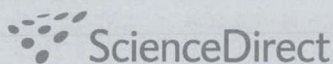


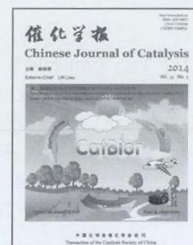


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## The production of light olefins by catalytic cracking of the microalga *Isochrysis zhanjiangensis* over a modified ZSM-5 catalyst

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## ABSTRACT

This study investigated the catalytic cracking of the microalga *Isochrysis zhanjiangensis* over a modified ZSM-5 catalyst with the aim of producing C<sub>2</sub>–C<sub>4</sub> light olefins. Compared with the thermal cracking process, the catalytic cracking of this microalga displayed higher selectivity for and greater yield of these olefins. The catalytic cracking of extracted lipids and the corresponding residues of the microalga was also examined, and the results showed that the lipids could be efficiently converted to light olefins. The catalytic cracking of lipids extracted by different solvents demonstrated that neutral lipids gave the highest yield of light olefins at 36.7%. The yields of light olefins obtained from catalytic cracking of the extraction residues were much lower than the yields obtained from lipids, and thus the lipids, especially the neutral lipids, are the primary contributors to the generation of light olefins. *Isochrysis zhanjiangensis* with an elevated neutral lipid content will therefore give the highest yield of light olefins through catalytic cracking.

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### 1. Introduction

Because of projected future decreases in fossil fuel resources, biomass has received increasing attention as an alternative energy source that is both renewable and environmentally friendly [1–4]. In this context, microalgae represent a very promising candidate for renewable biomass [5–9]. It is well known, however, that microalgae cells cannot be used as either fuels or basic chemicals without processing, and so the conver-

sion of microalgae to convenient and useful products is a very important field of research with regard to enabling the widespread application of microalgae. To date, the technologies available for converting microalgae-based biomass can be grouped into two basic categories depending on the conversion products: liquid bio-fuel and gas production processes [8].

The liquid products of microalgae conversion are primarily bio-diesel, bio-oil, and alcohols. Because many microalgae contain fatty acid esters, dry microalgae feedstock can be conven-

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iently converted to bio-diesel by extraction and transesterification processes [10]. In such processes, the yield of bio-diesel depends on the lipid content of the microalgae. However, it is noteworthy that not all the lipids in microalgae can be efficiently converted into bio-diesel; only the fatty acid esters can be effectively transformed into fatty acid methyl esters, while the phospholipids and glycolipids cannot because of the high proportion of phosphate groups and glycosyl they contain. High-pressure thermochemical liquefaction technology is employed in microalgae conversion to process the wet feedstock and maximize the production of liquid fuel [11]. Fast pyrolysis is another means of converting microalgae to liquid fuel and has been considered for the large-scale production of bio-fuel from microalgae [12]. However, the liquid bio-fuels derived from both thermochemical liquefaction and fast pyrolysis are typically of low quality and require upgrading before use. Catalytic pyrolysis technology has been extensively investigated as a technique for producing high-quality bio-oil, and ZSM-5 zeolite is an effective catalyst for the catalytic pyrolysis of microalgae, during which the microalgae is converted to high-quality liquid fuel containing a large proportion of aromatics [13–15]. The high nitrogen and oxygen content of the microalgae can be reduced using a ZSM-5 catalyst, and one study has shown an aromatic hydrocarbons yield (on a carbon basis) of 25.8% [13]. In addition, starch-rich microalgae can also be converted to alcohol by alcoholic fermentation processes [15].

Generating gaseous products from microalgae is another important technology, and a number of useful gaseous products are possible, such as bio-hydrogen, biogas, and synthesis gas (hydrogen and carbon monoxide). Some unicellular green algae and cyanobacteria, for example, can split water into bio-hydrogen and oxygen using solar energy [16] while anaerobic digestion can convert microalgae biomass into biogas, which consists primarily of methane and carbon dioxide [17]. Microalgae biomass can also be converted to synthesis gas by means of partial oxidation gasification at high temperatures [18]. The bio-hydrogen and methane products can be used directly as gaseous fuels, and the synthesis gas products (hydrogen and carbon monoxide) can serve as reactants for the production of methanol or oil through FT synthesis. Methane-rich gaseous fuels can also be produced by a novel catalytic gasification process using wet microalgae as the feedstock [8]. Furthermore, the nitrogen content in microalgae can be converted to ammonia, which can be used as a nitrogen fertilizer [15].

To date, studies on microalgae biomass conversion have primarily focused on the production of bio-fuel, synthesis gas, hydrogen, and methane, and the main product of the catalytic conversion of microalgae biomass has been aromatics-rich liquid fuel. At the same time, work on an efficient catalytic process for the conversion of microalgae biomass to light olefins (ethylene, propylene, and butene) has rarely been reported. This is unfortunate because light olefins, such as ethylene and propylene, are key building blocks in the petrochemical industry. The main technique currently used to produce light olefins is steam cracking of naphtha and other light alkane feedstocks, although alternative technologies such as methanol conversion

to olefins have been studied. The above processes constitute non-renewable routes to light olefin production, however, because they use fossil fuels as raw materials. The direct conversion of microalgae to light olefins offers a novel renewable route to light olefin production, and its exploration would be an important contribution to the development of microalgae biomass utilization technologies. In our previous work, the catalytic pyrolysis of the lipid-rich microalga *Chlorella pyrenoidosa* for the production of light olefins was investigated [19] after the microalga biomass was obtained by a heterotrophic culture process. Using a two-step process at a temperature of 650 °C and a water flow rate of 30 ml/h, the maximum carbon yield of light olefins was 31.9%. This research suggested that the catalytic pyrolysis of microalgae to produce light olefins represents another efficient means of microalgae utilization. In the present work, we investigated the catalytic cracking of *Isochrysis zhanjiangensis* as well as its lipids and residues to produce light olefins. *Isochrysis* is one of the most commonly used marine unicellular alga in a variety of mariculture systems and grows well as mass cultures in either indoor or outdoor environments [20,21]. Our laboratory has been culturing *Isochrysis zhanjiangensis* for many years and has produced a total of 10000 L of culture to date [20]. Therefore, we were able to obtain sufficient alga feedstocks for use in further research on cracking reactions. In these experiments, the catalytic cracking and thermal cracking of *Isochrysis zhanjiangensis* were compared, the cracking of its lipids and residues was investigated, and the catalysis of *Isochrysis zhanjiangensis* samples with different neutral lipids contents was also explored.

## 2. Experimental

### 2.1. Catalyst preparation

A catalytic cracking catalyst (FGTO-C106) was prepared by spray drying a modified ZSM-5 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 45$ ) powder mixed with clay, followed by calcination. The procedure has been described in detail in our previous publications [19,22,23]. The resulting catalyst was sieved to isolate the particles passing through a 300 mesh screen, which were then transferred to the reactor.

### 2.2. Cultivation of the microalga *Isochrysis zhanjiangensis*

*Wild I. zhanjiangensis* was photoautotrophically cultivated at  $25 \pm 1$  °C in sterilized natural seawater supplemented with f/2 culture medium and compressed air containing 2%  $\text{CO}_2$  [20]. The f/2 culture medium was composed of nutrient, trace metal and vitamin solutions. The nutrient solution included (per liter): 75 mg  $\text{NaNO}_3$  and 5 mg  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . The trace metal solution included (per liter): 3.15 mg  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 4.36 mg  $\text{Na}_2\text{EDTA}$ , 0.0098 mg  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 0.0063 mg  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , 0.022 mg  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.01 mg  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and 0.18 mg  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . The vitamin solution included (per liter): 0.001 mg vitamin  $\text{B}_{12}$ , 0.2 mg vitamin  $\text{B}_1$ , and 0.001 mg biotin [20]. Dry microalgae powder was obtained through centrifugation and drying at 60 °C.

### 2.3. Extraction of lipids from the microalga

Lipids were extracted from the microalga biomass using either methanol, ethyl acetate, or *n*-hexane in a Soxhlet extraction apparatus for 2 h. The resulting samples were referred to as Lipid-M, Lipid-E, and Lipid-H, respectively. The remaining residues consisted primarily of proteins and carbohydrates as well as some polar lipids and were referred to as Residue-M, Residue-E, and Residue-H, respectively.

### 2.4. Catalytic cracking of the microalga

A fixed bed reaction system was used for catalytic cracking of the microalga, as shown in Fig. 1. A 10 ml quantity of sieved catalyst was placed in the tail section of the reactor, and the feedstock was loaded into the top section. The catalyst and feedstock beds were heated by two independent electric furnaces. The catalyst was activated for 30 min and then flushed with nitrogen for 15 min at 550 °C prior to the reaction. During the reaction, the feedstock bed was heated at a rate of 10 °C/min to 650 °C. Water was pumped through the reactor via a syringe pump when the temperature of the feedstock bed reached 100 °C, and the resulting steam carried the volatile components through the catalyst bed. A condenser cooled by an ice water bath was used to trap the water and bio-oil. Gas phase products were collected using gas bags, and the gas volume was determined using the water displacement method. The composition of the gas product was analyzed using an Agilent 7890A gas chromatography system.

### 2.5. Analysis

The elemental composition of the microalga feedstock was determined with a C/H/N/O elemental analyzer (vario EL cube, Elemental Co.), and thermogravimetric analysis was performed using a TA Q600 at a rate of 10 °C/min from room temperature to 700 °C under nitrogen flow. The gaseous products were analyzed using an Agilent 7890A gas chromatography (GC) system equipped with flame ionization and thermal conductivity

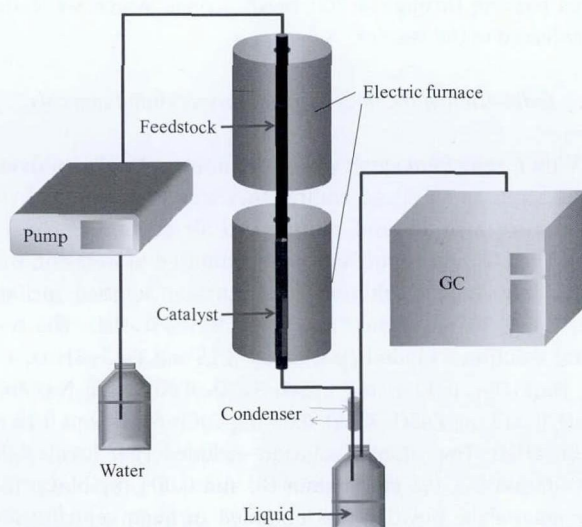


Fig. 1. The fixed-bed reactor system.

detectors (FID and TCD). An HP-AL/KCL column was employed in concert with the FID to separate and analyze hydrocarbons, while a TDX-01 column and TCD were used to separate and analyze CO, CO<sub>2</sub>, and hydrogen. The FID was maintained at 300 °C and the TCD at 250 °C. The following temperature ramp was applied: hold at 80 °C for 12 min, ramp to 200 °C at 20 °C/min, and hold at 200 °C for 16 min [19]. Extraction of total lipids from the dry microalga biomass was performed according to the procedure of Bligh and Dyer, while the carbohydrate content was determined based on the sulfuric acid-anthrone method and the protein content was analyzed by the Lowry method. The total lipid content was determined based on the procedure of Bligh and Dyer. The neutral lipids were extracted with *n*-hexane. An esterification-GC method was used for the analysis of fatty acids obtained from the microalgae, applying a procedure that has been described in our previous work [20].

## 3. Results and discussion

### 3.1. Analysis of the microalga

Elemental analysis (in wt%) data for the *Isochrysis zhanjiangensis* showed that the cells contain carbon, oxygen, hydrogen, and nitrogen in proportions of 49.0, 27.8, 7.1, and 6.5 wt%, respectively (Fig. 2). Based on these data, the molar composition of the cells was CH<sub>1.75</sub>O<sub>0.43</sub>N<sub>0.11</sub>. A typical biochemical composition (in wt%) of the microalga is presented in Table 1, demonstrating that lipids and proteins were the two main constituents, accounting for 84.2% to 92.3%. Later tests showed that while the total lipid content was above 40%, the neutral lipid content was only 10.1 wt%.

The thermogravimetric behavior of *Isochrysis zhanjiangensis* in a nitrogen atmosphere is shown in Fig. 3. In general, two weight loss regions were observed: between 200 and 400 °C, attributed primarily to the volatilization of bio-lipids, and be-

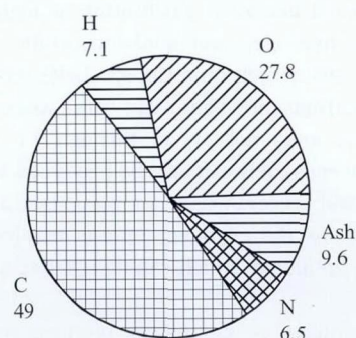


Fig. 2. Typical elemental analysis results (as wt% of dry weight) for the microalga *Isochrysis zhanjiangensis*. The amount of O was assumed to be the balance remaining after the other elements and ash were determined.

Table 1

Typical biochemical composition of the microalga *Isochrysis zhanjiangensis*.

Composition	Content (wt%)
Lipids	43.61±1.91
Carbohydrates	8.49±2.13
Proteins	44.64±2.12

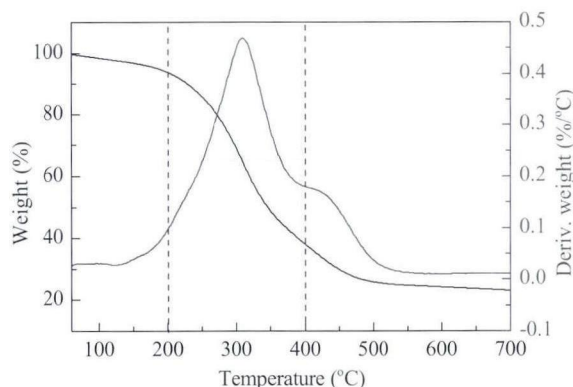


Fig. 3. Thermal analysis data for the microalga *Isochrysis zhanjiangensis* heated at 10 °C/min from room temperature to 700 °C under N<sub>2</sub> flow.

tween 400 and 500 °C, which could be due to the decomposition of carbohydrates and proteins. About 23 wt% residue was left above 650 °C, consisting mainly of coke and inorganic oxides.

### 3.2. Catalytic cracking of *Isochrysis zhanjiangensis*

ZSM-5 can provide the highest obtainable aromatic and olefin yields from certain types of biomass [24–27], and our previous research has successfully developed an efficient catalytic cracking catalyst, FGTO-106, which is composed of a ZSM-5 zeolite modified with P and La [19,22,23]. The FGTO-106 catalyst displayed high selectivity for light olefins when naphtha was used as the reactant. In the work reported herein, the same FGTO-106 catalyst was applied to the catalytic cracking of *Isochrysis zhanjiangensis* to produce light olefins. The selectivity for gaseous products and the associated yields obtained at different temperatures are summarized in Table 2. These results show that the selectivity for olefins decreased as the reaction temperature increased. The highest selectivity for light olefins (26.9%) was obtained at 550 °C, while the highest yield of 11.0% was obtained at 600 °C. The selectivity for ethylene increased from 6.8% at 550 °C to 7.6% at 650 °C. However, the selectivity for propylene decreased sharply from 14.4% to 8.0% as the temperature rose from 550 to 650 °C. Meanwhile, the selectivity for butene steeply decreased from 5.9% to 0.9%. The overall yield of gaseous products increased with increasing reaction temperature. For comparison purposes, the thermal cracking of *Isochrysis zhanjiangensis* at 650 °C was also investigated, and the results are provided in Table 2. These data show that the yield of light olefins from thermal cracking was only 5.8%, much lower than that obtained from the catalytic cracking process. The results indicate that the presence of the catalyst facilitates the production of light olefins. It is also worth noting that, under the catalytic cracking conditions, only the volatile microalga lipids would have been carried to the catalyst bed by the steam to undergo catalytic reactions. Other nonvolatile contents, such as proteins and carbohydrates, would have to first pyrolyze to small molecules and volatile liquids at the top portion of the reactor (the feedstock bed as shown in Fig. 1), and then pass through the catalyst bed before undergoing catalytic reactions.

Table 2

Performance data from catalytic and thermal cracking of *Isochrysis zhanjiangensis* at various temperatures.

Temperature (°C)	550 <sup>a</sup>	600 <sup>a</sup>	650 <sup>a</sup>	650 <sup>b</sup>
Gas product distribution (wt%)				
H <sub>2</sub>	4.3	3.7	3.5	5.3
CO	16.5	18.1	31.7	16.6
CO <sub>2</sub>	42.5	43.7	38.5	54.5
CH <sub>4</sub>	5.4	6.3	8.1	5.2
C <sub>2</sub> H <sub>6</sub>	1.7	1.6	1.1	1.4
C <sub>2</sub> H <sub>4</sub>	6.8	7.1	7.6	6.5
C <sub>3</sub> H <sub>8</sub>	1.2	0.8	0.4	0.5
C <sub>3</sub> H <sub>6</sub>	14.4	12.4	8.0	4.6
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.4	0.2	0.1	0.1
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.4	0.3	0.1	0.1
<i>t</i> -2-C <sub>4</sub> H <sub>8</sub>	1.4	1.1	0.2	0.2
<i>n</i> -C <sub>4</sub> H <sub>8</sub>	1.1	1.0	0.2	1.1
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	2.4	2.2	0.4	0.6
<i>c</i> -2-C <sub>4</sub> H <sub>8</sub>	1.0	0.8	0.1	0.1
C <sub>5+</sub>	0.8	0.9	0.1	3.3
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub> selectivity (wt%)				
	26.9	24.6	16.6	13.1
Yield (wt%)				
Total gas	34.4	44.8	58.8	44.3
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	9.3	11.0	9.8	5.8

Reaction conditions: 20:1 ratio of catalyst to feedstock, 0.12 ml H<sub>2</sub>O/h.

<sup>a</sup> Catalytic cracking; <sup>b</sup> Thermal cracking.

### 3.3. Catalytic cracking of lipids and residues of *Isochrysis zhanjiangensis*

In 1990, Milne et al. [28] first proposed the catalytic conversion of microalgae lipids over ZSM-5 catalyst and showed that the alkene (C<sub>2</sub>–C<sub>5</sub>) yield obtained from catalytic cracking of lipids extracted with chloroform was about 50%, while the yield of aromatics was about 15%. This work, however, did not establish clearly the lipid yield from the microalgae. In the same work, the alkene yield obtained from catalytic cracking of lipids extracted with butanol was only about 12%. The lipids in the microalgae included fatty glycerides, phospholipids, glycolipids, and steroids, each of which had different polarities. When the microalgae powder was extracted with solvents, the properties of the obtained lipids were thus dependent on the polarity of the solvent. In our work we applied three solvents with different polarities to the extraction of lipids from the microalgae: methanol, ethyl acetate, and *n*-hexane. The corresponding extracts were termed Lipid-M, Lipid-E, and Lipid-H, respectively. Methanol is a highly polar solvent, and the yield of Lipid-M was about 47.3%. This material had the appearance of a thick, black oil, was highly polar, and mainly contained fatty glycerides, phospholipids, glycolipids, and steroids. In contrast, *n*-hexane is a nonpolar solvent, and the Lipid-H yield was about 18.9%. Lipid-H was a yellow, semitransparent oil with low polarity primarily composed of fatty glycerides representing neutral lipids. Ethyl acetate is intermediate in polarity, and the yield of Lipid-E was around 27.7%. Lipid-E contained a mixture of fatty glycerides and other weakly polar lipids. The order of polarity of the three lipids, based on the polarities of their corresponding extraction solvents, was Lipid-M > Lipid-E > Lipid-H. The product selectivities and yields during catalytic

cracking of different lipids are summarized in Table 3. These results demonstrate that the total gaseous product yield decreased as the polarity of the lipids increased. This may be because phospholipids, glycolipids, and steroids are difficult to volatilize, and thus these compounds likely formed coke at high temperatures, so the total gaseous products yield of the Lipid-M was much lower than that of the Lipid-H. Furthermore, the light olefin selectivity and yield obviously increased as the polarity of the lipids decreased, suggesting that the low polarity lipids, such as the fatty glycerides, are readily transformed to light olefins by catalytic cracking, likely because their oxygen content is low compared with that of the high polarity lipids such as phospholipids and glycolipids. The light olefin selectivity and yield obtained from the lipids were much higher than those obtained from the original microalga biomass (as shown in Table 2), demonstrating that the microalga lipids are responsible for the majority of the olefins produced during the catalytic cracking process. Table 2 also shows that the catalytic performance of Lipid-H was similar to that of soybean oil because the light olefin yields of Lipid-H and soybean oil were 36.7% and 38.4%. The light olefin yield of the neutral alga lipids (Lipid-H) was thus almost the same as the yield obtained from soybean oil, highlighting the olefin's production potential of the catalytic cracking of algae-sourced lipids.

Pan et al. [29] explored the direct and catalytic pyrolysis of *Nannochloropsis sp.* residue. Lipids obtained from *Nannochloropsis sp.* were extracted with a mixed solvent composed of ethyl ether and petroleum ether, and the residue was found to account for about 70% of the microalga powder. The yield of light olefins obtained from the catalytic pyrolysis process was about 3%. In our work, the three kinds of residues were used as feedstocks for the catalytic process, and the selectivities and yields of gaseous products from catalytic cracking of the different residues are shown in Table 4. The light olefin selectivi-

ties and yields of the residues were lower than those associated with both the original microalga biomass and the extracted lipids. The residue of *Isochrysis zhanjiangensis* extracted with methanol (Residue-M) was primarily composed of proteins and carbohydrates and generated a light olefin yield of about 3.7%, which was slightly higher than yields previously reported in the literature. The residue remaining after extraction with *n*-hexane (Residue-H) contained not only proteins and carbohydrates but also some polar lipids, and the associated light olefin yield was about 7.6%. The light olefin yield of Residue-E was 5.1%, which was between that of Residue-M and Residue-H. The light olefin selectivity and yield of Residue-H were higher than those of Residue-M primarily because Residue-H contained some polar lipids while Residue-M mainly contained proteins and carbohydrates. L-alanine and glucose were used as model compounds for reference, and it was determined that L-alanine could be converted to light olefins by deamination and decarboxylation, with a resulting olefin yield of about 6.0%. The cracking of glucose produced the lowest reaction performance with regard to the generation of light olefins, with a yield of only 2.9%. These results suggest that amino acids and carbohydrates are not well suited to the production of light olefins under these reaction conditions.

The catalytic cracking of microalgae and their major components (carbohydrates, proteins, and lipids) with the goal of producing aromatics was explored by Du et al. [14]. Cellulose, egg whites, and canola oil were used as model compounds representing the three components, respectively. This work found that improving the lipid content in microalgae would be beneficial with regard to improving the yield of aromatics. Egg whites and cellulose had low aromatic yields, which suggested that proteins and carbohydrates can hardly be converted to aromatics with HZSM-5. Du et al. [14] also suggested a possible reaction mechanism for the catalytic pyrolysis of carbohy-

**Table 3**

The selectivities and yields of gas products during catalytic cracking of different lipids.

Feedstock	Lipid-M	Lipid-E	Lipid-H	Soybean oil
Gas phase composition (wt%)				
H <sub>2</sub>	3.1	2.7	3.3	0.9
CO	17.0	11.1	8.7	11.0
CO <sub>2</sub>	31.3	26.1	19.5	3.8
CH <sub>4</sub>	6.4	5.3	4.5	6.1
C <sub>2</sub> H <sub>6</sub>	2.0	1.8	1.8	2.6
C <sub>2</sub> H <sub>4</sub>	9.7	13.0	15.8	12.9
C <sub>3</sub> H <sub>8</sub>	1.3	1.6	2.2	1.8
C <sub>3</sub> H <sub>6</sub>	20.6	27.8	31.9	33.2
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.5	0.7	0.9	0.5
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.4	0.5	0.5	0.5
<i>t</i> -2-C <sub>4</sub> H <sub>8</sub>	1.7	1.4	2.2	4.0
<i>n</i> -C <sub>4</sub> H <sub>8</sub>	1.1	3.6	1.7	3.6
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	2.8	1.5	3.9	6.7
<i>c</i> -2-C <sub>4</sub> H <sub>8</sub>	1.2	0.9	1.6	3.0
C <sub>5+</sub>	0.9	2.0	1.5	9.3
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	37.1	48.1	57.1	63.5
selectivity (wt%)				
Yield (wt%)				
Total gas	41.0	47.3	64.2	60.5
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	15.2	22.8	36.7	38.4

**Table 4**

Product selectivities and yields from catalytic cracking of different residues under optimized reaction conditions.

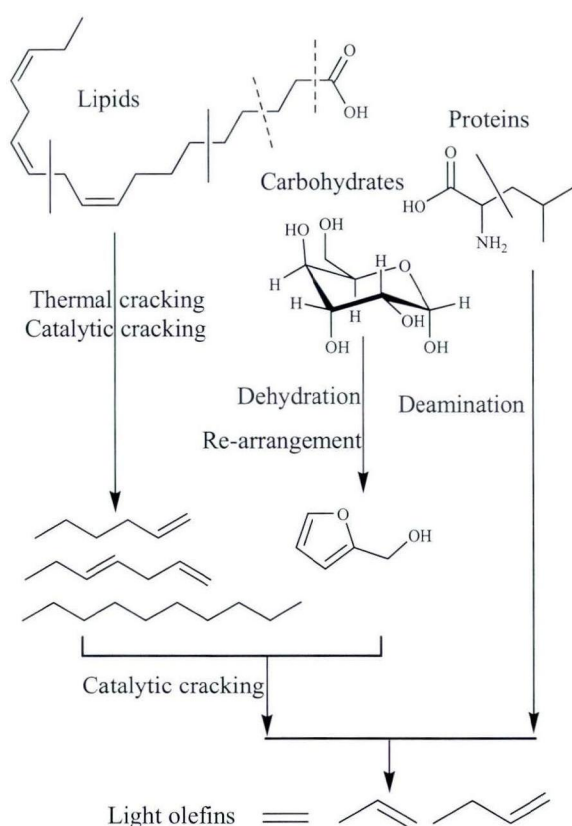
Feedstock	Residue-M	Residue-E	Residue-H	L-alanine	Glucose
Gas phase composition (wt%)					
H <sub>2</sub>	4.4	2.7	2.8	1.6	1.2
CO	12.2	11.8	15.4	42.6	37.4
CO <sub>2</sub>	58.3	58.2	53.8	20.4	39.3
CH <sub>4</sub>	6.1	5.4	4.2	8.0	6.5
C <sub>2</sub> H <sub>6</sub>	2.5	2.4	1.7	3.3	0.8
C <sub>2</sub> H <sub>4</sub>	3.7	4.9	6.0	11.6	3.0
C <sub>3</sub> H <sub>8</sub>	2.7	2.6	1.5	0.7	1.6
C <sub>3</sub> H <sub>6</sub>	5.6	6.7	9.9	7.0	4.4
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	1.1	1.3	0.6	0.3	1.6
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.6	0.6	0.4	0.1	0.0
<i>t</i> -2-C <sub>4</sub> H <sub>8</sub>	0.4	0.5	0.8	0.9	0.5
<i>n</i> -C <sub>4</sub> H <sub>8</sub>	0.3	0.3	0.5	0.6	0.2
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	0.8	0.8	1.4	1.1	0.6
<i>c</i> -2-C <sub>4</sub> H <sub>8</sub>	0.3	0.3	0.6	0.6	0.3
C <sub>5+</sub>	1.1	1.3	0.8	1.2	2.6
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	11.1	13.5	19.2	21.7	9.0
selectivity (wt%)					
Yield (wt%)					
Total gas	33.3	37.6	39.8	27.6	32.1
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	3.7	5.1	7.6	6.0	2.9

drates, proteins, and lipids to aromatics, although they did not report the yield of light olefins from the catalytic pyrolysis process. Light olefins could be obtained through the catalytic conversion of lipids, proteins, and carbohydrates as shown in Scheme 1. ZSM-5 zeolite exhibits strong acidity and unique pore structures and has been widely used as a catalyst for the production of both aromatics and light olefins from many different feedstocks, including naphtha, residue oils, and methanol. The neutral lipids or fatty acids could be thermally decomposed to long-chain ketones, aldehydes, and esters, which are then converted to alkanes and alkenes through thermal and catalytic processes. These alkanes and alkenes, in turn, could be cracked to generate light olefins, while aromatic hydrocarbons may be produced in the pores of the zeolite catalysts through a series of reactions such as oligomerization, cyclization, and aromatization [26,30]. The light olefin selectivity from catalytic cracking of Lipid-H achieved a maximum value of 57%, demonstrating that our modified catalyst can facilitate the production of light olefins (ethylene, propylene, and butene) when microalgae lipids are used as the reactant. Many studies have been performed concerning the catalytic pyrolysis of carbohydrates over HZSM-5 [24,25], and it has been found that carbohydrates can be thermally decomposed to anhydrosugars and other condensable oxygenated products, after which furans and smaller aldehydes are formed through dehydration and re-arrangement reactions. These oxygenates then diffuse into the pores of the zeolite catalyst where they undergo a series of decarbonylation, decarboxylation, dehydration, and oligomeri-

zation reactions to form aromatics and olefins. Amino acids can also be converted to olefins through deamination and decomposition reactions (Scheme 1).

#### 3.4. Catalytic cracking of *Isochrysis zhanjiangensis* with different neutral lipids

Catalytic cracking of the microalga cells showed poor reaction performance while the cracking of lipids resulted in high light olefin selectivity and yield. The catalytic cracking of the neutral lipids (Lipid-H) gave the highest light olefin yield, and so it follows that cultivation of *Isochrysis zhanjiangensis* should be conducted under conditions that increase its neutral lipid content. In our work, *Isochrysis zhanjiangensis* was photoautotrophically cultivated in sterilized natural seawater supplemented one to three times with f/2 culture medium to obtain microalga biomass with different lipid contents. The culture medium was added all at once such that, in the first 4 days, there were abundant nutrients in the culture and cell division took place rapidly, increasing the number of cells. As the nitrogen was consumed, the number of cells increased more slowly, and neutral lipids were accumulated such that, after 3 to 5 days of neutral lipids accumulation, a lipid-rich microalga was obtained. Table 5 and Fig. 4 summarize the product selectivities and yields obtained from the catalytic cracking of *Isochrysis zhanjiangensis* with different neutral lipid contents. When the neutral lipid content was 10.1%, the light olefin yield was 9.2%, and this yield is seen to increase with increasing neutral lipid content. The highest light olefin yield of 16.4% was obtained with a neutral lipid content of 33.9% although, when the neutral lipid content was higher, the culture time was longer and the growth rate was slower. It is also evident that, above a cer-



**Scheme 1.** Postulated pathways during the catalytic cracking of lipids, carbohydrates, and proteins.

**Table 5**

Product selectivities and yields from catalytic cracking of *Isochrysis zhanjiangensis* with different neutral lipid contents.

Neutral lipid contents (wt%)	10.1	16.1	23.8	31.2	33.9
Gas phase composition (wt%)					
H <sub>2</sub>	4.3	0.8	1.6	3.9	3.6
CO	16.5	27.0	18.5	14.9	21.7
CO <sub>2</sub>	42.5	20.4	26.8	40.4	35.9
CH <sub>4</sub>	5.4	9.7	7.4	5.1	8.2
C <sub>2</sub> H <sub>6</sub>	1.7	4.3	2.3	1.8	1.8
C <sub>2</sub> H <sub>4</sub>	6.8	8.4	10.6	7.5	8.8
C <sub>3</sub> H <sub>8</sub>	1.2	3.4	1.9	1.6	1.0
C <sub>3</sub> H <sub>6</sub>	14.4	15.5	21.9	16.2	14.6
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.4	0.7	0.7	0.6	0.2
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.4	0.7	0.6	0.5	0.2
<i>t</i> -2-C <sub>4</sub> H <sub>8</sub>	1.4	1.1	1.6	1.5	0.8
<i>n</i> -C <sub>4</sub> H <sub>8</sub>	1.1	2.5	1.3	1.0	0.6
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	2.4	1.1	2.9	2.5	1.3
<i>c</i> -2-C <sub>4</sub> H <sub>8</sub>	1.0	2.6	1.2	1.1	0.6
C <sub>5</sub> <sup>+</sup>	0.7	1.7	0.9	1.5	0.6
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	27.1	31.7	39.5	29.8	26.7
selectivity (wt%)					
Yield (wt%)					
Total gas	34.2	42.0	36.3	54.3	61.6
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub>	7.2	10.2	11.8	12.9	14.4
C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub> +C <sub>4</sub> H <sub>8</sub>	9.2	13.3	14.3	16.2	16.4

Reaction conditions: 600 °C, 0.12 ml H<sub>2</sub>O/h.

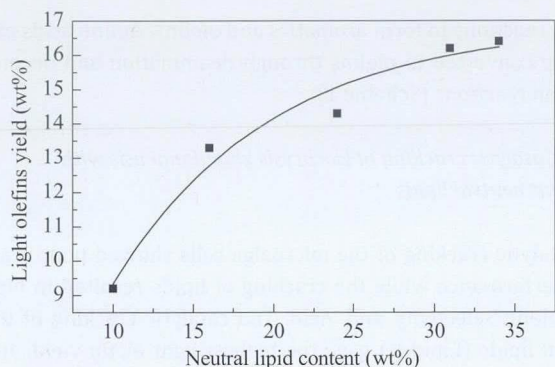


Fig. 4. Effects of neutral lipid contents on yield of light olefins.

tain point, further increases in the neutral lipid content do not lead to significant increases in the light olefin yield. Thus, increasing the neutral lipid content to an optimal value represents a means of improving the light olefin yield during catalytic cracking of microalgae.

#### 4. Conclusions

Light olefins can be produced directly from microalgae biomass. The catalytic cracking of the microalgae applied in our work resulted in an 11.0% yield of light olefins. Microalgae lipids were the predominant contributor to olefin production. Proteins and carbohydrates in the microalgae could also be converted to light olefins, however at much lower yields. The yield of light olefins increased with increases in neutral lipid content, such that a light olefin yield of 16.4% was achieved when the neutral lipid content was 33.9%. This research demonstrates that increasing the neutral lipid content to an optimal level is an effective way to improve the light olefin yield obtained from the catalytic cracking of microalgae.

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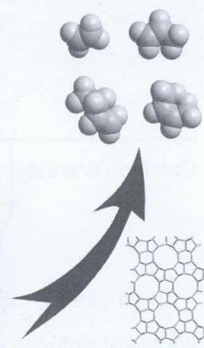
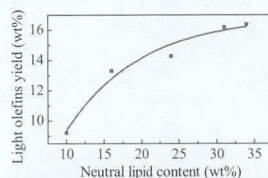
#### Graphical Abstract

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#### The production of light olefins by catalytic cracking of the microalgae *Isochrysis zhanjiangensis* over a modified ZSM-5 catalyst

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The catalytic cracking of a microalgae resulted in an 11.0% yield of light olefins. When the neutral lipid content in the microalgae was increased to 33.9%, the yield of light olefins was improved to 16.4%.



## 改性ZSM-5分子筛催化裂解湛江等鞭金藻制取低碳烯烃

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**摘要:** 研究了湛江等鞭金藻(*Isochrysis zhanjiangensis*)在改性ZSM-5分子筛上催化裂解制取低碳烯烃的过程。与热裂解过程相比, 湛江等鞭金藻催化裂解可以得到更高的低碳烯烃选择性和收率。同时还研究了湛江等鞭金藻中不同油脂和藻渣的催化裂解。结果表明, 微藻中的油脂能有效转化为烯烃, 其中中性脂的烯烃收率最高, 可达36.7%。不同溶剂抽提后得到的藻渣也可转化为低碳烯烃, 但收率远低于微藻中的油脂。微藻中的油脂, 特别是中性脂, 是烯烃的主要贡献者, 提高微藻中的中性脂含量能够得到更高的低碳烯烃收率。

**关键词:** 微藻; 湛江等鞭金藻; 催化裂解; ZSM-5; 低碳烯烃

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