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RESEARCH PAPER

Hydrothermal reaction of phenylalanine as a model compound of algal protein

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Abstract: The decomposition behavior of phenylalanine, as a model compound of algal protein, in water at high temperature was investigated in a quartz mini-batch reactor. The conversion of phenylalanine at 130–190°C as well as the decomposition pathways and nitrogen transition behavior in the hydrothermal process at 220–340°C with a batch holding time of 5–240 min were determined. The results showed that the conversion of phenylalanine is extremely low at 130–190°C, and that provided a reference for extracting high value-added protein during hydrothermal liquefaction of algae. The major product at 220–280°C is phenylethylamine; however, the yield of styrene is increased with the increase of reaction temperature and holding time. In water at high temperature, phenylethylamine is obtained via decarboxylation of phenylalanine, while styrene is produced via deamination of phenylethylamine under higher temperature and longer holding time; phenylethanol is further formed via the hydration of styrene. Most of nitrogen in phenylalanine is firstly transferred into phenylethylamine via the decarboxylation of phenylalanine, and then further transferred into water-soluble NH_4^+ via the deamination of phenylethylamine.

Keywords: algae; phenylalanine; hydrothermal reaction; protein; decomposition; nitrogen distribution

Algae is recognized as a promising energy source for the third-generation biofuels due to its high growth rates, high CO_2 fixation performance and the absence of competition with food production[1,2]; meanwhile, the hydrothermal liquefaction is considered to be an effective technique to get bio-oil from algae[2–4]. Compared with that from pyrolysis of lignocellulosic biomass, the bio-oil from hydrothermal liquefaction of algae has higher heating value due to its low oxygen content[5,6]; however, the high nitrogen content(4%–7%) in the bio-oil from algae may also be a barrier to its further utilization[7,8].

As one of the major components in algae, protein can account for up to 71%. During the processing of hydrothermal liquefaction, protein was broken into components of small molecules and then became the main source of nitrogen in the bio-oil[9–11]. Consequently, the study on the hydrothermal liquefaction of protein can gain a new insight into the attempts to improve the quality of algal bio-oil. Protein is a complex mixture of different kinds of amino acids. To better understand hydrothermal liquefaction of protein, amino acids were chosen as the model compounds[12]. Sato et al[13] investigated the hydrothermal behavior of five amino acids including phenylalanine under 200–340°C and 20 MPa for 20–180 s; they found that amines and organic acids were obtained by decarboxylation and deamination, respectively. Abdelmoez et al[14,15] also found that the major products were organic acids and ammonia during hydrothermal processing of amino acids. However, there were few investigations reported on the decomposition mechanism of amino acids at longer batch holding time, though longer batch holding time is necessary for the hydrothermal liquefaction of algae. Changi et al[12] examined the reaction behavior of phenylalanine in water under 250–350°C for 5–120 min by using a stainless steel batch reactor and illustrated that the decarboxylation to produce amines was the main decomposition pathway of phenylalanine. However, it is notable that the stainless steel might have potential effects on the hydrothermal reactions[16,17]; moreover, the conversion behavior of phenylalanine at lower temperature and the distribution of nitrogen during hydrothermal processing were ignored in these previous works.

To better understand the hydrothermal liquefaction

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mechanism of algal protein, phenylalanine, which occurs widely in algae protein(around 5%)[9], was chosen as a model compound of algal protein. The decomposition behavior of phenylalanine in water at high temperature was explored by using a quartz mini-batch reactor and the distribution of nitrogen in various products during the processing was then determined.

1 Experimental

1.1 Materials and apparatus

Phenylalanine, phenylethylamine, 2-phenylethanol were purchased from J&K in high purity(99%). Styrene was purchased from AccuStandard, Inc. in high purity(99.7%). 1-phenylethanol was purchased from TCI in analytical-reagent grade. All the hydrothermal reaction tests were carried out in a quartz mini-batch reactor with a length of 25 cm, outside diameter of 0.6 cm and inside diameter of 0.2 cm, which was heated in a tube furnace at the target temperature within ±2°C.

1.2 Hydrothermal test procedures

Prior to sealing the quartz reactor, phenylalanine solution(0.1 mol/L) was loaded into the reactors. To minimize the effect of phase variance between liquid and vapor on the hydrothermal reaction, the volume of the liquid phenylalanine solution loaded in the reactor at room temperature should be about 90% of the reactor volume. The reactor was then heated in the tube furnace. After the hydrothermal reaction, the reactor was cooled in cold water and then opened; and finally, the products were recovered with methanol.

1.3 Sample analysis

1.3.1 HPLC quantitative analysis

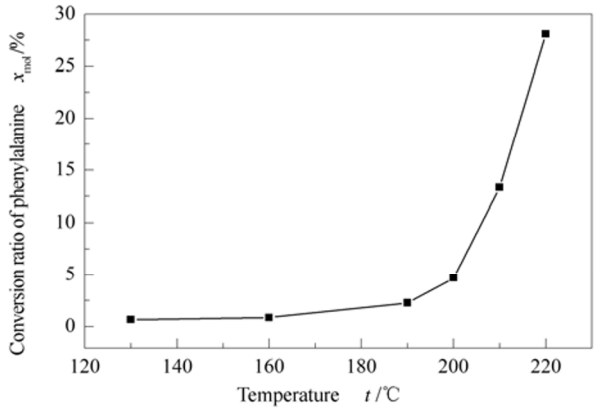

Fig. 1 Conversion of phenylalanine by hydrothermal liquefaction at 130–220°C for 240 min

High pressure liquid chromatography(HPLC, Waters 2695) was used to quantify phenylalanine and phenylethylamine with a UV detector at absorption wavelength of 258 nm and a column of Waters Xbridge C18. An isocratic method was adopted by using a mobile phase consisting of dilute sulfuric acid solution(0.005 mol/L, 90%) and acetonitrile(10%) at 1 mL/min for a total runtime of 20 min.

1.3.2 GC quantitative analysis

Gas chromatography(GC, Shimadzu GC2010) was used to quantify the contents of styrene and phenylethanol, with a flame ionization detector(FID) and a polar capillary column(RTX-WAX). The inlet temperature was 240°C and N_2 was served as carrier gas at 2 mL/min. The oven temperature program started at 40°C(isothermal for 1 min), followed by heating to 150°C at 10°C/min(isothermal for 4 min), and then to 240°C at 10°C/min(isothermal for 8 min), giving a total run time of 33 min.

1.3.3 IC quantitative analysis

Compact ion chromatography(IC, Metrohm 761) was used to quantify NH_4^+ with a conductivity detector and a cation-exchange column(C2-150). The mobile phase was dilute sulfuric acid solution(0.0094 mmol/L) at a flow rate of 1 mL/min.

2 Results and discussion

2.1 Hydrothermal liquefaction of phenylalanine at 130–220°C

Figure 1 shows the conversion of phenylalanine by hydrothermal liquefaction at 130–220°C for 240 min. The conversion of phenylalanine is extremely low at 130–190°C and then increased slowly from 2.28% to 28.1% with raising the temperature from 190 to 220°C.

A unique two-step sequential hydrothermal liquefaction method was recently considered as an economical measure for producing bio-oil from algae[18,19], where the value-added products such as protein and polysaccharide were obtained at low temperature and bio-oil was obtained at high temperature. Here, the processing temperature is a key factor for safely extracting the value-added products. Figure 1 indicates that phenylalanine is hardly decomposed at 130–190°C, suggesting that the high value-added products including protein may be safely extracted from algae at a low temperature of 130–190°C during the two-step sequential hydrothermal processing.

2.2 Products and decomposition pathway of the hydrothermal reaction of phenylalanine