

## Supplementary Information for

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

Xinglong Dong<sup>a,b</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>

<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.

<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

---

\* Corresponding authors: Tel./fax: +86 0411 84379998. E-mail addresses: [liuzm@dicp.ac.cn](mailto:liuzm@dicp.ac.cn) (Z. Liu) [xuyp@dicp.ac.cn](mailto:xuyp@dicp.ac.cn) (Y. Xu)

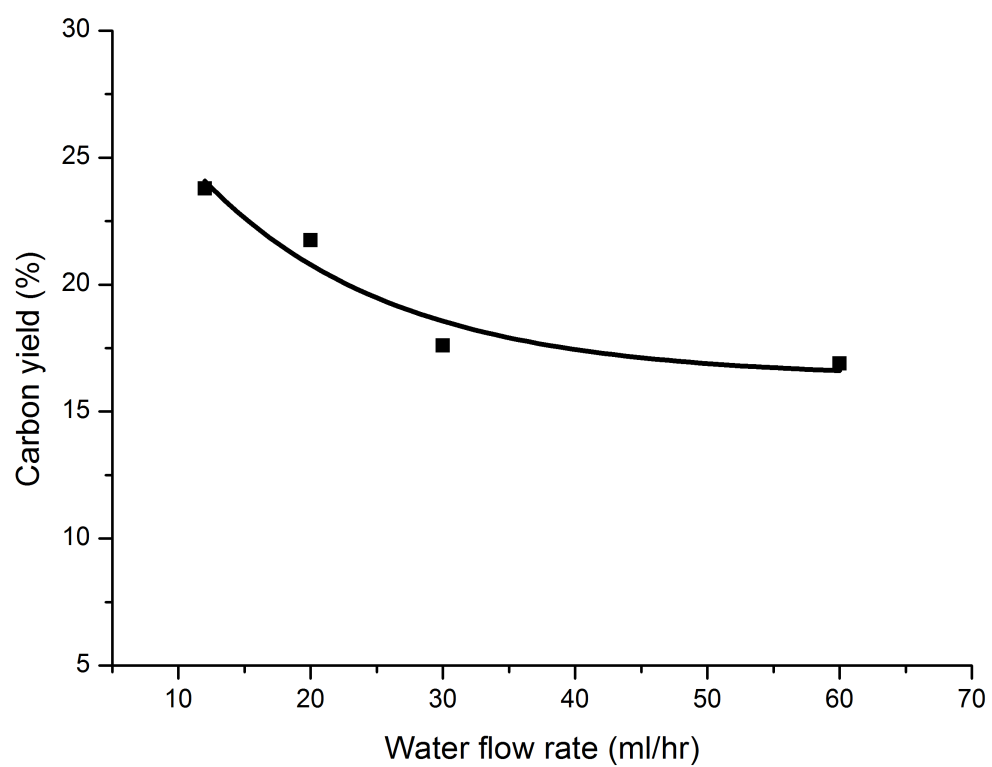


Fig. S1 Effects of water flow rates on carbon yields of biochar (reaction temperature:  
923K).

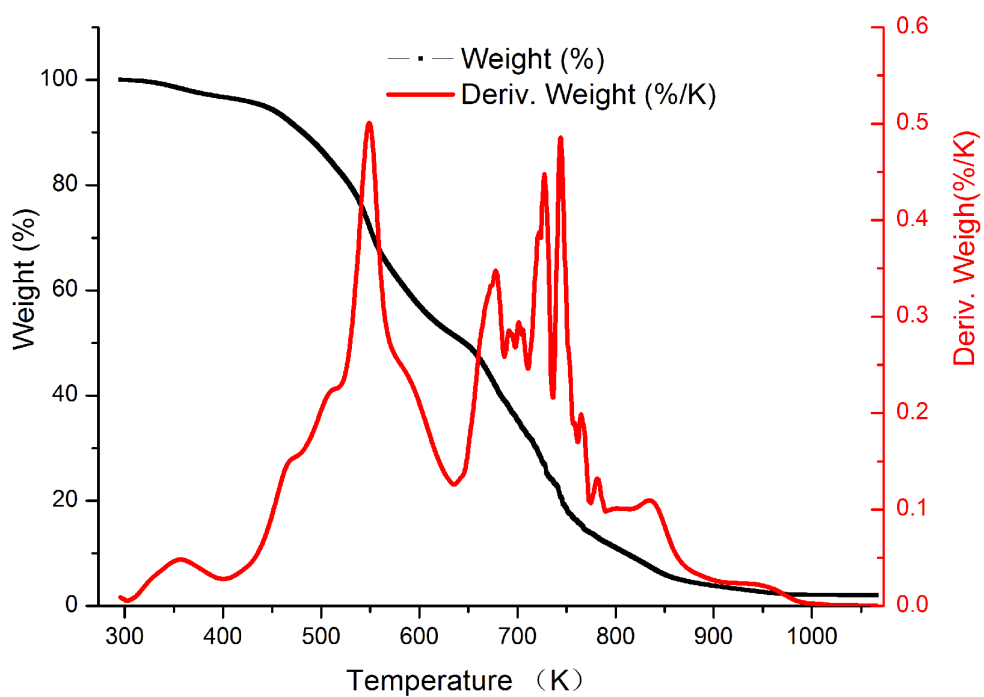


Fig. S2 Thermogravimetric behavior of heterotrophic *C. pyrenoidosa* at the heating rate of 10 K/min under air atmosphere.

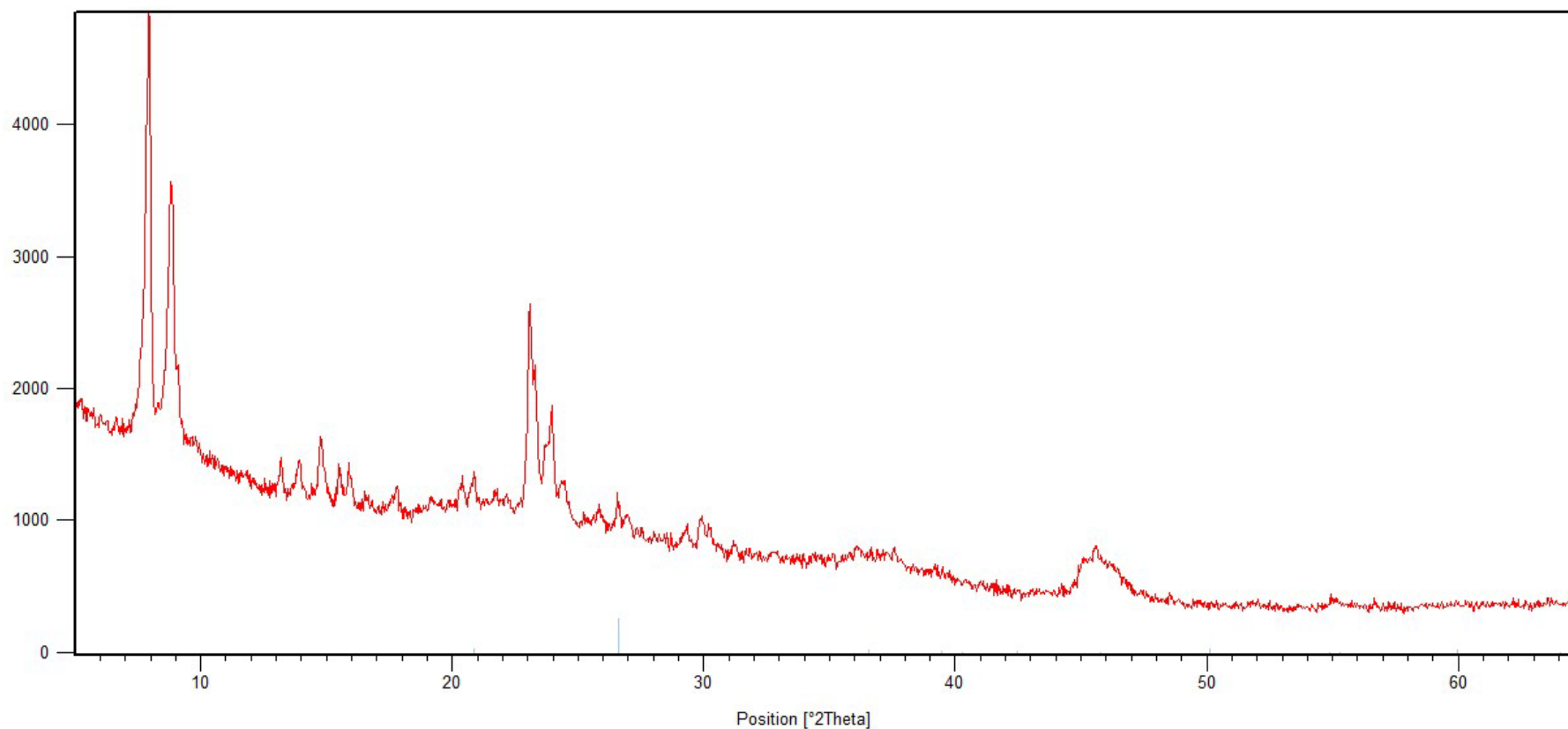


Fig. S3 The modified ZSM-5 zeolite catalyst used in the experiment was examined using X-ray powder diffraction (XRD). The X-ray diffraction pattern was recorded with a PANalytical X'Pert PRO X-ray diffractometer using the Cu-K $\alpha$  radiation ( $\lambda=1.54059\text{\AA}$ ), operating at 40 kV and 40 mA.

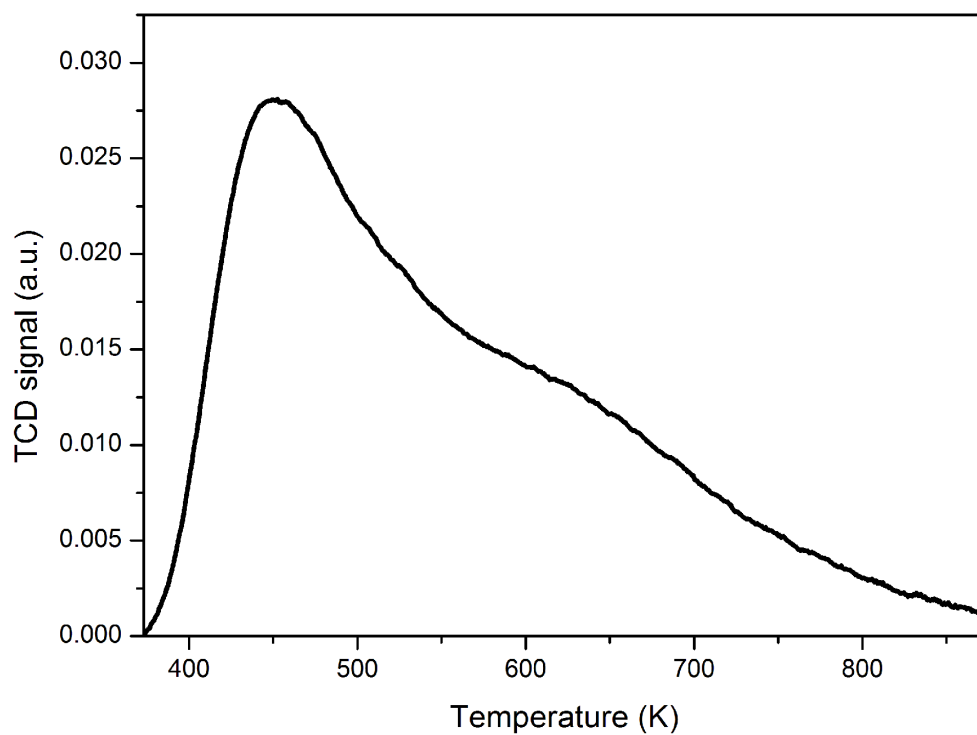


Fig. S4 Temperature programmed desorption of ammonia of the modified ZSM-5 catalyst.

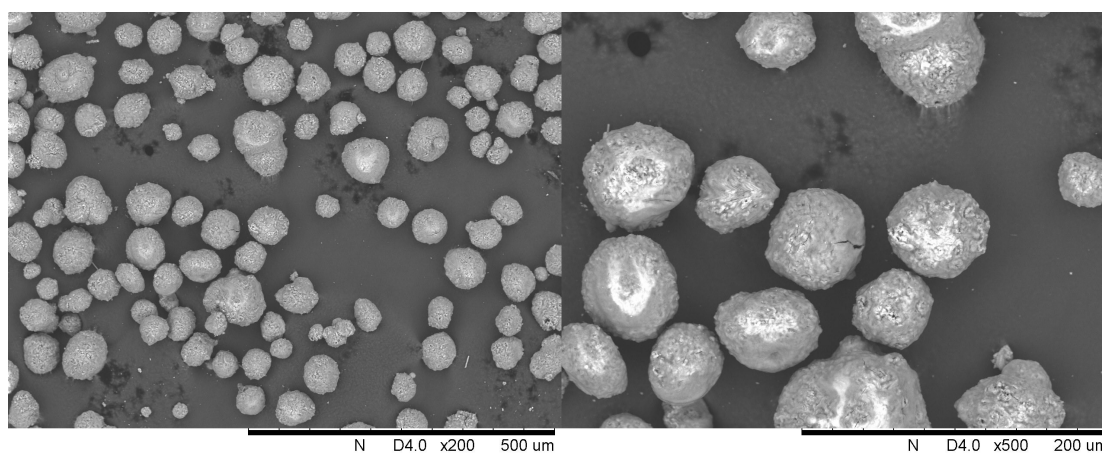


Fig. S5 SEM photos of the modified ZSM-5 catalyst.

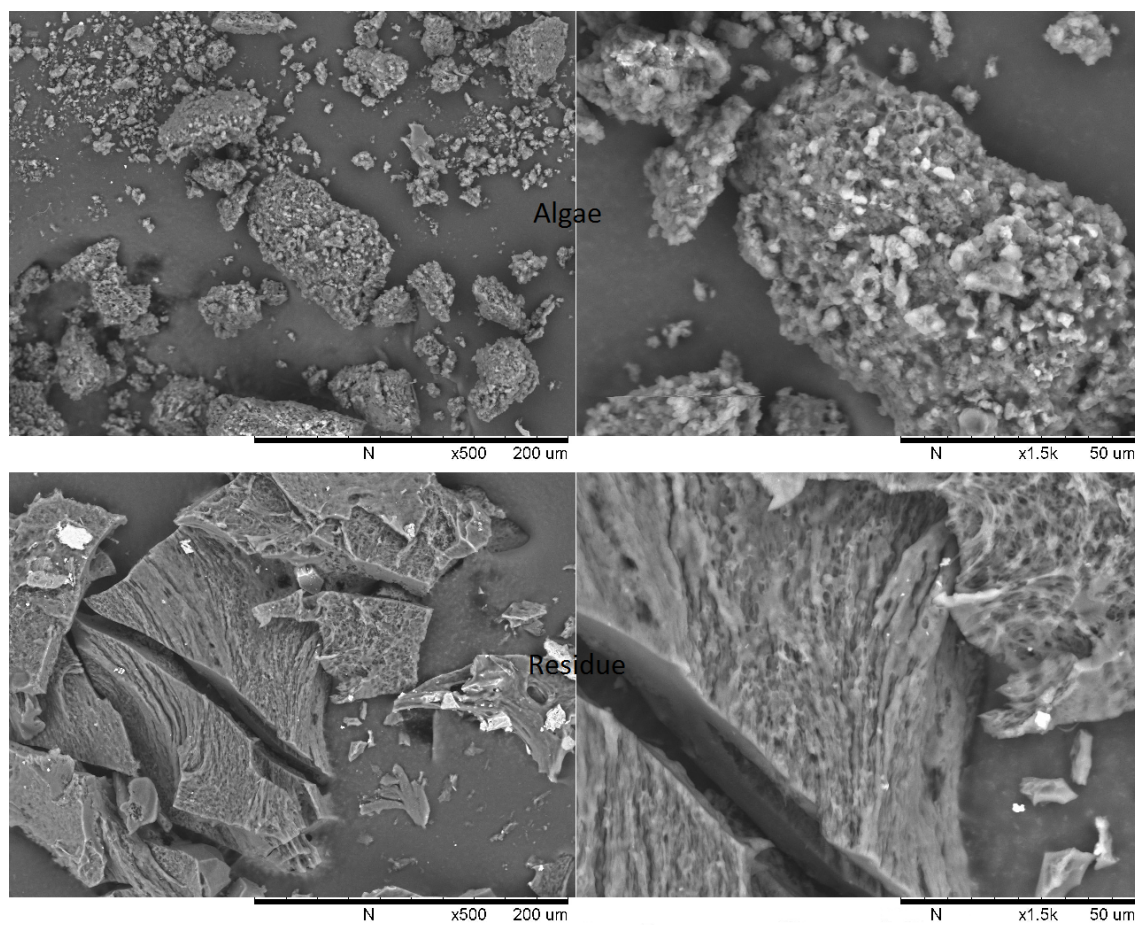
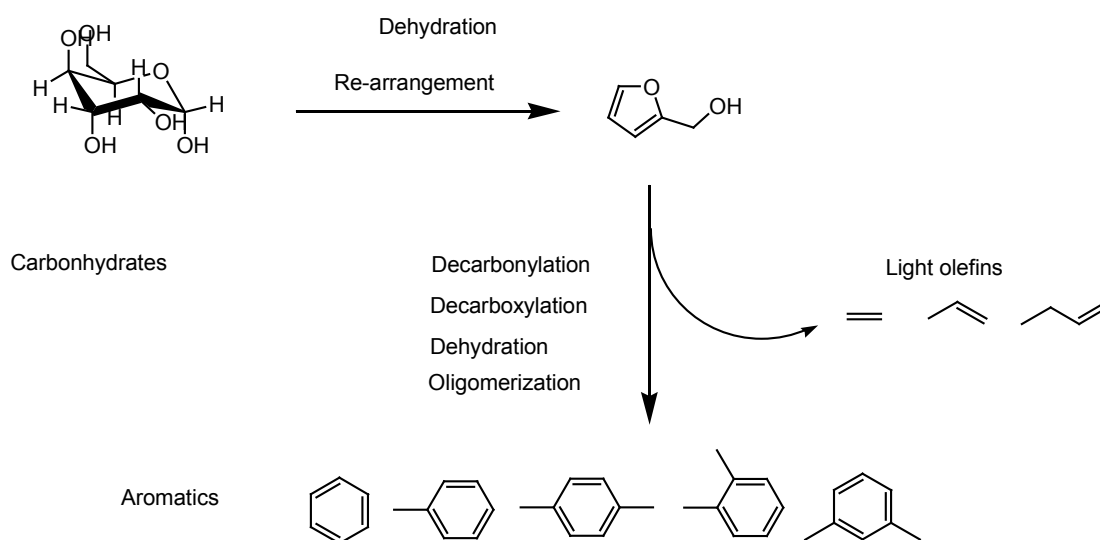
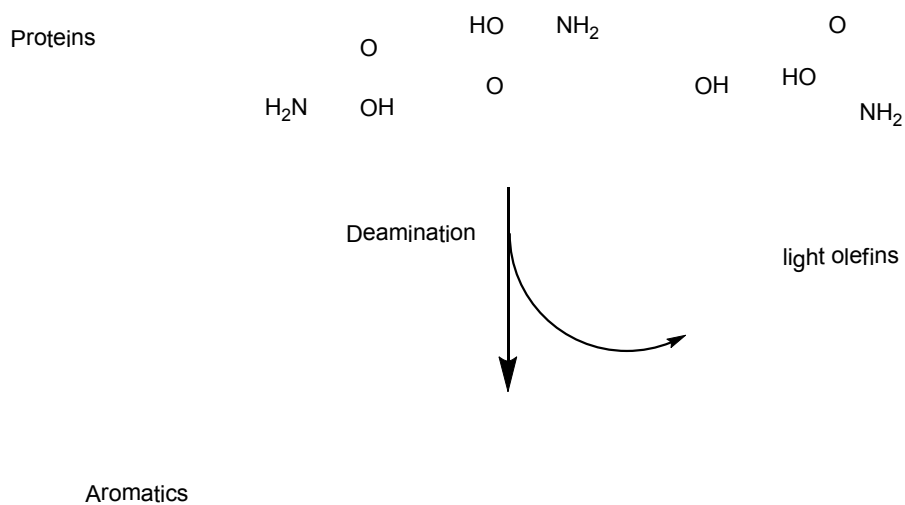


Fig. S6 SEM photos of algae and residue (catalytic pyrolysis).




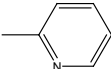
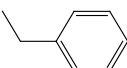
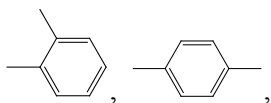
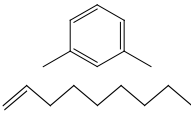

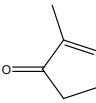
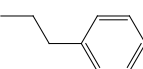
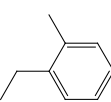
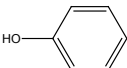
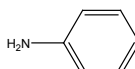



Scheme. S1 Postulated pathways for catalytic pyrolysis of carbohydrates.

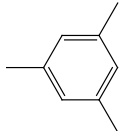
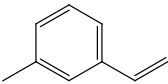
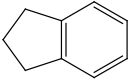
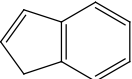
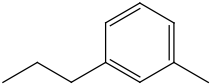
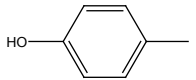

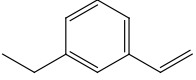
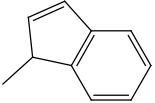
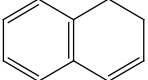

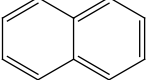
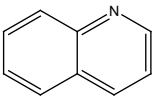
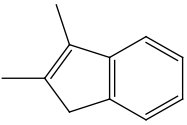
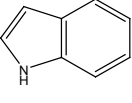
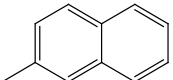



Scheme. S2 Postulated pathways for catalytic pyrolysis of proteins.

Table S1 Compositions (wt %) of liquid products from one-step process and two-step process (reaction atmosphere: steam).

RT /min	Compounds	Structural formula	Compositions / wt %	
			Catalytic cracking (One-Step)	Catalytic cracking (Two-Step)
4.706	Benzene		2.85	10.80
5.491	Pyridine		12.27	19.41
5.767	Toluene		8.23	18.65
6.474	2-methyl-Pyridine		2.71	8.22
7.252	Ethylbenzene		3.77	2.24
7.394	Xylene		9.39	4.87
7.654	1-Nonene		1.79	
7.809	styrene		5.48	3.72
8.071	2-methyl-2-Cyclopenten-1-one		1.21	
9.014	Propyl-Benzene		1.60	
9.194	1-ethyl-2-methyl-Benzene		6.06	-
9.298	Phenol		3.10	4.60
9.473	Aniline			1.99
9.602	1-Decene		2.16	



9.806	Mesitylene		4.59	1.20
9.879	1-ethenyl-3-methyl-benzene		1.78	
10.68	Indane		1.22	
10.85	Indene		1.90	2.08
10.96	1-methyl-3-propyl-benzene		3.42	
11.14	p-Cresol		2.58	1.50
11.48	1-Undecene		1.26	
11.50	1-ethenyl-3-ethyl-Benzene		1.43	
12.73	1-methyl-1H-Indene		5.20	1.15
12.79	1,2-dihydro-Naphthalene		1.32	1.53
13.16	1-Dodecene		1.05	
13.33	Naphthalene		1.71	3.24
14.17	Quinoline		1.58	2.92
14.43	2,3-dimethyl-1H-Indene		1.03	
14.87	Indole		1.88	4.47
14.99	2-methyl-Naphthalene		2.33	4.65
15.99	1-Tetradecene		0.66	

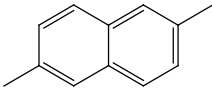


16.47	2,6-dimethyl-Naphthalene		0.94	2.77
17.32	Pentadecane		2.02	
24.99	Hexadecanenitrile		1.48	

Table S2 Mass yields (wt %) of products from catalytic pyrolysis of lipid-rich heterotrophic *C. pyrenoidosa*.

Compounds	One-Step		Two-Step
	Nitrogen	Steam	Steam
H <sub>2</sub>	0.4	0.1	1.4
CO	4.8	7.7	16.2
CO <sub>2</sub>	10.8	41.1	15.1
CH <sub>4</sub>	1.9	1.2	4.3
C <sub>2</sub> H <sub>6</sub>	1.3	0.5	1.0
C <sub>2</sub> H <sub>4</sub>	1.2	0.8	4.6
C <sub>3</sub> H <sub>8</sub>	1.2	0.3	0.5
C <sub>3</sub> H <sub>6</sub>	2.2	3.2	10.1
i-C <sub>4</sub> H <sub>10</sub>	0.1	0.1	0.1
n-C <sub>4</sub> H <sub>10</sub>	0.3	0.1	0.2
t-2-C <sub>4</sub> H <sub>8</sub>	0.4	0.6	1.3
n-C <sub>4</sub> H <sub>8</sub>	0.3	0.4	1.0
i-C <sub>4</sub> H <sub>8</sub>	0.6	1.3	1.9
c-2-C <sub>4</sub> H <sub>8</sub>	0.3	0.4	0.9
C <sub>5</sub>	2.0	0.0	0.0
C <sub>6</sub> +	0.1	2.0	2.0
Total olefins	4.8	6.7	19.7
Total gaseous products	27.8	60.0	60.3

Table S3 Effects of reaction temperatures on mass yields (wt %) of gaseous products from catalytic pyrolysis of lipid-rich heterotrophic *C. pyrenoidosa* (water flow rate: 30ml/hr).

Compounds	Temperature (K)			
	773	873	923	973
H <sub>2</sub>	0.4	0.8	1.4	1.2
CO	7.3	10.1	16.2	12.6
CO <sub>2</sub>	14.6	13.3	15.1	16.5
CH <sub>4</sub>	1.3	2.6	4.3	4.1
C <sub>2</sub> H <sub>6</sub>	0.5	0.9	1.0	0.9
C <sub>2</sub> H <sub>4</sub>	3.1	4.2	4.6	4.9
C <sub>3</sub> H <sub>8</sub>	0.3	0.5	0.5	0.5
C <sub>3</sub> H <sub>6</sub>	6.6	9.7	10.1	9.9
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>	0.1	0.2	0.2	0.2
t-2-C <sub>4</sub> H <sub>8</sub>	0.9	1.1	1.3	0.9
n-C <sub>4</sub> H <sub>8</sub>	0.7	1.1	1.0	1.0
i-C <sub>4</sub> H <sub>8</sub>	1.6	2.0	1.9	1.5
c-2-C <sub>4</sub> H <sub>8</sub>	0.6	0.8	0.9	0.7
C <sub>5</sub>	0.0	0.0	0.0	0.0
C <sub>6</sub> +	1.6	1.6	2.0	2.0
Total olefins	13.5	19.0	19.7	18.8
Total gaseous products	39.6	49.1	60.3	56.8

Table S4 Effects of water flow rates on mass yields (wt %) of gaseous products from catalytic pyrolysis of lipid-rich heterotrophic *C. pyrenoidosa* (reaction temperature: 923 K).

Compounds	Water flow rate (ml/hr)			
	12	20	30	60
H <sub>2</sub>	1.5	1.3	1.4	1.2
CO	12.7	13.2	16.2	10.3
CO <sub>2</sub>	9.6	10.9	15.1	9.8
CH <sub>4</sub>	3.9	4.7	4.3	2.8
C <sub>2</sub> H <sub>6</sub>	0.8	1.0	1.0	0.6
C <sub>2</sub> H <sub>4</sub>	3.4	4.1	4.6	2.4
C <sub>3</sub> H <sub>8</sub>	0.4	0.5	0.5	0.3
C <sub>3</sub> H <sub>6</sub>	6.9	8.4	10.1	6.1
i-C <sub>4</sub> H <sub>10</sub>	0.0	0.1	0.1	0.0
n-C <sub>4</sub> H <sub>10</sub>	0.1	0.2	0.2	0.1
t-2-C <sub>4</sub> H <sub>8</sub>	0.7	0.8	1.3	0.8
n-C <sub>4</sub> H <sub>8</sub>	0.5	0.6	1.0	0.7
i-C <sub>4</sub> H <sub>8</sub>	1.1	1.3	1.9	1.2
c-2-C <sub>4</sub> H <sub>8</sub>	0.5	0.6	0.9	0.6
C <sub>5</sub>	0.0	0.0	0.0	0.0
C <sub>6</sub> +	0.5	0.2	2.0	1.8
Total olefins	13.0	15.8	19.7	11.8
Total gaseous products	42.5	47.8	60.3	38.7