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Bio-oil Production from Different Algae: Hydrothermal Liquefaction of *Spirulina*, *Cyanophyta* and *Enteromorpha Prolifera*

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Abstract. Bio-oil based on algae has good development foreground and its manufacturing technology is the key problem for industrialized application. This study investigated HTL process and reaction mechanism of *Spirulina*, *Enteromorpha prolifera* (*EP*) and *Cyanophyta* through analysis and comparison of yields, HHV and organic compositions of bio-oil comprehensively. We found that *Spirulina* had the highest bio-oil yield of 30.4%. Severe conditions benefited more light bio-oil fraction and less heavy bio-oil fraction. HHV of bio-oil was nearly twice than algae feedstock and the highest value was 37.69 MJ/kg from *Cyanophyta* at 350℃, 30 min and a/w 1/4. GC-MS results showed that bio-oil from *Spirulina* and *Cyanophyta* mainly contained more amides, amines, phenols. Bio-oil from *Cyanophyta* and *EP* which had much carbohydrate could contain a portion of ketones, which could be intermediate products of Maillard reaction in HTL process.

Introduction

Bio-oil based on algae has many advantages such as high yield and no competition with land for food production. Hydrothermal liquefaction (HTL) is considered as a promising technique [1]. Under HTL condition, water is reactant so the process does not need to dry feedstock. Moreover, HTL can also convert protein and carbohydrates into bio-oil and benefit nutrients recycling for algae growth [2]. Therefore HTL is fit for conversion from algae with high moisture to bio-oil.

Recently, many researchers have mainly focused on HTLs of different algae such as *Spirulina* [3], *Chlorella* [4], *EP* [5], *Dunaliella* [6], *Cyanophyta* [7] and *Nannochloropsis sp.* [2]. Although previous research has provided some information, they were done in different reaction conditions and reactor types (batch, semi-continuous, continuous). Note that reaction environment is related to contact between algae cell and water, organics release rate, chemicals conversion and thus has significant influence on final production. Furthermore, different algae species have various chemical components, resulting in diverse products distribution. Besides, little previous research has addressed on systematical comparison among algae species, revealing potential of bio-oil production from algae. To fill this gap, *Spirulina*, *Cyanophyta* and *EP* were selected as sample feedstock because of their dramatically different chemical composition. We mainly investigated yields and properties of bio-oil from different algae HTL process systematically.

Experimental Study

Experimental Raw Materials and Chemical Reagents

In this investigation, *Spirulina* was purchased from Wudi Luqi Biological Engineering Co., Ltd., *EP* was from Jiangsu Qiangsheng International Trade Co., Ltd and *Cyanophyta* was colleted from Taihu in Wuxi China and it was dried at 80°C for > 72 hours, then grinded and screened to algae powder within 150 μm through a 100 mesh sieve. The proximate analysis and chemical composition analysis results of algae can be found in Table 1. The solvents used in this investigation were dichloromethane (AR, Tianjin Hongyan chemical reagent factory, China) and hexane (AR, Tianjin Fuchen chemical reagent factory, China).

Table 1. Proximate analysis and chemical composition analysis of algae.

Proximate analysis（%）	*Spirulina*	*EP*	*Cyanophyta*
Mositure	7.9	13.40	9.5
Ash	7.0	22.3	14.6
Volatile matter	87.7	91.2	90.9
Fixed Carbon	10.5	5.9	7.1
Chemical composition (%)			
Protein	66	21.1	52.7
lipid	3.0	0.3	4.5
Carbohydrate	4.2	6.1	9.1

Products Separation

The reactor with pre-added feedstock was mini batch reactor and was heated in a Techne fluidized sand bath. After reaction, cool and open the reactor and separate the production through adding dichloromethane and hexane. Light components were soluble in hexane and heavy ones insoluble in hexane. Besides, the residual in the centrifuge tube was dried in an electric constant temperature drying oven at 80°C for 6 h to drive off dichloromethane.

Analysis

The elemental composition (C, H, O, N and S) of the obtained bio-oil was determined by a Vario EL III elemental analyzer. The standard deviation for C, H, N, S element is less than 0.1 % and for O element is less than 0.2 %.

The bio-oil samples were analyzed on a Shimadzu gas chromatography and mass spectrometer (GCMS-QP2010 plus) equipped with a Restek Rtx-5ms capillary column operating in an electron ionization (EI, 70 eV) mode. The column was initially held at 60°C for 1 min. Then the temperature was ramped to 90°C at 5°C min^{-1} and held isothermally for 10 min. Following that the temperature was ramped again to 300°C at 3°C min^{-1} and held for 2 min, giving a total runtime of 81 min.

Data Interpretation

In this study, bio-oil yield, higher heating value (HHV) are defined as follows:

$$\text{Bio-oil yield (wt\%)}=\frac{\text{Mass of formed bio-oil}}{\text{Mass of algae feedstock}} \quad (1)$$

HHV of bio-oil derived from HTL of algae is calculated from Dulong formula:

$$\text{Higher heating value } \left(MJ/kg\right) = 0.338C+1.428\left(H-0.125O\right)+0.095S \quad (2)$$

where, C, H, O, S represent weight percentages of carbon, hydrogen and oxygen, respectively.

Results and Discussion

Hydrothermal Liquefaction of Algae

This section illustrates the liquefaction experiments of algae in subcritical water. On the basis of our previous research [7], temperature had the most influence on bio-oil yield than batch holding time and algae/water (a/w) ratio but the treating pressure reflecting by water density had little effect on it. Therefore, effect of pressure is not presented here and we conducted experiments of algae HTL at different temperatures (280℃ and 350℃).

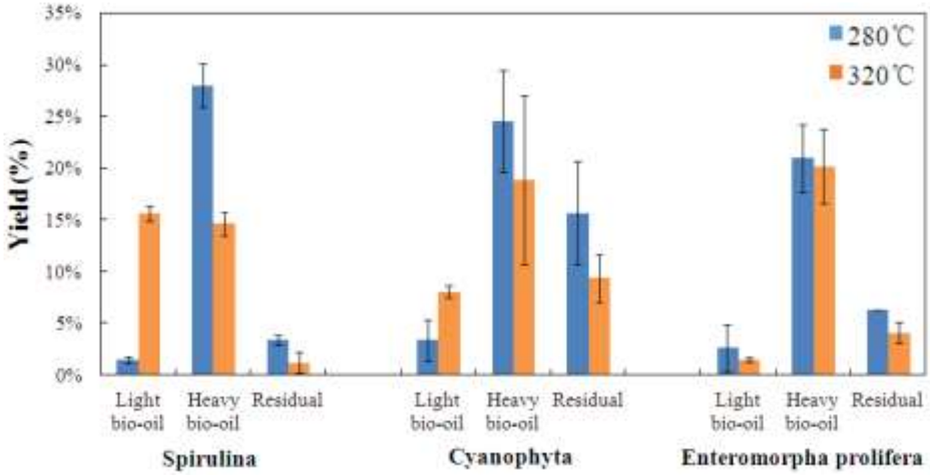

Figure 1. Yields of light and heavy bio-oil and solid residue obtained at 280°C, 350°C, 30 min reaction time, a/w ¼.

Figure 1 shows yields of light and heavy bio-oil, solid residue after HTL process at 280 and 350 ℃, 30 min and a/w 1/4. It is shown that the maximum total yield of 30.4% from *Spirulina* and then 27.9% and 23.4% from *Cyanophyta* and *EP*, respectively. Total chemical components content of *EP* was much lower than others, so the transferred fraction into bio-oil was much less, resulting in the lowest bio-oil yield. Note that higher temperature was conductive to more light bio-oil whereas less heavy bio-oil yielded for *Spirulina* and *Cyanophyata*. It could be due to that higher temperature enhanced depolymerization of free radical and heavy bio-oil fraction decomposed to short-chain organics into light fraction. For *EP*, both light and heavy bio-oil yield showed decreasing trend with temperature rising because its chemical components tended to generate more water-soluble compounds or gases through cracking gasification. For solid residue, higher temperature promoted decomposition of solid residue and the value remained below 10%, proving most of feedstock reacted under HTL process.

Elemental Analysis of Bio-oil

Analysis and comparison results of bio-oil and algae feedstock are shown in Table 2.

Table 2. Elemental composition analysis of algae and bio-oils（30 min，a/w 1/4）.

Algae and condition	Elemental analysis (wt%)					HHV (MJ/kg)
	C	H	N	S	O※	
Spirulina	45.53	6.98	9.25	3.33	45.53	17.54
280 ℃	68.12	8.56	7.07	0.75	15.51	32.54
350 ℃	72.56	8.76	6.72	0.67	11.29	35.08
EP	29.92	6.04	3.83	6.74	29.92	14.04
280 ℃	58.98	5.94	5.43	1.55	42.02	23.54
350 ℃	71.46	8.71	5.88	0.63	13.32	34.27
Cyanophyta	50.14	7.62	8.95	2.24	50.14	19.09
280 ℃	64.78	7.68	6.95	0.72	19.87	29.38
350 ℃	79.10	8.94	0.74	0.69	10.53	37.69

※：By difference.

Table 2 demonstrated carbon and hydrogen contents of bio-oil were much more whereas oxygen content was much less than feedstock. Note that HHV of bio-oil was much higher than algae, which was nearly twice. It proved combustion performance of bio-oil through HTL was better than original algae. The most HHV (37.69 MJ/kg) of bio-oil was obtained from *Cyanophyta* at 350℃, 30 min, a/w 1/4. And the lowest HHV of bio-oil was 23.54 MJ/kg from *EP* HTL, due to its low contents of protein, lipid and carbohydrate. In general, higher temperature was conductive to higher HHV of bio-oil and it possibly because it made HTL more acute and few unstable intermediate products or residual be converted into hydrocarbons access to bio-oil.

Analysis of Bio-oil

To study bio-oil properties and HTL reaction mechanism qualitatively and quantitatively, this section detected organic composition of bio-oil by GC-MS and the results are shown in Table 3-5.

Table 3. Main compounds in MS chromatogram of bio-oil of HTL of *Spirulina* (280℃).

Compounds	Percentage	Retention time
p-Cresol	2.36406	10.871
2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	1.27325	42.675
5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d] pyrazine	1.3544	45.704
Indolizine, 3-methyl-	1.41357	24.756
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	1.48194	45.817
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)-	1.50255	57.826
2-Pyrrolidinone, 1-butyl-	1.5441	23.062
Oxalic acid, hexadecyl 2-phenylethyl ester	1.70851	73.203
Benzene, (4-methyl-4-pentenyl)-	1.81069	39.495
5H-1-Pyrindine	1.90396	20.719
N-[2-Hydroxyethyl]succinimide	1.94076	24.503
7-Ethyl-4,6-pentadecandione	2.09462	41.82
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	2.2447	45.938
N(1)-(3-Methyl-1,2,4-oxadiazol-5-yl)-1-pyrrolidinecarboxamidi ne	2.49185	42.243
Octadecanamide, N-butyl-	2.62068	59.921
Fumaric acid, hexyl 2-phenylethyl ester	2.83345	39.191
10-Methyl-undecanoic acid, pyrrolidide	3.2837	64.634
Hexanoic acid, morpholide	3.68967	62.759
Dibenzofuran	3.88499	29.988
l-(+)-Ascorbic acid 2,6-dihexadecanoate	5.31744	46.832
Heneicosane	5.82307	37.244
Octadecanamide	6.22028	53.657
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	7.22123	60.463
Octanamide, N,N-dimethyl-	7.23331	56.013
N-Methyldodecanamide	10.16499	54.766

Table 4. Main compounds in MS chromatogram of bio-oil of HTL of *EP* (280℃).

Compounds	Percentage	Retention time (min)
Octadecanamide	1.12085	59.6
Pyrrolidine, 1-(1-oxoheptadecyl)-	1.18281	64.626
2-Hexadecanol, 1-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-, acetate	1.24317	58.62
Benzonitrile, 2,4,6-trimethyl-	1.39471	28.756
Eicosane	1.54248	41.315
2-Pyrrolidinone, 1-butyl-	1.55678	18.224
p-Cresol	1.56446	10.868
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	1.63919	60.454
Phenol, 2-ethyl-	2.1124	14.968
N-Decanoylmorpholine	2.19576	62.693
l-(+)-Ascorbic acid 2,6-dihexadecanoate	3.38117	46.823

continued

Table 4. Main compounds in MS chromatogram of bio-oil of HTL of *EP* (280℃) (Continued)

Compounds	Percentage	Retention time (min)
Hexanoic acid, morpholide	3.39763	62.747
2-Pyrrolidinone, 1-butyl-	3.97006	23.015
Octadecanamide, N-butyl-	4.82938	59.912
Heneicosane	5.41033	37.236
Octanamide, N,N-dimethyl-	8.43461	56.002
N-Methyldodecanamide	12.32599	54.757
Dibutyl phthalate	13.02958	46.73
Hexadecanamide	20.57812	53.65

Table 5. Main compounds in MS chromatogram of bio-oil of HTL of *Cyanophyta* (280℃)

Compounds	Percentage	Retention time (min)
Cyclotetrasiloxane, octamethyl-	0.14822	87.629
Decane, 4-cyclohexyl-	0.40495	60.28
3,6-Diisopropylpiperazin-2,5-dione	0.50645	42.394
Decane, 1-iodo-	0.58734	57.201
Heptadecane, 2,6,10,15-tetramethyl-	0.70559	54.301
Octacosyl acetate	0.86488	54.619
Sulfurous acid, 2-ethylhexyl isohexyl ester	1.16614	51.254
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	1.36509	45.479
2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	1.61232	42.675
Methanone, (2-carboxypyrrolidin-1-yl)-[1-(t-butoxycarbonyl)pyrrolidin-2-yl]-	1.84265	45.714
Oxalic acid, monoamide, N-(2-phenylethyl)-, isohexyl ester	2.08099	73.209
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	2.12395	45.805
3,4-Diethoxy-3-cyclobutene-1,2-dione	2.39796	45.31
Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	3.03025	45.927
2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	3.26139	42.241
Octadecanamide, N-butyl-	3.27461	59.917
Pyrrolidine, 1-(6-methyl-1-oxooctadecyl)-	3.57591	64.639
7-Ethyl-4,6-pentadecandione	3.61438	41.794
Fumaric acid, heptyl 2-phenylethyl ester	4.13141	39.199
Hexanoic acid, morpholide	4.53609	62.756
l-(+)-Ascorbic acid 2,6-dihexadecanoate	5.35606	46.805
Heneicosane	6.80676	37.243
Octanamide, N,N-dimethyl-	8.74475	56.014
Octadecanamide	10.63848	53.654
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	12.35897	60.455
N-Methyldodecanamide	14.86438	54.767

Table 3-5 show organic composition of bio-oil from HTL of different algae. It proved that organics species and contents were significantly various. *Spirulina* and *Cyanophyta* had much protein and bio-oil production included more amides, amines, phenols such as octadecanamide, palmitamide, octanamide, phenols and their congeners. It could be due to cracking of peptide bond in hydrolysis of protein and small molecular compounds reunited to long-chain components and aromatics through Fischer-Tropsch reaction into bio-oil phase. In addition, *EP* had some protein (21.1%) which was much more than lipid and carbohydrate, so bio-oil through HTL mainly had amides. Note that *Cyanophyta* and *EP* had much carbohydrate (9.1% and 6.1%, respectively), so their bio-oil had more ketones such as pyrrolidone, methanone. Their ketones could be intermediate products of Maillard reaction in HTL process. Moreover, algae had little lipid, so bio-oil included low contents of alcohols, acids and ethers, which could be from further decomposition of fatty acids and glycerins after lipid hydrolysis process.

Conclusion

This study investigated HTL process and reaction mechanism of *Spirulina*, *EP* and *Cyanophyta*. Analysis and comparison of yields, HHV and organic compositions of bio-oil was done comprehensively. We found that *Spirulina* had the highest bio-oil yield of 30.4% and *EP* had the lowest value of 23.4%. Severe conditions benefited more light bio-oil fraction and less heavy bio-oil fraction and it could be from the decomposition and conversion of high macromolecule compounds. HHV of bio-oil was nearly twice than algae feedstock and the highest value was 37.69 MJ/kg from *Cyanophyta* at 350℃, 30 min and a/w 1/4. GC-MS results showed that bio-oil from algae which contained much protein such as *Spirulina* and *Cyanophyta* mainly contained amides, amines, phenols and it could be due to reunion of protein hydrolysis productions. Bio-oil from *Cyanophyta* and *EP* which had much carbohydrate could contain a portion of ketones, which could be intermediate products of Maillard reaction in HTL process.

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