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# The direct pyrolysis and catalytic pyrolysis of *Nannochloropsis* sp. residue for renewable bio-oils

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ABSTRACT

*Nannochloropsis* sp. (a kind of green microalga) residue was pyrolyzed without catalyst or with different amount of HZSM-5 catalyst in a fixed bed reactor in nitrogen flow. The effects of pyrolysis parameters such as temperature and catalyst-to-material ratio on product yields were studied. The bio-oils obtained were analyzed by elemental, GC–MS and FTIR analysis. The results indicated that the bio-oils from catalytic pyrolysis of *Nannochloropsis* sp. residue (BOCP) had lower oxygen content (19.5 wt.%) and higher heating-value (32.7 MJ $kg^{-1}$) than those obtained from direct pyrolysis (BODP) which had an oxygen content of 30.1 wt.% and heating-value of 24.6 MJ $kg^{-1}$. The BODP mainly consisted of long carbon chain compounds with various terminal groups (LCTG), while the BOCP mainly consisted of aromatic hydrocarbons. These properties of bio-oils demonstrated that the *Nannochloropsis* sp. residue can be used as a renewable energy resource and chemical feedstock.



## 1. Introduction

Presently, the widely used energy sources are still limited to the conventional fossils such as coal, petroleum and natural gas, which are depleting, and their usage causes serious environmental problems. The exploitation of renewable and environmentally friendly energy resources is urgent and significant. Biomass, mainly including crops, forestry products and marine products, is widespread on the earth. With the exacerbation of energy crisis and environmental deterioration, biomass as an environmentally friendly and renewable energy resource has attracted more and more interests (Cercel, 2002; Goyal et al., 2008).

Biomass can be converted into fuel products by biological (fermentation and anaerobic digestion) or thermochemical (gasification, liquefaction) route. Among these conversion processes, pyrolysis is considered to be an effective technology, by which biomass can be converted to valuable bio-oils, char and gaseous products (Mohan et al., 2006). Especially, pyrolysis bio-oils are very attractive because of their high energy density and convenience in usage, storage and transport (Islam et al., 2004). Though numerous progresses on producing pyrolysis bio-oils have been reported with lignocellulosic biomass as raw materials (Karaosmanoglu et al., 1999; Mohan et al., 2006; Muller-Hagedorn and Bockhorn, 2007; Putun et al., 2004), the bio-oils obtained can not be used directly as fuel due to their high oxygen content, high viscosity, high corrosiveness and relative instability, and need to be upgraded by complicated process (Czernik and Bridgwater, 2004; Zhang et al., 2007). The poor quality of bio-oils is mainly attributed to the chemical components of lignocellulosic biomass (cellulose, hemicellulose and lignin), thus exploiting more appropriate biomass is necessary and valuable.

Microalga is a widely distributed low-grade water plant. Compared with lignocellulosic biomass, microalgae as energy resource have the following advantages: (1) microalgae have higher photosynthetic efficiency and higher biomass production (Peng et al., 2001; Schenk et al., 2008); (2) microalgae can be cultivated in an aquatic medium, and do not occupy arable land (Rodolfi et al., 2009); (3) the chemical composition of microalgae can be modulated easily by varying cultivation conditions, and high lipid content can be obtained (Rodolfi et al., 2009); (4) microalgae can utilize the salt and organic matter derived from waste water as fertilizers (Schenk et al., 2008). In addition, microalgae can effectively reduce greenhouse gas concentration in the atmosphere by their high capability in fixing carbon dioxide (Chiu et al., 2009; Kishimoto et al., 1994). So the exploitation and utilization of microalgae for fuel production can gain both economic and environmental benefits. However, for the large-scale usage of microalgae, there are still some fundamental challenges to be dealt with, such as the high cost of microalgae cultivation and its collection, as well as the efficiency in microalgae utilization (Li et al., 2007; Liliana et al., 2009).

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Generally, microalgae contain varying amounts of lipids, sugars, proteins and pigments etc. Presently, the attentions about the conversion of microalgae to fuel products mostly focus on the lipid which can be used to produce high-quality bio-diesel by the conventional esterification and transesterification (Chisti, 2007; Li et al., 2007; Miao and Wu, 2006). However, after lipid is extracted from microalgae cells (Li et al., 2007), numerous residues of microalgae which mainly contain almost all soluble polysaccharide, protein and some residual lipid are thrown away or sometimes used as animal feed. (Liliana et al., 2009) With the development of technology in producing low-cost fuel products derived from microalgae, the utilization of algal residues will become significant.

*Nannochloropsis* sp. has a high lipid content (about 46%, determined with Bligh–Dyer method, using methyl alcohol–chloroform mixture (2/1, v/v) as the extraction solvent), and is considered to be a promising green microalgae for fuel products (Gouveia and Oliveira, 2009; Rebolloso-Fuentes et al., 2001). In the present work, the direct pyrolysis of *Nannochloropsis* sp. residue was studied.

In addition, based on numerous researches on catalytic pyrolysis of lignocellulosic biomass, catalytic pyrolysis by using molecular sieves as catalysts can not only effectively upgrade the quality of bio-oils but also adjust the components of bio-oils to meet different demands (Adjaye and Bakhshi, 1995; Demiral and Şensöz, 2008; Vitolo et al., 1999; Williams and Horne, 1995a; Williams and Nugranad, 2000). Molecular sieves are well-known heterogeneous catalysts used in petroleum industry, and have been successfully applied in the interconversion of hydrocarbons, such as alkylation, isomerization, aromatization and thermal cracking reactions. Among various molecular sieve catalysts, HZSM-5 has gained great favors. ZSM-5 is an aluminosilicate zeolite with a high silica-to-alumina ratio and strong acidity. Its structure is based on channels with insecting tunnels. The substitution of $H^+$ for $Na^+$ made the acidity of zeolite stronger, which facilitates the conversion of hydrocarbons, such as thermal cracking (Pujadóa et al., 1992). At present, most studies are aiming at the pyrolysis or catalyzed pyrolysis of lignocellulosic biomass to obtained bio-oil (Demiral and Şensöz, 2008). And there is no literature available concerning the direct pyrolysis or catalyzed pyrolysis of algal residue to produce bio-oils. This paper will give some primary results.

## 2. Experimental

### 2.1. Material and catalyst

*Nannochloropsis* sp. was cultivated in laboratory. The culture medium was artificial seawater concocted by ourselves (using f/2 medium) (Guillard, 1975). Irradiance provided by fluorescent lamps was constant at 70 μmol $m^{-2}$ $s^{-1}$ and the ambiance temperature was maintained at 23 ± 0.2 °C. Cells of *Nannochloropsis* sp. were collected by centrifugation and washed with distilled water, and then dried in a vacuum desiccator at 65 °C for 24 h. The constitution of dry *Nannochloropsis* sp. was listed in Table 1.

Lipid in cells of *Nannochloropsis* sp. was extracted by the mixed solvent of ethylether and petroleum ether (1/2, v/v), and then used for the production of bio-diesel by esterification and transesterification. After residual solvent in algal residue was removed by vacuum distillation, the algal residue which occupied approximately 70 wt.% in cells dry weight was used as pyrolysis material. The proximate and ultimate analysis of *Nannochloropsis* sp. residue was shown in Table 1. Since metal salts contained in biomass exerted a significant impact on the pyrolysis process (Ross et al., 2008; Williams and Horne, 1994a), the contents of metals in the sample were determined by Inductively Coupled Plasma Spectrometry (ICP). The result was also listed in Table 1.

The HZSM-5 used in the catalytic pyrolysis of *Nannochloropsis* sp. residue was purchased from Nankai University. It had elliptical pore of 0.56 nm diameter, with a silica–alumina ratio of about 25 and pore volume of 0.19 $cm^3$ $g^{-1}$. The surface area was 347.9 $m^2$ $g^{-1}$. Before use, HZSM-5 was activated in a muffle furnace at 400 °C under air atmosphere for 4 h, with a heating rate of 10 °C $min^{-1}$.

### 2.2. Experimental apparatus

A fixed bed reactor designed by ourselves was used as experimental apparatus. The schematic diagram of the reactor was shown in Fig. 1. The outer tube was 35 mm diameter × 600 mm height. *Nannochloropsis* sp. residue (1 g) and catalyst (different amount) were mixed and packed in the inner vessel (25 mm diameter × 120 mm height), and were heated by an electric furnace. Temperature was controlled by a temperature controller (SKW-100). Nitrogen as a carrier gas was ventilated to the reactor from the inlet located in the top of the reactor and its flow rate was controlled by a flow meter. A condenser (ice trap) connected at the exit of the reactor was used to collect the liquid products.

### 2.3. Experimental procedure

The direct pyrolysis of *Nannochloropsis* sp. residue was performed in the fixed bed reactor mentioned above. The material was heated by an electric furnace with a heating rate of 10 °C $min^{-1}$ from room temperature to the final temperature, and then kept for 2 h at the final temperature. The volatiles produced in the pyrolysis process were swept out by carrier gas with a flow rate of 30 ml $min^{-1}$. The condensable components in volatiles formed liquid products which were collected in the condenser, and the incondensable components in volatiles formed gaseous products which were collected in a gas bag.

In the catalytic pyrolysis experiment of *Nannochloropsis* sp. residue, the same fixed bed reactor was used. Catalyst and material were mixed directly at the ratio from 0.2/1 to 1/1, and then placed in the inner vessel. Other experiment parameters were the same as those in the direct pyrolysis experiment.

**Table 1**
The proximate, ultimate and metal analysis of *Nannochloropsis* sp. residue[a].

| Proximate analysis (wt.%) | | Ultimate analysis (wt.%) | | Metal analysis (ppm) | |
|---|---|---|---|---|---|
| Moisture | 7.0 | C | 44.10 | Ca | 5503 |
| Volatile | 63.5 | H | 7.09 | K | 1660 |
| Fixed C | 19.6 | N | 5.51 | Na | 893 |
| Ash | 9.9 | O[b] | 33.40 | Mg | 7915 |
| | | Heating-value[c] | 20.7 MJ $kg^{-1}$ | | |

HHV (MJ $kg^{-1}$) = (3.55 $C^2$ − 232 C − 2230 H + 51.2 C × H + 131 N + 20600) × $10^{-3}$.

[a] Analyzed as received, after lipid in cells of *Nannochloropsis* sp. was extracted according to the depiction in the text.

[b] By difference, O (%) = 100-C–H–N-Ash sed as received.

[c] Heating-value was calculated by the following formula (Friedl et al., 2005).