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Effects of various reaction conditions on the hydrothermal treatment of polypeptone

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Abstract−This study investigated the production behavior of amino acids from polypeptone under various operation parameters and reactor modes (batch and continuous). In the batch experiments, the effect of heating time on amino acid production was studied using different type of reactor materials (Hastelloy (HAS) and SUS). The results showed that the production behavior of amino acids such as Gly, Ala, and Leu was quite similar regardless of reactor materials. To further investigate the relationship of reaction time on the amino acids production, experiments were conducted in batch and continuous reaction at the same conditions (T=523 K and P=30 MPa). The results showed that it is possible to get the same result at the same reaction time using a batch and continuous reaction mode if the reaction time is started after heating time in a batch reaction mode. From the study of reaction pressure, it was observed that the production of amino acids is not favored at reaction pressure between 4 and 30 MPa at 523 K.

Key words: Hydrolysis, Fish-Derived Wastes, Amino Acids, Reactor Material

INTRODUCTION

The use of high temperature and high pressure water (sub-and supercritical water) has been widely applied to various reactions such as reduction, pyrolytic, decomposition and dehydration [Savage et al., 1995]. Examples are oxidation of phenols [Martino and Savage, 1999], pyridine [Aki and Abraham, 1999a, b] and methanol [Anitescu et al., 1999], and hydrolysis of esters [Krammer and Vogel, 2000] and thiodiglycol [Lachance et al., 1999].

In the area of resource recovery from seafood processing wastes, Yoshida et al. [1999] applied subcritical water to produce organic and amino acids from fish meat by hydrolysis. They found that the liquefaction of fish meat occurred rapidly using subcritical water. Daimon et al. [2001] and Kang et al. [2004] investigated hydrolysis of proteins present in various marine wastes using sub- and supercritical water. They suggested that the yield of total amino acids from waste fish entrails was obtained at subcritical conditions (T= 523 K, P=4 MPa) using the batch reactor. Under supercritical conditions (e.g. T=653 K, P=45 MPa), the yield of amino acids decreased because of higher decomposition compared to production rate of amino acids. Even though they proposed an efficient process for converting organic wastes to useful resources, the information on the effect of operating parameters (e.g. heating time, reactor material, etc.) was not discussed in detail.

In the design of an applicable hydrothermal treatment process, information on the effects of various operating parameters is important. Among the parameters influencing hydrothermal reactions, temperature and time are usually the major concern of several researchers [Sasaki et al., 1998; Meyer et al., 1995]. These are the two most important parameters necessary for the technical and economic assessment of the process. To facilitate the design of an actual process, dependence of the behavior of products composition and yield on operating modes should also be studied.

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The main purpose of this study was to investigate the production of amino acids from polypeptone under various operating parameters and reactor modes (batch and continuous). Batch reaction mode takes about 5 min for a 66 cm^3 reactor made Hastelloy C-22 to reach a desired temperature of 523 K heated by a molten salt bath, while a 6 cm^3 reactor made of SUS 316 requires 2 min [Kang et al., 2001]. The transition in temperature and pressure might have an effect on reaction chemistry and therefore on the results. This would not give accurate results for the study of the effect of reaction parameters (temperature, pressure and time). For this reason, the effect of these parameters on the production behavior of amino acids using batch and continuous-flow reactors is quite difficult to analyze. In this regard, a study of the effect of reaction parameters between batch reaction and continuous reaction mode on the production behavior of amino acids is important. This information would be necessary in the design and economic evaluation of an applicable hydrothermal treatment process to recover amino acids from fish-derived wastes.

EXPERIMENTAL SECTION

1. Experimental Apparatus and Methodology

Polypeptone (acid hydrolysate of casein, Nihon Seiyaku Corp.) was used as a model material for fish-derived wastes. Before the experiments, the polypeptone was dissolved in distilled water to obtain a concentration of 1,000 mg/L.

The experimental apparatus and procedures for batch experiments have been described elsewhere in detail [Kang et al., 2001, 2004]. A reactor with a polypeptone solution was immersed into the preheated molten salt bath. After the desired reaction time, the reactor was plunged into a water bath to cool it down to room temperature.

For continuous flow experiments, peptone solution was prepared with deionized water at a sample to water weight ratio of 1 : 2. Small-scale continuous flow tubular reactor system is shown in Fig. 1. Inlet of a stainless steel tube (SUS-316) with inner diameter of 0.25 mm was connected to the backpressure regulator (Jasco, Model 880-81). This could be operated at a maximum operating temperature

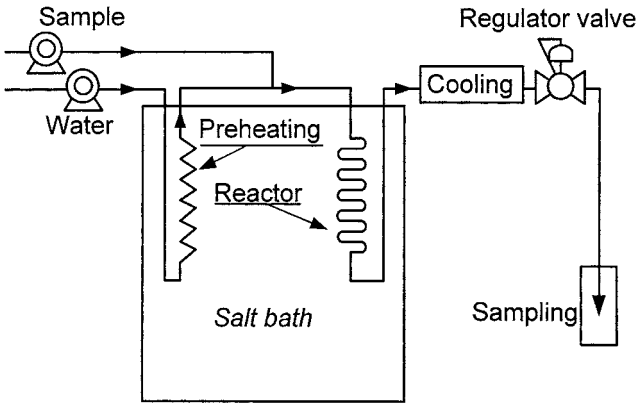

Fig. 1. Schematic diagram of small-scale continuous flow tubular reaction apparatus.

and pressure of 623 K and 35 MPa, respectively. Sample and deionized water were delivered at a constant flow rate. The apparatus was designed to mix two separate flows at a known temperature and fixed flow rates and to allow this mixture to react at isothermal conditions. The reactor pressure was controlled by adjusting the regulator valve. The temperature of deionized water was brought to the desired level by a preheating, and then mixed with sample solution before entering the main reactor.

2. Analytical Methods

The amino acid content of the reaction products was determined by using an amino acid analyzer (LC-10AD, Shimadzu Corp.). The amino acid analyzer is a combination of an ion exclusion column (Shim-pack Amino-Na, Shimadzu Corp.) and post-column labeling methods with spectrofluorophotometer (RF-10A, Shimadzu Corp.). In sample preparation for amino acid analysis, filtration was done by using an ultra-filtration membrane (30,000 fractional molecular weight, Millipore Ultra Free C3) to maintain good performance of the chromatographic system. The quantities of 17 kinds of amino acids (presented here according to elution order) - namely, aspartic acid (Asp), threonine (Thr), serine (Ser), glutamine (Glu), proline (Pro), glycine (Gly), alanine (Ala), cystine (Cys), valine (Val), methionine (Met), isoleucine (ILeu), leucine (Leu), tyrosine (Tyr), phenylalanine (Phe), histidine (His), lysine (Lys) and arginine (Arg)- were determined in each analytical run.

RESULTS AND DISCUSSION

1. Dependence of Heating Time at Different Types of Batch Reactor

The effect of heating time on amino acid production was studied by using different types of batch reactors (made from Hastelloy (HAS) and SUS). All reactions were conducted at 523 K, where the ion product of water is known to be maximum under saturated vapor pressure (4 MPa). Fig. 2 shows the experimental results. Others indicate the amount of other amino acids analyzed as described in the analytical methods. The reaction time of 0 min indicates the amount of initial free amino acids, also shown to serve as a reference.

As an intrinsic characteristic of a batch reactor, it took about 2 to 5 min for the temperature inside the rector (HAS and SUS types,

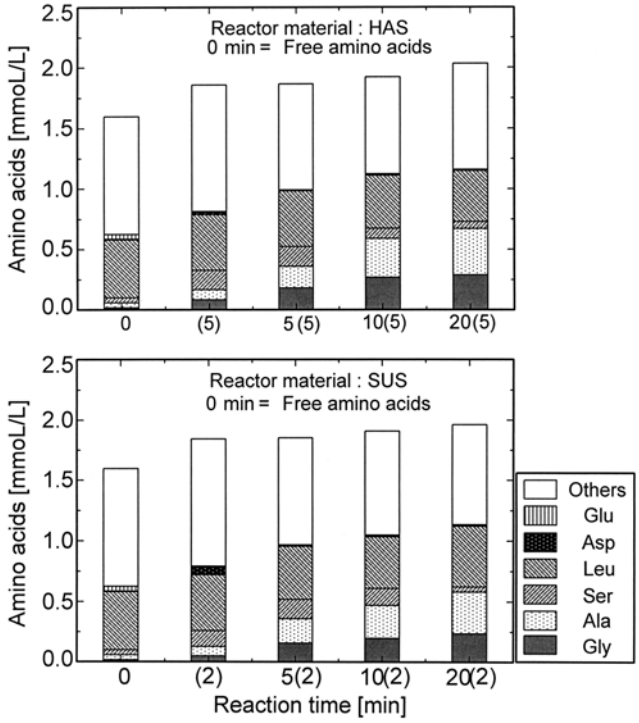

Fig. 2. Comparison of amino acids produced at each reaction time (Batch, RT=523 K, P=4 MPa, reaction time: (5), (2)=heating times).

respectively) to reach the temperature of the salt bath (523 K, 4 MPa). During the heating times of 2 to 5 min, at non-isothermal condition, the production yield of amino acid tended to increase compared to initial free amino acids. However, this result is not significant. In this work, reaction time is started after the heating times. After the heating times, the production behavior of amino acids such as Gly, Ala, and Leu was quite similar regardless of reactor materials (reaction time=10 min at HAS, reaction time=10 min at SUS). This result suggests that proper control of reaction time is necessary in order to get the same result using different types of reactor material. Hence we believe that the type of reactor materials does not affect the production of amino acids from the protein hydrolysis under high temperature and high pressure.

2. Relationship between Batch and Continuous Flow Reactor

It should be noted that it is quite difficult to get the same result at the same reaction time using a batch and continuous flow reactor due to the transition in temperature and pressure prior to reaching the desired reaction conditions. In addition, it is more economical to operate the system continuously if the production demand is high. A continuous process would not require a large scale, thus reducing the capital cost. In a laboratory scale, it is more practical if the experimental result of batch operation is applied in a continuous process. However, it needs to be verified whether experimental results obtained in batch process could be used in the design of an actual continuous operation.

To further investigate the relationship of reaction time on the amino acid production, experiments were conducted in batch and continuous flow reactors at the same conditions (T=523 K, time=10 min, and P=30 MPa). Fig. 3 shows a comparison of amino acids produced at batch and continuous reaction mode. The production yield

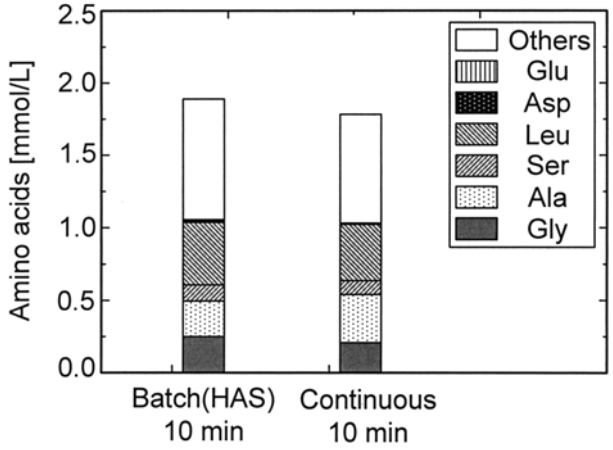

Fig. 3. Comparison of amino acids produced at batch and continuous reaction mode (RT=523 K, P=30 MPa).

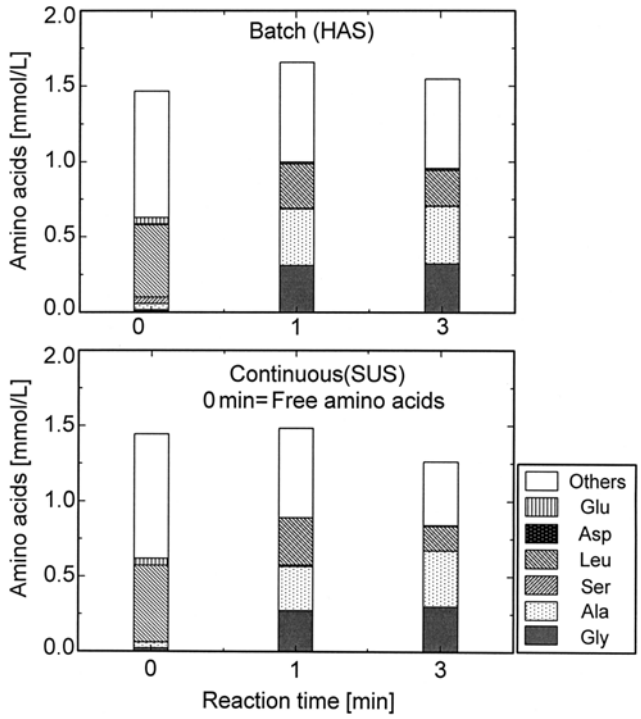

Fig. 4. Comparison of amino acids produced at batch and continuous reaction mode (RT=573 K, P=30 MPa).

of amino acids was quite similar in spite of different reaction modes. Regarding this, the production behavior of each amino acid also tends to correspond. Based on the results in Fig. 3, the effect of reaction time on the amino acid production between batch and continuous reactor was further investigated at higher temperature. Fig. 4 summarizes the effect of reaction time of up to 3 min on the production of amino acids at batch and continuous reaction. The reaction was conducted at 573 K and 30 MPa. It was observed from the results that the concentration of each amino acid is different from the concentration of original free amino acids. This difference in amino acid concentrations suggests that hydrolysis of protein took place to produce amino acids. The production behavior of each amino acids such as Gly, Ala, and Ser tends to corresponds at each reaction times

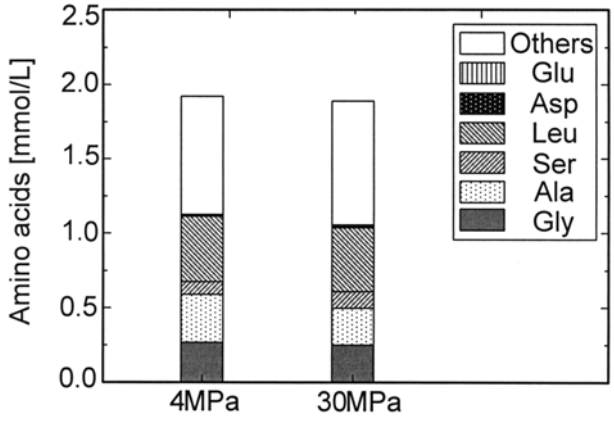

Fig. 5. The effect of reaction pressure on the production of amino acids in a batch reactor (RT=523 K, P=4 MPa).

(reaction time=3 min at batch, reaction time=3 min at continuous). This result showed that it is possible to get the same result at the same reaction time using a batch and continuous reaction mode if the reaction time is started after heating time in a batch reaction mode. In other words, this means that experimental results obtained in batch process could be used in the design of a continuous operation.

3. Effect of Reaction Pressure on the Production of Amino Acids

The ion products of water are strongly dependent on water density and weakly dependent on temperature [Pitzer, 1982; Tanger and Pitzer, 1989]. An increase in the reaction pressure causes a small increase in the water density so that the ion product of water increases, which could possibly accelerate hydrolysis of proteins. To determine the effect of reaction pressure on the production behavior of amino acids, the reaction was conducted at 523 K for 10 min with varying the reaction pressure from 4 to 30 MPa. Fig. 5 shows the effect of reaction pressure on the production of amino acids in a batch reactor. Gly, Ala, Ser, and Leu were the dominant amino acids obtained between 4 and 30 MPa. The ion product increases with increasing pressure (Kw=−11.2 at P=4 MPa and Kw=−10.98 at P=30 MPa). When the pressure was changed to 30 MPa, no significant changes in amino acids production were observed. Under these conditions, the reaction pressure has no significant effect on the amino acid production. Further investigation at a pressure higher than 30 MPa is necessary.

CONCLUSIONS

Production behavior of amino acids from the hydrolysis of polypeptone was investigated under various reaction conditions such as reactor material, heating time, and reaction pressure.

Experimental results demonstrate that different types of the reactor materials did not affect the amino acid production in high temperature and high pressure water reaction. The same results could be obtained in a continuous reaction mode if the reaction is starting after heating time (5 min at Hastelloy) in a batch reaction mode.

From the study on the effect of reaction pressure, it was observed that production is not favored at reaction pressure between 4 and 30 MPa at 523 K. This is due to the low ion product in this pressure ranges. This result suggests that proper control of reaction pres-

sure is necessary to clarify the effect of reaction pressure.

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