a higher content of ash-84.8% than initial bone (A^a– 63.5%) and strongly decreased content of carbon, hydrogen, nitrogen and oxygen. The caloric value of the char is 6.4 times lower than that of initial bone, which confirms the lower content (8.4%) of C in the char.

4. In the case of tar, the content of carbon, hydrogen and nitrogen increased almost 10 times in comparison with the char, except the content of oxygen, which remains the same in both cases. Increasing of the content of C, H and N in the tar indicates that these elements come from the bone organic matter released during the thermal decomposition of bone. The pyrolysis tar is a viscous liquid with black-brown color and unpleasant smell.

5. The FT-IR spectrum of bone char shows that the bands observed at 1640 and 3440 cm^{-1} indicate adsorbed H_2O in the char. The bands appearing at 875 and 1470 $cm^{-1}$are indicative of carbonate. The bands located around 1040, 607 and 560 cm^{-1}were related with phosphate group absorption.

6. The FT-IR spectra of bone tar in Figure 3 show weak absorption bands for H of aromatic -CH group at 1000-1300,700-800 cm^{-1} and strong bands for H of aliphatic $-CH_3$; $-CH_2$ and -CH groups at 2853-2924 cm^{-1} and also for H of -OH and –NH and $-NH_2$ groups at 3358 cm^{-1}. There are strong bands at 1400-1642cm^{-1} for skeletal vibrations of >C=O groups in ketones, aldehydes, esters and quinines. Therefore, the bone tar is a multicomponent mixture consisting mainly of organic substances with aliphatic chains and aromatic structures with oxygen and nitrogen functionalities.

7. Curing agents - tar and pyrolysis water were obtained from pyrolized animal bone with 18.95% and 76.05% degree of curing reaction for low molecular epoxy resin, respectively.

8. A new curing agent for the same epoxy resin was prepared by mixing bone tar and diethylenetriamine at a mass ratio of 1:1 (homogeneous mixture), displaying 96% degree of curing reaction.

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ПИРОЛИЗА НА ЖИВОТИНСКИ КОСТИ, ХАРАКТЕРИЗИРАНЕ НА ПОЛУЧЕНИТЕ ВЪГЛЕН И КАТРАН И ПРИЛАГАНЕТО НА КОСТЕН КАТРАН ЗА ОМРЕЖВАНЕ НА ЕПОКСИДНА СМОЛА.

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(Резюме)

В това изследване са определени техническите характеристики и елементният състав на животински кости, тяхната пиролиза, производството на твърд, течен и газообразни продукти и приложението на течния продукт като втвърдител на епоксидна смола. Животинските кости се характеризират с по-голямо съдържание на минерални компоненти - (A^a -63,5%), отколкото на органични - (V^a- 31,30%) ,а също и с по-малко съдържание на органичен въглерод- (C^{daf}-32,90%) отколкото на кислород и други елементи (O^{daf} + други -55,9%). Пиролизните опити на животински кости са проведени при различни температури на нагряване и са определени добивите на твърд (пиролизен въглен), течен (катран и пиролизна вода) и на газообразни продукти. Температурата около 600ºC бе определена като оптимална температура на нагряване и са получени около 66,35% пиролизен въглен, 4,34% катран, 18,02% пиролизна вода и 11,29% газове са получени при пиролизата. Пиролизният костен въглен има високо съдържание на пепел -84,8% в сравнение с костите (A^a -63,5%) и със интензивно намаление на съдържанието на въглерод, водород азот и кислород. В случая на катрана, съдържанието на въглерод, водород и азот нараства около 10 пъти в сравнение със съответното съдържание в костите. Пиролизата на проби от животински кости е проведена в лабораторен реактор. Във предишна наша работа бе получено втвърдяване на епоксидна смола ЕД – 20 със костния катран 18,95% и с пиролизна вода 76,05%. Ние приготвихме нов втвърдител на същата смола чрез смесване на костния катран с диетилентриамин в масово съотношение 1:1 (хомогенна смес), която дава 96% на омрежващата реакция.