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Hydrolysis technology of biomass waste to produce amino acids in sub-critical water

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Abstract

Hydrolysis of biomass waste (such as fish waste, chicken waste, hair and feather) to produce amino acids was studied in sub-critical water, with reaction temperatures from 180 to 320 °C and reaction pressures from 3 to 30 MPa. The product of amino acid was determined by Amino Acid Analyzer (BioLC), and 18 kinds of amino acid were obtained. The results show that the controlling of reaction atmosphere, pressure, temperature and time of hydrolysis is very important to obtain high yield of amino acid; most of amino acids reached maximum yield at reaction temperature range of 200–290 °C and reaction time range of 5–20 min. There are obvious changes of amino acids yield at reaction pressures of 6–16 MPa and reaction temperature around 260 °C, owing to the homogeneousness of the first two phases of water in the formation of vapor and liquid. There are different yields of the same amino acid in different reaction atmospheres (e.g. air, carbon dioxide and nitrogen).

Keywords: Hydrolysis; Biomass waste; Amino acid; Sub-critical water

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1. Introduction

Recently the enormous requirement of biomass (aquatic, livestock, bird, etc.) products is increasing around the world. China is the largest fishing nation in the world, and aquatic products output accounted for one-third of the world total output. The country had the largest market of aquatic products, but the utilized ratio of aquatic products was less than 30%, which was far less than 70% of advanced countries. Since it was banned to dump fish waste into ocean by Landon treaty in 1996, the process of fish waste has become a serious problem because about 40–45% of the fish mass is waste material such as bones, bony parts, entrails, and waste meats (Yoshida et al., 1999; Yoshida and Tavakoli, 2004), which contains a lot of protein and many kinds of biologic active matter. China also has the largest product output of livestock and poultry in the world. The annual output of hair (livestock) and feather (poultry) has reached 1 million tons. The processing and consumption of livestock and poultry will also produce a lot of residues (35–40), currently, which is mainly regarded as waste. The present common measures of processing biomass waste include disposed as trash, buried or composted into protein feedstuff. Therefore, the present measures of processing biomass waste not only take full use of valuable components, but also cause pollution and resource wasting.

Biomass waste hydrolyzed into high value-added products is a practical and effective way. Current industrial hydrolysis methods of biomass waste include chemical (acid, alkali or catalytic) hydrolysis and enzymatic hydrolysis. But the chemical hydrolysis needs violent reaction conditions and often brings serious pollution of the environment. Enzymatic hydrolysis is expensive, and with long production cycle. Therefore, the identification and development of a new environment-friendly method to overcome the shortcomings of the chemical and enzymatic hydrolysis is particularly important.

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Most of biomass waste is easily hydrolyzed in super- or sub-critical water, which is structurally different from normal liquid water, and possesses some marvelous properties: first, it behaves like non-polar organic solvent (similar with acetone), thus it can substitute for some of organic solvents, and become a clean medium for chemical reactions; second, it has density fluctuation, low dielectric properties, and molecular clusters, thus it can become an effective medium for energy and mass transfer; third, its ionic product (H^+ and OH^-) is thousands of times higher than normal water, thus it can take on a powerful catalysis based on acid and alkali at the same time, and it also can be a solvent or reactant participated in chemical reaction (Zhang et al., 2003; Su et al., 1998). Therefore, reaction rate can be accelerated in super- or sub-critical water. Without any pollution, hydrolysis in super- or sub-critical water is an environment-friendly technology. The biomass (Catallo and Junk, 2001; Horiuchi et al., 2004; Rogalinski et al., 2005; Yukihiko et al., 2005; Lamoolphak et al., 2006) and waste (Kang et al., 2001; Yoshida and Tavakoli, 2004; Tavakoli and Yoshida, 2006) can be hydrolyzed into high value industrial raw material: amino acid, unsaturation fatty acid, oil, polysaccharide (Toyoji, 2001), hydrogen and methane (Levin et al., 2007) and so on. Yoshida et al. (1999) studied hydrolysis of fish for producing amino acids in a set of stainless steel tube of 5 ml under argon atmosphere. We studied sub-critical hydrolysis of biomass waste (fish waste, chicken waste, hair and feather) in high pressure vessel with 400 ml capacity, and performed hydrolysis reaction in reaction atmosphere of air, nitrogen or carbon dioxide instead of argon. By controlling condition of reaction, cost can be reduced, and technology can be simplified, while the better result of hydrolysis was gained. The research can realize utilization of other biomass waste (food industries sludge, other biomass waste, etc.).

2. Methods

The samples of fish waste, chicken waste, feather and hair are purchased from market and barbershop. Reagents including 18 kinds of pure amino acids (Shanghai Kangda amino acid factory) and hydrochloric acid (36–38% SCMAIDO) are purchased.

The experimental system includes water tank, high pressure metering pump, electromotor, feeding vessel, nitrogen or carbon dioxide bottle, preheating vessel, feeding funnel, pressure reactor, sampling device, cooling device, collector and so on.

Sub-critical water hydrolysis was carried out using the experimental system. Emulsion of biomass is prepared by putting chopped biomass sample into colloid mill (JM850C). The vessel was pressurized to a pressure of 2 MPa with nitrogen (air or carbon dioxide) in order to prevent the emulsion from contact with other reaction atmosphere. After emptying apparatus and hunting leak, setting thermostat, putting deionized water quantified into vessel, shut valves and heat. When the temperature and pressure of vessel get to the condition of experiment, emulsion was injected, which has been preheated to 90 °C into vessel by high pressure metering pump. It is very important that the emulsion injected into vessel is a small enough quantity comparing with the deionized water in vessel. Thus, the reaction emulsion can be rapidly heated to the desired reaction temperature. Sample and analyze after each interval from finishing injection. Immediately after leaving the vessel, the sampling device was cooled down in order to obtain a well-defined reaction time.

The determination of the amino acids was performed by amino acid analyzer (AAA-Direct, DIONEX). A standard solution of 18 kinds pure amino acid was prepared and analyzed. Hydrolysate samples gained from biomass waste emulsion were analyzed afterward. The instrumentation consisted of a gradient pump (GP50), a chromatography oven (LC30), anion exchange columns (AminoPac PA10) include a analytical column and a guard column, AAA-certified gold electrodes and a electrochemical detector (ED50). Twenty-five microlitres of this mixture were injected after the samples were diluted with pure water and centrifuged at 16,000 r/min. The following gradient elution was performed: 80% A/20% B (pure water/NaoH, 0.25 M, v/v) hold 12 min; 4 min linear gradient of 80% A/20% B to 68% A/32% B; 8 min linear gradient of 80% A/20% B to 36% A/24% B/40% C (sodium acetate buffer 1.0 M, v/v/v), hold 16 min; 0.1 min linear gradient of 36% A/24% B/40% C to 50% B/50% C, hold 10 min; 0.1 min linear gradient of 50% B/50% C to 80% A/20% B, hold 10 min; equilibration time 20 min, flow rate 0.25 ml/min.

3. Results and discussion

Typical chromatograms show that peak positions of amino acids in hydrolysate sample are well in accord with that of standard.

3.1. Amino acid yield in dependency on reaction temperature and time

The effect of reaction temperature and time on amino acid yield in biomass waste hydrolysate was investigated at reaction temperature range of 180–320 °C for reaction time ranging from 1–50 min. The effect result of reaction temperature on amino acid yield in biomass waste hydrolysate for 30 min is shown in Table 1. Three kinds of amino acids (alanine, serine and leucine) are selected as representatives. It can be found that the yield of amino acids increases with rise of reaction temperature at first, and then decreases with continued rise of reaction temperature when reaction temperature rises to a certain value. Most of amino acids reach maximum yield values at the reaction temperature range of 200–290 °C.

The effect results of reaction time on amino acid yield in biomass (chicken and hair) waste hydrolysate at 5 MPa and 260 °C are shown in Figs. 1 and 2. It shows that at first