Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 743–748

INVESTIGATION ON PYROLYSIS OF CASEIN

B. Purevsuren and Y. Davaajav

Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar-51, Mongolia

(Received March 12, 2001; in revised form May 10, 2001)

Abstract

First casein was processed by pyrolysis and investigated under optimal thermal treatment condition to obtain a good quality adsorbent with high developed porosity structure and liquid product as a complex raw material for different kind of organic compounds with interesting properties and structures. The yields of hard residue, pitch, pyrolysis water and gases were determined and compared with the yields of pyrolysis products of other investigated different kind of organic materials.

The chemical composition of pitch was determined as following: free carbons – 4.52%, organic acids – 0.64%, organic bases – 38.00%, phenols – 7.75%, asphaltenes – 0.97%, paraffin's – 1.30%, neutral oils – 16.20% and preasphaltanes – 30.10%. The pitch was fractionated by air distillation into 3 liquid fractions with different boiling range and a bitumen like residue with a lower softening temperature.

Keywords: biochar, casein, pitch, pyrolysis

Introduction

Pyrolysis, or thermal decomposition of organic materials in the absence of oxygen is of practical importance in charcoal (semicoke or hard residue) making and in the production of so-called pyrolytic oils (liquid products or pitch) from the basic organic raw materials such as coal [1], oil shale [2], wood [3], polymer wastes [4], and some bioorganic materials including animal bone [5]. It is known that a good adsorbent and a filtering material for sugar industry can be obtained by pyrolysis of bone [6].

Unfortunately, we have found no information about the pyrolysis of other animal biomaterials including casein. In our previous work [7] first we have investigated the thermal stability and thermal decomposition kinetic of casein by thermogravimetric analysis and this paper contains the results on pyrolysis of casein aimed to obtain a biochar with high developed porosity structure and pitch with contents of unknown composition and properties.

1418–2874/2001/ $ 5.00
© 2001 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Pyrolysis of casein was performed in a laboratory horizontal cylindrical retort made by stainless steel which could contain 1000 g of sample. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 900°C. A chrome–alumel thermocouple was immersed in the casein bed to measure the actual heating temperature and an equipment for temperature control (potentiometer). The retort was connected with an air-cooled iron tube and water-cooled laboratory glass condenser and a collection vessel for the condensate of liquid product (pitch and pyrolysis water). The non-condensable gases after water-cooled condenser were left the system through a thin glass tube. The pyrolysis experiments at different temperature of heating (200, 300, 400, 450, 550 and 600°C), were carried out at the same heating rate (20°C min^{-1}) and the yields of products including solid residue, pitch, and pyrolysis water determined by weighing and the yield of gases by difference. The pyrolysis experiments at different heating rates were carried out at the same heating temperature until 550°C was reached inside the retort.

The chemical compositions of pitch in group organic compounds determined by methods described in [8] and air distillation of pitch was performed in a laboratory flask and fractions with different boiling temperature range were obtained.

Results and discussion

The basic characteristics of casein and other organic raw materials investigated by us are given in Table 1.

Table 1 The basic characteristics of casein and other organic materials in %

No.	Samples	Moisture[a]	Ash[b]	Volatile matter[c]	Carbon	Hydrogen	Other elements
1	Casein	8.73	4.72	78.28	52.49	7.14	40.37
2	Bone	4.07	64.69	26.89	32.91	8.00	59.09
3	Oil shale	5.88	61.12	36.59	65.29	13.14	21.57
4	Brown coal	6.78	10.96	44.86	66.82	5.21	27.90

a – analytical moisture; b – analytical ash; c – dry based volatile matter

As a pure bio-organic material casein has the highest content of volatile matter and the lowest content of mineral matter compared to others (Table 1). At the same time casein has lower thermal stability previously determined by us [7]. For this reason casein was chosen as a raw material for pyrolysis aimed to obtain biochare and pyrolytic oil with interesting properties.

For the determination of optimal temperature of pyrolysis casein was decomposed at different heating temperatures.

The yields of pyrolysis products at different heating temperatures with the same rate of heating (20°C min^{-1}) are shown in Fig. 1.

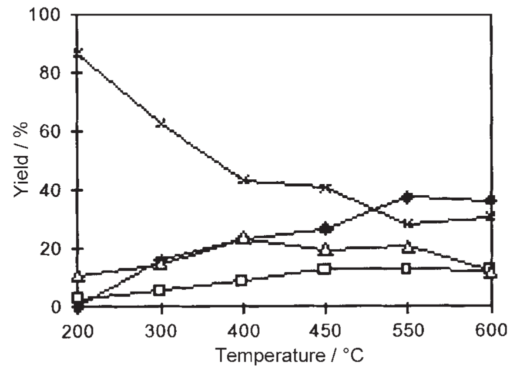

Fig. 1 The yields of casein pyrolysis *vs*. temperature; ◆ – pitch, Δ – pyrolysis water; × – hard residue; □ – gas and loss

These results show that the yield of pitch, pyrolysis water and gas increased with rising the temperature of pyrolysis. Only the yield of hard residue was decreased at the same time. The formed pitch and hard residue were the most important products for us. Certainly the yield of pitch is lower at lower temperature, because the thermal decomposition was not enough. The optimum temperature for pyrolysis of casein was selected 550°C, in which the yield of pitch is higher.

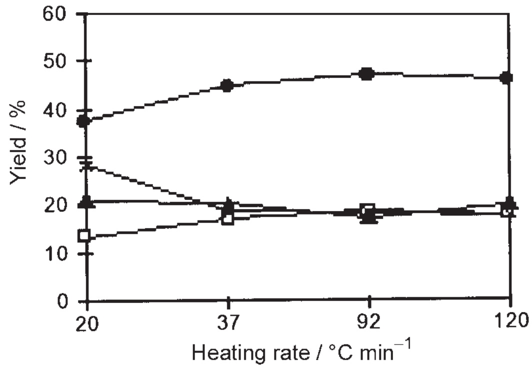

Fig. 2 The yields of pyrolysis products in different rate of heating; ● – pitch; □ – pyrolysis water; × – hard residue; ▲ – gas and loss

The determined specifications of pyrolysis hard residue is the following moisture – 4.56%, ash – 14.5% and volatile matter – 11.4% and it is a compact solid material with high developed porosity structure. The results of preliminary tests for using it as an adsorbent show that it has a good adsorbing properties for methylene blue from its solution (16.08 mg g^{-1}). The next experiments were carried out at this selected temperature, but the rate of heating was altered (Fig. 2).

Results in Fig. 2 show that the yield of pitch also increased with the rising rate of heating and 37°C min^{-1} was chosen as an optimum rate of heating. As a result of these investigations a heating temperature 550°C and heating rate of 37°C min^{-1} was determined as an optimal condition for the pyrolysis of casein. The yields of pyrolysis products of casein obtained in this condition compared with the yields of other organic materials investigated by us are given in Table 2.

Table 2 The yields of pyrolysis products of casein and other organic materials in %

No.	Samples	Hard residue	Pitch	Pyrolysis water	Gas
1	Casein	28.33	37.38	13.23	20.84
2	Bone	70.00	4.92	7.60	17.47
3	Oil shale	73.45	15.62	3.93	6.99
4	Brown coal	68.31	8.71	7.14	15.54

Casein as a pure organic material casein has the lowest ash content and the highest organic matter (Table 1) therefore casein gives the lowest yield of hard residue and the highest yield of pyrolysis liquid (pitch and pyrolysis water) and gas products (Table 2). In the case of bone the yields of hard residue and pyrolysis liquid products are similar or the same as for oil shale and brown coal as for casein (Table 2) because of its higher mineral matter and lower organic matter content (Table 1).

The pitch and pyrolysis water are formed in two unmixed layers and was easy to separate them in all cases of organic materials. Both smelt very bad. The casein pyrolysis pitch is viscous liquid with black-brown color and it becomes thicker during keeping under room condition which was the specific property compared to the pitches of other organic materials.

The chemical composition of casein pyrolysis pitch for a group of organic compounds is shown in Fig. 3.

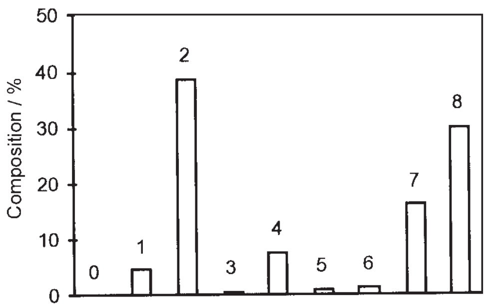

Fig. 3 The chemical composition of pyrolysis pitch; 1 – free carbons; 2 – organic bases; 3 – organic acids; 4 – phenols; 5 – asphaltanes; 6 – paraffins; 7 – neutral oils; 8 – preasphaltanes

The content of organic bases, neutral oils and phenols are higher than others. Certainly the higher content of organic bases depends on the higher nitrogen content (14.2%) of initial casein. Confirming this the pitch has strong alkaline reactions (pH>10). The casein pyrolysis pitch differs from the pitch of coal, oil shale and wood with its higher content of organic bases and thickening properties during storage time. This thickening and hardening properties indicate that they are sensitive to oxidation and polymerization. This property was an evidence for using it as a curing agent for cross-linking reactions of epoxy resins. The necessary amount of pitch for curing reaction of epoxy resin was determined experimentally as 7–10% for the stoichiometric amount of epoxy resin with 15–20% epoxy group content. The pitch has good compatibility with epoxy resin and the sample was cured at 80°C for 24 h in oven. It is known that most epoxy resins have excellent solubility in acetone, but after the curing reaction with pitch the sample was a solid material, more than 91% of which (the degree of curing reaction) is insoluble in acetone. Therefore, the casein pyrolysis pitch can be used successfully as a good curing agent for epoxy resin, because we have achieved the same degree of curing reaction with diethylenetriamine and maleic anhydride, which are the commercial curing agents for epoxy resins.

The pitch was also tested as an antioxidant for liquid casein glues. Adding a little amount (several drops) of pitch the time of using preparation of liquid casein glue is increased as long as well.

The casein pyrolysis pitch was treated by an air distillation and obtained several liquid fractions with different boiling range and bitumen like hard residue. The yields of these products are shown in Fig. 4.

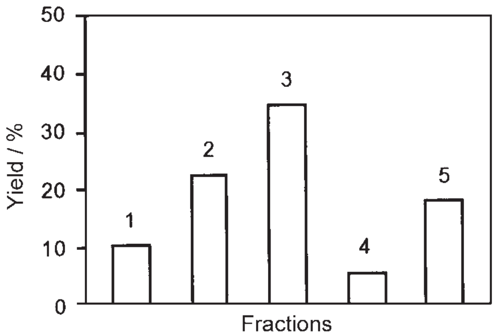

Fig. 4 Air distillation of pitch. Fractions with different boiling range; 1 – until 150°C (very light); 2 – 150–200°C (light); 3 – 200–250°C (middle); 4 – 250–300°C (heavy); 5 – >300°C (hard residue)

Figure 4 shows that the major part of the pitch was distilled at 150–200 and 200–250°C boiling temperature interval. The obtained four liquid fractions keep the consistence as a liquid for ever is comparison with the mother pitch. It means that components sensitive to oxidation and polymerization formed the greater part of the hard residue.

The pyrolysis pitch of casein was fractionated also by its solubility in different organic solvents: hexane – 31.92%, benzene – 47.89%, dioxane – 16.67% and water – 3.53%. This result demonstrates that the casein pitch consists of soluble in hexane aliphatic and soluble in benzene aromatic hydrocarbons, soluble in dioxane compounds with N and O containing high polar functional groups and water soluble parts.

It is important to emphasize that the casein pyrolysis pitch and its fractions are a complex raw materials for different kind of organic substances with interesting and new properties and unknown structure. For this reason it is necessary to investigate it in detail next time.

References

1 B. Purevsuren, J. Narangerel and D. Baljir, Proc. of the Mongolian Academy of Sciences, Ulaanbaater 1999, No. 2, p. 32 (in Mongolian).
2 B. Avid, B. Purevsuren and J. Dugarjav, Oil shale, 17 (2000) 241.
3 Sh. Munkhjargal, B. Purevsuren and B. Avid, Mongolian Academy of Sciences, 1998, p. 25.
4 S. L. Low, M. A. Connor and G. H. Covey, Proc. of the Second International Conference on Environmental Management, Australia, 10–13 February 1998, p. 269.
5 B. Purevsuren, T. Gerelmaa and Y. Davaajav, Proc. of the Mongolian Academy of Sciences, Ulaanbaatar 2001 (in press).
6 Kirk–Othmer, Encyclopedia of Chemical Technology, 3rd ed., Vol. 21, Wiley 1983, p. 897.
7 B. Prevsuren and Y. Davaajav, J. Therm. Anal. Cal., 65 (2001) 147.
8 A. M. Tarasova, Kratkoe rukovodstvo k praktikumu po khimii iskustvennogo jidkogo topliva, Izd-vo MGU, 1971, str. 45.