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Effect of pretreatment on microalgae pyrolysis: Kinetics, biocrude yield and quality, and life cycle assessment

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ABSTRACT

Effects of three different cell pretreatment methods on microalgae *Isochrysis* sp. pyrolysis kinetics, biocrude yields and quality, energy conversion efficiency and life cycle assessment (LCA) were investigated. From derived thermogrametry (DTG) curves, the decomposition reaction was apparently enhanced for acid pretreatment sample at 200 °C. The activation energy of pretreated microalgae pyrolysis was lower than that without pretreatment. The biocrude yields for raw microalgae were higher than pretreated samples at 450–475 °C and lower at 400–425 °C. Carbon distributions of biocrude from microalgae pyrolysis with ultrasonication and microwave pretreatment were similar and mainly in C6-10, C16, C18, and C20, while carbon distribution of biocrude from acid pretreatment mainly located in C7, C16, C18, and C20. Acid heating pretreatment improved fuel quality including N compounds reduction and increase of esters and ethers content, which was likely due to esterification reaction between carbohydrate derivative and lipid at acid conditions. From the point of energy conversion efficiency, pretreatment decreased the energy ratio and energy efficiency and increased the energy consumption/output ratio *ECR* (except *ECR* of acid heating pretreatment) during microalgae pyrolysis process. Based on the LCA, pretreatment increased the GHG emissions in the production process of alternative biofuels. Co-use of pretreatment process during biofuel production and valuable chemicals extraction can be further researched to enhance energy efficiency and cost-efficiency for microalgae.

1. Introduction

As a sustainable and renewable energy source, microalgae-derived biofuels have a growing potential in power generation and transportation sector. There are many thermochemical conversion technologies, such as pyrolysis [1], gasification [2] and combustion [3]. Fast pyrolysis to liquid biofuels is the conversion of biomass to liquid (termed biocrude), char and gaseous fractions, by heating biomass in the absence of oxygen at the temperature of 400–500 °C [4]. Pyrolysis biocrude yield can be predicted based on lipid, protein and carbohydrate content in microalgae with different liquefaction index *N* [5]. Indirect pyrolysis (defatted microalgae pyrolysis after oil extraction) has higher total oil yield (lipid and pyrolysis biocrude) comparing with direct pyrolysis [6]. But high nitrogen and oxygen compounds content is one of important problem for biocrude application.

As one of important operations for biochemicals extraction and biofuel production from microalgae [7,8], cell pretreatment can improve bio-crude quality [9] and reduce nitrogen content in pretreated microalgae [10], which also resulted in a slight increase in the liquid yield [11]. Microalgae pretreatment can disrupt microalgae cells and increase oil extraction efficiency. Commonly algae pretreatment methods include mechanical and non-mechanical methods, while non-mechanical methods include physical, chemical and enzymatic methods [7]. Ultrasonication, microwave and acids pretreatment are some pretreatment methods for microalgae lipid extraction. The disruption rate constant for ultrasonication was directly proportional to power level and followed a parabolic relationship with initial cell concentration [12]. The sonication method was found to be the most applicable and efficient method comparing with autoclaving, bead beating, and NaCl solution treatment [13]. Besides, hydrothermal microwave processing (HMP) can improve the biocrude quality following hydrothermal liquefaction [14].

For integration of microalgae cell pretreatment and pyrolysis process, some related researches have been conducted about chemical pretreatment [15] and hydrothermal pretreatment [10]. The sulfuric acid pretreatment significantly reduced the inorganic compounds but did not significantly affect the properties of the pyrolysis oil [15]. Hydrothermal pretreatment could reduce N content in algal feedstock, which results in less N-containing

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compounds [10]. Comparing with pretreated microalgae pyrolysis, lignocellulosic biomass pyrolysis with pretreatment has been conducted with many pretreatment methods including acids [16], microwave [17], hydrothermal [18], water washing [19] and catalytic methods [20], which can provide valuable information for microalgae pretreatment and pyrolysis. Moderate acid concentrations increased pyrolysis oil production and levoglucosan yield [16]. The levoglucosan yield from fast pyrolysis of corncob pretreated with microwave was higher than that of raw corncob [17]. Hydrothermal pretreatment improved bio-oil quality and especially enhanced levoglucosan content in bio-oils [18]. Combined water washing-torrefaction pretreatment improved the quality of pyrolysis products [19]. Although improved biocrude quality can be got, but the cell disruption energy requirement is an important consideration for biofuel production, which needs further research.

LCA has been an important method to assess energy and environmental impacts of biofuel production systems. LCA of microalgae hydrothermal liquefaction (HTL) and pyrolysis process indicated that pyrolysis pathway is not energetically or environmentally favorable due to drying process [21]. LCA analysis of lignocellulosic biomass feedstock indicated that pretreatment (drying and grinding) was one of the highest environmental impacts [22]. Fast pyrolysis of hybrid poplar and subsequent hydroupgrading is simulated and LCA results showed greenhouse gas (GHG) savings of 54.5% for the produced fuel compared to conventional gasoline and diesel [23]. However, there were few papers devoted to evaluating the environmental performance of algae-based hydrotreated pyrolysis jet fuel and especially focusing on effect of different pretreatment methods on environmental impact of pyrolysis process.

Based on our previous researches related to direct pyrolysis [5], indirect pyrolysis [6] and co-pyrolysis [24], this paper discussed the effects of three different pretreatment methods (microwave, acid and ultrasonic wave) on pyrolysis kinetics, biocrude yields and compositions, energy conversion efficiency and life cycle assessment in the pyrolysis process. It will supply basic and necessary information for microalgae pyrolysis process optimization and large-scale pyrolysis setup application.

2. Materials and methods

2.1. Samples

Microalgae *Isochrysis* sp. (ISO) were provided by Shenyang Research Institute of Chemical Industry (Shenyang, China), which was cultivated in laboratory condition. It was firstly dried at 105 °C for 24 h and then crushed into fine powders (less than 150 μm). Next, microalgae powders was pretreated by ultrasonication, hydrochloric acid and microwave and dried at 105 °C for 24 h, named ISO-U, ISO-A and ISO-M. The higher heating value (HHV) was measured by a bomber calorimeter (PARR1281, USA). Elemental analysis (Elementar Vario EL, Germany) was conducted to measure the level of C, H, N, S and O in the samples. The detailed measurement method can refer to previous researches [5].

2.2. Methods

2.2.1. Pretreatment methods

For acid heating pretreatment, the microalgae powder (100 g) was mixed and homogenized with 600 mL of 3 M hydrochloric acid for 60 min at ambient temperature. The mixture was then put in boiling water for 3 min and rapidly cooled to room temperature by cold ethanol (−20 °C) to avoid the further hydrolysis of protein and carbohydrate of microalgae in high temperature and long residence time. The pretreated microalgae were collected by sucking filtration and dried at 105 °C for 24 h.

For ultrasonic pretreatment, the microalgae powder (100 g) was dissolved and well-distributed with 300 mL of distilled water. Then the mixture was disposed by ultrasonic wave equipment (KQ5200DA, 40 kHz, 10 L, 30 cm × 24 cm × 15 cm) for 20 min at 160 W ultrasonic power. Finally the mixture was collected by sucking filtration and dried at 105 °C for 24 h.

For microwave pretreatment, 300 mL of distilled water was put into the microalgae powder (100 g) and mixed uniformly. The mixture was treated by microwave oven (Galanz, D80D23N1P-T7 (B0)) for 4 min at low-temperature defrost (800 W) and cooled once per minute by water at ambient temperature. The pretreated microalgae was collected by sucking filtration and dried at 105 °C for 24 h.

2.2.2. Pyrolysis by TGA analyzer

Raw microalgae and pretreated microalgae were analyzed using a thermal analyzer (Thermal Analysis Q50TGA, American) to create thermographs under a nitrogen flow of 60 mL/min. The samples were heated at heating rates of 5, 10, 15, 20, and 25 °C/min. The initial sample weight was controlled approximately at 8–10 mg for each run and the weight loss data were observed at temperature ranging from ambient to 900 °C. The detailed kinetic methods are based on Eqs. (1) and (2), which can refer to previous researches [5,25].

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{Ea}{R}\cdot\frac{1}{T} \tag{1}$$

$$\ln\left(\beta\frac{d\alpha}{dT}\right) + \frac{Ea}{R}\cdot\frac{1}{T} = \ln[A] + \ln[f(\alpha)] \tag{2}$$

where Ea, $f(\alpha)$ and A are the activation energy, mechanism function and pre-exponential factor. β, α and T are the heating rate, mass loss rate and temperature during pyrolysis process.

2.2.3. Pyrolysis by fixed bed

A fixed bed pyrolysis setup (Fig. 1) was used to study the pyrolysis biofuel yield of microalgae with and without pretreatment and the detailed introduction can refer to previous research [5]. Firstly microalgae samples (approximately 2.5 g in weight) were placed in the unheated zone 5′ and the oven was heated from ambient to the set pyrolysis temperatures (400–500 °C). When the pyrolysis temperature was up to aimed pyrolysis temperatures, the quartz tube was moved until microalgae samples were on heating zone 5 of oven. Before this, nitrogen flow was kept at least ten mins to ensure an oxygen-free condition.

These experiments were carried out to reveal biofuel characteristics from microalgae pyrolysis. The sample was heated from ambient to 400 °C, 425 °C, 450 °C, 475 °C and 500 °C with a nitrogen flow rate of 400 mL/min. All condensable volatile products were collected as biocrude, which were determined by weighting condenser mass. Char yield was weighted directly at ambient temperature and gas yield was calculated based on mass balance.

The biocrude obtained at the optimal pyrolysis temperature (responding to the maximum biocrude yield) was analyzed by gas chromatography mass spectrometry (GC/MS) (Agilent Technologies, 7890A/5975C), which was diluted with acetone (1:9, v/v) and filtered by 0.45 μm PTFE Filter. The GC column was HP-5 ms (30-m length × 0.25-mm i.d.) and column gas flow rate (He) was kept at 1 mL/min. A sample size of 1 μl was injected and the analysis time of each sample was about 60 min. Inlet temperature, quadrupole and detector temperature were 280 °C, 230 °C and 150 °C respectively. Oven temperature was maintained at 50 °C for 5 min followed by a ramp at 5 °C/min to 260 °C and