Direct catalytic hydrothermal liquefaction of spirulina to biofuels with hydrogen

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Abstract. We report herein on acquiring biofuels from direct catalytic hydrothermal liquefaction of spirulina. The component of bio-oil from direct catalytic hydrothermal liquefaction was similar to that from two independent processes (including liquefaction and upgrading of biocrude). However, one step process has higher carbon recovery, due to the less loss of carbons. It was demonstrated that the yield and HHV of bio-oil from direct catalytic algae with hydrothermal condition is higher than that from two independent processes.

1. Introduction
Due to the increase in oil demand and consumption of fossil fuels across the globe, biomass has attracted more and more attentions in world widely [1]. Currently, microalgae, as a biomass, has aroused extensive interests by its multiple advantages, including fast growth rate, high photosynthesis efficiency, maximum productivity, and no competition with food crops [2-4]. However, it suffers from relatively high heterogeneous atom content from microalgae, especially for pyrolysis [3]. To overcome these shortcomings, hydrothermal liquefaction has become an effective method to reduce large energy consumption and heterogeneous atom content, for it can avoid complicate drying process [4]. High temperature is conducive to algae decomposition, but the acidity of water is not high enough to decompose algae completely, so catalyst adding is essential [5-7]. Processing the wet microalgae at 300-350 °C using hydrothermal liquefaction has been studied extensively [3, 4]. Unlike crude oil used in industries, crude biofuels from HTL of algae contains quantities of oxygen, nitrogen and sulfur heteroatoms [8], which may decrease the stability of biocrude and create environmental problems such as production of SOx and NOx while combut [9,10]. Nevertheless, it takes two steps to conversion, which including liquefaction and upgrading processes. The two independent processes not only consume more energy, but also have high carbon loss. So, we need to take other method to solve this problem.

In this work, we report a method on directly catalytic converting microalgae into biofuels with hydrogen. 5wt% Pd/C was chosen as the catalyst in all of experiments, due to its steady
and high effective in hydrothermal condition. It was determined the influence of reaction temperature (250, 300, 350 °C), and holding time (30-180 min) on the yield of biofuels.

2. Material and methods

2.1. Material

*Spirulina*, as a kind of microalgae, was purchased from Xindaze Co. Ltd. (Fujian, China) in dry powder. The biochemical composition was provided by the supplier. The component results of the microalgae were shown in Table 1. Other chemicals (including catalysts) and solvents were from Sigma-Aldrich in >95 wt% purity and used as received. The reaction was conducted by a reactor, which was constructed from a 1/2 in Swagelok port connector and cap and a 1/8 in. to 1/8 in.

| Table 1. The composition and element of *Spirulina*. |
|--------------------------------------------------|
| **Biochemical composition (wt.%)** | **Ultimate analysis (wt%)** |
| **Proteins** | 69.6±8 | C | 44.45±3 |
| **Carbohydrates** | 16.4 ± 2 | H | 6.96±1.5 |
| **Lipids** | 7.9 ± 1.2 | N | 9.81±2.1 |
| **Ash** | 6.1 ± 0.8 | O | 38.06±4 |

2.2. Analysis of products

The chemical compositions of the bio-oil were determined using an Agilent Technologies 6890N GC equipped with an auto-sampler, auto-injector and mass spectrometric detector. The yields of bio-oil were calculated as follows:

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\text{Bio-oil yield (wt%)} = \frac{W_{\text{bio-oil}}}{W_{\text{algae}}} \times 100 \text{wt%}
\]

where the *W_algae* and *W_bio-oil* were weight of algal feedstock and bio-oil, respectively.

The elemental compositions of C, H, N and O in bio-oil were measured using a vario micro cube Elementar Analyser System. The higher heating value (HHV) of bio-oil was calculated by the Dulong’s formula (Eq.2) [11] with their elemental compositions.

\[
\text{HHV (MJ/kg)} = 0.3383 \times C + 1.422 \times (H-O/8)
\]

3. Results and discussion

3.1. Bio-oil elemental analysis

In Table 2, it showed that the result for the elemental analysis, carbon recovery and HHV of two process and direct catalytic liquefaction of algae. Higher carbon contents were achieved from direct catalytic liquefaction of algae, due to the less loss of carbons. Obviously, the HHV of biofuel from direct catalytic liquefaction of algae is 42.12 MJ/kg, which is similar to the crude oil. We also found that the carbon recovery was improved from 18.87wt%
Table 2. Elemental analysis, carbon recovery and the HHV of the bio-oil products.

| Method                      | Temperature (°C) | Time (min) | Elemental composition (%) | Carbon recovery (wt%) | HHV (MJ/kg) |
|-----------------------------|------------------|------------|---------------------------|-----------------------|-------------|
| Two processes of algae      | 350              | 60         | 78.73, 11.31, 6.72, 3.24  | 18.87                 | 41.56       |
| Direct catalytic liquefaction of algae | 350              | 60         | 79.59, 11.46, 6.13, 2.82  | 25.28                 | 42.12       |

3.2. GC-MS analysis for Bio-oil

The GC-MS was employed to obtain a detailed molecular characterization of the bio-oil from algae, which were categorized into groups based on the functionalities. In Figure 1, it was illustrated the major composition of bio-oil produced from direct catalytic liquefaction and two processes of algae. The amides and N-heterocyclics from direct catalytic liquefaction, such as pyridine, pyrrole, pyrrolidine, and piperdine, were similar with that from two independent processes. The trends of hydrocarbons and free fatty acids from the two different methods were opposite, which direct catalysis has higher hydrocarbons and less free fatty acids.

![Figure 1](image1.png)

3.3. Effect of reaction time on bio-oil yield

In Figure 2, it was shown that the effect of reaction time on yield of bio-oil from different methods. The trend of yield for bio-oil was similar before 120 min both of these two methods. However, the yield of bio-oil from two independent processes decreased, because the compounds from liquefaction of microalgae were small molecular component, which could be decomposed in the long time. In contrast, the trend for direct catalytic liquefaction could increase to 32wt% yield in 3h.
Figure 2. The effect of reaction time on the yield of bio-oil.

3.4. Effect of temperature on bio-oil yield
In Figure 3, it illustrated that the trend for the change of temperature on the bio-oil. Obviously, both of the two methods have the same trend, which the yield of bio-oil increased from 300 to 350 °C, and then decrease from 350 to 400 °C. It was because the decomposing process occurred above supercritical temperature.

Figure 3. The effect of temperature on the yield of bio-oil.

Conclusion
In this paper, we report a method to direct catalytic hydrothermal liquefaction of microalgae into biofuels. It demonstrated that the yield and HHV of bio-oil from direct catalytic algae with hydrothermal condition is higher than that from two independent processes (including liquefaction and upgrading of biocrude). The bio-oil from direct catalytic hydrothermal liquefaction of algae contained higher C element and was dominated by hydrocarbon substance hexadecane and tetradecane, which can be used as high-quality biofuel. Therefore, direct catalytic hydrothermal liquefaction of microalgae was effective for improving the quality of biofuels.

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