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# THERMAL ANALYSIS OF CASEIN

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## Abstract

Casein was analyzed during thermal treatment and pyrolysis. The thermal degradation process of casein was interpreted and thermostability indices, rate, order and activation energy of thermodestructive reaction of casein were determined on the basis of thermogravimetric analysis. The thermodestruction of casein has the characteristics of a first order reaction with activation energy $E_a$=3.87 kcal mol$^{-1}$ (16.2 kJ mol$^{-1}$).

The pyrolysis of casein was investigated and we determined optimal heating temperature – 550°C and yields of biochar, pitch, pyrolysis water and gases.

**Keywords:** biochar, casein, pitch, pyrolysis, thermal degradation

## Introduction

Casein, the main product of dairy industry is an important food protein [1]. Besides its relevance as a nutritional product, casein has been used for a long time in non-food applications, particularly as a binding material for plastics, man-made fibres, coatings and dyes [2–4]. Casein is used as a main component of glue in Mongolia [5, 6]. Other biomedical applications include gels [7], drug releasing microspheres [8] and edible films [9].

Uses of casein for technical applications are based on chemical modifications to the side groups of amino acid residues, crosslinking and its good binding properties [2]. For example, modified with diethylenetriamine casein is a good curing agent [10] in new synthetic epoxy oligomers [11].

Thermal treatment analysis is widely used in the investigation of thermodestructive reactions and determining kinetic parameters such as rate, order, energy of activation and thermostability indices for synthetic polymers [12] and other organic raw materials including oil shale [13]. However, this method is rarely used in the investigation of biopolymers. We have found no reports on the thermal treatment analysis of casein.

The biochar after pyrolysis and the condensed liquid product (pitch) usually have important applications as a good adsorbent and filtering material and the pitch

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can be an interesting source for different kinds of organic substances with unknown structure and properties. At last nitrogen-enriched carbons with interesting properties can be obtained from raw materials with high content of nitrogen e.g. from some biomass materials [16] or from other carbonaceous materials such as low-rank coal by chemical modification with N-reagents for instance urea, hydrazine, hydroxylamine and so on [17]. The pyrolysis hard residue (biochar) obtained from the selected nitrogen-enriched precursors have considerable effective surface areas and displayed excellent sulfure removal. For this reason casein was chosen as a nitrogen-enriched carbonaceous material for obtaining of a biochar which was not investigated before by thermogravimetric analysis and pyrolysis.

## Experimental

Yak milk casein was obtained from agricultural cooperatives, precipitated by 0.1 N hydrochloric acid solution and dried in air. It was swelled and washed at least two times with distilled water, then dried again at room temperature. Basic characteristics of casein were determined according to the Mongolian standard (UST-471-62).

Thermogravimetric analysis was carried out by using a derivatograph system (MOM, Hungary). Conditions of the analysis were: sample mass 506.6 mg, heating temperature – 20–1000°C, heating rate – 10°C $min^{-1}$, time – 100 min, in air.

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 equipped with an electrical heating system (tube furnace), temperature control equipment, a system for cooling and flask for condensed liquid product.

The elemental analysis of starting casein and its biochar were carried out using a CHN-600 analyzer of Leco Corporation.

## Results and discussion

The elemental composition and some physicochemical characteristics of casein before and after pyrolysis are summarized in Tables 1 and 2. The elemental composition of Mongolian yak milk casein is quite close to the bovine casein (Table 1).

**Table 1** Elemental composition of casein and its biochar

| No. | Elements/% | Yak casein/% | Biochar/% | Bovine casein [15]/% |
|---|---|---|---|---|
| 1 | Carbon | 52.49 | 60.68 | 52.96–53.50 |
| 2 | Hydrogen | 7.14 | 0.70 | 7.09–7.13 |
| 3 | Nitrogen | 15.75 | 9.02 | 15.63 |
| 4 | Oxygen and others | 24.62 | 29.60 | 24.12–24.51 |

As expected, chemical and physical changes occurring in amorphous casein with rising temperature were quite different from those of synthetic crystalline polymers. The DTA curve has an unsharp maxima and minima (Fig. 1). The TG curve

(Fig. 1) shows clearly distinct parts, which differ in thermodestruction rate ($W_r$) and mass loss ($G$). In the temperature range from 80 to 180°C an endoprocess takes place in which heat induces softening of casein.

**Table 2** Basic characteristics of casein and its biochar

| No. | Characteristics | Casein | Biochar |
|---|---|---|---|
| 1 | Colour | pale-yellow | grey-black |
| 2 | Appearance | 3.0–5.0 mm | porous solid |
| 3 | Specific gravity/g cm$^{-3}$ | 2.26–1.30 | 1.94 |
| 4 | Isoelectric pH | 4.6 | – |
| 5 | Moisture/% | 8.73 | 4.56 |
| 6 | Ash/% | 4.30 | 14.5 |
| 7 | Volatile matter/% | 78.5 | 11.4 |
| 8 | Fat/% | 1.53 | – |
| 9 | Viscosity (5% solution in 0.1 M NaOH)/mPas | 12.2 | – |
| 10 | Free acid/mL 0.1 M NaOH g$^{-1}$ | 0.21 | – |

This state facilitates intensive thermodestructive reactions causing vaporization of water and other volatile products. In the temperature range from 180 to 320°C a maximum rate of thermodestructive processes is observed. Above 400°C a minimal mass loss is exhibited, revealing the end of the thermodestructive reactions. The two clearly observed maxima in this part of the DTA curve correspond to the carbonizing and ashing process of the hard residues of casein. There is an unsharp minima (DTA curve) at 640°C, which is probably for a secondary pyrolysis of polymerized hard residue.

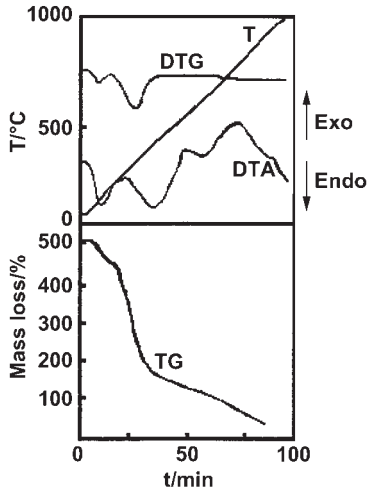


**Fig. 1** TG, DTG, DTA and T curves of casein

From the TG curve in Fig. 1 it was possible to follow the variation of mass loss ($G$%) with temperature and determine thermal indices ($T_{5\%}$ and $T_{50\%}$), which are regarded as specific thermostability indices of casein. These are indicated in Fig. 2. Activation energy ($E_a$), rate and order ($n$) of the thermodestructive reaction of casein were calculated using the method described in [14] from DTA, the differential thermogravimetrical (DTG) curve and temperature ($T$) curves shown in Fig. 1. From the logarithmic correlation between $W_r$ and $G$ (Fig. 3) and semilogarithmic correlation between $W_r$ and $1/T$ (Fig. 4) $E_a$ and n were found as $E_a$=2.0303$R$tg$\alpha$ and $n$(tg$\alpha$).

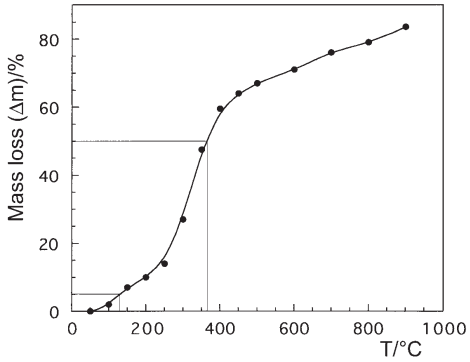


**Fig. 2** Correlation between mass loss and temperature

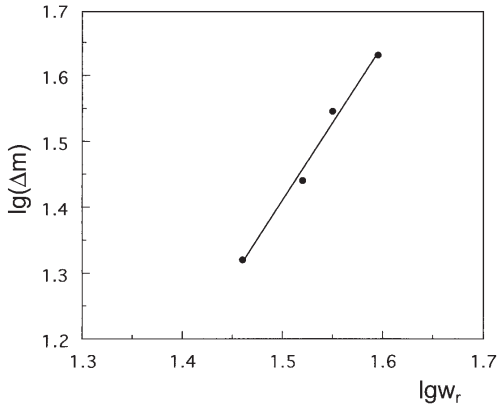


**Fig. 3** Logarithmic correlation between thermodesctructive reaction rate ($W_r$) and mass loss

Using the mass loss *vs*. temperature curve it is easy to find thermal indices of casein, for example $T_{5\%}$=125°C and $T_{50\%}$=355°C, showing the starting and half destruction indices, which correspond to the minimal and maximum reaction rates (Fig. 2). From the logarithmic correlation between the $W_r$ and $G$, it was found that the thermodestruction of casein has the characteristic of a first order reaction with $E_a$=3.87 kcal mol$^{-1}$ (16.2 kJ mol$^{-1}$). These data demonstrate a very low thermal stability of casein in comparison, for instance,

with that of a cured epoxy oligomer ($T_{5\%}$=293°C and $T_{50\%}$=600°C) synthesized and characterized earlier by us [11].

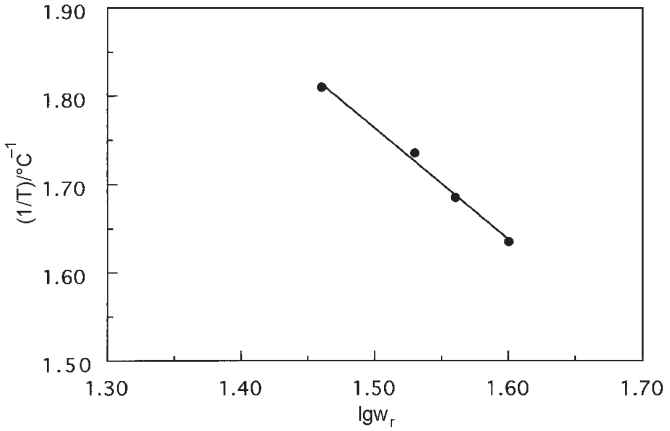


**Fig. 4** Semilogarithmic correlation between thermodestructive reaction rate ($W_r$) and reciprocal temperature

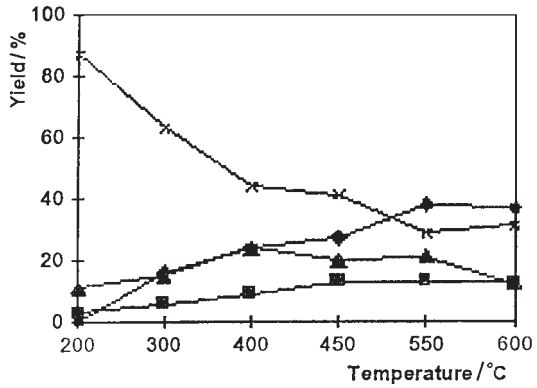


**Fig. 5** The yields of pyrolysis products at different temperatures × – biochar; ♦ – pitch; ▲ – pyrolysis water; ■ – gas

The yields of pyrolysis products at different heating temperature and same rate of heating (18°C min$^{-1}$) are given in Fig. 5. These results show that the yield of pitch, pyrolysis water and gas increased with the rising 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. Water, ammonia, alcohols, acids, bases and phenolic compounds

were obtained as a result of the thermodestruction and intermolecular reaction of pyrolysis products and functional groups of casein.

The amount of pyrolysis water formed during the thermal treatment was four times greater than the water calculated on the basis of moisture (Table 1). All liquid products had strong alkaline reactions (pH=11–12) indicating that considerable part of nitrogen was present as ammonia. The colour and viscosity of these liquid products changed with time at room temperature with an evolution toward a darker and thicker material. This indicates the formation, during the thermodestructive process, of unsaturated and oxidation sensitive products which were able to polymerize.

During the pyrolysis of casein the elemental composition has significantly changed, for instance, carbon and oxygen content increased and the content of hydrogen and nitrogen decreased in the biochar, because of thermal decomposition of casein. The obtained biochar is a compact solid material with highly developed porosity structure and the investigation of its adsorbing and filtering properties and chemical analyses of liquid products are in progress in our laboratory.

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