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ORIGINAL ARTICLE

# Kinetics of amino acid production from bean dregs by hydrolysis in sub-critical water

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**Abstract** Amino acids play an important physiological role in all life-forms and can be recovered from bean dregs waste using sub-critical water hydrolysis. This work deals with the hydrolysis kinetics of bean dregs. Kinetics was conducted in a temperature range of 200–240°C using a 300-ml stainless steel batch reactor. Since the reaction kinetics in sub-critical water is very complicated, a simplified kinetic model to describe the hydrolysis of bean dregs is proposed: a single consecutive reaction. The differential equations resulting from the model were fit to experimental data to obtain kinetic rate constants. By means of the Arrhenius plot, the activation energy as well as the pre-exponential factor was determined. A good agreement between the simplified model and the experimental data was obtained. The kinetic parameters provided useful information for understanding the hydrolysis reaction of bean dregs. The experimental results show that the best hydrolysis technology is: reaction temperature 200°C, reaction time 20 min. Under this condition, the total amino acid yield reaches 52.9%. Based on the results, this method could become an efficient method for bean dregs liquefaction, producing valuable amino acid.

**Keywords** Kinetics · Hydrolysis · Bean dregs · Sub-critical water · Amino acids

## Introduction

Amino acids play an important physiological role in all life-forms. However, not all of the 20 amino acids that are involved in the structure of natural proteins (so-called proteinogenic amino acids) can be metabolically synthesized by all creatures. Whereas plants can produce all of the 20 proteinogenic amino acids, some of them (so-called essential amino acids) cannot be produced by the human and animal organisms. These amino acids, therefore, have to be digested in sufficient amounts.

Soybean is one of the most staple human diets especially in Asian countries. China is rich in soybean and has a long history of soybean cultivation. Soybean is the main oil-bearing crop and an important food resource. Because soybean has comprehensive and rich nutrients, the soybean processing industries are in the ascendant. More than 80,000 tons wastes of bean dregs, the main by-product of soybean processing industry, are produced annually in recent years in China. Bean dregs have a high protein content which is about 20 wt% of bean dregs (Jiang and Hu 2008; Zhu and Zheng 2004). In order to recover its protein resource, bean dregs can be converted into valuable materials such as amino acids. Thus, technologies that would recover amino acids before disposal are needed.

Sub- and supercritical water has been gaining increasing attention as both an environmentally friendly solvent and attractive reaction medium for a variety of applications. It is cheap, non-toxic, non-flammable, non-explosive, and offers essential advantages compared to other substances, particularly in the field of "green chemistry". Its distinctly different behavior compared to water at ambient conditions is due to the dramatic changes in physical properties, namely dielectric strength and ionic product, which in turn can easily be altered by changing temperature and pressure (Alenezi et al. 2009). The ion product or dissociation constant is about three 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

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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 (Katritzky et al. 2001; Li et al. 2008) and for the recycling of different organic wastes, such as municipal solid wastes (Goto et al. 2004), refractory pollutants (Kim et al. 2003), sludge (Shanableh 2000; Zhang et al. 2010), different polymers (Chen et al. 2010; Li et al. 2009; Miyoshi et al. 2004), and wastes from seafood processing industries (Daimon et al. 2001; Kang et al. 2001a, b; Zhu et al. 2008a, b) and poultry processing industries (Zhu et al. 2010).

In the present study, sub-critical water hydrolysis was employed as a method for producing amino acids from bean dregs. This article concentrates on the hydrolysis kinetics of bean dregs. Rate constants for the hydrolytic conversion were determined based on a simplified reaction model following first-order kinetics. The results of this study could lead to the development of a value-added product from bean dregs, a cheap by-product of soybean industry.

## Materials and methods

### Substrate

Bean dregs wastes, used as substrate, came from Shanghai University canteen. In dry basis, bean dregs present a high content in protein (20 wt%). Before the experiments, the dried bean dregs were milled for 10 min using a mixer (HR170, Philips Corp.) at the maximum speed setting, and then were sieved. The portion under 140 mesh was collected for tests. Bean dregs were suspended in deionized water to about 5 wt% solids content (1.5 g in 30 ml of deionized water). Then, the feeding suspension was injected into a batch reactor when the temperature and pressure of the vessel got to the condition of experiment.

### Sub-critical water hydrolysis

Sub-critical water hydrolyses were carried out using a 300-ml batch reactor made of (316) stainless steel with temperature control. The schematic diagram of the batch reactor apparatus is shown in Fig. 1.

The experimental system includes water tank, high pressure metering pump, feeding vessel, nitrogen or carbon dioxide bottle, feeding funnel, pressure reactor, sampling device, collector, etc.

After emptying apparatus and checking no leakage, setting thermostat, putting 270 ml of deionized water into the vessel, shut valves and heat. When the temperature and pressure of the vessel got to the condition of experiment, 30 ml of the feeding suspension, which has been preheated to 90°C, was injected into vessel by high pressure metering pump and was diluted to 300 ml in the vessel. It is very important that the feeding suspension injected into vessel is a small quantity when compared with the deionized water in vessel. Thus, the feeding suspension can be rapidly heated to the desired reaction temperature. During the feeding suspension was added to the vessel, the temperature almost kept constant and temperature change did not exceed 1°C. In the experiment, the reaction pressure is the vapor pressure of water at the reaction temperature (temperature 200°C, pressure 1.8 MPa; temperature 220°C, pressure 2.5 MPa; temperature 240°C, pressure 3.4 MPa). Sample and analyze hydrolysate after each interval from finishing injection. Immediately after leaving the vessel, the sampling device was cooled down to obtain a well-defined reaction time.

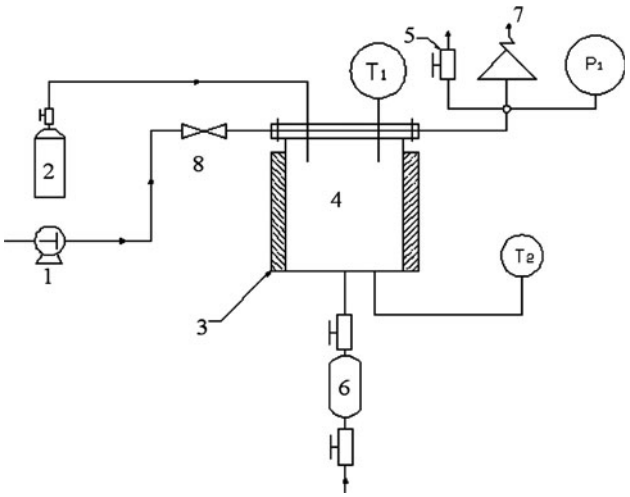



**Fig. 1** Apparatus and flow chart for sub-critical water experiments. *1* Metering pump, *2* nitrogen gas cylinder, *3* heating coil, *4* reactor, *5* emptying, *6* sampling device, *7* safety valve for pressure limitation, *8* valve, *T1*, *T2* temperature controller, *P1* piezometer for pressure indication

### Analysis

The determination of the amino acids was performed by amino acid analyzer (AAA-Direct, DIONEX). The instrumentation consisted of a gradient pump (GP50), a chromatography oven (LC30), an anion exchange columns (AminoPac PA10) including an analytical column and a guard column, AAA-certified gold electrodes and an electrochemical detector (ED50). The following gradient elution was performed: 80% A/20% B (with A = pure water and B = 0.25 M NaOH, 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. The eluents were delivered at a flow rate of 0.25 ml $min^{-1}$. Peak identification and quantification of the components detected with this system were accomplished by injecting standard solution with known composition. A comparison between the hydrolysate and standard amino acid samples is shown in Fig. 2.

## Results and discussion

Several experiments were conducted to examine the possibility of amino acids recovery from bean dregs using a batch reactor. These amino acids—namely, arginine, lysine, alanine, glycine, valine, serine, leucine, isoleucine, histidine, phenylalanine, glutamic acid, aspartic acid, cysteine acid, methionine, tryptophan, threonine and glutamic acid—were determined in the hydrolysates by amino acid analyzer. Amino acids compositions and contents of hydrolysates varied at different temperature or time. Table 1 shows the concentrations of eight main amino acids at different reaction times and the reaction temperature of 220°C. Table 2 shows the effect of reaction temperature on the concentration of eight main amino acids at reaction time 5 min. The amino acid concentration in mg $l^{-1}$ is given at temperature of the analysis (room temperature) in the two tables. In order to have a deep understanding of hydrolysis of bean dregs in sub-critical water, the kinetic of the process was investigated.

### Simplified reaction model

The following simplified reaction scheme based on consecutive reactions was used for the determination of the rate constants for the substrate degradation. The formation ($k_1$) and decomposition ($k_2$) of the desired products were described by a reaction model according to the pattern of a single consecutive reaction as Eq. 1:

$$\text{Substrate} \xrightarrow{k_1} \text{amino acids} \xrightarrow{k_2} \text{degradation products.} \quad (1)$$

Proteins are split by the cleavage of the peptide bonds within the molecule. The resulting amino acids are thermally labile and decompose to further products. The cleavage of the bean dregs molecule in smaller peptides could not be quantified, which could be summarized that the reaction is protein's splitting up to the free amino acids. It has to be stated that this reaction model is fairly simplified as long as the cleavage of bean dregs into their constituent amino acids is treated as one first-order step, thus the intermediate polypeptides are ignored.

Assuming that each stage is an irreversible first-order reaction, the model outlined above can be described in terms of the following differential equations:

$$r_s = \frac{-d[s]}{dt} = k_1[s] \quad (2)$$

where $r_s$ is substrate degradation rate (g $l^{-1}$ $s^{-1}$), $[s]$ is substrate concentration (g $l^{-1}$), $k_1$ is rate constant ($s^{-1}$), $t$ is reaction time (s):

$$r_a = \frac{d[a]}{dt} = k_1[s] - k_2[a] \quad (3)$$

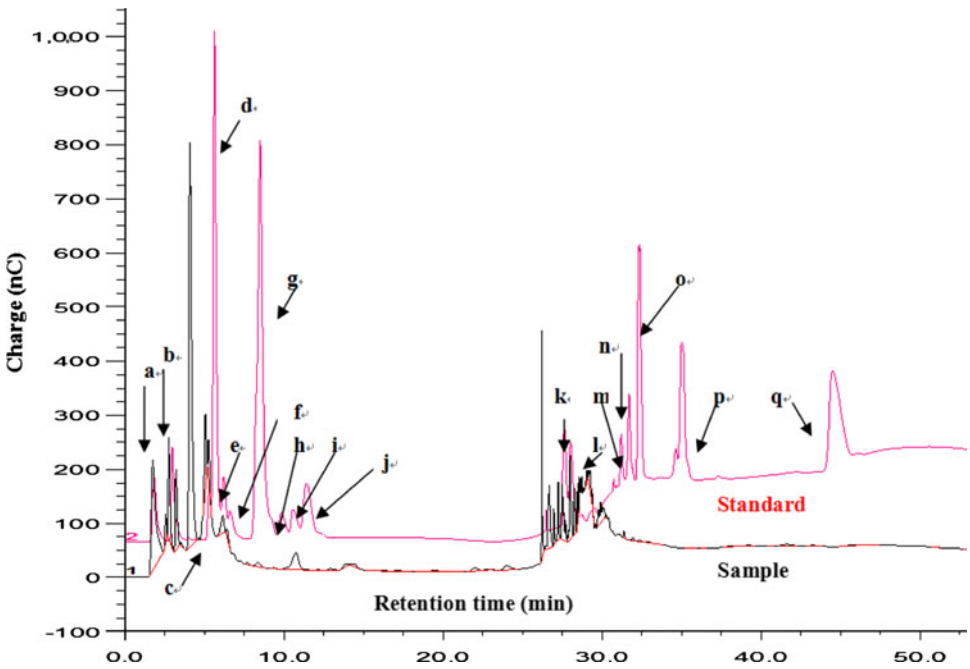



**Fig. 2** Comparison of amino acid chromatogram between standard and sample (temperature 220°C, pressure 2.5 MPa, reaction time 5 min): *a* arginine, *b* lysine, *c* alanine, *d* threonine *e* glycine, *f* valine, *g* serine, *h* isoleucine, *i* leucine, *j* methionine, *k* histidine, *l* phenylalanine, *m* glutamic acid, *n* aspartic acid *o* cystine, *p* tyrosine, *q* tryptophan

**Table 1** Concentrations (mg $l^{-1}$) of eight main amino acids at different reaction times and a reaction temperature of 220°C

| | Reaction time (min) | | |
|---|---|---|---|
| | 5 | 15 | 30 |
| Arginine | 14.32 | 15.81 | 13.12 |
| Alanine | 13.54 | 11.55 | 8.67 |
| Threonine | 0.15 | 0.31 | 0.17 |
| Histidine | 0.02 | 1.95 | 1.27 |
| Cystine | 0.10 | 0.02 | 0.02 |
| Tyrosine | 0.14 | 0.10 | 0.12 |
| Tryptophan | 0.02 | 0.05 | 0.04 |
| Serine | Not detected | Not detected | 0.22 |

**Table 2** Concentrations (mg $l^{-1}$) of eight main amino acids at different reaction temperature and reaction time 5 min

| | Reaction temperature (°C) | | |
|---|---|---|---|
| | 200 | 220 | 240 |
| Arginine | 4.79 | 14.32 | 16.23 |
| Alanine | 11.70 | 13.54 | 8.09 |
| Threonine | 0.98 | 0.15 | 0.23 |
| Histidine | 0.49 | 0.02 | Not detected |
| Cystine | Not detected | 0.10 | 0.16 |
| Tyrosine | Not detected | 0.14 | 0.13 |
| Tryptophan | 0.02 | 0.02 | 0.04 |
| Lysine | 4.54 | Not detected | Not detected |

where $r_a$ is amino acid production rate (g $l^{-1}$ $s^{-1}$), $[a]$ is amino acid concentration (g $l^{-1}$), $k_2$ is rate constant ($s^{-1}$).

The concentration of free amino acids is affected by two different factors: the amino acid production from bean dregs and the decomposition to further reaction products, as illustrated by Eq. 3.

Equation 2 shows the degradation rate of the substrate, where substrate concentration is expressed as g $l^{-1}$ of protein, and Eq. 3 shows the production rate of amino acids where amino acid concentration is expressed as g $l^{-1}$ of amino acid.

After integration of Eq. 2, the dependence of substrate concentration on time in the reactor is obtained:

$$[s] = [s]_0 \exp(-k_1 t) \tag{4}$$

where $[s]_0$ is initial substrate concentration (g $l^{-1}$).

Insertion of Eq. 4 into Eq. 3 leads to a first-order linear differential equation:

$$\frac{d[a]}{dt} + k_2[a] = k_1[s]_0 \exp(-k_1 t). \tag{5}$$

Taking into account the following boundary condition:

$$\text{At} \quad t = 0 \rightarrow [a] = 0 \tag{6}$$

the dependence of amino acid concentration on time is obtained by solving Eq. 5:

$$\frac{[a]}{[s]_0} = \frac{k_1}{k_2 - k_1}(\exp(-k_1 t) - \exp(-k_2 t)). \tag{7}$$

Equation 7 describes the amino acid yield based on the initial amount of bean dregs assuming a consecutive reaction. The rate constants $k_1$ and $k_2$ can be obtained by fitting them to experimental results. The parameters were evaluated using the method of nonlinear least squares regression analyses by MATLAB 7. Usually kinetics is described with molar concentrations, not with g $l^{-1}$ concentrations. Nevertheless, from Eq. 7, we can see that $\frac{[a]}{[s]_0}$ has the dimensions of concentration divided by concentration, so it is possible to use g $l^{-1}$ instead of molar concentrations. The amino acid yield is defined as $\frac{[a]}{[s]_0}$.

The rate constants' temperature dependence can be described by the Arrhenius equation:

$$k = A \exp(-E_a/RT) \tag{8}$$

where $k$ is rate constant ($s^{-1}$), $E_a$ is apparent activation energy (kJ $mol^{-1}$), $A$ is pre-exponential factor ($s^{-1}$), $R$ is universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$), $T$ is reaction temperature (K).

By plotting the logarithm of the rate constant against the reciprocal temperature, the results of (8) can be illustrated in the form of a straight line. By means of this so-called Arrhenius plot (9), the activation energy as well as the pre-exponential factor can be determined:

$$\ln k = \ln A - E_a/RT. \tag{9}$$

Determination of the kinetic parameters

In this experiment, the hydrolysis behaviors of bean dregs were studied at varying temperature of 200, 220 and 240°C. At these reaction conditions, the concentrations of arginine and alanine were relatively high in the hydrolysate. Therefore, the kinetic parameters of total amino acids, arginine and alanine were investigated. Figures. 3, 4 and 5 illustrate the time course of amino acid production at different temperatures.

Figures 3, 4 and 5 show the experimental data and the model predication. Theoretical values shown by solid lines were calculated for product concentrations using Eq. 7. The satisfactory agreement between experimental and

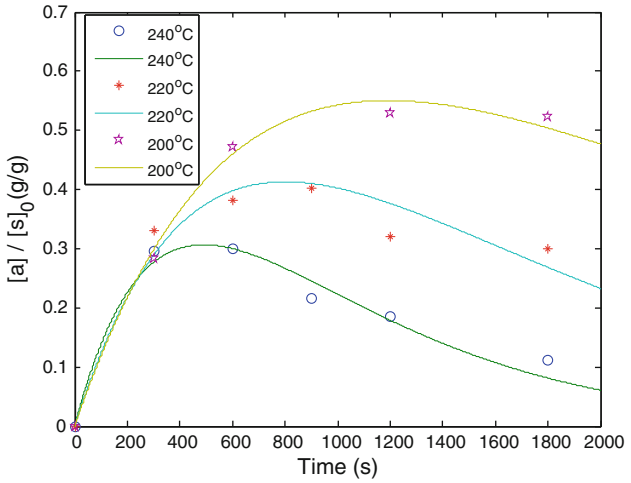



**Fig. 3** Experimental data and calculated curves for total amino acid concentration

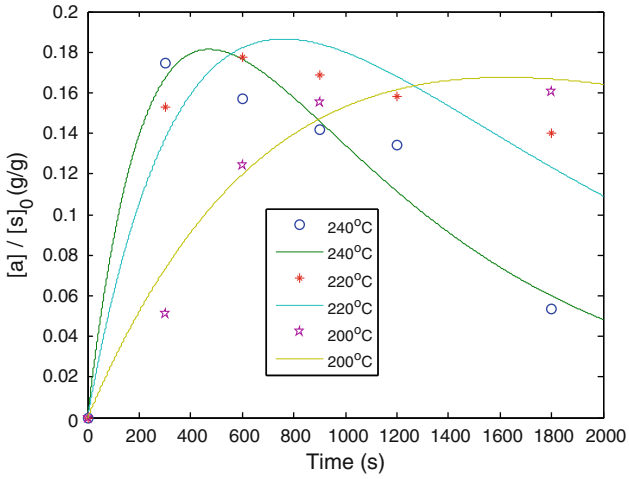



**Fig. 4** Experimental data and calculated curves for arginine

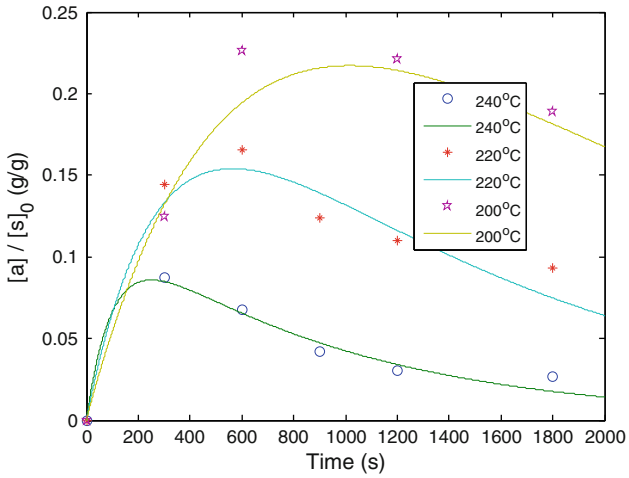



**Fig. 5** Experimental data and calculated curves for alanine

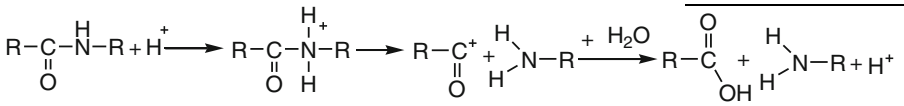
theoretical values could be observed. The obtained curves describe the data reasonably well. Due to the simplifications described in reaction model and the variation of the experimental data point only an approximate fit could be achieved. However, the reaction model is able to describe at least the tendential trends of the experimental data. From Fig. 3, we can see that the optimum hydrolysis conditions of bean dregs in sub-critical water to produce amino acids in the experiment are as follows: reaction temperature 200°C, reaction time 20 min. Under this condition, the total amino acid yield can reach 52.9%.

From Figs. 3, 4 and 5, we can see that the tendencies for yields of amino acids at different temperatures are similar. It shows that at first the yields of amino acids at different temperatures increase with extension of reaction time, and then decrease with continued extension of reaction time when reaction time is extended to a certain value. The significant influence of temperature and the shift of the maximum yield to lower reaction times with increasing temperature are evident. Similar behavior was obtained in the work of Rogalinski et al. (2005).

Proteins are important bio-polymers. In the hydrolysis reaction for proteins, first a proton is attached to the nitrogen atom of the peptide bonding. This leads to a splitting of the bonding, forming a carbo-cation and an amino group. In the next step, a hydroxide ion, from a dissociated water molecule, attaches to the carbon-cation, forming a carboxy group (Brunner 2009). The hydrolysis reaction mechanism described above can be shown as Eq. 10.

The amino acids produced may further decompose to different products, which could be supposed as their thermally labile and long time reaction. Reports exist about the chemical changes caused by hydrothermal treatments on the amino acids and the different decomposition products produced by these processes: deamination to produce ammonia and organic acids, and decarboxylation to produce carbonic acid and amines (Klingler et al. 2007; Sato et al. 2004).

In the presence of hydronium and hydroxide ions, peptide bonds are broken down into amino acids. At the beginning, with the increase of temperature, the concentration of hydronium increases, so the concentration of total



(10)

**Table 3** Rate constants for the sum of amino acids, arginine, and alanine production and decomposition for different temperatures as shown in Figs. 3, 4 and 5

| | 200°C | 220°C | 240°C |
|---|---|---|---|
| $k_1$ ($s^{-1}$) | 0.00127 | 0.0014 | 0.0017 |
| $k_2$ ($s^{-1}$) | 0.0005 | 0.0011 | 0.0024 |
| $k_{1,Arg}$ ($s^{-1}$) | 0.0003 | 0.0007 | 0.0011 |
| $k_{2,Arg}$ ($s^{-1}$) | 0.0011 | 0.0022 | 0.0036 |
| $k_{1,Ala}$ ($s^{-1}$) | 0.0006 | 0.0008 | 0.0011 |
| $k_{2,Ala}$ ($s^{-1}$) | 0.0015 | 0.0033 | 0.0097 |

amino acids in hydrolysate increases. However, with the further increase of temperature, some amino acids degrade to form low molecular weight carboxylic acids such as formic acid, acetic acid, propionic acids, etc., so the concentration of total amino acids in hydrolysate decreases (Sereewatthanawut et al. 2008). Therefore, the kinetic model for explaining the bean dregs degradation in sub-critical conditions has to include not only the production of amino acids but also the amino acid decomposition.

Table 3 shows the rate constants of the amino acid production and decomposition obtained by fitting the curve progressions to the experimental data according to Eq. 7. Nonlinear regression analysis was used for the fitting.

It can be observed that the reaction temperature has a large effect on reaction rate constants. With the increase of reaction temperature, the amino acid formation and decomposition rate constants increase. It is readily apparent that the degradation process has a strong influence on arginine and alanine because $k_{2,Arg}$ and $k_{2,Ala}$ are higher than reciprocal $k_{1,Arg}$ and $k_{1,Ala}$, respectively.

$E_a$ and $A$ were obtained by the plots of ln $k$ versus $1/RT$. Figure 6 shows the Arrhenius plots for the production and

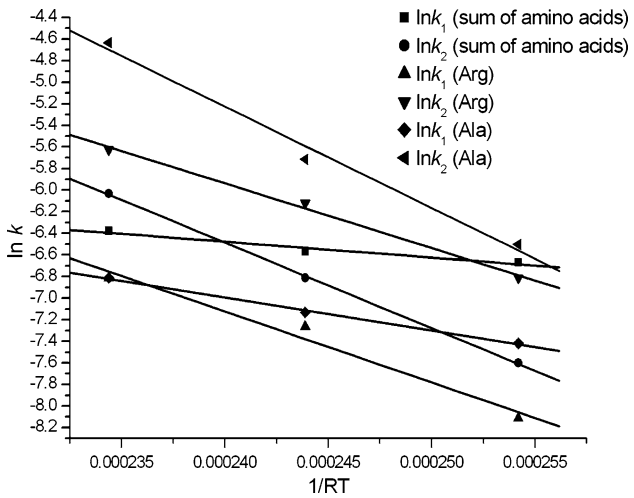



**Fig. 6** Arrhenius plot for the production and decomposition of the sum of amino acids as well as for arginine and alanine

**Table 4** Activation energies and pre-exponential factors for the sum of amino acids as well as for arginine and alanine

| | $E_a$ (kJ $mol^{-1}$) | $A$ ($s^{-1}$) |
|---|---|---|
| $k_1$ ($s^{-1}$) | 14.6 | 0.0516 |
| $k_2$ ($s^{-1}$) | 79.1 | $2.696 \times 10^5$ |
| $k_{1,Arg}$ ($s^{-1}$) | 65.8 | $5.831 \times 10^3$ |
| $k_{2,Arg}$ ($s^{-1}$) | 59.9 | $4.669 \times 10^3$ |
| $k_{1,Ala}$ ($s^{-1}$) | 30.6 | 1.404 |
| $k_{2,Ala}$ ($s^{-1}$) | 94.0 | $3.338 \times 10^7$ |

decomposition of the amino acid sum, arginine and alanine according to Eq. 9.

The rate constants calculated for different temperatures can be satisfactorily described by straight lines. The activation energies and pre-exponential factors for the production and decomposition reactions were calculated. Table 4 shows the activation energies and pre-exponential factors for the production and decomposition of the sum of amino acids as well as for arginine and alanine.

It could be seen that the apparent activation energy (14.6 kJ $mol^{-1}$) for the hydrolysis of bean dregs is much less than the one (79.1 kJ $mol^{-1}$) for the decomposition of total amino acids. The arginine formation apparent activation energy is 65.80 kJ $mol^{-1}$ and the decomposition one is 59.9 kJ $mol^{-1}$. The formation and decomposition apparent activation energy of alanine are 30.6 and 94.0 kJ $mol^{-1}$, respectively. The kinetic data are very useful in helping us understand the hydrolysis processes and mechanisms. Based on these results, it is proposed that sub-critical water hydrolysis could become a benign technology for bean dregs processing to recover amino acid.

## Conclusion

This study demonstrates that sub-critical water could be used to potentially hydrolyze bean dregs, a cheap by-product of soybean industry, into more valuable amino acids. The reaction rate constant, activation energy and pre-exponential factor were calculated. Two main reactions, hydrolysis of bean dregs to amino acids and decomposition of amino acids to other products, were observed in the treatment of the waste. The production and decomposition of amino acids could be described by a simple reaction model according to the pattern of a single consecutive reaction. A good agreement between experimental data and proposed equations was obtained. The optimum hydrolysis conditions of bean dregs in sub-critical water to produce amino acids in the experiment are as follows: reaction temperature 200°C, reaction time 20 min. Under this condition, the total amino acid yield can reach 52.9%.

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