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Synthesis of keratin foaming agent

Zh.B. Ospanova*, K.B. Musabekov and N. Abeu

*Faculty of Chemistry and Chemical Technology, al-Farabi Kazakh National University,
71, al-Farabi ave., 050040, Almaty, Kazakhstan
e-mail: zhanar.ospanova@kaznu.kz

The samples of technical protein foaming agents based on keratin materials like wool were obtained by method of alkaline hydrolysis. The optimal parameters for the hydrolysis of keratin-containing raw materials were established: the duration of the process was 3 hours, the concentration of the NaOH reagent solution was 5%, the reaction temperature was 403K, the feedstock ratio was NaOH = 1:7.5. Conducted by IR-spectroscopic studies of the hydrolysis reaction products were shown the identify of the samples of keratin foaming agents, obtaining at 403K and at 433K. It is established that at a temperature above 403K the quality of the product of hudrolysis significantly not improve. Proposed structure of the samples has α -helical configuration of laying chain and samples of amino acids with peptide bonds. The samples obtained by hydrolysis of keratin materials are natural surfactants and after modification ther can used as foaming agents in fire fighting and foamers for construction.

Key words: foaming agent, protein, keratin, wool, hydrolysis, foam stability, IR-spectroscopic studies.
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1 Introduction

In the south of Kazakhstan accumulate huge amounts of junk rough wool of sheep. Only fine-wool Merino wool is the production of textiles, and the bulk of coarse wool, finding the application is disposed of. Therefore, the creation of coarse wool processing technology is an urgent task.

Wool is 90% composed of keratin, a fibrillar structure [1, 2], which has an α -helical form (triple woven spiral). It is composed of 20 to 23 amino acids. The basic amino acid cystine peptide residues it contains disulphide bonds which are crosslinked spaced apart remains the same or different chain polypeptide chain. These crosslinks give keratin protein insolubility in water [3].

Depending on the destination of the final product offered considerable variety of methods of destruction of keratin materials, which allow to translate the keratin in soluble form [4-6]. One widely used method is the destruction of keratin hydrolysis in the presence of denaturing agents – acids, alkalis, and salts which, when dissolved in

water to form a hydrolyzed alkalis. Foaming agents obtained by hydrolysis of keratin materials are natural surfactants, and their solutions lyophilic colloids. At the interfaces they are able to form thin layers and films, which are formed as a result of surface phenomena (monolayers, asymmetrical adsorbtion layers, wettable film and symmetrical, double-sided thin film) [7, 8]. Such foaming agents are widely used in fire fighting and foams for construction [9].

The aim of this work was to determine the optimum reaction temperature hydrolysis of keratin material (wool), provides high-quality foam and IR spectroscopic study of alkaline hydrolysis products (hydrolysate) keratin, depending on the conditions of their receipt.

2 Experimental

To determine the effect on the process temperature hydrolysis hydrothermal bomb of stainless steel of at least 200 ml was charged with 20 g of wool were poured 150 ml of various concentrations of NaOH, the bomb sealed, and then the reaction mixture was

heated to the desired temperature. In this mode, the hydrolysis was carried out for a certain time. After hydrothermal bomb was cooled, and filtered hydrolyzate is neutralized with sulfuric acid solution with vigorous stirring until pH = 6 ÷ 7 [10, 11].

The foam is generated by passing air through the solution obtained foam for 1 min. Foam stability is determined by the time the destruction of the foam column.

To determine the composition and structure of the hydrolysis products pre-dried samples were keratin hydrolysates IR – Fourier spectrometer Spectrum – 65 were studied in the range 4000 – 400 cm⁻¹ at room temperature.

3 Results and Discussion

In order to obtain a qualitative keratinous foaming agent, alkaline hydrolysis of wool was carried out using NaOH. The main goal at this stage of work was to establish optimal parameters for the hydrolysis of keratin-containing raw materials (duration of the process, concentration of the reagent solution, reaction temperature, raw material: solution ratio), which ensures the production of a high-quality product.

To determine the effect of the duration of hydrolysis on the quality of the reaction product, the synthesis was carried out as described above, monitoring the appearance and color of the resulting hydrolyzate every hour.

In this mode, the hydrolysis process was carried out 1, 2, 3, 4, 5 hours (Table 1). Then, the hydrothermal bombs were cooled to a temperature of 291-293K, the cooled hydrolyzate was filtered and neutralized with a solution of acetic acid with vigorous stirring to pH = 6-7.

Table 1 – Study of wool hydrolysis as a function of reaction time

Time of hydrolysis, hour	Appearance of the product and color
1	Contains unreacted wool residues
2	Contains wool particles
3	Brown
4	Dark brown
5	Dark brown

It was found that the optimum hydrolysis time is 3 hours. When the time of hydrolysis is shortened, the remainder of undissolved wool is present in the product, which indicates that the duration of hydrolysis was insufficient and the reaction did not go to the end. As the hydrolysis time increases, the resulting product becomes viscous and clots appear in it, which is undesirable.

It is known [12-14] that the wool fibers can be converted to a soluble protein using denaturants – acids, alkalis, arsenic compounds, secondary amines, trialkyl phosphines, etc. The majority of researchers, compared to acid hydrolysis keratin preferred alkaline hydrolysis. Perhaps this is due to the fact that the acid hydrolysis reactor of the manufacturer requires acid-resistant materials, increasing chain process, which leads to higher production costs.

Solubility keratin depends on the alkali concentration, treatment time and temperature. As mentioned above, obtained by hydrolysis of protein hydrolysates comprise amino acid residues that are essentially macromolecular surfactants may be used as effective foam stabilizers.

To establish the influence of temperature, hydrolysis study was carried out at a temperature of 353, 373, 403, 433K at the other parameters constant. After each reaction, the samples neutralized hydrolysate obtained and examined its foam stability. The results of studies of the effect of temperature on the quality of the foam are shown in Figure 1.

As can be seen an increase in the data base concentration decreases wool unreacted (residue) and a total yield hydrolyser ≈ 88 % increase in temperature above 403K does not significantly improve the quality of foam leads to an additional overrun of electricity, so increasing the temperature above 403K is impractical.

Naturally occurring foam constituent and surfactant proteins with intriguing structures and functions are now being identified from a variety of biological sources [15].

The relatively non-specific foaming of denatured proteins is commonplace and widely exploited in food technology and other processes [16, 17]. However, this usually requires much higher protein concentrations (typically N=10 mg ml⁻¹) and much more vigorous physical treatment (whipping and sparging) than is the case with the specialized surfactant and related proteins to be described here. The process is generally acknowledged to be associated with the higher hydrophobicity and/or increased viscosity of denatured protein

in which physical entrapment of air bubbles is facilitated in concentrated viscous mixture. This is usually the dominant mechanism in common culinary processes such as the whipping of cream or preparation of meringue from egg white, for

example. Other familiar examples include the use of protein products to stabilize “instant whips”, beer foam, and other products. Denatured, fluorinated whey and soy proteins are also used on a large scale in fire-fighting foams [18, 19].

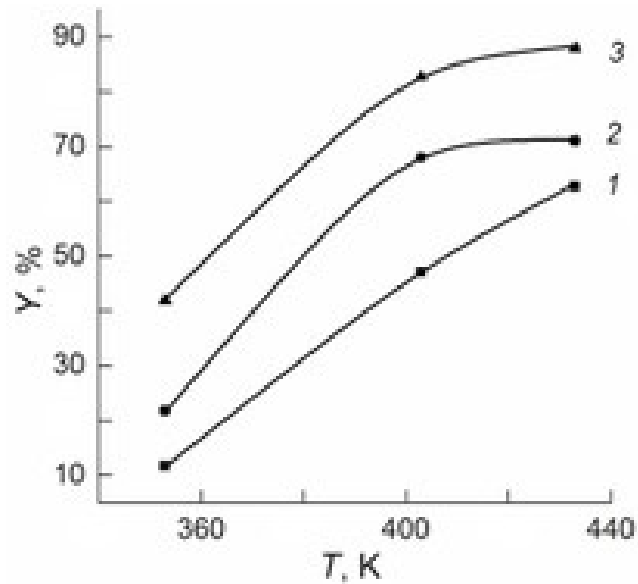


Figure 1 – Dependence of the reaction products from the hydrolysis temperature at a concentration of NaOH in the mixture:
1 – 1% 2 – 3% 3 – 5%.

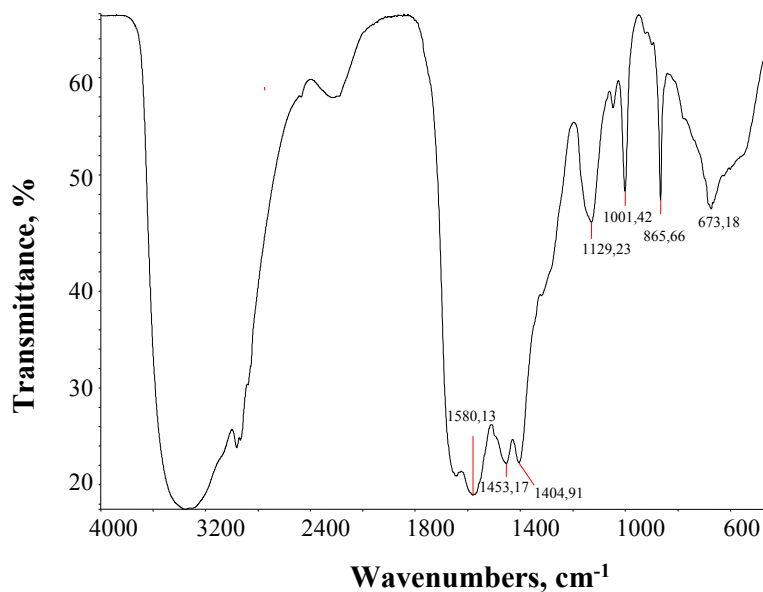


Figure 2 – The IR- spectrum of keratin hydrolysate is synthesized at 353K

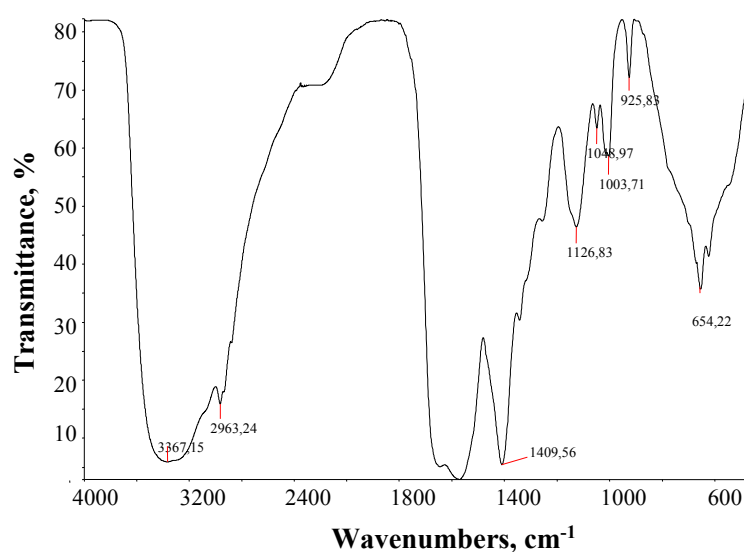


Figure 3 – The IR- spectrum of keratin hydrolysate is synthesized at 403K

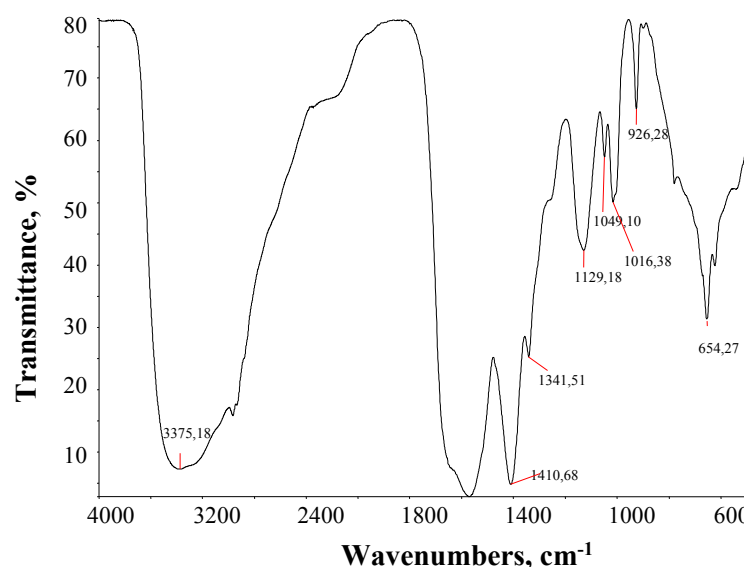


Figure 4 – The IR- spectrum of keratin hydrolysate is synthesized at 433K.

To determine the structure and composition of keratin hydrolysate were investigated IR spectra of samples hydrolysates synthesized at 353, 403, 433K. For the sample obtained at a temperature of 353K (Figure 2) fluctuations in the 3355cm^{-1} correspond to the presence of NH_2 groups, 2920cm^{-1} – CH_2 , CH , 1580cm^{-1} and 865cm^{-1} – NH groups 1453cm^{-1} and 404cm^{-1} – CH_2 and 1630cm^{-1} – the presence of the $\text{C}=\text{O}$.

In the samples obtained at a temperature of 403K (Figure 3), and 433K (Figure 4). IR – spectra are virtually identical: fluctuations in $3367\text{--}3371\text{cm}^{-1}$ –

indicate the presence of NH_2 groups, 2963cm^{-1} are assigned to the links CH , 1573cm^{-1} and NH – groups. Results IR – spectroscopic investigation indicates the presence of amino acids in the sample with a peptide bond.

The absorption bands in the region below 1400cm^{-1} are associated with fluctuations, which involved the entire polypeptide backbone of the molecule. Lack of absorption bands at 1685cm^{-1} , 1629cm^{-1} indicates that the protein virtually no β -configuration with laying anti parallel chains [20]. This eliminates the need for a hydrolysis at higher temperatures.

Proposed structure of the samples corresponds to the content in which α -helical configuration and laying chain amino acids present in the sample with a peptide bond.

To determine the ratio of raw materials: NaOH solution conducted a series of 4 experiments. To do this, the amount of wool needed to hydrolyze was changed in the initial mixture. Raw material ratio: NaOH solution was 1:30, 1:15, 1:7.5, 1:6. All other parameters of the hydrolysis reaction remained unchanged – temperature 403K, duration of the process – 3 hours. After the end of the reaction, the stability of the foams generated from the neutralized hydrolyzate samples was determined.

The stability of foams was 1:30 – 5 minutes, 1:15 – 8 minutes, 1:7.5 – 10 minutes, 1:6 – 5 minutes without the addition of a stabilizer. As can be seen from these data, with a low content of raw materials (wool), foaming agents are formed, giving insufficiently stable foam, and an increase in the content of wool in the reaction mixture leads to the formation of a poor-quality product with low foaming capacity. It was found that the optimum ratio of raw materials: NaOH solution is 1:7.5.

Thus, as a result of the studies, the optimal parameters for the hydrolysis of keratin-containing raw materials were established: the duration of the process was 3 hours, the concentration of the NaOH reagent

solution was 5%, the reaction temperature was 403K, the feedstock ratio was NaOH = 1:7.5. Conducted by IR spectroscopic studies showed the identity of keratin foam samples obtained at 403 and 433K.

4 Conclusions

As a result of the research, a technology has been developed for the synthesis of new polyfunctional foaming agents based on widely available domestic raw materials – keratin wool. It has been established that foaming of aqueous solutions of keratinous foaming agents depends on the ratio of keratin raw material, alkali, temperature and time of the process. The process was controlled by pH. Optimum parameters of hydrolysis of keratin containing raw materials (wool), ensuring the production of a quality product, were established: the duration of the process was 3 hours, the concentration of the NaOH reagent solution was 5%, the reaction temperature was 403K, the feedstock ratio was NaOH = 1:7.5.

The composition and structure of wool keratin hydrolysates synthesized at 353, 403, 433K, were studied by IR spectroscopy. The proposed structure corresponds to the content in the samples of the α -helical configuration of chain packing and the presence of peptide-bonded amino acids in the samples.

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