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Pyrolysis of wild cyanophyta from Chaohu lake for bio-oil

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Abstract. **To solve the environmental problems caused by the algae, pyrolysis experiment was studied to produce bio-oil with the wild cyanophyta from Chaohu lake for the first time. The results showed that the suitable temperature, carrier gas flow rate, and the smaller particle size were better for liquid products generation, the liquid (bio-oil) yield obtained maximum (66 %) at temperature of 450 ^{o}C, carried gas flow rate of 50 mL/min and particle size of less than 0.25 mm. The main ingredients of liquid product from cyanophyta pyrolysis consisted of hydrocarbons, nitrogenous compounds, acids and other organic compounds (such as alcohols, phenols esters and non-identified materials). Acid content was the highest and greatly affected by temperature. The content of hydrocarbons was about 15%.**

Keywords: **cyanophyta, pyrolysis, bio-oil, Chaohu lake.**

I INTRODUCTION

Chaohu lake is the main water resources and scenic spot in Hefei city of China, however, cyanophyta frequently occurred in August and September every year caused serious water pollution problem of eutrophication [1]. The previous research showed that the amount of cyanophyta (the dry biomass) was 5×10^5 t ~ 7×10^5 t every year [2]. There were no thorough methods to resolve the problem, the traditional interception and refloatation was the effective and emergency method [3]. A mass of wild cyanophyta by interception and refloatation able to be recycle very few, they were usually open piled up or landfill. Nonetheless, cyanophyta decay produced odor and poison, these polluted the air and surface water or even underground water, caused secondary pollution [4]. So it is urgently to properly resolve the refloatation of cyanophyta.

As we all know, biomass can accomplish thermal decomposition in a very short time under the condition of anaerobic or less oxygen, and then the yield rapidly condensed, the reaction process is biomass pyrolysis. It can reduce the secondary pyrolysis chance of the initial pysolysis products, and increase the yield of liquid products. The biomass pyrolysis can convert the abandoned biomass into the pyrolysis oil, which could use as chemical raw materials or alternative energy sources for fossil fuels. The process is simple, and easy to realize, it could achieve the biomass energy conservation and waste recycling use. So it's necessary to develop the biomass pyrolysis [5-10].

There were lots of researches on the algae for bio-oil by the pyrolysis process, but most of the algae was artificial cultivation. This study used the wild cyanophyta from Chaohu lake as raw material for bio-oil by the pyrolysis process for the first time. The influence of temperature, carrier gas flow rate, and particle size for cyanophyta pyrolysis were investigated, and the composition of pyrolysis liquid was analyzed. The research could provide technical and theoretical basis for the wild cyanophyta treatment and application of pyrolysis liquid.

II MATERIALS AND METHODS

Materials

The analytical grade of methyl alcohol, ethanol, sodium hydroxide, and the chromatographical grade of n-hexane were purchased from Sinopharm chemical reagent Co. Ltd., China. The secure without

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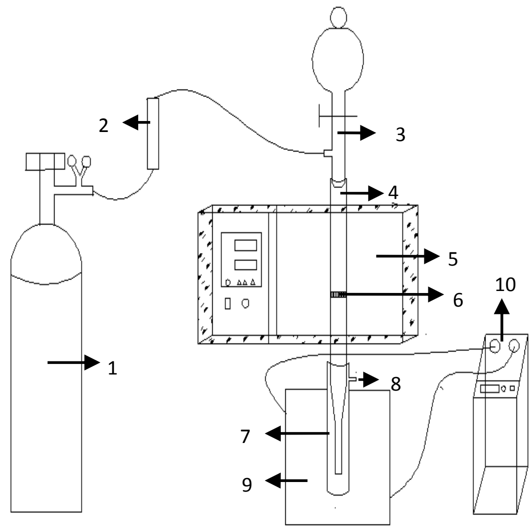
pyridine of Karl Fischer reagent was obtained from Shanghai Xin Zhong chemical science Co. Ltd., China.

The cyanophyta was refloated from the Caohu lake, then it was treated by dehydration, drying, crushing, and sieving. Afterward, it was stored in a dry vacuum oven for further investigate. The cyanophyta powder properties showed in Table 1.



Experimental device and procedure

Fig. 1 Schematic diagram of pyrolysis device

(1 nitrogen cylinder, 2 flow meter, 3 feed tube, 4 reaction tube, 5 vertical tube furnace, 6 quartz pads layer, 7 collection tube, 9 non-condensable outlet, 10 circulating cooling system)

The pyrolytic device schematic diagram was shown in Fig. 1, it constituted by three units of feedstock, reaction, and product collection. The unit of feedstock was comprised by pear type glass tube, the unit of reaction made of vertical tube furnace (OTF-1200X-S-V7) and quartz tube, the unit of product collection was consisted of oil collecting tube and circulating cooling system.

A mount of cyanophyta powder was sent to the feedstock, at the same time, a stream of pure nitrogen added to keep the anaerobic environment. When the vertical tube furnace reached the target temperature, turned on the reaction unit and the temperature was maintained for 10 min. The bio-oil collected by the collection tube from the circulating cooling system (0 ^{o}C).

Analytical methods

Elemental analysis was analysed by vario SL cube (Elementar, German). The composition was analysed by Clarus SQ8 GC-MS, the chromatographic column was Elite-5MS (50 m*0.25 mm*0.25 um), temperature of the injection port was set at 250 ^{o}C, the column kept at 50 ^{o}C for 2 min, then raised the temperature to 300 ^{o}C with heating rate of 10 ^{o}C/min and kept the temperature for 10 min. The carrier gas was helium, with the flow rate 1.0 mL/min, and split ratio 20:1. The GC transmission line temperature was 280 ^{o}C, ion source temperature was 230 ^{o}C, the scan quality range was 33 to 450, solvent delay was 2.8 min.

TABLE 1
PROPERTIES ANALYSIS OF THE CYANOPHYTA POWDER

Industry analysis (%)				Elemental analysis (%)				Main ingredients (%)		
Water content	Ash	Volatile matter	Fixed carbon	C	H	O	N	Crude protein	Crude fat	Crude polysaccharide
4.76	10.75	69.52	14.97	46.68	7.36	38.95	7.02	43.88	6.44	7.46

III RESULTS AND DISCUSSION

Effect of temperature on the pyrolysis product distribution of cyanophyta

Temperature is an important influencing factor in the biomass pyrolysis process, it can affect product yield and composition [11]. The product distribution of cyanophyta pyrolysis affected by temperature was showed in Fig. 2. When the temperature was raised, the change trend of liquid yield was increased first and then decreased. When the temperature between 300 to 450 ^{o}C, the liquid yield increased continuously, reached the maximum value at the 450 ^{o}C and then decreased slowly. The solid yield was decreased and the gas yield showed an increasing trend with increasing temperature. The reasons were analyzed as follows: thermal decomposition of cyanophyta can break chemical bonds with smaller bond energy and produced less volatile substances under the low temperature. Therefore, the pyrolysis liquid and gas yield were low. The pyrolysis reaction was occurred acutely at high temperature, so the temperature continuously raised, the pyrolysis reacted sufficiently and produced more volatile material, accordingly, the liquid and gas yield increased, the yield of solid declined [12]. But when the temperature increased further, the volatile substance produced by secondary pyrolysis of bio-oil in higher temperature, bio-oil was translated to small molecule non condensable gas, so the liquid yield decreased.

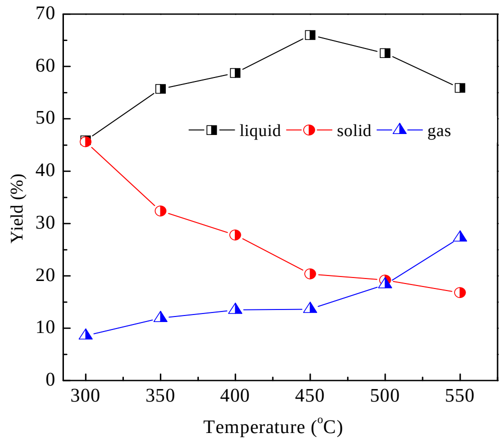


Fig. 2 Effect of temperature for cyanophyta pyrolysis

Effect of carrier gas flow rate for cyanophyta pyrolysis

The influence of carrier gas flow rate on the distribution of the pyrolysis products of cyanobacteria was exhibited in Fig. 3. It was observed that the temperature was maintained constant at 450 °C, when the carrier gas flow rate was lower than 30 mL/min, the liquid yield significantly increased with the enhance of flow rate. The liquid yield reached the maximum at flow rate of 50 mL/min, the liquid yield gradually decreased with the continue improve of flow rate, because of the lower carrier gas flow rate can prolong the retention time of volatile substances in the reactor and increase the possibility of secondary pyrolysis. Specifically, when the carrier gas flow rate was too high (e. g, more than 50 mL/min), the volatile was taken out of collecting pipe by the carrier gas rather than completely condensed, which reduced liquid yield. In addition, many cold gas carried by the high flow rate of carrier gas can reduce the temperature of reaction.

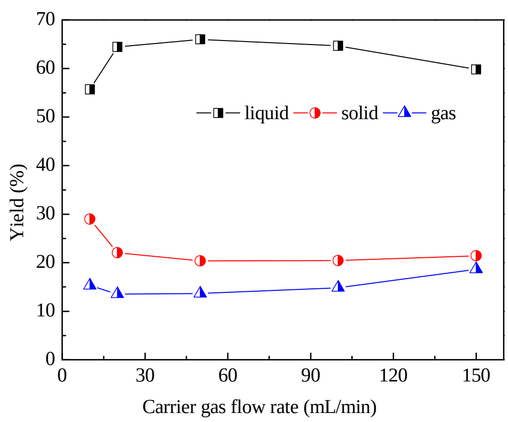


Fig. 3 Effect of carrier gas flow rate for cyanophyta pyrolysis

Effect of particle size of raw materials for cyanophyta pyrolysis

Raw material particle diameter was also an important factor affecting biomass pyrolysis [13]. Fig. 4 showed the influence of particle diameter on the cyanophyta pyrolysis product distribution. When the gradual increased of raw material particle diameter, liquid yield decreased, solid yield raised steadily, gas yield declined slightly. Due to the smaller particle diameter may be more beneficial to heat transfer, the raw material particles can rapidly reach the specified temperature of pyrolysis reaction. Furthermore, pyrolysis of volatile substances precipitation rate was speed among the smaller particles that reducing the possibility of the secondary pyrolysis reaction and improving the liquid yield. On the contrary, when the larger diameter of the particle was heated, the heating rate of the center of the particle was relatively slower than the surface. Based on this fact, the center of the particle was easy to generate carbon at lower pyrolysis temperature, so the higher solid yield.

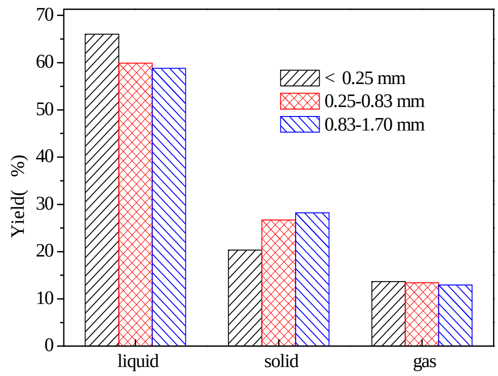


Fig. 4 Effect of particle size of raw materials for cyanophyta pyrolysis

Cyanophyta pyrolysis liquid analysis

Cyanophyta pyrolysis liquid was analyzed and exhibited in Table 2, the results showed that the moisture content was about 28.31 %, which was higher than the raw material, because of the process of pyrolysis produced by the combining of hydrogen and oxygen. It had a much greater density than light and heavy fuel, which was determined to be 1.16 g/cm^3. In addition, the pyrolysis liquid was very corrosive due to the high acidity (129.31 mg KOH/g). The calorific value of pyrolysis liquid (25.4 MJ/kg) was lower than that of bio-oil and gasoline, which may be related with the high moisture content.

TABLE 2
PROPERTIES OF LIQUID PRODUCED FROM CYANOPHYTA PYROLYSIS

category	fator	reuslt
React condition	temperature	500 °C
	carrier gas flow rate	50 mL/min
	raw material particle size	less than 0.25 mm
Chemical element	C	47.12 %
	H	9.31 %
	O	35.14 %
	N	8.44 %
Characteristics	moisture content	28.31 %
	density	1.16 g/cm^3
	acidity	129.31 mgKOH/g
	calorific value	25.4 MJ/kg

The main component of algae pyrolysate was investigated with the application of the GC-MS. The total ion chromatogram was showed in Fig. 5, the main content was demonstrated in Table 3.

TABLE 3
THE MAIN CONTENT IDENTIFIED BY GC-MS

No.	Retention time (min)	Compound	CAS#	Chemical formula	Area (%)
1	16.18	heptadecane	629-78-7	$C_{17}H_{36}$	11.95
2	17.24	octodecane	593-45-3	$C_{18}H_{38}$	3.46
3	17.62	phytol	102608-53-7	$C_{20}H_{40}O$	7.93
4	18.05	phytol	102608-53-7	$C_{20}H_{40}O$	4.05
5	18.99	palmitic acid	57-10-3	$C_{16}H_{32}O_2$	29.10
6	20.26	Phytosterol	150-86-7	$C_{20}H_{40}O$	4.77
7	20.66	oleic acid	112-80-1	$C_{18}H_{34}O_2$	4.65
8	20.81	stearic acid	57-11-4	$C_{18}H_{36}O_2$	6.01
9	20.95	hexadecanamide	629-54-9	$C_{16}H_{33}NO$	6.28
10	22.46	oleamide	301-02-0	$C_{18}H_{35}NO$	4.72
11	22.67	Octadecannamide	124-26-5	$C_{18}H_{37}NO$	3.93

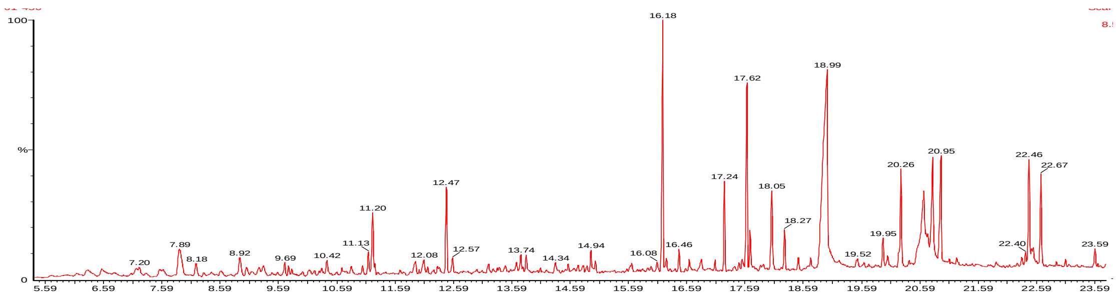


Fig. 5 Total ion chromatogram of product from cyanophyta pyrolysis liquid

From the analysis result in Table 3, it was obvious that the pyrolysis liquid composition was complex and the content of component was significantly different to each other. Some compounds had the higher content in the range of retention time 16～23 min, such as the peak area of palmitic acid, heptadecane and phytol were 29.10 %, 11.95 % and 7.93 %, respectively. All the detected components can be divided into four categories, for example, hydrocarbons, nitrogen-containing compounds, acids and other organic matter (such as alcohols, phenols, esters and so on).

The distribution of these four components at different reaction temperature was different. As showed in Fig. 6, whatever the temperature considered, the content of acids (including palmitic acid, oleic acid, stearic acid, etc.) were the highest. However, the percent of acids were reduced when the temperature was higher. The highest content of acids were mainly due to the high levels of ash of algae raw materials, which contained the alkali metals (such as sodium, potassium, etc) had catalytic effect on biomass pyrolysis process and produced large amounts of acids [14]. The pyrolysis liquid with high content of acidic substances was corrosive and instability, so it will adverse to long-term stable operation of the engine. The important issue of bio-oil preparation and refining was how to reduce the content of acids. The two common methods were the raw ash pyrolysis and pyrolysis liquid catalytic esterification.

There lative content of nitrogen-containing was increased from 12.02 % to 24.92 % as the temperature raised from 300 ^oC to 450 ^oC. It was increased significantly can be attribute to the breakage of C=N bond in the molecular structure of compound caused by high temperature. With respect to nitrogen-containing of cyanophyta pyrolysis liquid, this was mainly from the pyrolysis of peptide and amino acid of protein. Carbonyl compounds, indole, nitrile and other nitrogen-containing substances [15] were produced from many processes of the pyrolysis of amino acid, such as intramolecular elimination reaction of CO_2, stern depolymerization, etc.

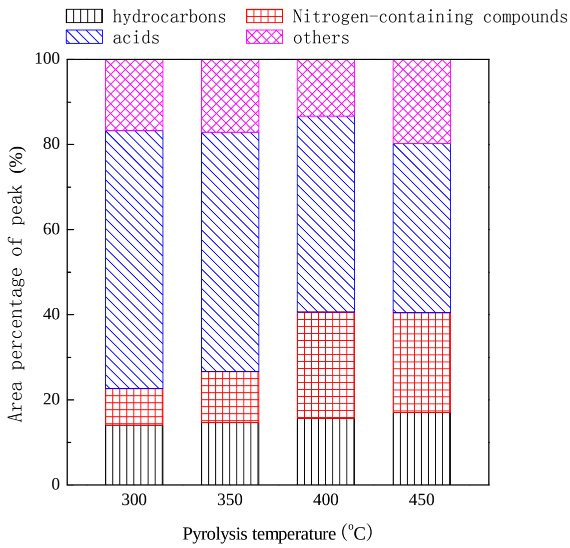


Fig. 6 The distribution of four components at different reaction temperature

Hydrocarbons mainly contained alkyl radical from the fracture of aliphatic groups of cyanophyta. It also included normal alkane and alkenes generated from these alkyl radical gain and loss of hydrogen free radical [15].The content of the hydrocarbons were about 15%, and less affected by the temperature, which was importance to instead of fossil fuels by refining the oil from the cyanophyta pyrolysis.

The other organics contained alcohols, esters, phenols and amount of an unknown substance. The alcohols were mainly refers to the phytol, which were lipophilic long-chain fatty alcohol as the main pyrolysis products of chlorophyll. The main esters were palmitic acid and stearic acid methyl ester, which were gained esterification of alcohol and acid in the process of pyrolysis storage rather than the direct product [15].

IV CONCLUSIONS

The main findings of this study can be summarized as follows:

(1) With the increasing temperature, cyanophyta pyrolysate liquid yield was increased at the early stage and then decreased, the solid yield reduced gradually, and the gas production rate was raised gradually. With the the increasing carrier gas flow rate, cyanophyta pyrolysis liquid yield was also increased firstly and then reduced, just change trend was relatively small. Additionally, the smaller the particle size of cyanophyta was more conducive to the formation of liquid products. In this experiment, cyanophyta pyrolysis liquid (bio-oil) yield was as high as 66 % when temperature was 450 ^oC, carrier gas flow rate was 50 mL/min, and the particle size was less than 0.25 mm.

(2) The main component of cyanophyta pyrolysis liquid was explored with the application of the GC-MS. Results showed that the mainly composed of hydrocarbons, nitrogen-containing compounds, acids and other organic matter (such as phenols, alcohols, esters and other substances). Furthermore, the hydrocarbon was about 15 %, which was little affected by temperature and helpful for cyanophyta pyrolysate. However, the ratio of acids and nitrogen-containing compounds of cyanophyta pyrolysis liquid were strongly influenced by temperature. The content of acids gradually reduced with the increasing temperature, while the high temperature was beneficial to production of nitrogen-containing compounds.

V ACKNOWLEDGMENTS

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