

## Catalytic pyrolysis of microalga *Chlorella pyrenoidosa* for production of ethylene, propylene and butene†

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Xinglong Dong,<sup>ab</sup> Zhaoan Chen,<sup>a</sup> Song Xue,<sup>c</sup> Jinling Zhang,<sup>a</sup> Jiannan Zhou,<sup>c</sup> Yanan Liu,<sup>c</sup> Yunpeng Xu<sup>\*a</sup> and Zhongmin Liu<sup>\*a</sup>

This paper investigated the process of catalytic pyrolysis of lipid-rich microalga *Chlorella pyrenoidosa* for the production of light olefins (ethylene, propylene and butene). A modified ZSM-5 zeolite catalyst was used in the reactions, and it had high selectivity for the light olefins production. The catalytic pyrolysis performances of microalga *Chlorella pyrenoidosa* in nitrogen and steam reaction atmospheres were investigated. The catalytic pyrolysis performances in one-step and two-step processes were investigated and compared. The effects of reaction temperatures and water flow rates on the catalytic pyrolysis performances were also explored. The results showed that higher yield of light olefins was obtained in the steam reaction atmosphere as compared with that in the nitrogen atmosphere. The carbon yield of light olefins obtained from two-step catalytic pyrolysis was nearly three times that from one-step catalytic pyrolysis. The two-step catalytic pyrolysis process also facilitated the production of aromatic hydrocarbons in the liquid products. The maximum carbon yield of light olefins could reach 31.9% in the two-step process under the reaction temperature of 923 K and water flow rate of 30 ml h<sup>-1</sup>.

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### 1. Introduction

In the face of declining fossil energy resources and increasing issues of environmental deterioration, worldwide researchers have focused on the study of renewable and environmentally friendly biomass since last century.<sup>1,2</sup> Of numerous types of available biomass, microalgae are believed to be the most promising candidate because of its high photosynthetic efficiency and biological productivity.<sup>3–5</sup> Microalgae can not be directly used as fuels or chemicals because of their complicated compositions.<sup>6</sup> Therefore, the study of converting microalgae to fuels or chemicals is of great significance.

Recently, Patel *et al.* gave a important review of algal bio-refinery, which described a completed idea of conversion of algae to available various products, such as methane, hydrogen, syngas and oil *etc.*<sup>7</sup> To date, the production of bio-fuels from microalgae biomass was mostly studied.<sup>8–17</sup> For instance, the biodiesel could be obtained by extraction of algae lipids and further transesterification processing, which was a mixture of fatty acid esters.<sup>8</sup> The direct pyrolysis of microalgae could

produced nitrogen- and oxygen-containing bio-oil, and the products needed further deoxygenating and denitrogenating processing in order to improve the quality of bio-oil.<sup>9–11</sup> Aromatics-rich high quality bio-oil could be produced by catalytic pyrolysis of microalgae biomass.<sup>12–16</sup> The catalytic pyrolysis of *Chlorella* microalga and its major components were studied.<sup>12</sup> It was found that high lipid content in microalga would provide a benefit to the yield of aromatics. The catalytic pyrolysis of green algae biomass using ZSM-5 zeolite catalyst resulted nearly 26% of carbon as aromatic hydrocarbons, and more than 60% of them were BTX (Benzene, Toluene and Xylene).<sup>13</sup> A recent study in 2013 showed that catalytic pyrolysis of lipid-lean green algae produced 24% of aromatics, and the selectivity of BTX was above 70%.<sup>14</sup> Light olefins (ethylene, propylene and butene) are important and widely used base chemicals just as aromatics, while the efficient conversion of microalgae biomass to light olefins (ethylene, propylene and butene) was rarely reported. In 1990, Milne *et al.* first proposed the catalytic conversion of microalgae lipid over ZSM-5 catalyst, and the results showed that the yield of alkenes was about 50%, and the yield of aromatics was about 15%.<sup>18</sup> Pan *et al.* explored the direct pyrolysis and catalytic pyrolysis of *Nannochloropsis* sp. residue.<sup>15</sup> The yields of light olefins in the direct pyrolysis process and catalytic pyrolysis process were very low (<3 wt%). Campanella *et al.* explored the fast pyrolysis of microalgae in a falling solids reactor.<sup>16</sup> The total yield of light olefins was only about 4 wt% since the low yield of gas product (23 wt%).<sup>16</sup>

This study presented a more efficient process of catalytic converting microalgae to light olefins (ethylene, propylene and

<sup>a</sup>National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: liuzm@dicp.ac.cn; xuypp@dicp.ac.cn; Fax: +86 0411 84379998; Tel: +86 0411 84379998

<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup>The Laboratory of Biotechnology, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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butene) by using a modified ZSM-5 zeolite catalyst. Lipid-rich microalga *Chlorella pyrenoidosa* biomass obtained by heterotrophic culture process was used as the feedstock of catalytic pyrolysis. The catalytic pyrolysis performances of microalga *Chlorella pyrenoidosa* in nitrogen and steam atmospheres were investigated. The reaction performances of one-step and two-step catalytic pyrolysis were compared and discussed. Catalytic pyrolysis of microalgae biomass at various reaction temperatures and water flow rates were also explored in the experiments.

## 2. Experimental

### 2.1 Feedstock preparation

*Chlorella pyrenoidosa* (FACHB 9) was obtained from Freshwater Algae Culture Collection of the Institute of Hydrobiology, Chinese Academy of Sciences. It was cultured for 10 days at  $298 \pm 1$  K in autoclaved natural seawater, supplemented with SE culture medium ( $\text{NaNO}_3$   $0.25 \text{ g l}^{-1}$ ,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$   $0.075 \text{ g l}^{-1}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   $0.075 \text{ g l}^{-1}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$   $0.025 \text{ g l}^{-1}$ ,  $\text{KH}_2\text{PO}_4$   $0.175 \text{ g l}^{-1}$ ,  $\text{NaCl}$   $0.025 \text{ g l}^{-1}$ , Soil extract 40 ml,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$   $0.005 \text{ g l}^{-1}$ , Fe-EDTA 1 m  $\text{l}^{-1}$ , A5 solution 1 ml  $\text{l}^{-1}$ ). For the heterotrophic growth of lipid-rich *Chlorella pyrenoidosa*, 40 g  $\text{l}^{-1}$  glucose and 8 g  $\text{l}^{-1}$  yeast extract were added to the basal medium. Dry microalga powder was obtained through centrifugation and drying at 333 K.

### 2.2 Catalyst preparation

The detailed procedure of ZSM-5 modification and catalyst preparation was described elsewhere.<sup>19,20</sup> ZSM-5 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 45$ ) was obtained from Catalyst Plant of Nankai University, China. The catalyst was composed of about 35 wt% modified ZSM-5 zeolite and 65 wt% clay, and prepared by spray-drying method. The catalyst was calcined at 923 K for 3 h, then sieved to a particle size to pass through 300-mesh before being placed into the reactor. The XRD patterns,  $\text{NH}_3$ -TPD performance, and SEM images of catalyst were shown in the ESI.† The catalyst was proved having high selectivity of light olefins (ethylene, propylene and butene) in catalytic cracking reactions when naphtha was used as the reactant.<sup>19</sup> In this research, the catalyst also displayed high selectivity for the light olefins production from catalytic pyrolysis of microalga *Chlorella pyrenoidosa*.

### 2.3 Experimental setup

**2.3.1 One-step catalytic pyrolysis.** In one-step catalytic pyrolysis process, 0.5 g of microalgae powder and 10.0 g of catalyst were mixed and loaded in the reactor. Nitrogen or steam was used as the carrier gas. When the steam was used as the carrier gas, water was pumped into the reactor by a syringe pump when the temperature of reactor reached 373 K. During the reactions, the mixtures of microalgae powder and catalyst were heated from room temperature to 923 K at a rate of 10 K  $\text{min}^{-1}$ . An ice-water bath condenser was used to trap the water and bio-oil. Gas phase products were collected using a gas bag,

and the gas volume was determined using the water displacement method.

**2.3.2 Two-step catalytic pyrolysis.** The two-step catalytic pyrolysis system was shown in Scheme 1. In two-step process, 10.0 g of sieved catalyst was placed in the tail section of the reactor, and 0.5 g of microalgae powder feedstock was placed on the top section of the reactor. The catalyst bed and microalga feedstock bed were heated by two independent electric furnaces. The catalyst was activated for 30 min and flushed with nitrogen for 30 min at 823 K before the reactions. In the experiments, the catalyst bed was firstly heated to the reaction temperature, and then the feedstock bed was heated from room temperature to 923 K at a rate of 10 K  $\text{min}^{-1}$ . When the steam was used as the carrier gas, water was pumped into the reactor by a syringe pump when the temperature of the feedstock bed reached 373 K. An ice-water bath condenser was used to trap the water and bio-oil. Gas phase products were collected using a gas bag, and the gas volume was determined using the water displacement method.

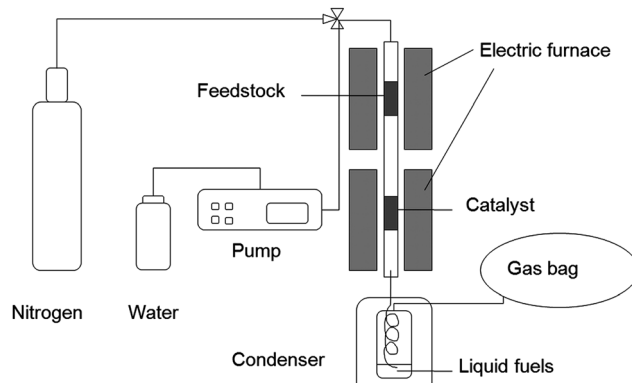
### 2.4 Analysis

Elemental composition of microalga feedstock was measured with an C/H/N/O elemental analyzer vario EL cube of elemental Co.

The thermogravimetric analysis was performed using a TA Q600 with the temperature-programmed rate of 10 K  $\text{min}^{-1}$  from room temperature to 1073 K under air/nitrogen flow.

Extraction of total lipids from dry microalgae biomass was performed according to the procedure of Bligh and Dyer.<sup>21</sup> The carbohydrate content was determined based on the sulfuric acid-anthrone method.<sup>22</sup> The protein content was analyzed by the Lowry method.<sup>23</sup> A esterification-GC method was used for the analysis of fatty acids of microalgae, and the detailed procedure was described elsewhere.<sup>24</sup>

The gaseous products of microalga catalytic pyrolysis were analyzed using an Agilent 7890A GC system equipped with FID and TCD detectors and HP-AL/KCL and TDX-01 columns. HP-AL/KCL column and FID were used for separation and analysis of hydrocarbons, and TDX-01 column and TCD were used for separation and analysis of  $\text{CO}_x$  and hydrogen. FID detector was



**Scheme 1** Two-step catalytic pyrolysis reaction system.

maintained at 573 K, and TCD detector was maintained at 523 K. The following temperature ramp was used: hold at 353 K for 12 min, ramp to 473 K at 20 K min<sup>-1</sup> and hold at 473 K for 16 min.

The total carbon content of the liquid products was quantified by an instrument of total organic carbon (TOC) (Shimadzu TOC-L CPH). The temperature of combustion tube of Shimadzu TOC-L was 993 K. The liquid products were treated by ultrasonic wave to achieve good emulsification. Then the emulsifying liquid was diluted 1000 times for TOC determination. Liquid product composition was identified by GC-MS and quantified by GC-FID (Agilent 7890A). HP-5 column was used for separation of components in liquid product. FID detector was held at 573 K. The GC oven was programmed with the following temperature regime: hold at 313 K for 5 min, ramp to 473 K at 15 K min<sup>-1</sup> and hold at 473 K for 5 min.

An instrument of total organic carbon (Shimadzu TOC-L CPH) with solid sample module (SSM-5000A) was used for the determination of total carbon content in the residue (coke/char) after reactions. The temperature of total carbon combustion tube of SSM-5000A was 1173 K. About 50 mg of solid sample was loaded in a ceramic sample boat and analyzed by further combustion.

## 2.5 Data evaluation and analysis

$$\text{Carbon yield} = \frac{\text{Moles of carbon in a product}}{\text{Moles of carbon feed in}} \times 100\%$$

## 3. Results and discussion

### 3.1 Feedstock analysis

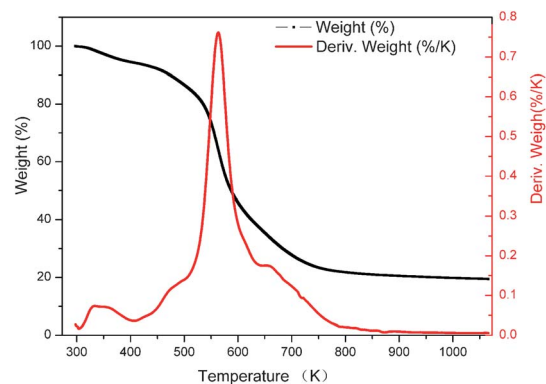
A typical elemental and biochemical analysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* sample was shown in Table 1. The ash content of lipid-rich heterotrophic *Chlorella pyrenoidosa* (2.0 wt%) was much lower than that of photoautotrophic *Chlorella* (15.64 wt%)<sup>14</sup> due to the less accumulation of inorganic salts from the culture media. Because of the high lipid content, the carbon content of lipid-rich heterotrophic *Chlorella pyrenoidosa* was as high as 52.8 wt%. Based on the

**Table 1** A typical elemental and biochemical analysis data of lipid-rich heterotrophic *Chlorella pyrenoidosa* sample

Elements	Content (wt%)
C	52.8
H	8.1
N	5.7
O (for balance)	31.4
Ash	2.0
Biochemicals	Content (wt%)
Proteins	19.8
Lipids	24.3
Carbohydrates	18.9

**Table 2** The fatty acid analyses of lipid-rich heterotrophic *Chlorella pyrenoidosa*

Compounds	Content (wt%)
Myristic acid (C14:0)	1.2 ± 0.3
Palmitic acid (C16:0)	25.4 ± 2.2
Palmitoleic acid (C16:1n7)	0.7 ± 0.3
Hexadecatrienoic acid (C16:3n4)	1.2 ± 0.1
Oleic acid (C18:1n9)	27.4 ± 1.1
Linoleic acid (C18:2n6)	33.1 ± 1.2
Linolenic acid (C18:3n3)	10.7 ± 0.5
Arachidic acid (C20:0)	0.1 ± 0.1
Docosapentenoic acid (C22:5n3)	0.1 ± 0.1



**Fig. 1** Thermogravimetric behavior of lipid-rich heterotrophic *Chlorella pyrenoidosa* in N<sub>2</sub> atmosphere under the heating rate of 10 K min<sup>-1</sup>.

elemental analysis, the chemical formula can be written as (C<sub>4.4</sub>H<sub>8.1</sub>O<sub>2.0</sub>N<sub>0.4</sub>)<sub>n</sub>. The lipid content in lipid-rich heterotrophic *Chlorella pyrenoidosa* cells was 24.3 wt%, which was much higher than that in photoautotrophic microalga cells (2–11.9 wt %).<sup>25</sup>

The fatty acid analysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* were shown in Table 2. The main fatty acids were hexadecanoic acid, oleic acid, linoleic acid and linolenic acid, their total content could reach 96.6 wt% around.

The thermogravimetric behavior of lipid-rich heterotrophic *Chlorella pyrenoidosa* in N<sub>2</sub> atmosphere was shown in Fig. 1. In general, there were two weight loss regions in thermogravimetric analysis. The first region was in the range of 373 to 423 K, which was mainly attributed to water volatilization. The second region was between 423 and 773 K, which could ascribe to the biolipids volatilization, decomposition of carbohydrates and proteins. About 20 wt% residue was left above 923 K, which was mainly coke and inorganic oxides.

### 3.2 One-step catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* in nitrogen and steam atmospheres

In one-step process, the catalyst and microalga feedstock were mixed together and placed in the middle section of reactor. The carbon yields of gaseous products from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* in nitrogen and steam atmospheres were shown in Table 3. When the reactions were conducted under nitrogen atmosphere, 7.8% carbon yield

**Table 3** Carbon yield (%) of products of catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa*

Compounds	One-step		Two-step
	Nitrogen	Steam	Steam
C <sub>2</sub> H <sub>4</sub>	1.9	1.3	7.4
C <sub>3</sub> H <sub>6</sub>	3.5	5.1	16.4
t-2-C <sub>4</sub> H <sub>8</sub>	0.6	1.0	2.0
n-C <sub>4</sub> H <sub>8</sub>	0.4	0.6	1.6
i-C <sub>4</sub> H <sub>8</sub>	0.9	2.2	3.0
c-2-C <sub>4</sub> H <sub>8</sub>	0.4	0.7	1.5
CH <sub>4</sub>	2.7	1.8	6.1
C <sub>2</sub> H <sub>6</sub>	2.0	0.7	1.4
C <sub>3</sub> H <sub>8</sub>	1.9	0.5	0.8
i-C <sub>4</sub> H <sub>10</sub>	0.2	0.1	0.1
n-C <sub>4</sub> H <sub>10</sub>	0.4	0.2	0.3
C <sub>5</sub> <sup>+</sup>	3.5	3.3	3.3
CO	3.9	6.3	13.1
CO <sub>2</sub>	5.6	21.2	7.8
Total olefins	7.8	10.9	31.9
Total gaseous hydrocarbons	18.4	17.5	43.9
Total gaseous products	27.9	45.1	64.8
Liquid	13.8	18.0	19.4
Residue (coke/char)	54.7	34.6	17.6
Total carbon balance	96.4	97.7	101.8

of light olefins could be obtained, and the total gas carbon yield was 27.9%. When the reactions were carried out under steam atmosphere, the carbon yield of light olefins reached 10.9%, and the total gas carbon yield was 45.1%. It was obvious that steam facilitated the production of gas as well as the light olefins.

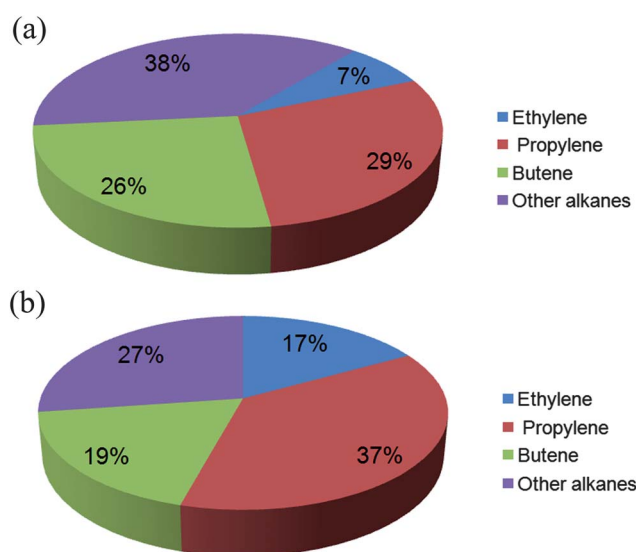
Putun *et al.* explored catalytic pyrolysis of biomass in inert (nitrogen) and steam atmospheres, and the results showed that higher bio-oil yield was obtained in steam atmosphere.<sup>26</sup> They explained that nitrogen was an inert agent, it only acted as a carrier gas for transporting the volatiles from the hot zone to minimise the secondary thermal pyrolysis and coking reactions. However the steam not only acted as a carrier gas but also penetrated into solid materials and efficiently removed the volatile product from solid materials, thus enhanced the yield of bio-oil.<sup>27</sup> As to the reactions studied here, another function of steam was that steam could eliminate coke on the ZSM-5 catalyst, interact with the acidic centers of ZSM-5 and facilitate the dehydrogenation process, and finally enhance the catalytic cracking process to produce light olefins efficiently.<sup>28</sup> It was shown in Table 3 that under steam atmosphere, less alkanes (methane, ethane, propane and butane) and more olefins (ethylene, propylene, and butene) were produced as compare with nitrogen atmosphere. Higher yields of CO and CO<sub>2</sub> could also be observed, which proved that steam could participated in the reactions and reacted with coke on the catalyst.

### 3.3 Catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* in one-step process and two-step process

In the experiments, the reaction ways of microalga pyrolysis were classified into one-step process and two-step process

according to locations of catalyst and microalga feedstock in the reactor. In one-step process, the catalyst and microalga feedstock were mixed together and placed in the middle section of reactor. In two-step process, the microalga feedstock was placed in the top section of reactor and the catalyst was placed in the tail section of reactor. In one-step process, the catalyst and microalga biomass mixtures were heated with a program rate of 10 K min<sup>-1</sup>, the final temperature was 923 K. In two step process, the catalyst bed was heated to a certain reaction temperature firstly, then the microalga feedstock bed was heated with a programed rate of 10 K min<sup>-1</sup>, and the final temperature was 923 K.

The carbon yields of products from different reaction processes were shown in Table 3. The results showed that one-step and two-step catalytic pyrolysis processes displayed very different reaction performances. In one-step catalytic pyrolysis process, the carbon yield of total gaseous hydrocarbons and CO<sub>x</sub> was 17.5% and 27.5%, respectively, and the carbon yield of liquid product and residue was 18.0% and 36.4%, respectively. The carbon yield of light olefins (ethylene, propylene and butene) was 10.9%. Two-step pyrolysis process could get higher carbon yield of total gaseous hydrocarbons, which could reach as much as 43.9%. 19.4% carbon yield of liquid product could be obtained in two-step process, which was slightly higher than that of one-step process. 20.9% carbon yield of CO<sub>x</sub> and 17.6% carbon yield of residue were obtained in two-step process, those were lower than one-step process. Most importantly, the carbon yield of light olefins from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* in two-step process was 31.9%, which was nearly three times as much as that in one-step process (10.9%). The results revealed that two-step process was more efficient for the light olefins production than one step process. As to the products distribution of light olefins (Fig. 2a and b), no matter one-step or two step catalytic process, the

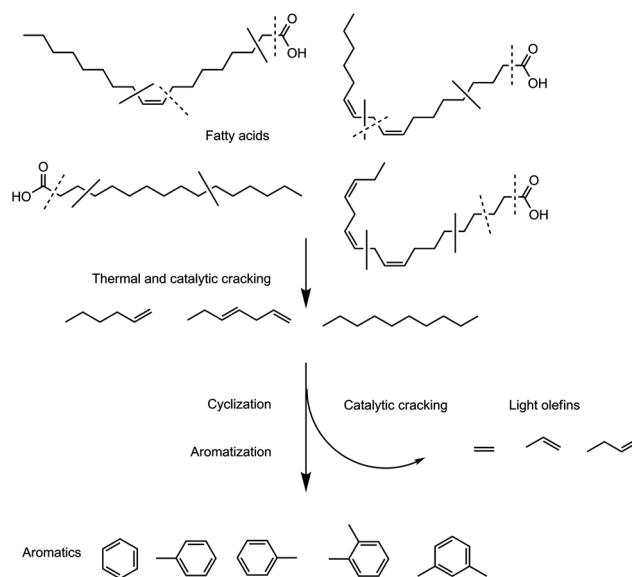


**Fig. 2** (a) Carbon distributions (%) of gaseous hydrocarbons from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* with one-step process. (b) Carbon distributions (%) of gaseous hydrocarbons from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* with two-step process.

carbon yield sequence was propylene > butene > ethylene, which displayed the characteristic of catalytic cracking reactions.<sup>29</sup>

ZSM-5 zeolite has strong acidity and unique pore structures, can be used as the catalyst for production of both aromatics and light olefins from hydrocarbons or alcohols, such as naphtha, residue oils and methanol *etc.*<sup>28–30</sup> The catalytic pyrolysis of microalga with unmodified ZSM-5 zeolite as catalyst could produce aromatics-rich bio-oil, wherein light olefins products were not specified.<sup>12–15</sup> The ZSM-5 zeolite catalyst used in our experiment was modified by P and La. Our previous research showed that such modification would stabilize the zeolite structure and optimized the acidity of zeolite, and facilitate the production of light olefins (ethylene, propylene and butene) when naphtha was used as the reactant.<sup>19,20</sup> The data in Table 3 showed that the modified ZSM-5 zeolite catalyst was also efficient for light olefins production from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa*. Especially in two-step process, the light olefins (ethylene, propylene and butene) were the predominant products, their carbon yield could reach nearly 32%.

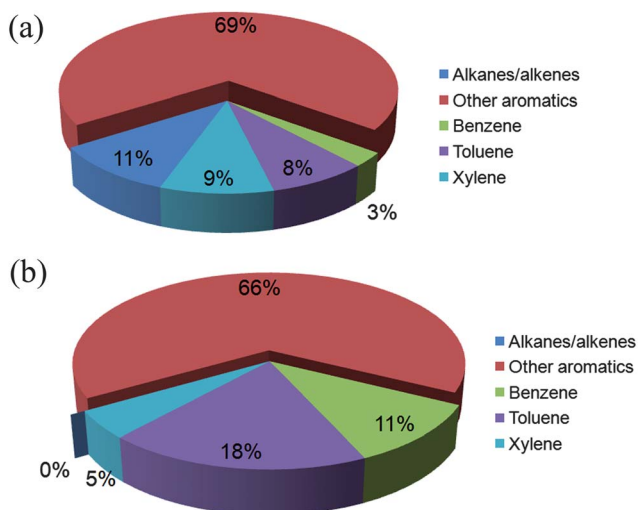
Lipid-rich heterotrophic *Chlorella pyrenoidosa* contains three major biochemical contents: lipids, proteins and carbohydrates. Lipids are volatile, they can contact with the active centers of catalyst and conduct catalytic reactions directly. Since lipids have similar molecular structures and elemental compositions with petroleum based oils, they can be converted to light olefins (ethylene, propylene and butene) with high yield (40–47.5 wt%).<sup>31–33</sup> For the non-volatile properties of protein and carbohydrate, they can not contact with the active centers of catalyst and can not conducted catalytic reactions directly. However, proteins and carbohydrates can produce volatile bio-oil by thermal pyrolysis,<sup>8,15</sup> the bio-oil can contact with the zeolite catalyst and conduct catalytic reactions to produce light olefins and other liquid products.



**Scheme 2** Postulated pathways for catalytic pyrolysis of lipids.

The experiments results displayed that two-step catalytic pyrolysis was a better way for production of light olefins from microalga than one-step process. Güngör *et al.* studied the pyrolysis of pine bark with one-step and two-step pyrolysis systems.<sup>34</sup> They also found that ReUS-Y produced more alkane and alkene in gas products in two-step process as compared to one-step process (39.3% to 23.5%). The different results of two reaction processes might be attributed to following reasons. In the case of one-step process, the catalyst was mixed with microalga feedstock, and the catalytic reaction temperature was changed with the time. Under such reaction conditions, some volatile contents of microalga would not contact with the catalyst and directly went out of the reacting zone, thus the reaction would display a mixed result of thermal pyrolysis and catalytic pyrolysis. Moreover, the catalytic reaction temperature varied all the time, the total result should be a mixed result of a wide range of reaction temperatures. While in the case of two-step process, the temperatures of microalga feedstock bed and catalyst bed were controlled independently. The catalytic pyrolysis temperature could be set at an optimized value. Furthermore, as the microalga feedstock bed temperature rising, the steam would bring the volatile contents to pass through the catalyst bed and conduct catalytic cracking reactions very fully. Hence, the carbon yields of gaseous hydrocarbon products and light olefins of two-step process were higher than those of one-step process, and the carbon yield of residue was also lower in the two-step process.

The carbon yields of liquid products with one-step process and two-step process were similar, those were both around 20%, but their compositions were very different (Fig. 3a and b and Table S1†). In one-step catalytic pyrolysis system, the share of straight chain alkanes/alkenes was about 11% and the main products of oil phase were aromatic hydrocarbons. The selectivity of BTX in the oil phase was about 20%. In the case of two-step catalytic pyrolysis, there were negligible amount of straight chain alkanes/alkenes in the liquid products, the aromatics



**Fig. 3** (a) Carbon distributions (%) of liquid products from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* with one-step process. (b) Carbon distributions (%) of liquid products from catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* with two-step process.

were the predominant contents in the liquid products and the selectivity of BTX in the oil phase reached 34%. The results proved that the modified ZSM-5 catalyst could produce not only light olefins but also aromatics effectively, though the yield of aromatics-rich liquid was lower than previous report.<sup>13,14</sup> Just as discussed in above section, because of the optimized catalytic reaction temperature and fully contacting of reactant with catalyst, two-step process displayed high yield of aromatics in liquid product.

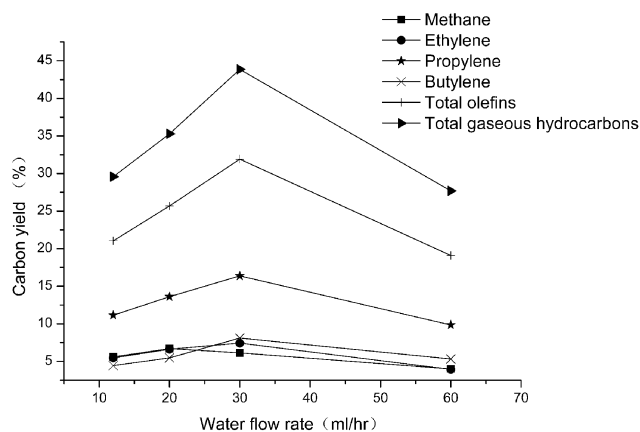
The aromatic hydrocarbons could be obtained through the catalytic conversion of lipids, proteins and carbohydrates as shown in Scheme 2, S1 and S2.<sup>31,35–38†</sup> The catalytic cracking of triglycerides such as canola oil on HZSM-5 has been studied extensively.<sup>31,35</sup> The triglycerides could be thermally decomposed to long-chain fatty acids, ketones, aldehydes and esters, which were then converted to hydrocarbons through thermal and catalytic processes. The hydrocarbons could be cracked to light olefins and paraffins, and those products could produce aromatic hydrocarbons in the pores of the zeolite catalysts through a series reactions of oligomerization, cyclization and aromatization. Meanwhile, carbohydrates could be thermally decomposed to anhydrosugars and other condensable oxygenated products such as dihydroxyacetone and glyceraldehyde, those could subsequently undergo dehydration and re-arrangement reactions to form furans and smaller aldehydes.<sup>36,37</sup> These oxygenates then diffused into the zeolite catalyst pores and formed aromatics and olefins through a series of decarbonylation, decarboxylation, dehydration, and oligomerization reactions.<sup>36,37</sup> While the catalytic pyrolysis of proteins on HZSM-5 was rarely reported. From the view of molecular structure, some amino acids could be converted to olefins and aromatics through deamination<sup>38</sup> and decomposition reactions. In general, lipids were the prominent contributors for the production of light olefins and aromatics during the catalytic pyrolysis of microalga.

### 3.4 Effects of reaction temperatures on carbon yield of light olefins

The effects of reaction temperatures on carbon yields of gaseous products and light olefins were shown in Table 4 and Fig. 4. The data showed that carbon yields of gaseous hydrocarbons and light olefins increased from 27.9% and 21.8% to 43.9% and 31.9% in the temperature range of 773 K to 923 K, respectively. When the reaction temperature further increased to 973 K, the carbon yield of gaseous hydrocarbons and light olefins decreased to 42.0% and 30.6%, respectively. From the viewpoint of thermodynamics, high temperature facilitated the formation of light olefins.<sup>20</sup> Nevertheless, too high reaction temperature, such as 973 K, would make thermal cracking and coking reactions seriously, those would lead to low yield of total gaseous hydrocarbons. It was noteworthy that propylene was always the predominant olefin product, which increased when the temperature increased from 773 K to 923 K, and decreased at 973 K. Butene displayed the same trend as propylene while the yield of ethylene increased with increasing temperature from 773 K to 973 K. From the viewpoint of reaction mechanism, the catalytic reactions on ZSM-5 zeolite catalyst followed the

**Table 4** Effects of reaction temperatures on carbon yields (%) of gaseous products of catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* (water flow rate: 30 ml h<sup>-1</sup>)

Compounds	Temperature (K)			
	773	873	923	973
C <sub>2</sub> H <sub>4</sub>	5.1	6.9	7.4	8.0
C <sub>3</sub> H <sub>6</sub>	10.7	15.8	16.4	16.1
t-2-C <sub>4</sub> H <sub>8</sub>	1.4	1.8	2.0	1.5
n-C <sub>4</sub> H <sub>8</sub>	1.1	1.8	1.6	1.6
i-C <sub>4</sub> H <sub>8</sub>	2.6	3.2	3.0	2.4
c-2-C <sub>4</sub> H <sub>8</sub>	1.0	1.4	1.5	1.1
CH <sub>4</sub>	1.8	3.6	6.1	5.8
C <sub>2</sub> H <sub>6</sub>	0.8	1.4	1.4	1.3
C <sub>3</sub> H <sub>8</sub>	0.5	0.7	0.8	0.7
i-C <sub>4</sub> H <sub>10</sub>	0.1	0.1	0.1	0.1
n-C <sub>4</sub> H <sub>10</sub>	0.2	0.3	0.3	0.3
C <sub>5</sub> <sup>+</sup>	2.7	2.7	3.3	3.2
CO	5.9	8.2	13.1	10.2
CO <sub>2</sub>	7.5	6.9	7.8	8.5
Total olefins	21.8	30.8	31.9	30.6
Total gaseous hydrocarbons	27.9	39.6	43.9	42.0
Total gaseous products	41.3	54.7	64.8	60.7



**Fig. 4** Effects of reaction temperatures on carbon yields (%) of gaseous hydrocarbons and light olefins (water flow rate: 30 ml h<sup>-1</sup>).

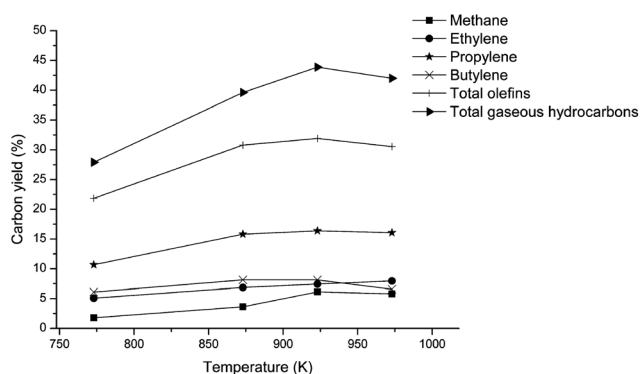
carbonium mechanism, which facilitated the formation of propylene.<sup>39,40</sup> The thermal cracking (steam cracking) process followed the radical mechanism, which facilitated the formation of ethylene.<sup>40</sup> In the range of 773 K to 973 K, the modified ZSM-5 zeolite catalyst used in our experiments displayed affective catalytic functions, and carbonium mechanism played the dominant role in reactions, so propylene was always the predominant olefin product. Only at temperature as high as 973 K, the radical cracking reactions took place seriously, which displayed increased yield of ethylene and decreased yields of propylene and butene.

### 3.5 Effects of water flow rates on carbon yield of light olefins

The carbon yields of gaseous products and light olefins from the catalytic pyrolysis of lipid-rich heterotrophic *Chlorella*

**Table 5** Effects of water flow rates on carbon yields (%) of gaseous products of catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* (reaction temperature: 923 K)

Compounds	Water flow rate (ml h <sup>-1</sup> )			
	12	20	30	60
C <sub>2</sub> H <sub>4</sub>	5.5	6.6	7.4	3.9
C <sub>3</sub> H <sub>6</sub>	11.1	13.6	16.4	9.8
t-2-C <sub>4</sub> H <sub>8</sub>	1.1	1.4	2.0	1.3
n-C <sub>4</sub> H <sub>8</sub>	0.8	1.0	1.6	1.1
i-C <sub>4</sub> H <sub>8</sub>	1.7	2.1	3.0	2.0
c-2-C <sub>4</sub> H <sub>8</sub>	0.8	1.0	1.5	1.0
CH <sub>4</sub>	5.6	6.7	6.1	4.0
C <sub>2</sub> H <sub>6</sub>	1.1	1.5	1.4	0.9
C <sub>3</sub> H <sub>8</sub>	0.6	0.8	0.8	0.5
i-C <sub>4</sub> H <sub>10</sub>	0.1	0.1	0.1	0.1
n-C <sub>4</sub> H <sub>10</sub>	0.2	0.3	0.3	0.2
C <sub>5</sub> <sup>+</sup>	0.9	0.3	3.3	2.9
CO	10.3	10.7	13.1	8.4
CO <sub>2</sub>	4.9	5.6	7.8	5.1
Total olefins	21.1	25.7	31.9	19.1
Total gaseous hydrocarbons	29.6	35.3	43.9	27.7
Total gaseous products	44.8	51.6	64.8	41.1



**Fig. 5** Effects of water flow rates on carbon yields (%) of gaseous hydrocarbons and light olefins (reaction temperature: 923 K).

*pyrenoidosa* at different water flow rates were shown in Table 5 and Fig. 5. The carbon yields of gaseous hydrocarbons and light olefins were 29.6% and 21.0% at water flow rate of 12 ml h<sup>-1</sup>, and then reached a maximum of 43.9% and 31.9% at water flow rate of 30 ml h<sup>-1</sup>. Further increasing the water flow rate to 60 ml h<sup>-1</sup> decreased their carbon yields to 27.7% and 19.1%. The trends of carbon yields of ethylene, propylene and butylene were the same as gaseous hydrocarbons. At low water flow rate, thermal cracking reactions took place before the volatile species were carried to the catalyst bed, and the contact time of volatile species with catalyst was also too long. So that thermal cracking, deep cracking and coking reactions were serious at low water flow rate, those would lead to low carbon yields of gaseous hydrocarbons and light olefins. When the water flow rate was too high, the contact time of volatile reactant was too short to undergo sufficient catalytic reactions, which also resulted in low carbon yields of gaseous hydrocarbons and light olefins.

Furthermore, the increasing of water flow rate decreased the production of biochar obviously. As shown in Fig. S1,<sup>†</sup> the carbon yield of biochar decreased from 23.8% to 16.9% as water flow rate increased from 12 ml h<sup>-1</sup> to 60 ml h<sup>-1</sup>.

## 4. Conclusion

Light olefins (ethylene, propylene and butene) were efficiently produced by catalytic pyrolysis of lipid-rich heterotrophic *Chlorella pyrenoidosa* with a modified ZSM-5 zeolite catalyst. The total carbon yield of light olefins could reach 31.9% in two-step catalytic process at temperature of 923 K and water flow rate of 30 ml h<sup>-1</sup>, and 19.4% carbon yield of aromatics-rich liquid product was also obtained at the same time. Higher yield of light olefins was observed when the reactions were conducted in steam atmosphere than in nitrogen atmosphere. The carbon yield of light olefins obtained from two-step catalytic pyrolysis was nearly three times of the yield from one-step catalytic pyrolysis. The aromatics were the predominant contents of the liquid products in two-step process, and the selectivity of BTX could reach 34%. This research suggested that the catalytic pyrolysis of microalga to produce light olefins (ethylene, propylene and butene) was another efficient candidate route of microalga utilization.

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