Hydrothermal liquefaction of Undaria pinnatifida residues to organic acids with recyclable trimethylamine

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HIGHLIGHTS
- Trimethylamine had positive effect on hydrothermal liquefaction.
- The temperature of hydrothermal liquefaction does not exceed 260 °C.
- Cellulose cleaved into organic acids by peeling reaction in low temperature.
- The hydrothermal route of glycolic acid was presented.
- The highest recovery rate of TMA was 98.89%.

ABSTRACT
This study investigated the effect of trimethylamine (TMA) on the hydrothermal liquefaction (HTL) process and the recycle of TMA. The results suggest that the peeling reaction occurred on the surface and the cleavage of cellulose leading to water-soluble substances and bio-oil. The highest content of organic acids was found in the water-soluble phase. Model compounds, different glucides with TMA were used to investigate the mechanism of the HTL. Results suggest that the OH appeared to selectively interact with C–O–C bonds, and thus causing the key linkages of cellulose to become much easier to be cleaved under mild conditions. In addition, the conditions for TMA recovery were optimized and the highest TMA recovery rate reached 98.89%. The recovered TMA had the same properties as the original compound, and it was perfectly re-usable in the conversion process of HTL.

1. Introduction
Biomass is an abundant and potential renewable energy resource for the production of bio-fuels and various valuable chemicals (Kim et al., 2016; Zhang et al., 2016a,b). The utilization of marine biomass is a relatively new concept, and it demands an assessment of how much the marine biomass can contribute to the total biomass resources (Anastasakis et al., 2011). The marine biomass especially edible algae have a great potential as the raw material for food and pharmaceutical industries. However, it is unavoidable of producing some waste and scraps in these industrial processes. This offers an opportunity for material and energy valorisation, and to develop a bio-based economy. Therefore, better
utilization of algal residues that from food and pharmaceutical industries will improve the economics of algal production. At the same time, various conversion routes have been researched for the production of liquid fuels from microalgae or macroalgae (Barreiro et al., 2015). However, most of these researches require dry biomass, which leads to a significant increase in energy costs as a result of the need for drying. Therefore, the possibility of producing chemicals from food and pharmaceutical industries residues, without drying and at lower temperatures is very interesting.

In general, hydrothermal liquefaction (HTL) processing is one of the most promising technologies that can convert the biomass to more readily utilizable materials for production of high value-added products through bio-refinery processes at one step. In order to improve the conversion rate of HTL process, the hydrothermal agent or catalyst is usually added. For example, Yan et al. (2010) investigated the hydrothermal conversion of carbohydrates including glucose and cellulose into lactic acid using NaOH and Ca(OH)₂ as alkaline hydrothermal reagents. A number of metal catalysts have been studied extensively (Onda et al., 2008; Choudhary et al., 2015; Wang et al., 2016). Meanwhile, plenty of literatures have been reported utilizing ionic liquid as solvent to convert biomass with solid or liquid catalysts (Li et al., 2008; Zhou et al., 2013). The results of these researches lay the foundation of further study of transformation from biomass to chemicals. Although the above mentioned hydrothermal agents or catalysts can improve the conversion rate of biomass, it still faces the problems of environmental pollution, high recovery costs and high production cost and so on. As far as we know, no research has studied hydrothermal agent transform biomass to chemicals both efficient and recoverable which can reduce the complexity of products development and the environment pollution. Therefore, it is necessary to study the efficient and recyclable hydrothermal agents.

The principal objective of the present work is to investigate the hydrothermal agent which has a good hydrothermal effect and recyclable. The purposes of this study are: (1) investigating the effect of TMA on the product of the hydrothermal process; (2) investigating the production of organic acids by the TMA hydrothermal treatment of Undaria pinnatifida residues and optimizing the conditions for maximal production; (3) researching TMA recovery and utilization; (4) full use of marine resources.

2. Materials and methods

2.1. Materials and chemical composition analysis

TMA aqueous solution (chemically pure, TMA not less than 33%), sodium hydroxide (chemically pure, not less than 96%), sodium bicarbonate (technical grade 99.8%), sodium carbonate anhydrous (technical grade 99.8%), disodium hydrogen phosphate (technical grade 99.0%) were purchased from Sinopharm Chemical Agent Co. Ltd. Undaria pinnatifida residues was supplied by Yuansheng Biological Engineering Co. Ltd. Feedstock analysis revealed the biochemical composition contained cellulose 52.35 ± 0.54 wt.%, moisture 14.86 ± 0.37 wt.%, ash 7.51 ± 0.10 wt.%, protein 5.69 ± 0.14 wt.%, polysaccharides 7.74 ± 0.72 wt.% and lipid 6.83 ± 0.57 wt.%. The polysaccharides content was analyzed by the sulfuric acid-anthron method (Somani et al., 1987). The moisture and ash contents were determined according to the procedures of Chinese standard. The protein content was determined by the method of Bradford. Cellulose content was analyzed by cellulose analyzer.

2.2. Experimental procedures and equipments

HTL experiments were conducted in a 0.5 L high pressure autoclave under different reaction conditions including temperature, residence time, hydrothermal agent concentration. In each experiment, in order to facilitate the calculation 11.77 g Undaria pinnatifida residues (equal to 10 g of dry matter) was mixed with 100 ml TMA aqueous solution and the mixed slurry was added into the reactor. The reactor was flushed with argon gas 3 min to remove the air. Reactants were agitated vertically at 200 rpm using stirrer. The temperature of HTL reaction was raised to the desired value in about 30 min and then kept for 1 h. The retention time in this study does not include the heat-up time. The pressure during the process was autogenous and the maximum pressure was 5 Mpa. After reaction, the reactor was left to cool down to the room temperature. The experiments were repeated three times and the deviation of the liquid yields were within ±0.5%. Cryogenic vacuum distillation was used to recover TMA as initial step before the HTL liquid was adjusted to pH 2 using H₂SO₄. The acidified HTL liquid was filtered under vacuum with a filter paper and the filtrate was collected for extraction with dichloromethane to remove the bio-oil. The raffinate phase (water-soluble products under acidic conditions (WSPAC)) was used to analyze the concentration of organic acids. The water-insoluble substances remained on the filter paper were rinsed by ethanol. The insoluble residues were recovered again for hydrothermal liquefaction and the ethanol-soluble substances were distilled to obtain bio-oil. The experiment scheme was shown in Fig. 1.

2.3. Analysis method

The chemical compositions of liquefaction were analyzed with an Agilent 7890GC/5975MS using DB-FFAP column (30 m × 0.32 mm × 0.5 μm). Helium (99.999%) was used as the carrier gas with a flow rate of 2 ml/min. The inlet temperature and the detector temperature were 250 °C and 240 °C, respectively. The column temperature was programmed initially at 50 °C for 10 min, increased to 200 °C with a rate of 5 °C/min and held for 10 min, then increased to 240 °C with a rate of 5 °C/min and held for 15 min. Compounds were identified using NIST (National Institute of Standards and Technology) mass spectral library. The concentration of the carboxyl acid in the acidic aqueous solution samples were analyzed by high-pressure liquid chromatography (HPLC) with Agilent ZORBAX SB-Aq column (250 mm × 4.6 mm, 5 μm) and a UV spectrophotometer (Two-channel UV detector). The sample was prepared and filtered through a 0.45 μm hydrophilic polyethersulfone membranes. The mobile phase was an aqueous mixture containing 10% of methanol and 3.90 g/L of NaH₂PO₄ with pH adjusted to 2.50 using phosphoric acid. The flow rate was 0.6 ml/min at 30 °C. The detection wave length was 210 nm. The pH value of the aqueous phase was measured by a pHS-2 type acidimeter with an accuracy of about 0.01 pH units. Each of the experiments was repeated 3 times, and the relative deviation did not exceed 0.5%.

2.4. Data interpretation

The yields of the products are calculated based on dry mass of initial biomass as following:

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\text{Yield of water-soluble substances (wt%) = } \left(1 - \frac{\text{Bio-oil (g)}}{\text{Residue (g)}} \right) \times 100\%
\]  

(1)

\[
\text{Yield of bio-oil (wt%) = } \left(\frac{\text{Bio-oil (g)}}{\text{Mass of biomass (g)}}\right) \times 100\%
\]  

(2)

All of the calculations based on dry mass of biomass which contain ash mass.