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# Microwave-assisted direct liquefaction of *Ulva prolifera* for bio-oil production by acid catalysis

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ABSTRACT

Production of bio-oil by microwave-assisted direct liquefaction (MADL) of *Ulva prolifera* was investigated, and the bio-oil was analyzed by elementary analysis, Fourier transform infrared spectroscopic analysis (FT-IR), and gas chromatography–mass spectrometry (GC–MS). The results indicate that the liquefaction yield is influenced by the microwave power, liquefaction temperature, liquefaction time, catalyst content, solvent-to-feedstock ratio and moisture content. The maximum liquefaction yield of *U. prolifera* (moisture content of 8%) was 84.81%, which was obtained under microwave power of 600 W for 30 min at 180 °C with solvent-to-feedstock ratio of 16:1 and 6% $H_2SO_4$. The bio-oil was composed of benzenecarboxylic acid, diethyl phthalate, long-chain fatty acids ($C_{13}$ to $C_{18}$), fatty acid methyl esters and water. The results suggest that *U. prolifera* is a viable eco-friendly, green feedstock substitute for biofuels and chemicals production.

## 1. Introduction

With the reduced availability of fossil fuels and current focus on global environmental problems, energy shortages and environmental pollution have become key factors affecting the development of the world economy. The exigency of the situation has mandated the search for alternative, sustainable, renewable, efficient, and cost-effective energy sources with fewer green house gas emissions (Nigam and Singh, 2011). Biomass can serve as an excellent alternative source to meet present and future fuel demands. It include wood, energy crops, aquatic plants, agricultural crops, animal wastes, and algae (Williams and Laurens, 2010; Zou et al., 2009a). Among these, algae afford the advantages of fast growth, higher biomass production, high photosynthesis efficiency compared with lignocellulosic material (Li et al., 2011; Ye et al., 2010; Zou et al., 2009a), and mature breeding techniques that can mass produced. Algal is beneficial to the environment and helps maintain the ecological balance (Clarens et al., 2010).

*Ulva prolifera* belongs to the Chlorophyta division, Ulvales order, and Ulvaleae family. From the year of 2007, there are *U. prolifera* blooming in coastal areas along the shore of Yellow Sea of China. Up to mid-July, 2008, 1 million tons of algae had been cleared from one of the severely affected areas in Qingdao city, China. These algae caused a threat to the coastal environment (Li et al., 2010). So their rational treatment will become more and more important in the future. As a kind of renewable resources, the cycling process of its growth, liquefaction, or combustion can reduce carbon emissions. Therefore, *U. prolifera* is a good raw material for bioenergy (Li et al., 2008).

Liquefaction is a process by which biomass undergoes complicated thermochemical reaction in a solvent medium to form mainly liquid products. In the liquefaction process, macromolecules of the feedstock are decomposed into fragments of light molecules by dehydration, dehydrogenation, deoxygenation, and decarboxylation in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, rearrange through condensation, cyclization, and polymerization, leading to oily compounds having appropriate molecular weights (Balat, 2008; Zou et al., 2009b). Current processes include high temperature and high pressure liquefaction (Yokoyama et al., 1994), direct catalyst liquefaction (Zou et al., 2009a), and supercritical liquefaction (Lee and Ohkita, 2003). Among these methods, direct catalyst liquefaction takes place under normal pressure with a reaction mixture consisting of solvent and catalyst. A small amount of the catalyst can greatly improve the liquefaction efficiency (Zhang et al., 2007). Catalytic liquefaction is mainly used in the liquefaction of wood and agricultural crops (Kržan and Kunaver, 2006; Xiao et al., 2011) and little about algae which worth pursuing. As a good new energy carrier, microwaves are helpful in reducing energy

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consumption and reaction time compared to conventional heating (Kržan and Kunaver, 2006; Krzan and Zagar, 2009). MADL of *U. prolifera* has the potential to provide an effective and environmentally harmless way to recycle raw materials such as algae.

A method employing MADL of *U. prolifera* was developed, and the bio-oil obtained under optimum conditions was analyzed by elemental analysis, infrared spectroscopy (IR), and gas chromatography–mass spectrometry (GC–MS). This study provides theoretical basis for evaluating the feasibility of using *U. prolifera* to produce bio-oil.

## 2. Methods

### 2.1. Raw materials and reagents

*Ulva prolifera* were collected in July of 2011 from Zhanqiao Piers in Qingdao, China. The fresh raw materials were washed with filtered seawater four times and sun-dried for 4 days. They were then pulverized in a plant disintegrator and passed through a 60-mesh sieve and stored in a desiccator. All chemicals and reagents were of analytical grade.

### 2.2. Apparatus and experimental procedure

MADL experiments were performed in a microwave synthesis/extraction workstation (Xinyi Microwave Chemical Technology Co., Ltd., Shanghai, China) equipped with a microwave instrument and a three-neck flask. Above the flask, there is a tube for direct temperature measurement and a reflux condenser. All liquefaction reactions were carried out under normal pressure with magnetic stirring at 500 rpm to ensure homogeneous reactions.

Ethylene glycol (EG), polyethylene glycol (PEG) 400, *n*-octyl alcohol, and phenol as solvent, while concentrated sulfuric acid, concentrated hydrochloric acid, phosphoric acid, sodium hydroxide, and sodium carbonate as catalysts were used in *U. prolifera* liquefaction (Krzan and Zagar, 2009; Lee and Ohkita, 2003; Zou et al., 2009b; Zhang et al., 2007).

What is more, some key factors that may have significant effects on the liquefaction were also investigated. Liquefactions in EG using sulfuric acid as catalyst were conducted at different microwave powers (300, 400, 500, 600, 700, and 800 W), liquefaction times (2, 5, 10, 20, 30, and 40 min), temperatures (140, 150, 160, 170, 180, and 190 °C), and solvent-to-feedstock ratios (4, 8, 12, 16, and 20). The influence on the liquefaction yield of different catalyst contents (0%, 1%, 2%, 4%, 6%, and 8%) and moisture contents (0%–14%) were also investigated.

Accurately weighed *U. prolifera* powder was subjected to different masses of solvent and catalyst under different experimental conditions. After liquefaction, the reactor was cooled to room temperature in a beaker of cold water. The flask, filled with the solid and liquid reaction mixture, was washed with acetone to recover the bio-oil, and the reaction mixture was filtered under vacuum to separate the solid residue and liquefaction products. Then acetone was removed from the liquefaction products at 36 °C using a rotary evaporator and water was eliminated by anhydrous sodium sulfate. The residue was dried at 105 °C to constant weight. The yield was calculated by averaging the results of three runs and expressed as average ± stander deviation. The separation process for the reaction products is illustrated in Fig. 1. The liquefaction yield was determined from the following equation (Shin et al., 2009):

$$\text{liquefaction yield}\ (\%) = \left(1 - \frac{\textit{weight of residue}}{\textit{weight of feedstock powder}}\right) \times 100 \tag{1}$$

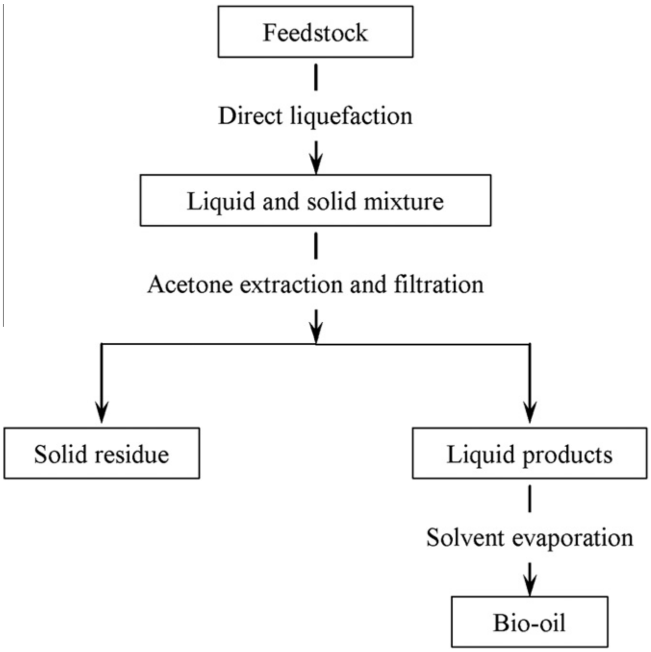

**Fig. 1.** Separation process of the bio-oil.

### 2.3. Analytical methods

#### 2.3.1. Analysis of U. prolifera

Proximate analyses were conducted according to ASTM standards (E871-82, 2006; E872-82, 2006; E1755-01, 2007). The fixed carbon was calculated as follows: 100% − ash content − moisture content − volatile matter. The C, H, S, and N contents of the raw materials were determined by a Vario EL III CHNS/O Elemental Analyzer (Vario EL III, Elemental Analysis System GmbH, Germany). The oxygen contents were calculated from the equation O (wt.%) = 100 − (ash + C + H + N) (wt.%). The chemical content (elemental composition, wt.%) and proximate analysis (received basis, wt.%) of *U. prolifera* are shown in Table 1.

#### 2.3.2. Analysis of the bio-oil

The elemental compositions of the bio-oil were determined using a Vario EL III CHNS/O Elemental Analyzer (Vario EL III, Elementar Analysen Syetem GmbH, Germany). The higher heating value (HHV) of the bio-oil was calculated from the Dulong formula (Landau and Lifshitz, 1976).

$$\text{HHV (MJ/kg)} = 0.3383\text{C} + 1.422(\text{H} - \text{O}/8) \tag{2}$$

where C, H, and O are the weight percentages of carbon, hydrogen, and oxygen in the oil, respectively. The chemical content (elemental composition, wt.%) and proximate analysis of the bio-oil are shown in Table 1.

An FT-IR spectrometer (Nicolet-5700, Thermo Nicolet Corporation, USA) was used to determine the functional groups of the bio-oil. For each spectrum, a 32-scan adsorption interferogram was gathered with 4-$\text{cm}^{-1}$ resolution in the 4000 to 400 $\text{cm}^{-1}$ region at ambient temperature.

GC–MS analysis of the bio-oil was carried out on an Agilent 6890N/5973 with an HP-5 ms column (5% phenyl and 95% dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm). As a carrier gas, helium (purity 99.999%) was used at a flow rate of 20 mL/min. 0.1 μL of the bio-oil/methanol solution (0.06 g/mL) was injected. After an initial 2 min isothermal period, the oven temperature was programmed from 70 to 280 °C with a heating rate of 10 °C/min, and then the final temperature was held for 15 min.