Analytical study on pyrolyzed products of *Desmodesmus* sp. cultivated in BG11

Li Gang[1], Ji Fang[2], Xiang Shunan[3], Zhou Yuguang[4,5], Jiang Mengmeng[4,5], Huang Zhigang[1*]

(1. *School of Material Science and Mechanical Engineering, Beijing Technology and Business University, Beijing 100048, China*; 2. *Chinese Academy of Agricultural Engineering, Beijing 100125, China*; 3. *China Agricultural Machinery Testing Centre, Beijing 100122, China*; 4. *College of Engineering /National Center for International Research of BioEnergy Science and Technology, China Agricultural University, Beijing 100083, China*; 5. *Key Laboratory of Clean Production and Utilization of Renewable Energy, Beijing 100083, China*)

Abstract: Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC/MS) was adopted to determine the changes in component of BG11-cultivated *Desmodesmus* sp. (BG11/8-10) pyrolyzed products at different temperatures (300°C-800°C). The results of analysis on a series of total ions chromatogram (TIC) showed that pyrolyzed products of BG11/8-10 at different temperature mainly included aliphatic hydrocarbons, nitrogen compounds, aromatic hydrocarbons, fatty acids, ketones, alcohols, aldehydes and furan compounds. Compared to the bio-oil (42.36%) generated by pyrolysis at 700°C, the relative content of bio-oil generated at 800°C was the highest up to 56.96%. However, higher temperature could easily cause the generation of large quantities of such pollutants as nitrogen compounds and polycyclic aromatic hydrocarbons (PAHs). Therefore, based on lower pollutant discharge and higher bio-oil yield, the optimal pyrolysis temperature of BG11/8-10 was around 700°C.

Keywords: *Desmodesmus* sp., microalgae, pyrolyzed products, pyrolysis temperature, bio-oil

DOI: 10.3965/j.ijabe.20171003.2942

Citation: Li G, Ji F, Xiang S, Zhou Y G, Jiang M M, Huang Z G. Analytical study on pyrolyzed products of *Desmodesmus* sp. cultivated in BG11. Int J Agric & Biol Eng, 2017; 10(3): 218–226.

1 Introduction

The massive use of fossil energy causes that the pollution by hazardous substances is serious increasingly so as to produce such global ecological problems as greenhouse effect, climate change, destruction for diversity of species and desertification. The biomass energy is a kind of renewable energy resources with rich reserves in the nature which may be converted as solid, gaseous and liquid fuel and can replace the fossil energy to some extent. The biomass energy that the microalgae is served as the representative may form beneficial supplement with other energy forms, the microalgae is provided with such advantages as high photosynthesis efficiency, short growing period and high oil content as well as the advantage that the production with high density and large scale may be completed[1]. Therefore, as a kind of vital source for new type of biofuel, microalgae are one of resources with most potential to replace fossil fuel in future.

The thermal-chemical conversion way of biomass covers the direct combustion, liquefaction, gasification

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Received date: 2016-10-26 **Accepted date:** 2017-03-06

Biographies: Li Gang, PhD, research interests: microalgae conversion and bioenergy, Email: ligang@btbu.edu.cn; **Ji Fang,** PhD, research interest: microalgae cultivation, Email: ji_fang1984 @163.com; **Xiang Shunan**, Engineer, research interest: biomass engineering, Email: xiangshunan17@163.com; **Zhou Yuguang**, PhD, Asociate Professor, research interests: bioenergy clean utilization, Email: zhouyg@cau.edu.cn; **Jiang Mengmeng**, Graduate student, research interest: bioenergy conversion, Email: jmm2457674939@qq.com.

***Corresponding author: Huang Zhigang**, Professor, research interests: agricultural product processing engineering. School of Material Science and Mechanical Engineering, Beijing Technology and Business University, No. 11 Fucheng Road, Haidian District, Beijing 100048, China. Tel/Fax: +86-10-68985249; Email: huangzg@btbu.edu.cn.

and pyrolysis[2,3]. The rapid pyrolysis reaction of biomass mainly covers Class-I activation, fragmentation reaction and Class-II gaseous phase pyrolysis reaction[3]; and in the process of reaction, the enthalpy change relevant with pyrolysis reaction may influence the pyrolysis mode of substances[4]. In the pyrolysis process of biomass, such multiple energy products as pyrolysis gas (main ingredients cover CO_2, H_2, CO and CH_4), bio-oil (mainly composed of oxy-organics) and biochar were produced, but at the same time also generated some potential pollutions such as nitrogen compounds and Polycyclic Aromatic Hydrocarbons (PAHs) which were carcinogenic for human body[5]. The study shows that the pyrolyzed products may be utilized to synthesize various energy products[2]. However, the pyrolysis reaction mechanism of microalgae biomass is still unclear and required to be explored further. Py-GC/MS has been widely used for characteristic study of complex compounds due to these advantages such as no require to implement the pre-treatment for sample; less sample consumption; diversified samples; rapid analysis speed; high efficiency and high sensitivity[6-10]. In this study, it is proposed to test the pyrolyzed products and components content of BG11/8-10 under different temperature as well as the optimal conditional parameters in the pyrolysis conversion process of BG11/8-10.

2 Materials and methods

2.1 Algae strain and culture condition

Microalgae strain was a wild-type *Desmodesmus* sp. EJ 8-10, which was isolated from local river in Fangshan District, Beijing, China. It was preserved in BG11 medium and listed in Table 1. EJ 8-10 were inoculated at 10% (v/v) in 250 mL Erlenmeyer flasks containing 100 mL liquid medium. Culture conditions were: illumination strength ((6000±100) lx); temperature ((25±1)°C); illumination period (14 h : 10 h) (light : dark). The BG11 medium and Erlenmeyer flasks were sterilized at 121°C for 20 min.

2.2 Raw materials and sample preparation

EJ 8-10 was preserved in BG11 medium for 14 d and the culturing condition was described as 2.1. After 14 d of cultivation, algae cells were harvested by centrifugation at 10 000 r/min for 10 min and dried by a vacuum freeze dryer (Savant Instruments Inc., USA), then stored at 4°C before being analyzed, which was named as BG11/8-10 for short.

Table 1 The chemical composition of BG11 medium

No.	Chemicals	Concentration/g·L^{-1}
1	$NaNO_3$	1.5
2	K_2HPO_4	3×10^{-2}
3	$MgSO_4\cdot7H_2O$	7.5×10^{-2}
4	$CaCl_2\cdot2H_2O$	36×10^{-2}
5	Citric Acid combined with Ferric	6×10^{-3}
6	Ammonium Citrate	6×10^{-3}
7	EDTA	1×10^{-3}
8	Na_2CO_3	6×10^{-3}
9	H_3BO_3 $MnCl_2\cdot4H_2O$ $ZnSO_4\cdot7H_2O$ $NaMoO_4\cdot5H_2O$ $CuSO_4\cdot5H_2O$ $Co(NO_2)_2\cdot6H_2O$	2.86×10^{-3} 1.81×10^{-3} 2.22×10^{-4} 3.9×10^{-4} 7.9×10^{-5} 4.94×10^{-4}

2.3 Compositional analysis

The carbon, hydrogen, nitrogen and sulfur contents in BG11/8-10 were measured using an elemental analyzer (Flash EA-1112, Thermo, USA) at the Institute of Chemistry, Chinese Academy of Sciences. Reported values were from the average of at least triplicate samples. The Bligh and Dyer method was used to determine the total lipid content of BG11/8-10[11]. The protein content (wt%) of BG11/8-10 indicates that content of BG11/8-10 nitrogen element multiplies by 6.25[12], referring to Equation (1):

$$\text{protein} = \text{nitrogen} \times 6.25 \tag{1}$$

The Equations (2) and (3) that has been established below for high heating value (HHV) of BG11/8-10 was employed[13].

$$HHV\,(\text{OLS}) = 1.87C^2 - 144C - 082H + 63.8C\times\text{H}+ 129N + 20147 \tag{2}$$

$$HHV\,(\text{PLS}) = 5.22C^2 - 319\ C - 1674H + 38.6C\times H + 133N + 21028 \tag{3}$$

where, C, H and N represent the content of carbon, hydrogen and nitrogen elements, respectively.

Equations (2) and (3) were obtained respectively through regression analysis of ordinary least square (OLS) and partial least square (PLS) of high heating value for sample. According to the suggestions of Friedl et al.[14], the mean value of HHV (MJ/kg) was calculated according to Equation (4):

$$HHV=\frac{HHV(\mathrm{OLS})+HHV(\mathrm{PLS})}{2}=(3.55C^2-232C-2230H+51.2C\times H+131N+20600)\times 10^{-3} \quad (4)$$

2.4 Analytic pyrolysis of BG11/8-10

The analyzer (Py-GC/MS) used for BG11/8-10 pyrolysis was composed by a pyrolysis device (Frontier Labs 3030i, Japan) and gas chromatography-mass spectrometer (GC/MS, Agilent 7890A/5975C, USA).

The Py-GC/MS real-time testing was performed between 300°C-800°C (100°C for temperature interval) for BG11/8-10 sample to obtain the total ion current (TIC) diagrams of BG11/8-10 pyrolysis product components. The analysis condition of GC refers to Table 2.

Table 2 Analytical condition of GC settings

Name	Parameters
Capillary column	HP-5 (30 m × 0.25 mm × 0.25 μm)
The carrier gas and flow rate	He, 1.0 mL/min, constant current
Inlet temperature	250°C
Split ratio	1:10
Temperature programming	Initial temperature 40°C, keep for 3 min; up to 200°C by 5°C/min, keep for 5 min; up to 250°C by 10°C/min, keep for 5 min.

2.5 Analysis of BG11/8-10 pyrolysis components

The TIC diagrams of BG11/8-10 pyrolyzed products under different temperature conditions were obtained. Results were analyzed using Agilent MSD Productivity Chem Station for GC and GC/MS System Data Analysis application software (Version D 03.00.552, Agilent, USA). Retention time and peak area percentages of different compounds in pyrolyzed products were determined by comparing with NIST 2011 Database (Version 2.0, National Institute of Science and Technology, USA). The concentrations of each individual compound were of right proportion to its corresponding peak area percentage.

3 Results and discussion

3.1 Composition analysis

Table 3 lists the contents of carbon, hydrogen, nitrogen and sulphur elements, HHV value, protein content and lipid content of BG11/8-10. Since *Desmodesmus* sp. belongs to generalized *Scenedesmus* sp., Table 3 also shows the data of *Scenedesmus* sp. as comparison[15].

The element analysis showed that, except that the content of sulphur element was around 0.5%, the content of carbon, hydrogen and nitrogen of BG11/8-10 were greater than those of in *Scenedesmus* sp., especially the carbon element content was about 6% higher. In the chemical analysis, the protein content of BG11/8-10 was far higher than *Scenedesmus* sp., mainly because the content of nitrogen element of BG11/8-10 was higher than *Scenedesmus* sp.; the lipid content of BG11/8-10 was also higher than *Scenedesmus* sp.; the HHV value of BG11/8-10 (16.14 MJ/kg) was slightly higher than *Scenedesmus* sp. It was reported by Harman-Ware et al.[15] that the obtained HHV value of bio-oil was 18.4 MJ/kg when *Scenedesmus* sp. pyrolysis at 480°C, while various indexes of BG11/8-10 were higher than *Scenedesmus* sp., showing that BG11/8-10 has greater energy production potential with comparison to *Scenedesmus* sp.

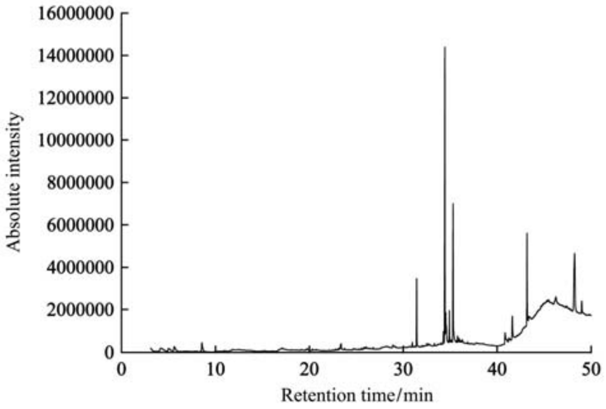
Table 3 Compositional analysis of feedstock for pyrolysis

Feedstock	Elemental analysis/%				HHV /MJ·kg^{-1}	Chemical analysis/%	
	C	H	N	S		Lipid content	Protein content
BG11/8-10	38.05	6.30	7.67	0.56	16.14	16.6	47.94
Scenedesmus sp.	32.1	4.8	5.3	0.5	14.69	11.5	27.8

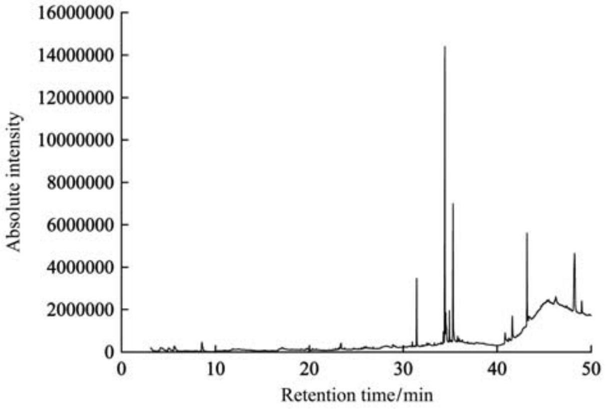
3.2 Compositional analysis of BG11/8-10 pyrolyzed products

Temperature is one of the important factors in the process of biomass pyrolysis. When the temperature is up to certain degree, the secondary pyrolysis reaction might occur simultaneously. The primary pyrolyzed products in biomass portion may produce the secondary pyrolysis to obtain the secondary pyrolyzed products.

Figure 1 shows the TIC diagrams of BG11/8-10 pyrolytic bio-oil at 300°C and 400°C. At 300°C, the pyrolyzed products of BG11/8-10 mainly covered such 19 kinds of substances as hydrocarbons, acids, ketones, alcohols and other organic substances. Therein, the substances that the content was greater than 3% cover bicyclo [3.1.1] heptane, 2,6,6-trimethyl-, [1R-(1.alpha., 2.beta., 5.alpha.)]-(30.64%), squalene (16.72%), 2-propylcyclohexanol (16.58%), heptadecane (6.44%), succinic acid, di(2-ethylhexyl) ester (6.2%), phytol (3.49%) and 7,11-hexadecadien (3.06%), the retention time were 34.43 min, 48.24 min, 35.31 min, 31.43 min, 43.18 min, 41.61 min and 46.25 min, respectively.



a. 300°C

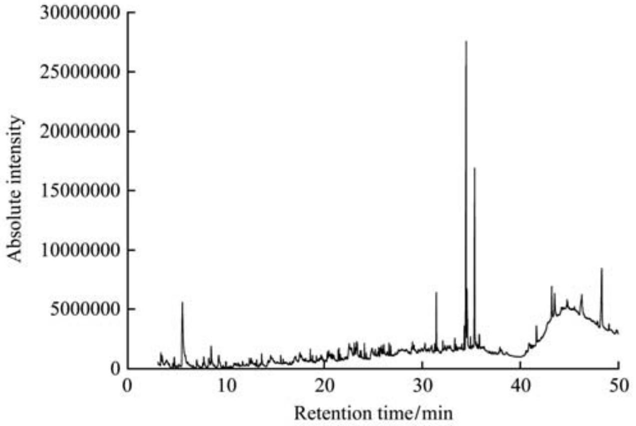


b. 400°C

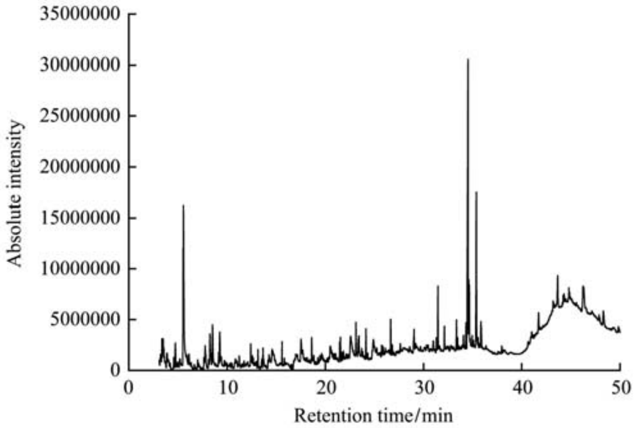
Figure 1 Total ion current diagram of BG11/8-10 pyrolytic bio-oil at 300°C and 400°C

The pyrolyzed products of BG11/8-10 at 400°C mainly covered such 95 kinds of substances as hydrocarbons, nitrogenous compounds, alcohols and other organic substances. Therein, the substances that the content was greater than 3% successively refer to 9-octadecyne (18.05%), m-menth-1(7)-ene, (R)-(-)-(10.55%), 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-(4.24%), hexadecanamide (3.97%) and 9-octadecenamide, (Z)-(3.27%), the retention time were 34.49 min, 35.35 min, 34.58 min, 43.51 min and 46.27 min, respectively.

Figure 2 shows the TIC diagrams of BG11/8-10 pyrolytic bio-oil at 500°C and 600°C, after further analysis and summarized, it can be conclude that the pyrolyzed products of BG11/8-10 mainly covered such 113 and 173 kinds of substances at 500°C and 600°C, respectively. Among which that more than 3% at 500°C consisted of 9-octadecyne (14.43%), 1H-imidazole-4-propanamine (8.32%), toluene (6.92%), 6,10,14-hexadecatrien-1-ol, 3,7,11,15-tetramethyl-, [R-(E,E)]-(5.4%), cyclobutanecarboxylic acid, tridecyl ester (5.21%), 5,9-dimethyl-2-(1-methylethylidene)-1-cyclodecanol (3.23%); while 600°C included 9-octadecyne (9.46%), toluene (8.01%) and cyclopentylcyclohexane (4.51%).



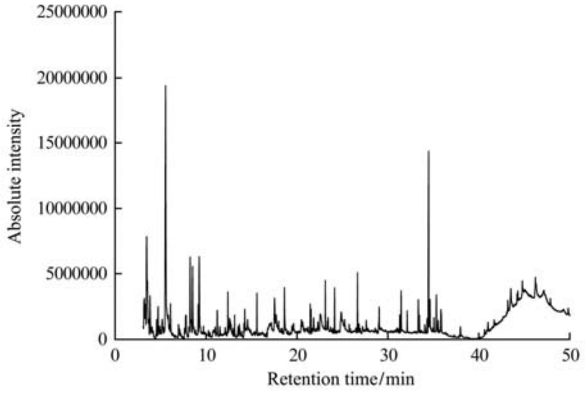
a. 500°C



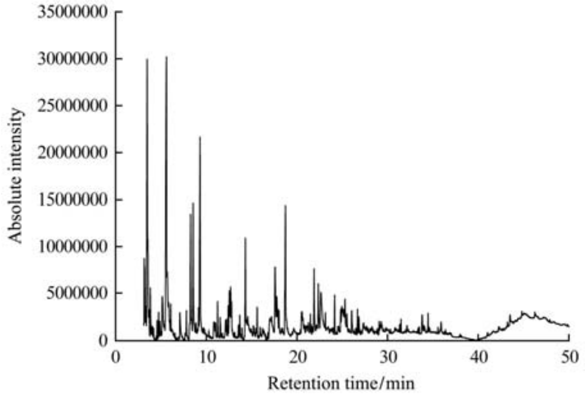
b. 600°C

Figure 2 Total ion current diagram of BG11/8-10 pyrolytic bio-oil at 500°C and 600°C

As we can see in Figure 3, pyrolysis products of BG11/8-10 pyrolyzed at 700°C was similar with 800°C, which was primary made up of hydrocarbons, nitrogenous compounds, phenols, ketones, alcohols and other organic substances. However, the specific substances pyrolyzed at 700°C and 800°C was not the same, except toluene and and benzene, which was (10.4%) and (3.03%) at 700°C, and (14.38%) and (10.04%) at 800°C. Besides, the pyrolyzed products of BG11/8-10 at 700°C also comprised bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1.alpha.,2.beta.,5.alpha.)]- (4.24%); while the pyrolyzed products of BG11/8-10 at 800°C covered styrene (8.01%), naphthalene (5.65%), indole (4.21%), o-xylene (4.18%), 1H-indene, 1-methyl-(3.34%), indene (3.25%) and ethylbenzene (3.12%).



a. 700°C



b. 800°C

Figure 3 Total ion current diagram of BG11/8-10 pyrolytic bio-oil at 700°C and 800°C

3.3 Effects of various temperatures on BG11/8-10 pyrolyzed products

In order to better study the influence of temperature on pyrolyzed products, the pyrolyzed products with larger peak area and stable testing results under each temperature shall be summarized and compared, the substances that the match quality were over 80% in BG11/8-10 pyrolyzed products shall be classified and summarized according to chemical compounds, as shown in Table 4, and then, the influence of BG11/8-10 pyrolyzed products along with temperature variation was discussed.

The pyrolyzed products of BG11/8-10 at 300°C-800°C were classified into the following categories: aliphatic hydrocarbons (alkanes and olefins), aromatic hydrocarbons (benzenes, indenes and both derivatives), acids, nitrogenous compounds (amides, nitriles, indoles and miazines), phenols, PAHs, ketones, alcohols, aldehydes and furans. This result was similar to the results of studies by Thangalazhy-Gopakumar et al.[8] and Li et al.[16] Table 4 also showed the relative peak area of various substances at different temperatures.

Table 4 Identification and quantification of chemical compounds from BG11/8-10 pyrolyzed at 300°C-800°C (Qual.>80%)

Groups	Compounds	Percent content/%					
		300°C	400°C	500°C	600°C	700°C	800°C
Aliphatics							
Alkanes	Cyclopropane, octyl-	-	-	-	-	0.73	-
	Cyclohexane, 1-(1,5-dimethylhexyl)-4-(4-methylpentyl)-	-	-	-	0.71	1.48	-
	7-Thiabicyclo[4.1.0] heptane, 2-methyl-	-	-	-	0.33	-	-
	Cyclooctane, 1,2-dimethyl-	-	-	-	0.96	-	-
	endo-2-Methylbicyclo [3.3.1]nonane	-	-	-	-	0.04	-
	(7R,8S)-cis-anti-cis-7,8-Epoxytricyclo [7.3.0.0(2,6)] dodecane	-	-	-	-	0.59	-
	Cyclododecane	-	0.44	0.55	-	-	0.55
	Tridecane, 7-methylene-	-	-	-	0.50	-	-
	Tetradecane	-	-	0.46	-	-	-
	Cyclotetradecane, 1,7,11-trimethyl-4-(1-methylethyl)-	-	-	0.41	-	-	-
	Pentadecane	-	-	0.35	-	0.27	-
	Heptadecane	6.44	2.61	1.97	1.40	0.81	0.27
	Heneicosane	-	-	-	-	0.06	-
	Sum	6.44	3.05	3.74	3.90	3.98	0.82
Alkenes	1-Phenyl-1-butene	-	0.15	-	-	-	-
	(Z)-Hex-2-ene, 5-methyl-	-	-	-	-	0.69	-
	1,4-Hexadiene, 2,3,4,5-tetramethyl-	-	-	-	0.25	-	-
	1,3,5-Hexatriene, 3-methyl-, (Z)-	-	-	-	-	0.54	-
	1-Heptene	-	-	-	-	1.19	1.37
	1,3-Cycloheptadiene	-	-	-	-	0.93	-
	1-Nonene	-	-	-	0.35	0.72	0.48
	1-Decene	-	-	-	0.60	0.97	0.60
	1-Undecene	-	-	-	-	-	0.60
	5-Undecene	-	-	-	0.45	-	-
	1-Dodecene	-	-	-	1.21	1.44	-
	1,9-Dodecadiene	-	-	-	-	0.09	-
	1-Tridecene	-	-	-	0.43	0.48	-
	1-Tetradecene	-	-	0.48	0.68	0.91	-
	2-Tetradecene, (E)-	-	-	0.32	-	-	-
	1-Pentadecene	-	-	0.44	0.77	1.10	-
	1-Hexadecene	-	-	-	-	0.77	-
	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	1.15	5.49	3.05	2.68	0.95	-
	1-Heptadecene	-	-	-	0.56	-	-
	3-Heptadecene, (Z)-	-	-	-	-	-	-
	8-Heptadecene	-	1.07	0.36	0.37	-	-
	cis-1-Chloro-9-octadecene	-	-	-	0.087	-	-
	1-Nonadecene	3.73	0.68	-	0.77	2.21	-
	1-Eicosene	-	-	-	-	0.74	-
	1,19-Eicosadiene	-	-	-	-	0.16	-
	Limonene	-	-	0.72	-	-	-
	Sum	4.88	7.39	5.37	9.21	13.89	3.05

Groups	Compounds	Percent content/%					
		300°C	400°C	500°C	600°C	700°C	800°C
Sum		11.32	10.44	9.11	13.11	17.87	3.87
Aromatics							
Benzenes	Benzene	-	-	-	0.96	3.03	10.04
	Benzene, propyl-	-	-	-	0.54	0.93	1.01
	Benzene, 1-propenyl-	-	-	-	-	1.65	0.59
	Benzene, 1-butenyl-, (E)-	-	-	-	-	-	0.18
	Benzene, 3-butenyl-	-	-	-	-	0.29	-
	Benzene, 1,3-dimethyl-	2.42	-	1.45	-	-	-
	Benzene, 1-isocyano-2-methyl-	-	-	-	1.75	-	-
	Benzene, 1-ethyl-3-methyl-	-	-	-	-	0.48	0.72
	Biphenylene	-	-	-	-	-	0.93
	Toluene	-	2.46	6.92	8.01	10.4	14.38
	p-Xylene	-	1.27	-	1.63	2.50	-
	o-Xylene	-	-	-	-	-	4.18
	Ethylbenzene	-	-	-	-	2.18	3.12
	Styrene	-	-	1.63	1.27	2.67	8.01
	Benzocycloheptatriene	-	-	-	-	-	1.62
	Sum	2.42	3.73	10	14.16	24.13	44.78
Indenes	Indene	-	-	-	-	-	3.25
	1H-Indene, 1-methyl-	-	-	-	-	-	3.34
	2-Methylindene	-	-	-	-	-	0.73
	1H-Indene, 1,1-dimethyl-	-	-	-	-	0.15	-
	Sum	0	0	0	0	0.15	7.32
	Fluorene	-	-	-	-		0.13
	Phenanthrene	-	-	-	-		0.86
Sum		2.42	3.73	10	14.16	24.28	53.09
Acids	Z-8-Methyl-9-tetradecenoic acid	-	-	-	0.47	-	-
	Octadec-9-enoic acid	-	-	-	0.62	-	-
	Oleic Acid	-	-	-	0.24	0.21	-
	Sum	0	0	0	1.33	0.21	0
Nitrogen compounds							
	Octadecanamide	-	-	-	1.97	1.5	-
	Tricyclo[3.1.0.0(2,4)]hex-3-ene-3-carbonitrile	-	-	-	-	-	1.42
	Heptadecanenitrile	-	0.93	-	-	-	-
	Benzyl nitrile	-	0.30	1.09	1.10	1.9	-
	Benzonitrile, 2-methyl-	-	-	-	-	-	0.52
	Benzonitrile, 4-methyl-	-	-	-	-	-	0.36
	Indole	-	3.26	3.39	3.5	2.1	4.21
	1H-Indole, 2-methyl-	-	1.77	1.98	-	-	-
	1H-Indole, 3-methyl-	-	-	-	1.06	0.44	0.6
	1H-Indole, 4-methyl-	-	-	-	0.48	1.41	-
	Pyridine	-	-	-	0.53	1.13	2.29
	Pyridine, 2-methyl-	-	-	-	-	0.46	1.36
	1H-Pyrrole, 3-methyl-	-	-	-	-	-	0.55
	Isoquinoline	-	-	-	-	-	0.68
	3-Azabicyclo[3.3.1]nonan-9-ol,3-methyl-6-(1-pyrrolidinyl)-, (endo,anti)-	-	-	0.06	-	-	-
Sum		0	6.26	6.52	8.64	8.94	11.99
Phenols	Phenol	-	-	-	-	0.69	-
	Phenol, 3-methyl-	-	-	-	-	0.96	-
	Phenol, 4-methyl-	-	-	-	2.78	1.43	1.93
	Sum	0	0	0	2.78	3.08	1.93
PAHs	Naphthalene	-	-	-	-	-	5.65
	Naphthalene, 2-methyl-	-	-	-	-	-	2.2
	Naphthalene, 2-ethenyl-	-	-	-	-	-	0.74
	Naphthalene, 2,3-dimethyl-	-	-	-	-	-	0.69
	Naphthalene, 2,6-dimethyl-	-	-	-	0.25	-	0.84
	Naphthalene, 2,7-dimethyl-	-	-	-	0.21	0.29	-
	1,4-Dihydronaphthalene	-	-	-	-	-	0.70
	2(1H)-Naphthalenone, octahydro-4a-methyl-7-(1-methylethyl)-, (4a.alpha.,7.beta.,8a.beta.)-	-	-	-	0.88	-	-
	Naphthalene, 1,2-dihydro-1,1,6-trimethyl-	-	0.91	0.72	0.68	0.34	-
	Naphthalene,1,2,3,4-tetrahydro-1,1,6-trimethyl-	-	1.08	0.86	1.03	0.35	-
	Sum	0	1.99	1.58	3.05	0.98	10.82
Ketones	8-Cyclohexadecen-1-one	-	-	-	-	0.16	-
Alcohols	2,4,7,14-Tetramethyl-4-viny-tricyclo[5.4.3.0(1,8)] tetradecan-6-ol	-	0.32	-	-	-	-
	1,16-Hexadecanediol	-	-	0.29	0.086	-	-
	6,10,14-Hexadecatrien-1-ol, 3,7,11,15-tetramethyl-, [R-(E,E)]-	-	-	5.4	-	-	-
	9,12-Octadecadien-1-ol, (Z,Z)-	-	-	-	-	0.15	-
	E,E,Z-1,3,12-Nonadecatriene-5,14-diol	-	-	-	-	0.23	-
	Phytol	3.49	1.73	1.07	-	-	-
	Sum	3.49	2.05	6.76	0.086	0.38	0
Aldehydes	Butanal, 3-methyl-	-	0.48	-	-	-	-
	cis-9-Hexadecenal	-	-	-	0.24	-	-
	7-Hexadecenal, (Z)-	-	-	-	-	0.18	-
	E-11-Hexadecenal	-	-	-	-	0.03	-
	7,11-Hexadecadienal	3.06	-	-	-	-	-
Sum	Sum	3.06	0.48	0	0.24	0.21	0
		6.55	2.53	6.76	0.326	0.75	0
Furans	Furan, 2,5-dimethyl-	-	-	-	-	-	0.2
	2,5-Furandione, 3-dodecyl-	-	-	1.11	-	0.17	-
Sum		0	0	1.11	0	0.17	0.2

Aliphatic hydrocarbons exist in the fossil fuel naturally and are of components with very high value on the aspect of fuel application[8]. Along with temperature rose, aliphatic hydrocarbons with different species and different contents would generate. When the temperature rose up to 500°C from 300°C gradually, the relative content of aliphatic hydrocarbon compounds reduced gradually; when the temperature rose to 700°C from 500°C, the relative content of aliphatic hydrocarbon compounds rose gradually and reached maximum 17.87% at 700°C. These results were uniformly higher than the maximum 10.65% and 8.4% reported by Li et al.[16] and

Thangalazhy-Gopakumar et al.[8] There were three possible causes to this phenomenon: (i) the lipid content of BG11/8-10 was higher, and more aliphatic hydrocarbon compounds might be transferred and generated during pyrolysis; (ii) at high temperature, the fatty acid produced the decarboxylation chemical reaction as well as generates aliphatic hydrocarbon compounds and CO_2; (iii) with increasing temperature, the long and medium-chain aliphatic hydrocarbon compounds produce the short-chain ones from the carbon chain breakage[6,10]. When the temperature was higher than 700°C, the relative content of aliphatic hydrocarbon compounds began to reduce.

As important industrial chemical substances and transportation fuel additives, aromatic hydrocarbon compounds may improve the octane value of fuel and fuel quality[10]. Except for plenty of benzenes and benzene derivatives, there were indene and indene derivatives in the aromatic hydrocarbon compounds. The relative content of aromatic hydrocarbon compounds increased along with gradual raised temperature. When the temperature reached 800°C, the relative content of aromatic hydrocarbon compounds reached maximum 53.09% and was higher than the one in previous literature report[17]. Maggi et al.[18] deemed that these aromatic hydrocarbon compounds were not the direct products by flash pyrolysis of biomass, they might be generated through secondary reaction under high temperature (polymerization or condensation function); meanwhile, it was demonstrated that the high-temperature (over 600°C) pyrolysis shall generate plenty of aromatic hydrocarbon compounds.

Miao et al.[19] deemed that the fatty acid compounds in the pyrolyzed products mainly came from the lipid pyrolysis. There were quite a little fatty acid compounds in BG11/8-10 pyrolyzed products. Between 300°C-500°C, the generation of fatty acid compounds were not detected; between 600°C-700°C, very little long-chain fatty acid compounds generated (C14-C18). This was probably because the lipid compositions in BG11/8-10 converted more aliphatic hydrocarbon compounds during the process of pyrolysis.

The nitrogen compounds in the process of pyrolysis mainly came from degradation of protein and chlorophyll and produce potential nitrogen oxides pollution[8,16,20]. Therefore, the high protein content in the sample may produce large amount of nitrogen compounds in the process of pyrolysis. When the temperature was up to 800°C gradually from 300°C, the relative content of nitrogen compounds increased with temperature raised and was up to maximal 11.99% at 800°C. The tendency that the relative content of nitrogen compounds changed with temperature showed that low temperature helped the reduction of discharge for nitrogen compounds in the process of pyrolysis.

In BG11/8-10 pyrolyzed products, there were small amounts of phenolic compounds as well. Until the temperature raised up to 600°C, were detected, the phenolic compounds and alky derivatives increased along with temperature raised and reach maximum 3.08% at the time of 700°C. When the temperature rose up to 800°C, the relative content of phenolic substances began to decline.

Polycyclic aromatic hydrocarbons (PAHs) belong to typical pollutants, not only existing in the fossil fuel but also producing in the process of fuel combustion and pyrolysis as well. At 300°C, PAHs was not detected. Between 400°C-600°C, along with temperature raised, the relative content of PAHs increased gradually. At 700°C, the relative content of PAHs dropped down to 0.98%. When the temperature was up to 800°C, the relative content of PAHs increased sharply, rapidly raised up to maximum 10.82%. During the pyrolysis process, there were three ways to generate the PAHs[10]: (i) Diels-Alder reaction; (ii) deoxygenation of oxygenated aromatic hydrocarbon compounds; (iii) pyrolysis of protein substances, especially under the condition that the carbohydrate substances exist, the content might increase. It can be shown that the sharp increase of PAHs under high temperature was possibly caused by secondary reaction of pyrolyzed products under high temperature. Therefore, in order to avoid generating the PAHs, it is suggested to adopt lower temperature.

Except small amounts of furan generated, partial ketoaldehyde and alcohol compounds could generate as well during the pyrolysis process, those substances changed with temperature changed. When the temperature was up to 500°C, the ketoaldehyde and acolohol compounds reach maximum 6.76%; when the temperature was over 600°C, the relative content of these substances began to drop.

In above-mentioned pyrolyzed products, as valuable organic compounds, the aliphatic hydrocarbon compounds can generate the energy[16]; Aromatic hydrocarbon compounds are important industrial chemical substances and may increase the octane value of fuel and improve the fuel quality[17]; the long-chain fatty acid substances not only produce the aliphatic hydrocarbon compounds via deoxygenation but also generate the fatty acid methyl ester (FAME) through transesterification process, namely, main components of biodiesel, having energy utilization potential[20]. Figure 4 showed the sum of relative content under each temperature for the three substances, the sum of relative content of the three substances reached maximum 56.96% at 800°C and reached 42.36% at 700°C. However, 800°C generated more pollutants (nitrogen compounds and PAHs, 12.89%) than 700°C. Based on lower pollutants discharge and higher bio-oil yield, the optimal pyrolysis temperature of BG11/8-10 was around 700°C.

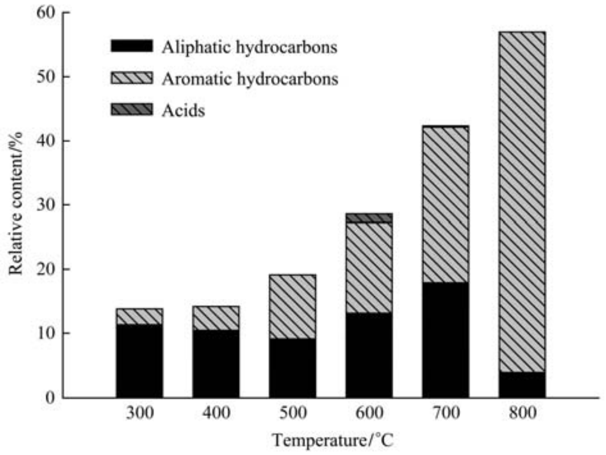


Figure 4 Sum of relative percentages of aliphatic hydrocarbons, aromatic hydrocarbons and acids under different pyrolysis temperatures (300°C-800°C)

4 Conclusions

Relative higher carbon content (38.05%) and relative lower nitrogen content (7.67%) of BG11/8-10 showed that there was huge potential in terms of energy regeneration utilization. BG11/8-10 pyrolyzed products mainly include aliphatic hydrocarbons (alkanes and olefins), aromatic hydrocarbons (benzenes, benzene alkyl derivates and indenes), fatty acids, nitrogen compounds (amides, nitrites and indoles), phenols and PAHs. Temperature was one of the important factors influencing the composition of BG11/8-10 pyrolyzed products. Compared to bio-oil content at 700°C, the bio-oil content of BG11/8-10 produced at 800°C was the highest that reached 56.96%. However, higher temperature can easily lead to massive generation of such pollutants as nitrogen compounds and PAHs. After a comprehensive consideration of higher conversion ratio of bio-oil and generation of fewer pollutants, around 700°C was the optimal temperature for BG11/8-10 bio-oil conversion.

Acknowledgments

This research was supported by Beijing Municipal Science and Technology Plan Projects (No. D161100006016001), and Beijing Municipal Key Discipline of Biomass Engineering.

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