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Fractional Pyrolysis of Algae and Model Compounds[†]

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Pyrolysis of algae from Taihu Lake water blooms for bio-oil production was conducted from 473 K to 773 K by a fractional way in six steps. Palmitic acid, agarose and egg white were used as model compounds to study the origin of bio-oil ingredients and interaction of the intermediates from the algae components. In the first step at 473 K, the bio-oil obtained was composed of *n*-heptadecane and some small molecule acids. Quantities of carboxylic acids (mainly palmitic acid) and some amides, hydrocarbons, esters *etc.* were evolved in the second step at 523 K. For the third step at 573 K, except the carboxylic acids (still mainly palmitic acid), amides, nitriles, and phenols also accounted for a large proportion whereas respectable amount of indoles and alcohol ketones were attained. The main products in the later three steps were nitriles and phenols at 623 K, hydrocarbons and phenols at 673 K, and only phenols at 773 K, respectively. A higher heating value (HHV) of 36.0 MJ/kg of the bio-oil was obtained at 673 K. The hydrocarbons, palmitic acid and esters in the bio-oil were derived from lipids. The phenols, indoles, pyrroles, small molecular acids, amides like acetamide and some nitriles like phenyl-acetonitrile were generated from proteins. Amides and nitriles were also dated from the interaction of pyrolytic intermediates of lipids and proteins. Fewer products directly from the direct pyrolysis of saccharides were detected in the algae bio-oil due to the interaction of pyrolytic intermediates of saccharides and proteins in algae, and those interactions resulted in the formation of oligomers in the bio-oil at 473 and 523 K. Whereas very weak interaction was observed between lipids and saccharides. The process of fractional pyrolysis by varying temperature provided an advisable way for improving the selectivity of bio-oil from direct pyrolysis, and made the bio-oil much more applicable in down streaming utilization.

Key words: Fractional pyrolysis, Algae, Interaction, Model compound

I. INTRODUCTION

With the continual exploitation and consumption of fossil energy, biomass as an alternative plays a significant part in the development of renewable energy [1, 2]. Microalgae is one of the most promising raw materials because of their short growth cycle, high biomass value, strong capability of CO_2 capture and no occupation of arable lands compared to many other biomass resources [3−5]. Therefore, the conversion of microalgae draw more and more attention for bio-energy production.

Many studies on microalgae conversion have been reported recent years, and thermochemical conversion was a commonly used method [6−8], in which direct pyrolysis as an effective and conventional method had been widely used and great efforts had been devoted to this respect [9−12]. The results obtained presented big difference due to the diversity of algae species and complexity of algae composition. Liu *et al.* investigated the thermochemical characteristics of *Hapalosiphon sp.* and *Botryococcus braunii* [13]. The results indicated that not only the low calorific value of the bio-oil showed big difference but also the pyrolysis activation energy presented large disparity for the two kinds of microalgae. Gong *et al.* studied the pyrolytic characteristics of the two low lipid microalgae, *Chlorella vulgaris* and *Dunaliella salina* [14]. They concluded that the two kinds of microalgae were not just diverse in thermochemical characters, and there were big differences in the distribution and characteristic parameters of the pyrolytic products. The blue-green algae blooms were used as feedstock by Hu *et al.* for bio-oil production [15]. The effects of nitrogen flow rate, particle size and pyrolysis temperature on pyrolysis products were investigated. A maximum oil yield of 54.97wt% with a higher heating value of 31.9 MJ/kg and an O/C molar ratio of 0.16 was attained under optimum conditions. However, the products got in most direct pyrolysis of microalgae were very complex. In the early 2001, fractional vacuum

[†]Dedicated to Professor Qing-shi Zhu on the occasion of his 70th birthday.

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pyrolysis of birch wood chips for the products of phenolic compounds was reported by Pakdel *et al.* [16]. They considered that fractional pyrolysis approach with different temperature range could simplify the pyrolysis oil composition, and facilitate the separation and purification of phenol products formed. In the next year, Agblevor *et al.* [17] utilized catalytic pyrolysis and fractional condensation to selectively convert hybrid poplar wood. Furthermore, Westerhof *et al.* [18] and Gooty *et al.* [19] both attempted to fractionally condense the biomass pyrolytic vapor and made certain achievements in fractionating the biomass pyrolysis products.

In our previous work [20], fractional pyrolysis-stepwise pyrolysis at a series of different temperatures based on the characteristics of components in algae, was used for improving the selectivity of algae bio-oil. The results suggested that pyrolysis fractionated by temperature was an effective way to enhance the quality of algae bio-oil. In the present work, the Taihu Lake water blooms were used as algae feedstock to investigate the fractional pyrolysis behavior of components in algae using comparatively palmitic acid, agarose and egg white as model compounds.

II. MATERIALS AND METHODS

A. Feedstock

The Taihu Lake water blooms, mainly *Cyanobacteria*, outbroke in the warm seasons every year because of the eutrophication of water body. The algae samples used in the present work were collected in Taihu Lake, Jiangsu Province of China on the summer of 2013, which were washed with freshwater and dried in sunlight after collection. The dried algae were then milled and sieved into powder with a particle size of less than 80 meshes and dried again in an oven at 373±1 K overnight before use.

B. Pyrolysis experiment

The device used was modified on the basis of Zeng *et al.* [21]. As shown in Fig.S1 (in supplementary material), an electric furnace with a hole across one side was used. The reactor was composed of an outer quartz tube, a thermocouple in appropriate position hung on the furnace through the hole, and an inner quartz tube with algae in the top pool inserted into the outer tube. Carrier gas of nitrogen controlled by a rotameter was introduced into the reaction system from the bottom of the outer tube. A condenser immerged in ice water was used for condensates collection. An absorption bottle with water linked to the condenser was used for ammonia absorption, after which all the non-condensable products was collected with a vacuum gas bag.

In a typical run, 3.0 g algae powder was added into the inner tube and the system was swept with N_2 about 10 min at a flow rate of 40 mL/min to get a completely inert atmosphere. The feedstock firstly pyrolyzed at 473 K for 2 h, and then the remaining char was subjected to pyrolysis at 523 K for 2 h. The char obtained at 523 K was consecutively pyrolyzed at 573, 623, 673, and 773 K, respectively. The liquid and gaseous products were collected separately at each temperature. The pyrolysis of model compounds was carried out in the same way as that of algae.

The yields of products were calculated as follows: the weight difference of both the condenser and the outer tube before and after the pyrolysis was recognized as total liquid weight, and the water in liquid products was removed by rotary evaporation, the remained liquid was considered as bio-oil weight, and the weight difference before and after rotary evaporation was the weight of water. The weight of char was calculated by the weight difference of inner tube before and after pyrolysis. The gas quantity was calculated by overall mass balance, and in which the ammonia was quantified by titration. All data were an average of replicates (at least, 3 times) and calculated on the basis of algae feedstock weight, the relative deviation was about ±0.3%.

C. Analysis methods

The main chemical composition of algae feedstock and char from fractional pyrolysis were analyzed. The Soxhlet extraction was used for the total lipids extraction with a mixture solvent of chloroform/methanol (2:1, volume ratio) [22, 23]. A certain amount of solid with a filter paper surrounded was placed into the Soxhlet extractor and a flask with moderate solvent was connected to the extractor. The system was extracted at 343±2 K in water bath under condensation reflux condition until the solvent in the extractor was colorless. Then the flask was rotary evaporated and weighted, the weight difference of the empty and rotary evaporated flask was considered as the amount of total lipids. It was observed that the extractives from the thermally-treated algae (char) contained nitriles and amides *etc.* Meanwhile, the major component of lipids was palmitic acid. Therefore, the quantitative content of palmitic acid in the total lipids was used to represent the lipids content. The content of saccharides was measured by the the dinitrosalicylic acid (DNS) method [24]. The solid was treated with 3 mol/L HCl at 373 K for 60 min and then cooled to room temperature, filtered, washed with water, neutralized the solution to pH=7 with NaOH, transferred to a volumetric flask and diluted to the scale mark with water. A certain amount of mixture of the neutralized filtrate and DNS solution were steamed for 5 min in boiling water. Then the absorbance of the solution was determined by ultraviolet visible spectrophotometer at a wavelength of λ_{max}=540 nm. The content of saccharides was calcu-

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lated by the standard equation obtained from standard glucose concentration to absorbance, and multiplied by a glucose-to-saccharide conversion factor of 0.9. The proteins content was determined by combustion method (National Standard in China, GB 5009.5-2010) with a nitrogen-to-protein conversion factor of 6.25. The determination of inorganics was conducted by inductively coupled plasma spectrometry (ICP).

The bio-oil components were analyzed by GC-MS (Agilent Technologies, 6890N GC and 5973 MS) with a HP-INNOWAX capillary column (30 m×0.25 mm× 0.25 μm). Helium with a flow rate of 1.0 mL/min was used as carrier gas. The detector temperature and injector temperature were both 553 K. The temperature program of GC oven was set as follows: the temperature ramp to 383 K at 10 K/min from 313 K followed by ramping to 483 K at 4 K/min, and then the temperature ramp to 513 K at 5 K/min and hold at 513 K for 7 min. The gel permeation chromatography (GPC) of bio-oil was conducted by a HLC-8320 analyzer with two columns of TSK gel super HZM-M and TSK gel super HZ3000 (6.0×150 mm).

The composition of gaseous products (except NH_3) was identified by GC 9710 with a thermal conductivity detector (TCD) using a TDX-1 carbon molecular sieve packed column (2 m×3 mm I.D.). A flow rate of 20 mL/min nitrogen was used as carrier gas. The temperature parameters were as follows: column temperature of 393 K, inlet temperature of 418 K, and detector temperature of 433 K.

Furthermore, all the C, H, and N element contents were attained using a Italy CARLO ERBA 1106 Element Analyzer, while the content of O was calculated by difference.

III. RESULTS AND DISCUSSION

A. Characteristics of feedstock

The proximate analysis of algae feedstock showed the chemical compositions of lipids, saccharides, proteins and ashes are 7.6wt%, 20.4wt%, 42.6wt%, and 21.7wt%. Due to the eutrophication of water body, a large number of proteins and plenty of saccharides were detected in algae feedstock, but only 7.6wt% of lipids were observed. Except these main components, quantities of ashes combined with much inorganics were also found with K, Ca, Na, Mg, Al, Fe, and Si being 0.6wt%, 0.9wt%, 0.4wt%, 0.3wt%, 2.1wt%, 0.8wt%, and 3.2wt%, respectively. Moreover, element analysis showed C, H, N, and O are 38.5wt%, 7.4wt%, 6.6wt%, and 39.3wt%, where Owt%=100−C−H−N−inorganics. Affluent nitrogen was measured in element analysis because of the massive content of proteins and a low higher heating value of 15.9 MJ/kg (HHV=3.55×C^2−232×C−2230×H+51.2×C×H+131×N+20600 kJ/kg) was obtained due to the high amount of oxygen and varieties of inorganics [25].

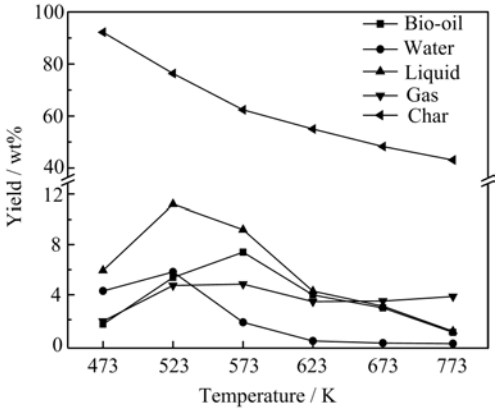

FIG. 1 Yields of products in each step of algae fractional pyrolysis.

TABLE I The composition of liquid products in fractional algae pyrolysis (based on the weight of feedstock) at different temperature.

Product	Composition of products/wt%					
	473 K	523 K	573 K	623 K	673 K	773 K
Water	4.3	5.8	1.8	0.3	0.1	0.1
Carboxylic acids	0.4	2.8	1.3			
Hydrocarbons	1.2	0.5	0.1	0.2	1.1	
Amides		0.6	1.7	0.2	0.2	
Nitriles		0.1	1.3	1.5	0.2	
Phenols			1.3	1.4	1.1	1.0
Indoles		0.1	0.6	0.5	0.1	
Pyrroles			0.2	0.2	0.2	
Alcohol ketones		0.3	0.6			
Esters		0.6	0.1			
Others		0.4	0.4	0.1		

B. Distribution of the products from fractional pyrolysis of algae

Figure 1 illustrates the yields of products from fractional pyrolysis of algae feedstock at different temperature, and the distribution of liquid and gaseous products are presented in Table I and II.

The algae feedstock was firstly pyrolyzed at 473 K, and a few bio-oil and gas were obtained with relatively high amount of water. Only carboxylic acids (mainly small molecule acids) and hydrocarbon (*n*-heptadecane) were detected in the bio-oil. A lot of CO_2 and a spot of CO and NH_3 were attained in the gaseous products.

When the char remained at 473 K was further pyrolyzed at 523 K, respectable amount of bio-oil and gas were attained, and the high water content of 5.8wt% was accounted for more than 50wt% of the total liquid products. The kinds of bio-oil components greatly in-

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TABLE II Distribution of gas products from algae fractional pyrolysis (based on the weight of feedstock) at different temperature.

Product	Composition/wt%					
	473 K	523 K	573 K	623 K	673 K	773 K
H_2				Trace	0.1	0.8
CO	0.2	0.2	0.2	0.4	0.3	0.4
CH_4			Trace	0.1	0.3	0.8
CO_2	1.4	4.4	4.2	2.7	2.7	1.6
NH_3	0.2	0.1	0.5	0.3	0.2	0.3

creased. The main component of bio-oil was carboxylic acids, and the quantity of palmitic acid exceeded 50% of the bio-oil at 523 K. There were also some amides, hydrocarbons, esters *etc.* in the bio-oil. Plenty of CO_2 and a little amount of CO and NH_3 were detected in the gaseous products.

The char obtained at 523 K was used for the next-step pyrolysis at 573 K, where a high bio-oil yield with modest water content was got and the quantity of gas was almost equivalent to that got at 523 K. The bio-oil was still very complex and there was not an obvious main product. Besides carboxylic acids (still mainly palmitic acid), amides, nitriles and phenols also accounted for a large proportion. In addition, respectable amount of indoles and alcohol ketones were detected, and a little other compounds like esters, pyrroles, *etc.* were also detected in the bio-oil. Abundant CO_2 and little CO existed in the gas. The amount of NH_3 apparently increased and trace CH_4 was observed in the gaseous products.

The char attained at 573 K was further pyrolyzed sequentially at the following temperatures of 623, 673, and 773 K by fractional way. The conversion of char at each temperature apparently decreased compared to those at preceding temperatures. The yield of bio-oil descended from 4.0wt% to 1.0wt% and the low water yield descended as well from 0.3wt% to 0.1wt%, whereas the gas amount slightly ascended from 3.5wt% to 3.9wt%. The main products became gradually explicit at these temperatures. That is, mainly nitriles and phenols at 623 K, hydrocarbons and phenols at 673 K, and only phenols at 773 K, respectively. The main gas component was still CO_2 but the quantity decreased to a certain extent. The quantity of CH_4 obviously increased from 0.1wt% to 0.8wt%. H_2 formed and its amount rapidly increased from trace to 0.8wt%. The CO amount got little change.

In the fractional pyrolysis of algae feedstock, the bio-oil was mainly produced in the temperature interval of 523−673 K, but most water was obtained below 573 K. It means that dehydration reactions of algae components mainly occurred at low temperature. Additionally, the majority of gas products was accumulated between 523 and 773 K. The ratio of gas content in all products except char was obviously augmented with the change of pyrolysis temperature, which suggested that high temperature was in favor of scission reaction. The reducing conversion of char indicated the part that could pyrolyze in algae dwindled, *i.e.* the char remained at 773 K was not easily to be thermally cracked any more.

C. Analysis of products from fractional pyrolysis of model compounds

To study the origin of algae bio-oil and interaction of algae components, model compounds of palmitic acid, agarose, egg white and their mixture (mixed in accordance with the ratio of the components in algae feedstock) were pyrolyzed in the same way of algae. The results of liquid products were listed in Table S1−S3 (see supplementary material).

The model compound of palmitic acid changed little at each temperature. The condensed products at 473, 523, and 573 K were mainly quantities of palmitic acid and small amount of water, which indicated that main series of physical changes of fusion, gasification, liquefaction and solidification occurred to palmitic acid. There were a loss of 7.4wt%, 52.0wt%, and 39.6wt% to palmitic acid at 473, 523, and 573 K, respectively. Only 1.0wt% feedstock remained at 573 K. It was indicated that the pyrolysis behavior of palmitic acid was almost completed at 573 K. Only slight dehydration and decarboxylation (only CO_2 detected in gaseous products) reactions occurred at each temperature under inert atmosphere.

For agarose, water was the main product at each temperature and only water was detected at 473 K. Much furan derivatives, a few acetic acid and alcohol ketones were obtained at 523 K. At 573 K, only a bit of furan derivatives and alcohol ketones were achieved. Water alone was detected at the temperature of 623, 673 and 773 K, namely that the pyrolysis of agarose was almost done at 573 K.

The liquid products from pyrolysis of egg white were relatively much more complicated. At 473 K, a little acetic acid and acetamide were attained besides water. Each product category was emerged at 523 and 573 K. Amides, phenols, and sulfur compounds were the main products at 523 K, and much more amides and phenols as well as considerable indoles and nitriles were achieved at 573 K. Phenols were the main products detected at 623 and 673 K, and only water was detected at 773 K.

Almost all the products at each temperature from fractional pyrolysis of the model compound mixture could be found in the algae bio-oil, as shown in Table I. The distribution of liquid products from the mixture was in line with the bio-oil attained from algae pyrolysis. However, there were no hydrocarbons, pyrroles or esters in the liquid products from the model compound mixture. Another variation was that some products

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like indoles and nitriles, which were mainly produced at 473−623 K from model compound mixture, could be only obtained at 523−623 K in the bio-oil from algae. It was indicated that the algae needed a higher temperature to be pyrolyzed than the model compound mixture. Which might be caused by the fact that the combination of algae components might possess some special structure so that it was harder to be pyrolyzed than the model compounds.

D. Analysis of the origin of algae bio-oil ingredients

The conversion of algae components (lipids, saccharides, and proteins) and model compounds (palmitic acid, agarose, and egg white) in fractional pyrolysis was presented in Table III.

The pyrolysis behavior of lipids and saccharides in algae were consistent with the pyrolysis of palmitic acid and agarose. However, the pyrolysis behavior of proteins in algae and model compounds of egg white were different. The maximum conversion of proteins in algae appeared at 523−573 K, whereas the maximum conversion of egg white were at 473−573 K. It was shown that the egg white was easier to be pyrolyzed than proteins in algae. It was also possible that the egg white powder could not completely represent the proteins in algae.

In the first pyrolysis step at 473 K, the three main components were all presented small conversion (0.2wt% for lipids, 1.7wt% for saccharides and 2.8wt% for proteins). The most predominant product was water. The hydrocarbon of *n*-heptadecane in bio-oil was derived from sound lipids, and the small molecule acids of 3-methyl-butanoic acid and 3-methyl-pentanoic acid came from proteins, The postulated formation route from valine and leucine was shown in Scheme I of Fig.S2 (see supplementary material). Dehydration reaction occurred to both saccharides and proteins, otherwise, proteins also underwent decarboxylation and deamination reaction. Due to the interactions existed among the algae components, 473 K was not enough to make palmitic acid, acetic acid and acetic amide escape from algae. Additionally, the GPC results of algae bio-oil and agarose liquid products are shown in Fig.2. It was indicated that there were oligomers in both the algae bio-oil and agarose liquid products at 473 K. In fact, a number average molecular weight (M_n) of 484 with a weight average molecular weight (M_w) of 507 were obtained in the algae bio-oil, and the corresponding M_n and M_w of agarose liquid products at 473 K were 477 and 618, respectively. It was deduced that the oligomers in the algae bio-oil at 473 K might come from the polymerization of the pyrolytic intermediates of saccharides.

At 523 K, the pyrolyzed percentage of lipids, saccharides and proteins were 2.7wt%, 9.3wt% and 2.6wt%, respectively. Although the conversion of saccharides was the highest, the bio-oil contained mainly palmitic acid with the content over 50% of the bio-oil. It was

TABLE III Conversion of main components of algae and model compounds in fractional pyrolysis.

Component	Conversion/wt%					
	473 K	523 K	573 K	623 K	673 K	773 K
Lipids	0.2	2.7	1.4	0.3		
Saccharides	1.7	9.3	3.0	1.7	2.1	1.0
Proteins	2.8	2.6	9.1	5.5	4.1	3.1
Palmitic acid	7.4	52.0	39.6	1.0		
Agarose	10.8	33.8	10.3	6.6	5.2	4.3
Egg white	5.0	20.5	19.9	8.9	6.4	5.1

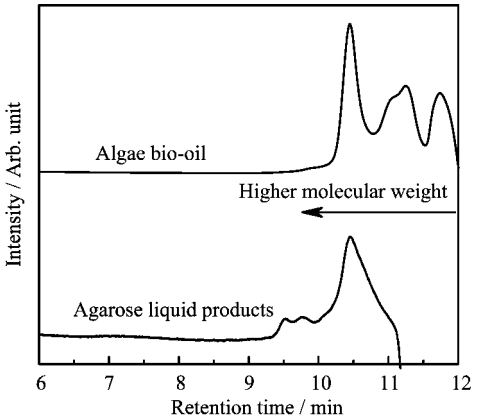

FIG. 2 GPC results of algae bio-oil and agarose liquid products from fractional pyrolysis at 473 K.

dated from lipids with stearic acid, oleic acid and esters in the bio-oil. The small molecule acids of pentanoic acid, 4-methyl-pentanoic acid and crotonic acid came from proteins and the probable formation paths were proposed in Scheme II of Fig.S2 (see supplementary material). Additionally, according to the pyrolysis results of agarose and egg white, both proteins and saccharides might generate acetic acid in the pyrolysis process. Almost all amino acids had the capability of forming acetic acid and the presumptive formation pathways of acetic acid from proteins were proposed in Scheme III of Fig.S2. The formation of acetic acid from the pyrolysis of saccharides was also reported, where pyrolysis of carbohydrates was conducted [26, 27]. The amides, mainly palmitamide, were generated from the reaction of carboxylic acids and ammonia, and the dehydration of amides formed nitriles [20, 28]. Furthermore, a control experiment of mixture of egg white/palmitic acid in ratio of the content of proteins/lipids in algae feedstock was conducted in the same way of algae feedstock. The liquid product distribution given in Table S4 (see supplementary material) suggested that the amides and nitriles (mainly palmitic amide and palmitonitrile) were both increased especially at 573 K. Which proved the existence of interaction between the intermediates from the pyrolysis of lipids and proteins. The biggest contribution of saccharides at this temperature was a

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lot of water production, and the total water yield was more than 50wt% in the liquid products at 523 K. It was different from the pyrolysis of agarose, where the main pyrolysis products were furan derivatives. This phenomenon might be caused by the interaction of the pyrolytic intermediates from saccharides and proteins. Therefore, another two control experiments of pyrolyzing the agarose/palmitic acid and agarose/egg white mixture proportioned based on the content of saccharides/lipids and saccharides/proteins in algae feedstock were also respectively conducted, and the distribution of liquid products were presented in Table S5 and S6 (see supplementary material). The results revealed that furan derivatives existed in the agarose/palmitic acid pyrolysis products but hardly existed in the agarose/egg white pyrolysis products. Moreover, almost all the furan derivatives products in the pyrolysis of agarose were reserved in the agarose/palmitic acid pyrolysis products. Similarly, nearly all the egg white pyrolysis products could be found in the pyrolysis products of agarose/egg white mixture. That is to say, the pyrolysis intermediates from egg white greatly influenced the pyrolysis products of agarose but the reverse was not obvious. In addition, there was no interaction between agarose and palmitic acid or only very weak interaction existed. Thus, NH_3, as one of the most important pyrolysis products of proteins, was used as a reactant added into the carrier gas in the pyrolysis of agarose for another control experiment.

Figure 3 shows the TIC of GC-MS of liquid products from agarose pyrolysis at 523 and 573 K with or without NH_3. When the agarose was pyrolyzed with NH_3 in the carrier gas, only few furan derivatives except water with very small peaks were detected in the liquid products at 523 K, and there were no nitrogenous compounds except NH_3 detected. That is to say, the furan derivatives obtained without NH_3 in the carrier gas were fiercely reduced when NH_3 was added into the carrier gas. Namely, that the small molecule products from agarose might polymerize or decompose in alkalescent circumstance rather than directly interacted with NH_3.

Meanwhile, the GPC results of the liquid products in Fig.4 revealed the change of molecule weight of M_n and M_w of the liquid products from agarose pyrolysis with or without NH_3 in the carrier gas. The M_n of 268 and M_w of 355 of the liquid products increased to 698 and of 821 at 523 K, respectively. Whereas the M_n and M_w at 573 K also greatly augmented from 253 and 346 to 1567 and 1581, respectively. The change of molecular weight proved the enhancement of the formation of oligomers in the liquid products, *i.e.* the furan derivatives from pyrolysis of agarose were polymerized under alkaline condition. Hence there was no products of furan derivatives from saccharides detected in the bio-oil of algae pyrolysis. The pyrolysis of polysaccharides formed oligomers and furan derivatives polymerized under certain condition were also reported previously [29−33]. Consequently, the main pyrolysis products from saccharides

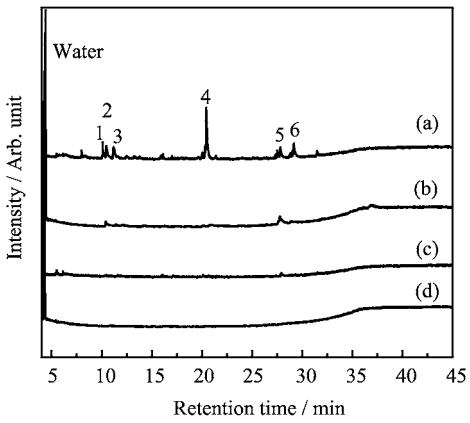

FIG. 3 TIC of GC-MS of liquid products from agarose fractional pyrolysis with or without NH_3 in the carrier gas. (a) 523 K, without NH_3, (b) 523 K, with NH_3, (c) 573 K, without NH_3, (d) 573 K, with NH_3. 1: acetic acid, 2: furfural, 3: 1-(2-furanyl)-ethaone, 4: methyl-2-furoate, 5: 2-furancarboxylic acid, 6: 5-hydroxymethyl-furfural.

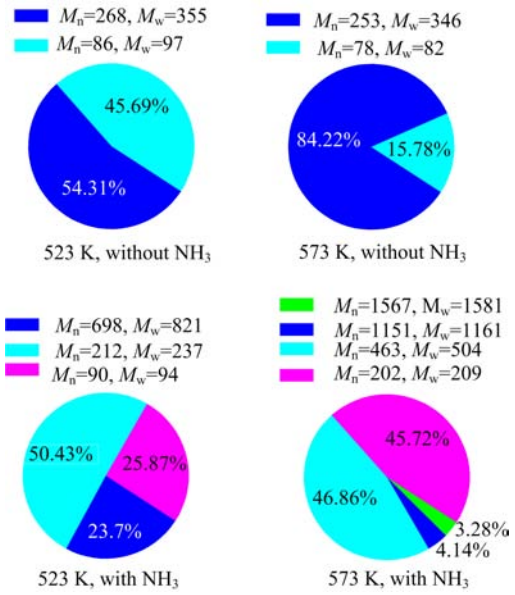

FIG. 4 GPC distribution of liquid products from agarose fractional pyrolysis with or without NH_3 in the carrier gas.

were polymerized due to the effect of NH_3 from the pyrolysis of proteins.

At 573 K, the conversion of lipids, saccharides and proteins were 1.4wt%, 3.0wt% and 9.1wt%, respectively. Lipids contributed to all the palmitic acid and the interaction of palmitic acid with ammonia contributed to the formation of the palmitic amide and palmitonitrile. These products were consistent with the products from the pyrolysis of palmitic acid/egg white mixture. The small molecule amides like acetamide and pentanamide *etc.* were mainly formed by the interaction of small molecule acids with ammonia except δ-valerolatam. The postulated formation mech-

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anism of δ-valerolatam from proline was displayed in Scheme IV of Fig.S2 (see supplementary material). The phenols, indoles, pyrroles (imidazoles at 573 K) and phenyl-acetonitrile were originated from the pyrolysis of proteins and the postulated formation mechanisms of phenol, indole and phenyl-acetonitrile were identical with the research of Du *et al.* [34]. In spite of an absence of pyrroles in the egg white pyrolysis products, proteins were the only source of forming pyrroles, and none of any nitrogenous compounds were detected in the products of agarose pyrolysis with ammonia in the carrier gas. The postulated mechanisms of forming imidazoles from histidine are shown in Scheme I of Fig.S3 (see supplementary material), where many rearrangement reactions occurred in this process. Because the conversion of saccharides at 573 K was small and the content of bio-oil reached a maximum quantity, the proportion of oligomers in bio-oil was too small so that the M_n and M_w were only 205 and 226, respectively. The relatively complicated alcohol ketones were derived from both saccharides and proteins.

The conversion of the three components and the yields of bio-oil above 573 K were all reducing. Only 0.3wt% of lipids pyrolyzed at 623 K and 4.8wt% in total of saccharides pyrolyzed at 573−773 K. Hence the relatively higher conversion of proteins (12.7wt% in total at 573−773 K) was the main bio-oil source. Thus the selectivity of bio-oil was improved to a certain degree. The dehydration and demethanation reactions were intensified and the decarboxylation reaction was attenuated. The formation of pyrroles at 623 and 673 K was similar to the reverse reaction of Diels-Alder reaction. In fact, the cracking of indoles finally formed pyrroles. The postulated mechanisms of pyrroles from trytophan were displayed in Scheme II of Fig.S3. Plenty of hydrocarbons with carbon number between 10 and 15 arose at 673 K. Hence the bio-oil with maximum C content and minimum O content was achieved at 673 K, the maximum HHV was 36.0 MJ/kg, as shown in Table IV.

In summary, the hydrocarbons, palmitic acid, and esters were derived from lipids. The phenols, indoles, pyrroles, small molecular acids, amides like acetamide and nitriles like phenyl-acetonitrile were generated from proteins. Amides and nitriles were also dated from the interaction of pyrolytic intermediates of lipids and proteins. The alcohol ketones and acetic acid might come from both proteins and saccharides. Moreover, saccharides generated most of the water. Most of the pyrolysis intermediates of saccharides polymerized in the pyrolysis process because of the interaction with the pyrolytic intermediates of proteins. Only very weak interaction existed between saccharides and lipids.

TABLE IV Element composition and higher heating value (HHV, MJ/kg) of the bio-oil from fractional pyrolysis of algae at different temperature.

Element	Composition/wt%					
	473 K	523 K	573 K	623 K	673 K	773 K
C	62.3	63.3	66.0	69.1	72.1	71.3
H	8.7	8.4	8.6	8.1	8.4	7.4
N	7.5	6.8	10.7	11.2	10.9	5.1
O[a]	21.4	21.6	14.8	11.6	8.7	16.2
HHV	29.3	29.5	32.0	33.6	36.0	33.3

[a] Owt%=100−Cwt%−Hwt%−Nwt%.

IV. CONCLUSION

Pyrolysis of algae from Taihu Lake water blooms fractionated by temperature can improve the selectivity of bio-oil to a certain degree. The main components in algae not only respectively presented different pyrolysis characteristics but also certain interactions occurred among them. The hydrocarbons, palmitic acid and esters in the bio-oil came from lipids, and the proteins generated the phenols, indoles, pyrroles, small molecular acids, amides like acetamide and nitriles like phenyl-acetonitrile. Amides and nitriles also might form by the interaction of pyrolytic intermediates from lipids and proteins. Only small amount of alcohol ketones, acetic acid and plenty of water dated from saccharides were detected due to the formation of oligomers via polymerization promoted by the pyrolytic intermediates from proteins. The interaction of lipids and proteins formed amides and nitriles. Very weak interaction occurred to lipids and saccharides. Although the selectivity of bio-oil improved to a certain extent, it is not enough for the application of bio-oil because of the complexity and diversity caused by the own complicacy of algae and the interaction of algae components. The oligomers generated at low temperature is not conductive for the down streaming process of bio-oil. To further improve the selectivity and applicability of bio-oil, much more work is still needed.

Supplementary material: The Schematic diagram of the pyrolytic experimental apparatus, postulated formation pathways of small molecule acids and δ-valerolatam from proteins, and postulated route of formation of pyrroles and imidazoles from proteins, were shown in Fig.S1−S3 respectively. The distribution of liquid products in fractional pyrolysis of agarose, egg white, palmitic acid/agarose/egg white mixture, egg white/palmitic acid mixture, egg white/agarose mixture and agarose/palmitic acid mixture were presented in Table S1−S6, respectively.

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