Comparative study on thermal cracking characteristics and bio-oil production from different microalgae using Py-GC/MS

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Abstract: The yield and chemical composition of pyrolysis products of *Chlorella pyrenoidosa* and *Schizochytrium limacinum* were determined using thermogravimetric analyzer (TGA) and pyrolysis-gas chromatographic mass spectrometry (Py-GC/MS) by varying the temperature ranges. After further analysis of the total ion current (TIC) diagrams of *Chlorella pyrenoidosa* and *Schizochytrium limacinum*, it was concluded that both the pyrolysis products of each sample were mainly comprised of hydrocarbons, aromatics, fatty acids, nitrogen compounds, PAHs, phenols, etc, however, the relative content of each compound from *Chlorella pyrenoidosa* and *Schizochytrium limacinum* was different. The pyrolysis of *Chlorella pyrenoidosa* and *Schizochytrium limacinum* at 350℃ produced a maximum yield of bio-oil production (44.32% and 60.99%); moreover, *Chlorella pyrenoidosa* could lead to more pollutants (nitrogen compounds and PAHs) release (2.71%) compared to that of *Schizochytrium limacinum* (0.7%). Considering the reasonable bio-oil production and minimum release of pollutants, *Schizochytrium limacinum* was found to be superior for producing biofuel against *Chlorella pyrenoidosa*.

Keywords: microalgae, *Chlorella pyrenoidosa*, *Schizochytrium limacinum*, bio-oil production, thermal cracking, Py-GC-MS
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1 Introduction

The pollution caused by hazardous substances that emitted from the massive use of fossil energy is serious increasingly so as to create global ecological problems such as greenhouse effect, climate change, destruction for diversity of species and desertification. It has been paid increasing attention on searching for renewable and alternative energy sources[1]. Among all the proposed alternatives, biomass for bioenergy production is considered as a sustainable, renewable and geographically evenly distributed resource[2]. Microalgae, as one of the major feedstocks for the third-generation biofuel production, have been attractive due to their advantages such as high photosynthesis efficiency, short growth period and high oil content as well as the advantage that the production with high density and large scale can be accomplished[3-5].

At present, it is still not fully understood for the mechanisms of generation as well as modification of products for the microalgae biomass via pyrolysis. The major compounds in microalgae involve oil, protein, soluble polysaccharides, and so on[6]. Research has shown that the ecological situation during cultivation of microalgae pose effects on the concentration process of any dominated element involved[7]. Therefore, the study on pyrolysis of *Chlorella pyrenoidosa* and *Schizochytrium limacinum* is of great significance to detect the basic principles behind the first and the second-order pyrolysis processes, and their application.

Generally, thermochemical conversion of biomass consists of direct combustion, liquefaction, gasification, and pyrolysis[8]. As a promising thermochemical conversion, it is well-known that fast pyrolysis can convert biomass directly into solid, liquid, and gaseous products by thermal decomposition of biomass in an oxygen-free atmosphere[3]. Pyrolyzer-gas chromatography-mass spectrometer (Py-GC-MS) is one of the most effective ways for complicated compound analysis. Separation and extraction of substances are required before spectrum methods. After combing with a pyrolyzer, the application of GC-MS has been extended to a wider aspect and can be suitable for more compounds to be analyzed, including the non-volatile solid organic samples. The best effect is to provide better performance of sample injection[9-12].

In most cases, several micrograms of samples can be instantly pyrolyzed at 300°C-800°C. The series of spectrum of pyrolyzed product can be obtained since its volatility gets weaker along with the increasing in molecular weight. If Py-GC-MS was employed

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in the study of *Chlorella pyrenoidosa* and *Schizochytrium limacinum*, the spectrum is expected to provide more abundant information about the bio-oil production and its composition, in addition with the specific differences of bio-oil from each microalgae.

2 Materials and methods

2.1 Sample preparation

The *Chlorella pyrenoidosa* and *Schizochytrium limacinum* samples were purchased from Wudi Bioengineering Co., Ltd. (Shandong, China) and preserved at 4℃ in sealed plastic bags.

2.2 Compositional analysis

The carbon, hydrogen, nitrogen, and sulfur contents in sample 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. Based on the elemental composition, the high heating values (HHV) of samples were calculated using the well-established correlations[13].

2.3 Thermogravimetric analysis

The sample was tested by thermogravimetric analyzer (SDT-Q600, TA Instruments, USA) for the determination of decomposition behavior. Weight calibration of the analyzer was conducted according to the operation manual[14]. Approximately 2-4 mg of each sample was measured, put into an alumina oxide pan and loaded into the furnace. Compressed air was purged into the furnace at the rate of 100 mL/min. The analyzer was programmable controlled and temperature of furnace was ramped from standby temperature (40℃) to 1000℃ with an increasing rate of 25℃/min.

2.4 Analytic pyrolysis by Py-GC/MS

Real-time chemical composition of pyrolysis sample was analyzed using a single-shot pyrolyzer (Frontier Labs 3030i, Japan) connected to a GC-MS (Agilent 7890A/5975C, USA), which was equipped with an inert XL mass spectrum detector and a capillary column (30 m in length, 0.25 μm in internal diameter, HP-5 MS, HP19091s-433, Agilent, USA). Concentration level and percentage of different compounds in the pyrolysis products of *Chlorella pyrenoidosa and Schizochytrium Limacinum* were determined by online Py-GC/MS under a ramping temperature gradient from 350℃ to 750℃ at a temperature interval of 100℃. The analysis condition of GC refers to Table 1.

Table 1 Analysis 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℃
Split ratio	1 : 10
Temperature programming	Initial temperature 40℃, keep for 3 min; up to 200℃ by 5℃/min, keep for 5 min; up to 250℃ by 10℃/min, keep for 5 min.

The total ion current (TIC) diagrams of *Chlorella pyrenoidosa and Schizochytrium Limacinum* pyrolysis 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 pyrolysis 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

The results of element analysis and moisture content and higher heating value (HHV) of two kinds of microalgae are shown in Table 2[23,24]. As a comparison, the results of typical lignocellulosic biomass samples, including sawdust and straw, are also listed[13]. Both of the C and H contents for *Schizochytrium limacinum* were higher than *Chlorella pyrenoidosa*, and especially the C content was much higher (about 13%). On the contrary, *Chlorella pyrenoidosa* showed the highest N and S amounts in Table 2. It was reported that higher nitrogen percentage may lead much NOx emissions during combustion[15]. Due to the relative high C and H content, the HHV of *Schizochytrium limacinum* was much higher than that of *Chlorella pyrenoidosa*. Compared with the typical lignocellulosic biomass, the HHV of microalgae was higher, which indicates that microalgae have a great potential in energy production, especially microalgae *Schizochytrium limacinum*.

Table 2 Compositional analysis of feedstock for pyrolysis

Feedstock	Elemental analysis/%				Moisture content (dry basis)/%	HHV /MJ·kg^{-1}
	C	H	N	S		
Chlorella pyrenoidosa	46.025	6.41	8.48	1.2	4.06	19.36
Schizochytrium limacinum	59.61	8.135	2.295	0.9	3.18	26.37
Sawdust	47.4	6.2	0.2	0.1	4.7	18.83
Straw	39.3	6.2	1.4	0.7	8.5	15.80

3.2 Thermogravimetric analysis

As it reported that the main decomposition temperatures of *Chlorella pyrenoidosa* and *Schizochytrium limacinum* were 294.53℃ and 428.16℃, respectively. Which followed by a significant weight loss of 46.7% and 65.5% due to that most carbohydrates and proteins had decomposed[16]. Another decomposition peak point was found at 642.64℃ (*Chlorella pyrenoidosa*) and 760.17℃ (*Schizochytrium limacinum*), which can be taken as the complete decomposition temperature of each sample owing to the ash decomposition[17,22-23].

3.3 Pyrolysis products of sample by GC/MS

Pyrolyzed products within diverse degradation levels of each sample were obtained by different temperatures. It was suggested that the pyrolyzed products of sample might be pyrolyzed again, and then re-pyrolyzed products could be collected. GC-MS analysis was carried out to determine the percentage of major compounds present in the pyrolysis products derived from the two algae samples, which would provide important references for biomass thermochemical conversion and utilization in industry.

TIC diagram of *Chlorella pyrenoidosa* obtained at 350℃ is presented in Figure 1. After further analysis, it can be concluded that the pyrolyzed products of *Chlorella pyrenoidosa* at 350℃ mainly contained 161 kinds of substances such as acids, hydrocarbons, alcohols and other organic substances. Therein, the substances whose content was greater than 3% included 9,12,15-octadecatrienoic acid, (Z,Z,Z)- (34.26%), bicycle[3.1.1]heptane, 2,6,6-trimethyl- (19.82%), 3,7,11,15-tetramethyl-2-hexadecen-1-ol (9.79%), *n*-hexadecanoic acid (5.18%), 2-hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]- (3.85%) and eicosane, 2-methyl- (3.64%); the retention time were 28.4 min, 22.67 min, 23.4 min, 25.88 min, 22.72 min and 26.97 min, respectively.

Figure 2 shows the TIC diagrams of *Schizochytrium limacinum* pyrolytic bio-oil at 350 ℃. The pyrolyzed products were primarily made up of 176 kinds of compounds such as hydrocarbons, alcohols, acids and so on. Among which that had more than 3% consisted of *n*-hexadecanoic acid (42.87%), 6-octadecenoic acid (6.61%), 1,2-benzenediol (6.36%) and tetradecanoic acid (5.92%); the retention times were 25.13 min, 27.44 min, 14.17 min and 21.25 min, respectively.

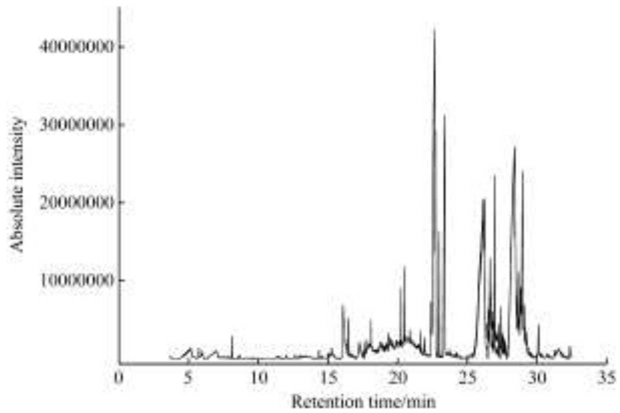

Figure 1 TIC diagram of *Chlorella pyrenoidosa* pyrolytic bio-oil at 350 ℃

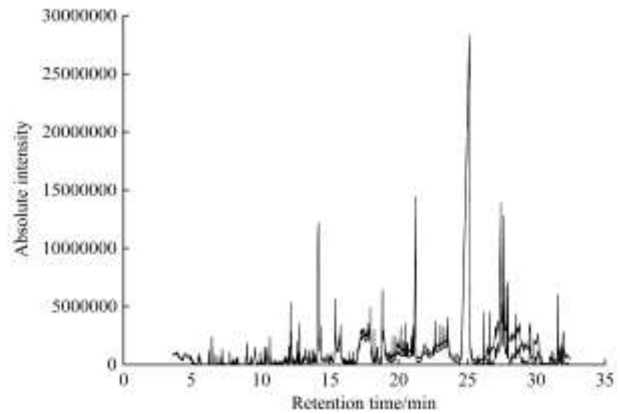

Figure 2 TIC diagram of *Schizochytrium limacinum* pyrolytic bio-oil at 350 ℃

Based on the further analysis of TIC diagrams of each sample, it can also be obtained that the chemical compounds of *Chlorella pyrenoidosa* identified by GC/MS was the same as those of *Schizochytrium limacinum*, which could be classified in to several groups such as hydrocarbons, acids, aromatics, nitrogen compounds, phenols and polycyclic aromatic hydrocarbons (PAHs). However, the constituents of each compound were not the same at all. In order to better study the influences on pyrolyzed products by temperature, the substances that the match quality were over 80% in each sample under each temperature shall be classified and summarized according to chemical compounds[1,3-4].

Hydrocarbons that naturally present in fossil fuel, are valuable organic components in bio-oil for fuel application[21,24]. Among the compounds listed in Tables 3, the relative content of hydrocarbons in *Chlorella pyrenoidosa* firstly decreased from 350 ℃ to 450 ℃, then up to the highest content of 6.51% at 550 ℃, and finally decreased to 0.05% with increasing temperature from 550 ℃ to 750 ℃. Long-chain fatty acids could not only generate biodiesel, but also produce straight-chain hydrocarbons via the denitrification and deoxygenation reactions[3]. Only three kinds of fatty acids were detected and identified as long-chain compounds (C_{16}-C_{18}) that were suitable for biodiesel production[18]. The relative content of fatty acids decreased with the increasing temperature in the range of 350 ℃ to 750 ℃ and the highest content (39.44%) was obtained at 350 ℃. As important fuel additives, aromatics could increase octane number of transportation fuel[22]. The aromatics listed in Table 3 were consisted of benzene and its derivatives, and of which was not detected until 450 ℃, the relative content of aromatics increased from 450 ℃ to 650 ℃ and reached up to the highest content of 28.24% at 650 ℃, then followed by a little decrease with increasing temperature from 650 ℃ to 750 ℃.

Table 3 Effects of temperature on identification and quantification of chemical compounds from *Chlorella pyrenoidosa*pyrolyzed at 350 ℃-750 ℃ (Quality>80%)

Compounds	Relative content /%				
	350 ℃	450 ℃	550 ℃	650 ℃	750 ℃
Hydrocarbons					
Tricyclo[4.3.1.0(2,5)]decane	-	-	1.19	-	-
Tridecane	-	0.52	-	-	-
Nonadecane	1.03	-	-	-	-
Bicyclo[4.2.0]octa-1,3,5-triene	-	-	-	4.78	-
1,3,5,7-Cyclooctatetraene	-	-	2.02	-	0.05
2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-(E)]]-	3.85	2.81	3.30	-	-
Sum	4.88	3.33	6.51	4.78	0.05
Fatty acids					
n-Hexadecanoic acid	5.18	6.49	2.24	0.89	2.22
9,12-Octadecadienoic acid (Z,Z)-	-	0.22	-	-	-
9,12,15-Octadecatrienoic acid, (Z,Z,Z)-	34.26	9.48	-	-	-
Sum	39.44	16.19	2.24	0.89	2.22
Aromatics					
Benzene, 1-propynyl-	-	-	-	-	2.04
Benzene, 1-ethyl-2-methyl-	-	-	-	-	0.30
Benzene, 1-ethyl-4-methyl-	-	-	-	-	0.25
Benzene, 1,3,5-trimethyl-	-	-	-	-	0.33
Toluene	-	-	17.07	24.72	18.59
Ethylbenzene	-	0.78	4.56	3.62	4.02
Sum	0	0.78	21.63	28.24	25.33
Nitrogen compounds					
Hexadecanamide	1.03	0.25	-	-	0.96
Benzyl nitrile	-	0.99	-	0.07	-
Indole	1.68	2.86	6.66	-	7.35
Aniline	-	-	-	0.29	-
Pyridine, 2-methyl-	-	-	-	-	0.99
Sum	2.71	4.10	6.66	0.36	9.30
Phenols					
Phenol	-	3.24	2.38	4.30	1.98
Phenol, 4-methyl-	-	-	5.76	7.02	5.64
Sum	0	3.24	8.14	11.32	7.62
PAHs					
Naphthalene, 1-methyl-	-	-	-	-	1.14
Naphthalene, 1,4-dimethyl-	-	-	-	-	0.39
Naphthalene, 1,5-dimethyl-	-	-	-	0.44	-
Sum	0	0	0	0.44	1.53

Besides, nitrogen compounds were mainly comprised of amides, nitriles, indoles and pyridines, which account for potential emission of nitrogen oxides during fuel combustion[19-21]. The content of nitrogen compounds increased with increasing temperature from 350 ℃ to 550 ℃, then had a huge decline in the range of 550 ℃ to 650 ℃, and finally reached the maximum content of 9.3% at 750 ℃.

A few typical pollutants called PAHs which naturally exist in fossil fuels were also detected. The relative content of PAHs was not detected until the temperature reached 650 ℃, which was only 0.44%. Then with the increased temperature the highest content of 1.53% was shown at 750 ℃. Furthermore, the relative content of phenols and its derivatives, which are of commercial importance, increased with the rising temperature in the range of 350 ℃ to 650 ℃, and reached the highest content of 11.32% at 650 ℃.

As for *Schizochytrium limacinum*, different hydrocarbon compounds were released at different temperatures as the temperature increased (Table 4). The hydrocarbons of pyrolysis products from *Schizochytrium limacinum* were mainly consisted of alkanes and alkenes, which had a steady increase with the elevated temperature from 350 ℃ to 650 ℃. The highest content of 17.58% was obtained at 650 ℃, which was much higher than *Chlorella pyrenoidosa* (6.51%). Table 4 further shows that the trend of fatty acids content showed a gradual descending trend accompanied by an increase in temperature from 350 ℃ to 750 ℃, which was in accordance with *Chlorella pyrenoidosa*. The relative content of fatty acids from *Schizochytrium limacinum* reached its highest value (59.73%) at 350 ℃, and was also higher than *Chlorella pyrenoidosa* (39.44%) due to its high lipid content which was mainly converted to fatty acids during pyrolysis process[21]. Both results (*Chlorella pyrenoidosa* and *Schizochytrium limacinum*) were in accordance with previous reports that lower temperature could generate more fatty acids during the pyrolysis process[21,22]. However, the relative content of aromatics for *Schizochytrium limacinum* showed a step increase with the elevated temperature from 350 ℃ to 750 ℃, especially in the range of 650 ℃ to 750 ℃, the aromatics content had a huge generation and climbed up to the highest value of 33.27% at 750 ℃ which was much higher than *Chlorella pyrenoidosa* (28.24%).

The relative content of nitrogen compounds increased with increasing temperature from 350 ℃ to 650 ℃ and up to its highest value of 3.94%, which was lower than *Chlorella pyrenoidosa* (9.30%), this was probably due to the N content of *Schizochytrium limacinum* was much lower than that of *Chlorella pyrenoidosa*[19,23]. The relative content of PAHs showed a step increase with elevated temperature in the range of 350 ℃ to 650 ℃; when the temperature raised up to 750 ℃, the PAHs content had a huge boost and reached its highest value of 6.52% which was also higher than *Chlorella pyrenoidosa* (1.53%). Besides, a few phenols compounds were detected and decreased with elevated temperature from 350 ℃ to 750 ℃, and the highest content (6.66%) obtained at 350 ℃ was lower than *Chlorella pyrenoidosa* (11.32%).

In order to perform a better comparison of the bio-oil production potential with these two microalage strains, Figure 3 showed the sum of relative content of hydrocarbons, aromatics and acids for *Chlorella pyrenoidosa* and *Schizochytrium limacinum* as a function of temperature. As seen, the sum of relative content of the three substances achieved maximum of 44.32% and 60.99% at 350 ℃ respectively. Pollutants release of nitrogen compounds were respectively 2.71% (*Chlorella pyrenoidosa*) and 0.7% (*Schizochytrium limacinum*) at the same time, while pollutants release of PAHs were not detected. It was clear that the pyrolysis products obtained from *Schizochytrium limacinum* had higher relative content of the three substances and lower pollutants than *Chlorella pyrenoidosa*, which suggested that *Schizochytrium limacinum* was more suitable for the exploitation of energy through pyrolytic conversion.

Table 4 Effects of temperature on identification and quantification of chemical compounds from *Schizochytrium limacinum*pyrolyzed at 350 ℃-750 ℃ (Quality>80%)

Compounds	Peak area/%				
	350 ℃	450 ℃	550 ℃	650 ℃	750 ℃
Hydrocarbons					
Cyclopropane, 1-methyl-2-pentyl-	-	-	2.67	5.27	1.83
Cyclopropane, 1-pentyl-2-propyl-	-	-	-	3.05	-
cis-1-Butyl-2-methylcyclopropane	-	-	2.00	-	1.85
Cyclododecane	-	-	3.27	-	5.82
Tridecane	0.01	-	0.72	0.38	0.37
Tetradecane	-	1.86	0.33	3.23	-
Pentadecane	1.25	5.75	4.75	-	1.46
1-Heptene	-	-	0.58	2.51	-
1,3,5-Cycloheptatriene	-	1.36	-	-	0.31
1-Decene	-	-	3.80	5.89	2.67
1-Undecene	-	-	1.18	-	2.51
1-Dodecene	-	-	1.50	3.57	-
1-Tridecene	-	-	0.86	2.00	1.94
Sum	1.26	7.97	13.72	17.58	9.26
Fatty acids					
Dodecanoic acid	1.74	0.2	-	-	-
Tetradecanoic acid	5.92	9.48	7.87	-	1.64
n-Hexadecanoic acid	42.87	33.83	18.97	2.18	1.07
Heptadecanoic acid	0.09	-	-	-	-
Octadecanoic acid	2.5	2.22	-	-	-
6-Octadecenoic acid	6.61	-	-	-	-
9,12-Octadecadienoic acid (Z,Z)-	-	0.78	-	-	-
Sum	59.73	46.51	26.84	2.18	2.71
Aromatics					
Benzene, propyl-	-	0.28	1.31	1.24	1.19
Benzene, butyl-	-	0.41	0.36	-	-
Benzene, 1-butynyl-	-	-	-	1.57	4.75
Benzene, 1,3-dimethyl-	-	-	-	-	1.91
Benzene, 1-ethenyl-2-methyl-	-	-	-	-	2.41
Benzene, 1-ethyl-2-methyl-	-	-	-	-	1.75
Benzene, 1-ethyl-3-methyl-	-	-	-	1.08	0.04
Biphenyl	-	-	-	0.29	0.62
Toluene	-	-	1.86	7.94	9.85
p-Xylene	-	0.74	-	1.26	-
Ethylbenzene	-	-	-	2.67	3.44
Styrene	-	0.03	-	4.32	6.87
cis-.beta.-Methylstyrene	-	-	-	1.23	0.44
Sum	0	1.46	3.53	22.60	33.27

Compounds	Peak area/%				
	350℃	450℃	550℃	650℃	750℃
Nitrogen compounds					
Tetradecanamide	-	-	-	1.27	0.66
Hexadecanamide	0.70	0.20	1.27	2.18	2.09
Hexadecanenitrile	-	-	0.55	0.46	-
Indole	-	0.24	-	-	-
Pyridine	-	0.19	-	0.03	-
Sum	0.70	0.63	1.82	3.94	2.74
Phenols					
Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-	0.3	-	-	-	-
1,2-Benzenediol	6.36	1.39	0.05	-	-
Sum	6.66	1.39	0.05	0	0
PAHs					
Naphthalene	-	-	-	0.10	0.03
Naphthalene, 1-methyl-	-	0.06	-	0.59	2.06
Naphthalene, 2-ethenyl-	-	-	-	-	0.74
Naphthalene, 1,3-dimethyl-	-	-	-	-	0.57
Naphthalene, 1,2-dihydro-	-	-	0.55	-	2.1
1,4-Methanonaphthalene, 1,4-dihydro-	-	0.07	-	0.02	1.02
Sum	0	0.13	0.55	0.71	6.52

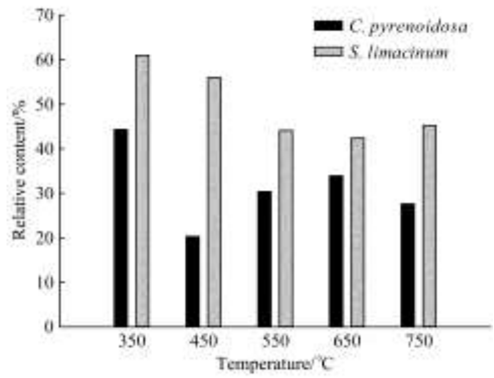

Figure 3 Sum of relative percentages of hydrocarbons, aromatics and acids under different pyrolysis temperatures (350℃-750℃)

4 Conclusions

The main categories of pyrolysis products of *Chlorella pyrenoidosa* were hydrocarbons, aromatics, fatty acids, nitrogen compounds, PAHs, phenols and so on, which were the same as that of *Schizochytrium limacinum*. The pyrolysis of *Chlorella pyrenoidosa* at 350℃ produced a maximum yield of bio-oil (44.32%) compared to 60.99% that *Schizochytrium limacinum* generated at 350℃; furthermore, the generation of such pollutants (nitrogen compounds) during *Chlorella pyrenoidosa* pyrolysis at 350℃ was 2.71% which was much higher than that of *Schizochytrium limacinum* (0.7%) at 350℃. Hence, *Schizochytrium limacinum* is more suitable for producing bio-oil in terms of optimal quality and yield against *Chlorella pyrenoidosa*.

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