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Hydrothermal conversion of microalgae into N-containing compounds

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Abstract. With the respect to the depletion of fossil fuels, numerous approaches have been developed to mitigate the problem, among which production of chemicals from microalgae is a substantially new way to contribute to the economic viability. In the present study, one new and straightforward method for the conversion of microalgae into nitrogen-containing compounds such as 2-pyrrolidone under hydrothermal conditions was demonstrated. Furthermore, protein in microalgae was proved to be the source of N-containing compounds production.

1. Introduction

Huge consumption of fossil fuels has led to a serious energy crisis and associated environmental issues. Utilization of chemicals and energy derived from renewable biomass resources could alleviate the dependence on petroleum-derived feedstock and global warming resulted from the use of fossil fuels. In this regard, methods to convert microalgae have been extensively studied due to its ability of photosynthesis, fast growth speed, high lipid content, ability to sequester CO₂ and potential for producing useful chemicals [1]. In addition, microalgae make no demands on rigorous living conditions or agriculturally productive land [2]. Recent interest of using microalgae is mainly focused on biodiesel extraction [3], but its utilization efficiency is very low due to its low oil content (only 10%) [4]. Production of chemicals from microalgae can take the advantage of various components in microalgae and their intermediates, and therefore maximize the value derived from the microalgae.

Hydrothermal reactions using high-temperature water (HTW) as both reaction media and reactant is receiving increasing attention because HTW has lower dielectric constant, fewer and weaker hydrogen bonds, and higher ion-product constant than ambient water [5]. In our previous researches, we demonstrated that biomass feedstocks, such as carbohydrate, fatty acid and lignin, can be selectively converted into acetic acid under hydrothermal conditions [6-9]. However, only few of studies involved the conversion of microalgae.

Unlike most other types of biomass such as glucose and cellulose, microalgae contains nitrogen. Nitrogen-containing compounds which are widely applied in carbon dioxide fixation, pharmaceutical industry, textiles and beyond, are crucial for modern manufacture. For example, the nitrogen-containing



organic compound pyrazine is integral to several best-selling drugs such as eszopiclone (for sleeping difficulties) and varenicline (to treat nicotine addiction), and ethanolamine (ETA) is used in power plants for CO₂ sequestration and in skin-friendly soaps, household cleansers and surfactants [10].

Thus, in this research, the potential of the conversion of microalgae into nitrogen-containing compounds under hydrothermal conditions was studied. Results indicated that nitrogen-containing compounds such as lactam could be produced efficiently. Mechanism study indicated that protein in microalgae is responsible for N-containing compounds production.

2. Experimental Sections

2.1. Materials

Spirulina (solid content > 95%) was selected as the representative of microalgae and was purchased from Yunnan Natural Biotech Co., Ltd. NaOH was obtained from Sigma-Aldrich.

2.2. Experimental Procedure

All experiments were conducted in a batch reactor (3/8 in. diameter, 1 mm wall thickness, and 120 mm length) made of SUS 316 alloys with an internal volume of 5.7 mL. Schematic drawing of the experimental setup can be found in our previous report [11]. In a typical reaction, desired amounts of *Spirulina*, NaOH, and deionized water were added to the reactor, which was then sealed and immersed into a salt bath that had been preheated to desired temperature to initiate the reaction. After the reaction, the reactor was lifted out from the salt bath and placed into a cold-water bath immediately to quench the reaction. The reaction time was defined as the duration that the reactor was kept in the salt bath. A water filling rate was used to denote the liquid amount in the reactor, which is defined as the ratio of the liquid volume to the inner volume (5.7 mL) of the reactor. After the reaction, liquid sample was collected, and filtered through a 0.22 μm syringe filter for further analysis.

2.3. Analytical methods

Liquid samples were analyzed by an Agilent 1200 high-performance liquid chromatography (HPLC) analyzer equipped with two KC-811 columns (SHODEX) on a tunable ultraviolet/visible (UV/vis) absorbance detector adjusted to 210 nm and a differential refractometer detector. The mobile phase of the HPLC system was a 2 mmol/L HClO₄ with a flow rate of 1 mL/min. Liquid samples were also analyzed by a gas chromatography-mass spectrometer (GC-MS, Agilent GC7890A-MS5975C) equipped with an HP-Innowax column (30 m × 0.25 mm × 0.25 μm).

3. Result and discussion

3.1. Confirmation of N-containing compounds formation from *Spirulina*

First, *Spirulina* was selected as the representative of microalgae to study its conversion under hydrothermal conditions. The chemical composition of *Spirulina* used in this study is summarized in Table 1. It can be seen that protein, carbohydrate and lipid are the major components of *Spirulina*. Our previous research of biomass conversion indicated that alkaline condition could promote biomass conversion efficiently under hydrothermal conditions. Thus, in the present study, alkali was added in the first place.

Table 1. Basic chemical composition of *Spirulina*

Chemical composition	Protein	Carbohydrate	Lipid	Water	Ash
Relative amount in <i>Spirulina</i> (%)	70	12	9	6	3

As shown in Fig. 1, when *Spirulina* reacted under alkaline hydrothermal conditions, 15 products were produced, which mainly includes organic acids (peaks 1, 2, 3), chain-amides (peaks 4, 5, 8), N-substituted 2,5-diketopiperazine (DKP, peaks 9,10) and lactam (peaks 6, 7, 11, 12, 13). The

corresponding quantities of the detected products are summarized in Table 2 (only commercially-available products were quantified). It can be seen that lactam are produced mostly, followed by acetate, formate and propionate. These results indicate that microalgae can be converted into N-containing compounds under hydrothermal conditions, with lactam as the major N-containing compounds.

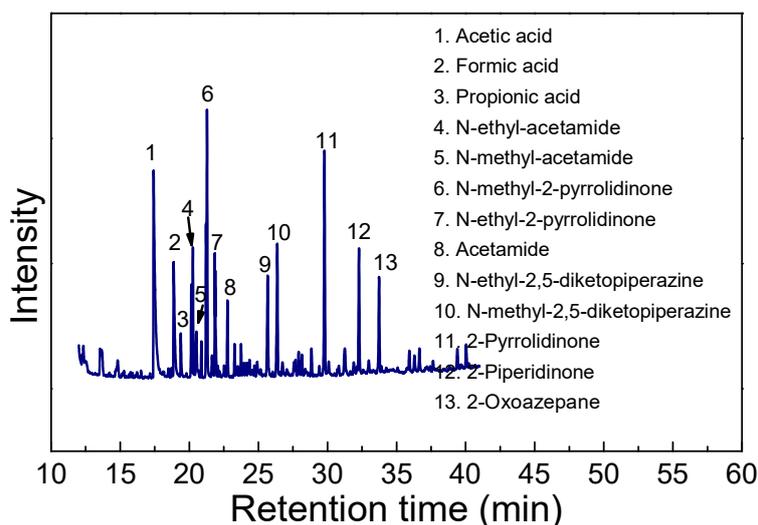


Figure 1. GC-MS chromatograms for the reaction of Spirulina under hydrothermal conditions (1 mol/L NaOH, 0.28 g Spirulina, 1 h, 300 °C, 50% water filling).

Table 2. Major products after the Spirulina reaction under hydrothermal conditions ^a.

Products	Concentration (mmol/L)
Formate	5.3
Acetate	19.2
Propionate	3.4
N-methyl-2-pyrrolidinone	7.5
2-pyrrolidinone	40.9
2-piperidinone	35.6

^a Reaction conditions: 0.28 g Spirulina, 1 mol/L NaOH, 300 °C, 1 h, 50% water filling.

Then, we selected 2-pyrrolidinone as the target product to study the kinetics of lactam production from Spirulina. As shown in Fig. 2, 2-pyrrolidinone was formed quickly in the first 5 min, and then gradually accumulated till 30 min. The reaction temperature had a significant effect on the 2-pyrrolidinone production, and increasing the reaction temperature from 275 to 325 °C significantly promoted the 2-pyrrolidinone generation.

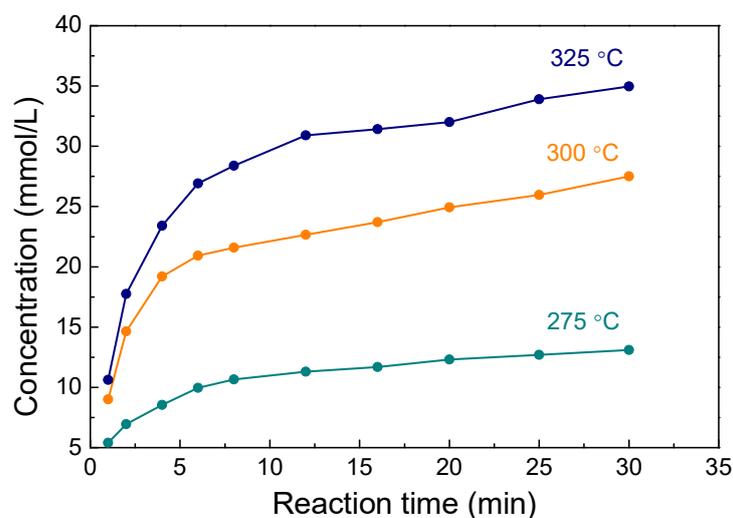


Figure 2. Kinetic information of 2-pyrrolidinone formation from the reaction of Spirulina (1 mol/L NaOH, 0.28 g Spirulina, 300 °C, 50% water filling).

3.2. Determination of the source of N-containing compounds production from Spirulina

The chemical composition of *Spirulina* indicates that N-containing compounds should be produced from protein contained in Spirulina. To study the assumption, bovine serum albumin (BSA, a typical protein contained in the microalgae) is used as the representative of protein to study its conversion under hydrothermal conditions. As shown in Fig. 3, similar products distribution to Spirulina conversion were observed for the reaction of BSA, and the concentration of the N-containing compounds from BSA were almost the same to the products from Spirulina (Table 3). These results indicate that protein in Spirulina is the source of N-containing products.

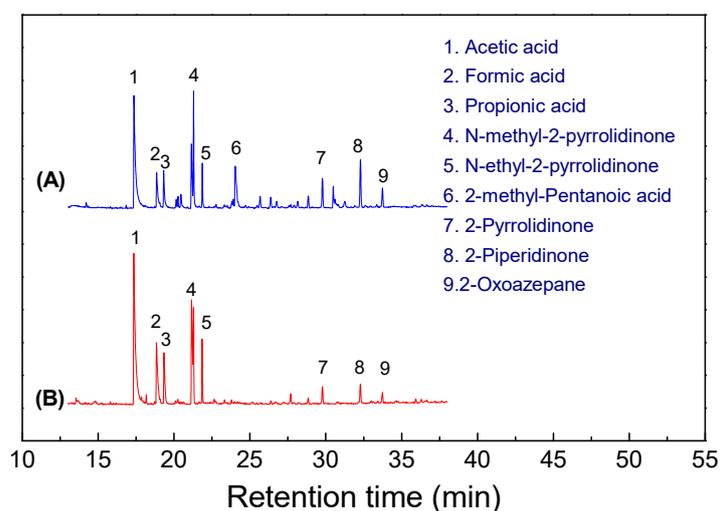


Figure 3. GC-MS chromatograms of liquid samples for the reaction of bovine serum albumin (BSA) (A) or Spirulina (B) (1 mol/L NaOH, 0.75 mol/L BSA, 0.28 g Spirulina, 1 h, 300 °C, 50% water filling).

Table 3. Major products concentration for the reaction of Spirulina or BSA^a.

	Products concentration (mmol/L)					
	Formate	Acetate	Propionate	N-methyl-2-pyrrolidinone	2-pyrrolidinone	2-piperidinone
<i>Spirulina</i>	5.3	19.2	3.4	7.5	40.9	35.6
BSA	3.5	16.2	3.2	6.8	42.7	36.4

^a Reaction conditions: 1 mol/L NaOH, 0.28 g Spirulina, 0.75 mol/L BSA, 300 °C, 1 h, 50% water filling.

4. Conclusion

In conclusion, a novel method of microalgae conversion into N-containing compounds was developed. With 2-pyrrolidinone as the target products, the kinetic study of microalgae conversion indicates that 2-pyrrolidinone could be produced in less than 30 min, and higher temperature was beneficial for microalgae conversion. Control experiments indicate that protein in microalgae is responsible for N-containing compounds production.

Acknowledgments

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