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Kinetics of amino acid production from hog hair by hydrolysis in sub-critical water

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ABSTRACT

Amino acids can be recovered from hog hair using sub-critical water hydrolysis. Since the reaction kinetics in sub-critical water is very complicated, a simplified kinetic model to describe the hydrolysis of hog hair is proposed: the reaction follows a cero order reaction for the first 45 min and a single consecutive reaction after this time. The differential equations resulting from model were fit to experimental data to obtain kinetic rate constants. A good agreement between the simplified model and the experimental data was obtained.

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1. Introduction

Since waste treatment is one of the most important subjects in the preservation of environment throughout the world, development of an efficient technology for industrial waste is much desired. Regarding wastes, hog hair obtained from slaughterhouses can cause a negative impact on the environment if it is managed by an improper method. Technologies that would treat these wastes or, even better, recover some useful organic materials before disposal, are important. Hog hair is very high in protein which is almost exclusively keratin. In order to recover its protein resource, keratin can be converted into valuable materials such as amino acids. One of the possible technologies to carry out this process is hydrolysis in sub-critical water. In recent years, sub-critical water has been used as a cheap, environmentally friend and cheap solvent for the recycling of different organic wastes: municipal solid wastes [1], refractory pollutants [2], sludges [3], different polymers [4,5], and wastes from seafood processing industries [6–8].

Hydrothermal reaction has been attracting many researchers, because of the fascinating physical and chemical characteristics of water near its critical point. In these conditions water exhibits a much lower dielectric constant and a much larger ion product. The ion product or dissociation constant is about 3 orders of magnitude higher near critical point than it is for ambient liquid water. Under these conditions, there is a high H_3O^+ and OH^- ion concentration. As such, some acid-catalyzed organic reactions can be carried out without acid addition. However, the ion product decreases greatly above the critical point. This fact makes sub-critical water an ideal reaction medium for the hydrolysis of organic compounds [9–11].

Since sub-critical water hydrolysis can be applied for converting various organic wastes into raw material, information about the kinetics of the sub-critical water hydrolysis is very important for the design of the main component of the equipment: the reactor.

The complicated structure of most of the organic wastes makes the kinetic study very difficult. In such cases, simplified and generalized reaction models are useful to describe the involved reactions.

Several researches reported kinetics of reactions for different organic wastes by sub- and super-critical water. These studies propose generalized models based on simplified reaction schemes where substrate is treated as a single component, but they allow quantify the global reaction rate which is necessary and sufficient for engineering purposes. For example, Li et al. [12] considered acetic acid as the rate limiting substrate for wet oxidation of organic compounds. Mizuno et al. [13] considered acetic acid and ammonia for the decomposition of municipal solid waste by supercritical water oxidation. Fromenteil et al. [14] used total organic carbon and chemical oxygen demand to described hydrolysis of epoxy resins. Kinetics of hydrolysis of different protein sources were found in the literature too. Yoshida et al. [15] described the hydrolysis of fish meat and Rogalinski et al. [16] the hydrolysis of bovine serum albumin considering that the substrate split to amino acids that are thermally labile and decompose to different products.

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Nomenclature

[aa]	Amino acid concentration (g/l)
k_A	rate constant (g l^{-1} min^{-1})
k_B	rate constant (min^{-1})
k_C	rate constant (min^{-1})
[S]	substrate concentration (g/l)
$[S]_0$	initial substrate concentration (g/l)
t	time (min)
τ	time for the consecutive reaction (min)
r_a	amino acid production rate (g l^{-1} min^{-1})
r_s	substrate degradation rate (g l^{-1} min^{-1})

Thus, the goal of this work is to propose a kinetic model that describes the sub-critical hydrolysis of hog hair into amino acids.

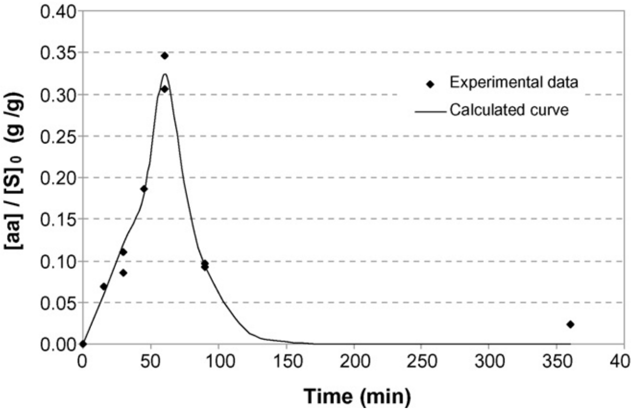

Fig. 1. Experimental data and calculated curve for total amino acid concentration.

2. Materials and methods

2.1. Substrate

The hair, used as substrate, came from a slaughter of hogs and shows two main components: water and protein. The high content in water (65.71%) is due to the pig treatment before obtaining the hair: the hog hair is removed by scalding the pigs in hot water at around 60 °C for a few minutes before singeing. In dry basis, hair presents a high content in protein (94.21%), also containing ash (3.32%) and fat (2.47%) determined in accordance to specific methods [17]. Falla [18] and Moran et al. [19] showed similar values for the composition of the hair.

2.2. Hydrolisis reaction

Sub-critical water hydrolysis was performed in a 500 ml batch reactor made of 316 stainless steel with temperature control and stirring. In the experiments, hair and water were placed into the reactor in order to obtain a concentration of 10 g/l of protein. Then, the reactor was sealed and immersed in a cylindrical heater. The reaction was carried out at 250 °C and temperature in the reactor was measured by a thermocouple. Previous studies proved that 250 °C is the optimum temperature for the hydrolysis of hog hair in sub-critical conditions: temperatures higher and lower than 250 °C showed a negligible production of amino acids in comparison with experiences at 250 °C [20]. Therefore, heating and cooling times of reactor are not important in the process. The reaction pressure corresponds to the saturated vapour pressure of water and was estimated from a steam table. The reaction time was varied from 0 to 360 min at 250 °C. After the desired reaction time, the reactor was allowed to cool down. Subsequent to the reaction, samples were centrifuged at 5500 rpm for 5 min and supernatant liquors were used for amino acids analysis.

2.3. Amino acid analysis

The amino acid content of the hydrolysates was determined by HPLC. Samples were coupled with AccQ-Fluor (aminoquinolil-*N*-hidroxysuccinimidyl carbamate) for further analysis by reverse-phase HPLC using a C18 column (WATERS 600) and an UV detector (WATERS 2487).

3. Results

Figs. 1 and 2 illustrate the time course of amino acid production at 250 °C. The yields of total and individual amino acids gradually increased with reaction time up to 60 min and above that gradually decreased with reaction time. These results indicate that amino acids, produced from hair, are not stable under the reaction conditions after 60 min of reaction time.

Similar behaviour was obtained in a work of Kang et al. [7] where water hydrolysis in sub-critical conditions showed a maximum yield of total amino acids from waste fish entrails at 250 °C for a reaction time of 60 min in a batch reactor.

Kang and Chun [21] also observed a significant decrease in the amino acid production from a hydrothermal process of fish-derived wastes due to the decomposition of amino acids into organic acids or volatile materials.

In general, thermal degradation of amino acids occurs at temperatures above 250–300 °C, depending on the raw protein and the corresponding contact time [6,15,22–24].

Then the kinetic model for explaining the hair degradation in sub-critical conditions has to include the production of amino acids but also the amino acid decomposition.

The models usually proposed for justifying the reactions of production and decomposition of the amino acids from organic wastes consider the same kinetic behaviour from the beginning to the end of the reaction. The consequence of this supposition is a discrepancy between the experimental and calculated data. Thus the simplified empirical reaction model based on a single consecutive reaction of first order proposed by Rogalinski et al. [16] for the production of amino acids from bovine serum albumin by sub-critical water hydrolysis shows the calculated curves clearly displaced in relation to the experimental data points.

This disagreement seems to indicate a change in the kinetic order with the reaction time.

Kajavi et al. [25] also observed this kinetic change in the degradation of monosaccharides in sub-critical water: the degradation of glucose at short residence times obeyed first-order kinetics, but for longer residence times, the first-order kinetics was not applicable.

In order to avoid this discrepancy, in this work two different kinetics have been considered for different reaction times: one for the first 45 min where decomposition of amino acids is not produced and another one for higher reaction times where production and decomposition of amino acids take place.

Although the keratin is split by the cleavage of the peptide bonds within the molecule, the cleavage of the keratin molecule in smaller peptides could not be quantified so that this reaction was summarized as protein splitting up to the free amino acids. Similar assumption was made for other authors [16].

The linear relationship between the amino acid concentration and the time observed for the first 45 min suggests zero-order kinetics at the beginning of the reaction when an excess of substrate

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