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Formation of nitrogen-containing compounds during microwave pyrolysis of microalgae: product distribution and reaction pathways

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ABSTRACT

The formation of nitrogen-containing compounds in bio-oil during microwave pyrolysis of *Chlorella* and *Spirulina* microalgae has been investigated in this study. Activated carbon (AC) and magnetite (Fe₃O₄) were used as microwave receptors during microwave pyrolysis experiments. It has been found that the use of Fe₃O₄ increased the total yield of bio-oil. The use of different microwave receptors did not seem to have affected the total yield of nitrogen-containing compounds in the bio-oil. However, Fe₃O₄ promoted the formation of nitrogen-containing aliphatics, thereby reducing the formation of nitrogen-containing aromatics. The use of AC promoted the dehydration reactions during amino acid decomposition, thereby enhancing the formation of nitrogen-containing aromatics during pyrolysis. From the gas chromatography-mass spectrometry (GC-MS) analysis results, the major high-value nitrogen-containing compounds in the pyrolysis bio-oil of *Chlorella* and *Spirulina* were indole and dodecamide. The formation mechanisms of nitrogen-containing compounds have been proposed and discussed.

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Keywords: Nitrogen-containing compounds; microalgae; microwave pyrolysis; microwave receptor; bio-oil.

1. Introduction

Biomass is one of the most important carbon-based energy sources after crude oil, coal and natural gas, and accounts for about 14% of the world's total primary energy resources. Biomass feedstock with high energy application potential include agricultural residues (Huang et al., 2013; Li et al., 2016), forestry waste (Undri et al., 2015), aquatic biomass (Watanabe et al., 2014; Yuan et al., 2011) and organic waste materials (Xie et al., 2014). Biomass pyrolysis is seen as an important thermochemical conversion technique to convert biomass into gas, bio-oil and bio-char (Corton et al., 2016). Bio-oil products contain more than 400 kinds of organic compounds among which many of them are widely recognized as high-value chemical substances, including hydrocarbons, phenols, furans and sugars.

Nitrogen-containing fine chemicals are some of the most value-added compounds in bio-oil. High value-added nitrogen-containing chemicals can be produced through pyrolysis of biomass with high nitrogen content (Chen et al., 2016). Nitrogen compounds in bio-oils are the main ingredients or precursors of pharmaceuticals and fine chemicals. The nitrogen content in microalgae is higher than that of other biomass species. For instance, the nitrogen content of chlorella microalgae is about 8%. The production of high value-added nitrogen-containing chemicals through pyrolysis of microalgae is one of the promising ways for efficient utilization of microalgae. Compared with terrestrial biomass, microalgae have the advantages of faster growth, higher oil content and wider distribution (Du et al., 2011; Harman-Ware et al., 2013). In addition, the main components of microalgae are proteins, lipids, and carbohydrates, which are

different from woody biomass (Du et al., 2013). Proteins, much more complex polymers than carbohydrates, are intricate macromolecular compounds with the amino acid sequence, which decomposes in a temperature range of 200-900 °C (Boon & De Leeuw, 1987). Bio-oil obtained from pyrolysis of microalgae contains hundreds of different compound species, such as oxygen-containing organic compounds, nitrogen-containing organic compounds and linear hydrocarbons. Among these, nitrogenous organic compounds are primarily important compounds, some of which are indispensable to life activity substances.

Previous studies on the pyrolysis behavior of microalgae were mainly focused on the effects of experimental parameters such as microalgae type, pyrolysis temperature and catalyst type on the yields and characteristics of pyrolysis products (Borges et al., 2014; Chen et al., 2017b; Du et al., 2013; Harman-Ware et al., 2013; Zainan et al., 2015). Chen and co-workers (Chen et al., 2017b) investigated pyrolytic poly-generation of three algae species (*Enteromorpha prolifera* (EP), *Spirulina platensis* (SP) and *Nannochloropsis sp.* (NS)) using a fixed bed reactor in a temperature range of 400-800 °C. They observed that pyrolysis temperature and feedstock composition has a significant effect on the yield and composition of pyrolysis products. At 400-600 °C, EP bio-oil was rich in furans, while SP bio-oil mainly contained amines, amides, nitriles and N-heterocyclic compounds. NS bio-oil showed a different composition and was mainly composed of aliphatic hydrocarbons and carboxylic acids. At temperatures higher than 700 °C, aromatics were the major component of bio-oil. Zainan et al. (Zainan et al., 2015) studied the catalytic pyrolysis of microalgae *Tetraselmis suecica* and in a temperature range of 300-600 °C using zeolite catalyst and reported that the optimum temperature for pyrolysis of microalgae was 400 °C. The main nitrogen-containing compounds detected in bio-oil were

indole, pyrrole, and amide compounds. Herman-Ware and co-workers (Harman-Ware et al., 2013) investigated the fast pyrolysis behavior of *Scenedemus sp.* microalgae using isothermal spouted bed reactor at 480 °C and a dynamic pyrolysis-GC/MS unit. The main N-containing species detected in bio-oil were amines, amides, pyridines, pyrroles, pyrazoles, nitriles, imidazoles, and indoles, amides being the majority. They postulated that cyclic amides were formed as a result of protein and amino acid intermolecular cyclization, while linear amides were formed during primary protein decomposition. Chen and co-workers (Chen et al., 2017a) investigated the transformation and evolution of nitrogen during microalgae pyrolysis in a fixed bed reactor. They reported that protein-N in algae cracked in the temperature range of 400-600 °C to form pyridinic-N, pyrrolic-N and quaternary-N in char. Deamination or dehydrogenation of amino acids at high temperatures led to an increase in formation of Pyridinic-N and pyrrolic-N. Concentration of amides decreased at higher temperatures while an opposite trend was observed for nitriles and N-heterocyclic compounds (pyridines, pyrroles, and indoles).

The advantages of the microwave pyrolysis over conventional pyrolysis systems include uniform internal heating and instantaneous response. Thermal cracking or polymerization reactions during secondary pyrolysis reactions may decrease the yield of N-containing compounds in bio-oil in favor of light gas (NH₃, HCN) or char formation (N retention in char). Therefore, the secondary pyrolysis reactions need to be minimized to achieve higher bio-oil yields and higher concentrations of N-containing compounds. Under microwave heating conditions and as a result of selective heating of microwave, the temperature of sample bed is higher than its surroundings during pyrolysis. Therefore, once the volatiles are released, they move from high temperature region to low-temperature region and the secondary pyrolysis

reactions are minimized. The generation of renewable fuels and fine chemicals via microwave pyrolysis of biomass has been researched in recent years, including microwave pyrolysis of microalgae for bio-fuel (Bu et al., 2011), microwave pyrolysis of eucalyptus pulverulenta for methoxyaromatics (Xu et al., 2016), microwave pyrolysis of lignocellulosic biomass for phenol-rich bio-oil (Omoriyekomwan et al., 2016) and microwave pyrolysis of sewage sludge for bio-oil (Huang et al., 2015; Xie et al., 2014), etc.

High nitrogen contents in microalgae species make them suitable as feedstock for production of high-value nitrogen containing fine chemicals. However, the study of N-containing fine chemicals formation from microalgae is scarce in the literature and the mechanism of formation of these compounds is not fully understood. This study focuses on the formation of high-value nitrogen-containing compounds during catalytic microwave pyrolysis of two types of microalgae, *Chlorella* and *Spirulina*. The influence of process parameters such as temperature and type of catalyst on the yield and composition of bio-oil was investigated systematically with a particular focus on the yield and type of nitrogen-containing species. The formation mechanisms and reaction pathways of the major nitrogen-containing compounds during microwave pyrolysis were also proposed and discussed.

2. Materials and methods

2.1. Materials

Two microalgae species, *Chlorella* and *Spirulina* (purchased from Dongtai Spirulina Bio-Engineering Inc., China), were used in microwave pyrolysis experiments. The particle size of microalgae samples was less than 48 μm . Microalgae samples were dried at 80 $^{\circ}\text{C}$ under nitrogen for 24 h. The proximate and ultimate analyses and compositions of the microalgae are

given in Table 1. The protein content of microalgae was determined by the Kjeldahl method and was calculated using a nitrogen conversion factor of 6.25 (Akgul et al., 2015). The lipid content was determined using the one-step extraction adapted from Folch method (Li et al., 2011). The carbohydrate contents were determined using Phenol-Sulfuric Assay method (Zainan et al., 2015). The *Chlorella* and *Spirulina* samples used in this study contained 18 kinds of amino acids, mainly glutamic acid, leucine, aspartic acid, arginine and alanine. AC and Fe_3O_4 were used as microwave receptors during microwave pyrolysis experiments. AC was grinded and sieved to a particle size of 75-200 μm and Fe_3O_4 was purchased in powder form with a particle size of 75-150 μm . Both microwave receptors were dried at 80 °C for 24 h prior to experiments.

2.2. Microwave pyrolysis experiments

The microwave pyrolysis experiments of microalgae were carried out using a microwave oven (Tangshan Microwave Thermal Instrument Inc., China) with a maximum microwave output power of 2000 W at a frequency of 2.45 GHz. The microwave pyrolysis experimental setup is shown in Fig. 1. AC and Fe_3O_4 were used as the microwave receptors and are believed to catalyze the microalgae pyrolysis reactions. The microalgae samples were evenly blended with microwave receptor (AC or Fe_3O_4) at the mass ratio of 8:2. During each pyrolysis experiment, the mixture of microalgae and microwave receptor was placed in a specially designed quartz reactor and subjected to microwave heating under high purity nitrogen gas flow with a flow rate of 500 ml/min. Microwave pyrolysis experiments were carried out in a temperatures range of 350-650 °C. Pyrolysis temperature was measured at 2 s intervals by inserting a thermocouple into the sample bed. Once the desired temperature was achieved, the temperature/power control system of the microwave oven automatically adjusted the output

power to maintain the desired final temperature. The evolved volatiles were collected using three consecutive condensers containing dichloromethane (Sinopharm Chemical Reagent Inc.) placed in ice-water baths. The reaction time was set for 50 min. After pyrolysis, the bio-char was separated from microwave receptors by sieving based on their particle size difference. The yields of solid and liquid products were calculated from the weight of each fraction, while the gas yield was calculated by difference.

2.3. Characterization of bio-oil

Distillation separation method was used to separate the bio-oil from the dichloromethane. The bio-oil composition was analyzed by gas chromatography-mass spectrometry (GC-MS, Thermo Scientific ISQ) with a TR-5MS column (30m×0.25mm×0.25μm). Helium was employed as the carrier gas with a flow rate of 1 ml/min. The injection size was 1.0 μl with a split ratio of 1:10, and the MS source was set to 70 eV. The inlet was set at 300 °C, and the initial oven temperature was 40 °C. The temperature program was as follows: from 40 °C increased to 100 °C at the rate of 15 °C/min and hold for 2 min, and then ramp to 280 °C at 10 °C/min and hold for 15 min. The identification of the compounds was done by comparing the respective mass spectra with those from the National Institute of Standards and Technology (NIST) mass spectral data library. The areas% from the total chromatogram peak area was used in calculating the relative proportions of compounds in bio-oil.

2.4. Characterization of bio-char

Elemental analysis technique was used to study the nitrogen retention in bio-chars. A Euro Vector EA3000 element analyzer was used to determine the nitrogen content in microalgae and

bio-chars and calculate the nitrogen conversion during pyrolysis.

3. Results and discussion

3.1. Product yields

The product yields (bio-oil, bio-char and gas) from catalytic microwave pyrolysis of *Chlorella* and *Spirulina* using AC and Fe_3O_4 as microwave receptors are shown in Fig. 2 as a function of temperature. Bio-oil was the main pyrolysis products of microalgae under microwave pyrolysis conditions, especially at higher temperatures. Bio-char was the byproduct of microalgae microwave pyrolysis, which can be used as solid fuel or for waste water treatment, and improving soil properties.

The yield of bio-oil during microwave pyrolysis of *Chlorella* using AC as catalyst was in the range of 44.7-49.4 wt.%. A higher bio-oil yield was obtained in the temperature range of 350-500 °C, and the bio-oil yield decreased slightly as the pyrolysis temperature was further increased. The yield of bio-char was in the range of 23.3-37.3 wt.%, which was higher at lower temperatures and decreased with increasing the pyrolysis temperature. The gas yield showed an increasing trend with increasing pyrolysis temperature. When Fe_3O_4 was used as the microwave receptor during microwave pyrolysis of *Chlorella*, the yield of bio-oil increased with increasing temperature and was in the range of 38-53.8 wt.%, which was higher than that with AC. The yield of bio-char was in the range of 14.8-27.4 wt.%, which was lower than that with AC as catalyst.

During microwave pyrolysis of *Spirulina*, the yield of bio-char decreased with increasing pyrolysis temperature, accompanied by an increase in the yield of non-condensable gases. The yield of bio-oil during the pyrolysis of *Spirulina* in presence of AC and Fe_3O_4 were in the range

of 30.7-46.4 wt.% and 33.4-48.4 wt.%, respectively, and reached its maximum value at 500 °C.

These results showed that although slightly higher bio-oil yield was reached using Fe₃O₄, in case of AC a higher yield of bio-char was obtained as the by-product of microwave pyrolysis of microalgae.

3.2. Bio-oil compositions

The bio-oil derived from microwave pyrolysis of *Chlorella* and *Spirulina* under different experimental conditions were complex mixture of organic compounds. To further investigate the effects of pyrolysis temperature and microwave receptors on bio-oil composition, the identified compounds were grouped into: nitrogen-containing aliphatics, nitrogen-containing aromatics, oxygen-containing aliphatics, oxygen-containing aromatics, aliphatic hydrocarbons, aromatic hydrocarbons, and others. A semi-quantitative analysis was performed by calculating the relative area percentage of the chromatographic peaks.

3.2.1. Effect of microwave receptor on bio-oil compositions

The effect of microwave receptor on bio-oil composition is shown in Fig. 3. It can be seen that the type of microwave receptor had a significant influence on the chemical composition of bio-oil. The products of microwave pyrolysis of *Spirulina* blended with AC were mainly nitrogen-containing aliphatics and oxygen-containing aliphatics, accounting for 20-35 area% and 20-30 area% of bio-oil, respectively. In addition, nitrogen-containing aromatics accounted for 10-20 area%. The proportion of nitrogen-containing aliphatics decreased with increasing pyrolysis temperature. The amount of oxygen-containing aliphatics and nitrogen-containing aromatics in bio-oil increased with increasing pyrolysis temperature. The proportion of aliphatic

compounds in the bio-oil obtained during microwave pyrolysis of *Spirulina* in presence of Fe_3O_4 was higher than that of AC. However, the amount of aromatic compounds was lower than that of *Spirulina* blend with AC. The proportion of nitrogen-containing aliphatics and oxygen-containing aliphatics in the bio-oil obtained during microwave pyrolysis of *Spirulina* and using Fe_3O_4 as catalyst decreased with increasing pyrolysis temperature, while that of nitrogen-containing aromatics and the oxygen-containing aromatics showed an increasing trend. The main chemical compounds in bio-oil obtained from microwave pyrolysis of *Spirulina* were aliphatic compounds, including nitrogen-containing aliphatics and oxygen-containing aliphatics. The addition of microwave receptors changed the distribution of products in bio-oil to a certain extent. The main chemical compounds identified in bio-oils derived from the microwave pyrolysis of *Spirulina* as a function of temperature are shown in Table 2. The major nitrogen-containing compounds in the bio-oil obtained during microwave pyrolysis of *Spirulina* were nitriles, amides, and indole.

The main chemical compounds in bio-oil obtained from microwave pyrolysis of *Chlorella* in presence of AC were oxygen-containing aliphatics, the proportion of which increased with increasing pyrolysis temperature, accounting for 40-60 area% of bio-oil. In addition, the nitrogen-containing aliphatics accounted for 5-10 area% of compounds in bio-oil, and the nitrogen-containing aromatics accounted for about 15 area%. The nitrogen-containing compounds reached a maximum at 450 °C and decreased with further increasing pyrolysis temperature. The proportion of aliphatic compounds in the bio-oil obtained from microwave pyrolysis of *Chlorella* and using Fe_3O_4 as catalyst was higher than that of AC. However, the proportion of aromatic compounds when Fe_3O_4 was used as microwave receptor was lower than

that the case where AC was used as catalyst. The oxygen-containing aliphatics accounted for 50-60 area% of chemical compounds in bio-oil. The concentrations of nitrogen-containing aliphatics and nitrogen-containing aromatics in bio-oil were 15-20 area%, and about 10 area%, respectively. The main chemical compounds identified in bio-oils obtained from the microwave pyrolysis of *Chlorella* as a function of temperature are shown in Table 3. The major nitrogen-containing compounds in the bio-oil were amides and indole. Since the composition of the protein in *Chlorella* and *Spirulina* was similar, the type of the main nitrogen-containing compounds in the pyrolysis bio-oil did not vary. During the microwave pyrolysis of microalgae, the AC and Fe_3O_4 were not only microwave receptor, but also acted as catalyst to control the distribution of aliphatics and aromatics by promoting the dehydration and decarboxylation reactions. It can be concluded that the addition of Fe_3O_4 resulted in formation of more aliphatic compounds, while AC promoted the formation of aromatic compounds.

3.2.2. Effect of microwave receptors on nitrogen-containing compounds in bio-oil

The effects of microwave receptor on the nitrogen-containing compounds during the microwave pyrolysis of microalgae are shown in Fig. 4. Regardless of the type of microwave receptor used, the total amount of nitrogen-containing compounds in the bio-oil at any given temperature was similar during microwave pyrolysis of microalgae, suggesting that the types of microwave receptors had little influence on the total amount of nitrogen-containing compounds that can be obtained during microwave pyrolysis of microalgae. As shown in Fig. 4, although the effects of AC and Fe_3O_4 on the total amount of nitrogen-containing compounds during microwave pyrolysis of *Spirulina* and *Chlorella* were negligible, they had a significant influence on the type of the compounds, i.e. nitrogen-containing aliphatics and nitrogen-containing

aromatics. During microwave pyrolysis of *Chlorella*, the amount of the nitrogen-containing aliphatics reached a maximum value of 26.5 area% at 450 °C when Fe₃O₄ was used as the microwave receptor, while the amount of the nitrogen-containing aromatics was 8.53 area%. When AC was used as the microwave receptor, the amount of the nitrogen-containing aromatics reached a maximum value of 18.5 area% at 450 °C and the amount of nitrogen-containing aliphatics was 14.89 area%. Fe₃O₄ promoted the formation of nitrogen-containing aliphatics, while AC promoted the formation of nitrogen-containing aromatics during microwave pyrolysis of microalgae. The concentration of nitrogen-containing aliphatics in bio-oil reached a maximum value of 36 area% at 350 °C when Fe₃O₄ was used as the microwave receptor during pyrolysis of *Spirulina*. When AC was used as the microwave receptor, the concentration of nitrogen-containing aromatics reached a maximum value of about 24 area% at 650 °C. It can be concluded that AC promoted the formation of nitrogen-containing aromatics, while Fe₃O₄ promoted the formation of nitrogen-containing aliphatics.

3.3. Mechanism of formation of nitrogen-containing compounds

The types of nitrogen-containing compounds in bio-oil were affected by factors such as the composition of microalgae, the type of microwave receptor, and pyrolysis temperature, implying that the formation mechanism of nitrogen-containing compounds could be altered. The nitrogen-containing compounds in the bio-oil mainly originated from the protein in the microalgae. Amino acids are the basic unit of protein and are considered as the precursors of N-containing species in bio-oil. Each of these nitrogen-containing compounds may be the result of primary or secondary reactions that occurred during microwave pyrolysis of microalgae (Moldoveanu, 2010). Low molecular weight amino acids, such as glycine, serine, alanine, and

threonine are completely decomposed into CO_2 , NH_3 , H_2O and other volatile fragments (Simmonds, 1972). One other pathway is the decarboxylation reaction which is the most common decomposition pathway followed by reactions typical for amines (Liu et al., 2016). Dehydrogenation and formation of nitriles is one of the typical reactions of amines. After the loss of the first hydrogen molecule, the intermediate can also react with other molecule of amine and expelled ammonia (Ratcliff Jr., 1974). The amine also can react with carboxylic acid to form an amide. The second mode of thermal decomposition involves dehydration reaction between two amino acid molecules leading to formation of diketopiperazine (DKP), which subsequently decomposes (Chiavari & Galletti, 1992). The third mode of decomposition is homolysis of the aliphatic chain that leads to the formation of the hydrocarbons or substituted hydrocarbons. The structure of the product depends on the structure of amino acids (Tsuge & Matsubara, 1985). The fourth decomposition path is intramolecular dehydration or deamination to form cyclic compounds (Chiavari & Galletti, 1992).

The experimental results showed that the AC promoted the formation of nitrogen-containing aromatics during microwave pyrolysis of microalgae (Fig. 3). Dehydration was one of the major reactions during decomposition of amino acids to form nitrogen-containing aromatics and AC has been reported to promote the dehydration reaction during pyrolysis (Wang et al., 2017). On the other hand, decarboxylation is the major reaction during decomposition of amino acids, resulting in the formation of nitrogen-containing aliphatics. Transitional metals such as iron have been reported to promote the decarboxylation reactions (Srifa et al., 2015). Fe_3O_4 promoted the formation of nitrogen-containing aliphatics (Fig. 4) by promoting the decarboxylation reactions during microalgae decomposition. Amino acids absorption on the surface of Fe_3O_4 formed

organic complexes, followed by transition of Fe that promoted the decarboxylation of amino acid. Transitional metals can stabilize unsaturated intermediates, and can activate the relatively inactive molecules through the coordination role. As discussed above, indole was one of the important nitrogen-containing compounds present in pyrolysis bio-oil of *Chlorella* and *Spirulina*, which can be used as additives in food industry. The formation of indole was mainly due to the homolysis of the aliphatic chain of the tryptophan in the microalgae. Dodecanamide was another important nitrogen-containing compound in pyrolysis bio-oil, which can be used as organic synthesis intermediates. During decomposition of amino acids, dodecanamide was obtained through the reaction of an amino and a dodecanoic acid. Considering that linear and unbranched C12 structural units do not exist in microalgae structure, it can be postulated that the dodecanoic acid was obtained through the chemical reaction among amino acids containing C, H, O, and N elements and non-branched units such as lysine and glutamic acid. The formation of dodecamide included three steps: (1) amino acid decarboxylation or deamination reactions; (2) polymerization reaction between the products of the previous step to form dodecanoic acid; (3) reaction of dodecanoic acid with amino to form dodecamide.

3.4. Nitrogen conversion during microalgae pyrolysis

Fig. 5 shows nitrogen conversion during microwave pyrolysis of microalgae in presence of AC and Fe₃O₄. It can be seen that nitrogen conversion during *Spirulina* pyrolysis was higher than that of *Chlorella*. Furthermore, the nitrogen conversion during the pyrolysis of microalgae using AC as microwave receptor was higher than that of Fe₃O₄.

Amino acids with/without reactive side chains affect the char yield and the nitrogen content in the char depends on the presence/absence of nitrogen containing reactive side chains. Thus,

the structure of the amino acid in the microalgae has an important effect on nitrogen conversion during pyrolysis. Amino acids without reactive side chains such as leucine, isoleucine and glycine do not produce any char during pyrolysis, while amino acids with reactive side chains such as phenylalanine, aspartic and tryptophan could form char (Ren & Zhao, 2013). The nitrogen and the amino acid content of *Spirulina* were higher than *Chlorella*. However, *Chlorella* contained more nitrogen-containing reactive side chains such as lysine, tryptophan and histidine compared with *Spirulina*, resulting in higher nitrogen retention in char during pyrolysis. Therefore, the nitrogen conversion during *Chlorella* pyrolysis was lower than that of *Spirulina*. Compared with Fe₃O₄, AC seemed to promote the thermal decomposition of the nitrogen containing compounds in char leading to higher nitrogen conversions.

4. Conclusions

Nitrogen-containing compounds have been efficiently produced via microwave pyrolysis of microalgae. The highest bio-oil yields during microwave pyrolysis of *Chlorella* and *Spirulina* was obtained at 500 °C. The bio-oil derived from *Chlorella* pyrolysis was mainly composed of oxygen-containing aliphatics while the *Spirulina* bio-oil contained both nitrogen-containing aliphatics and oxygen-containing aliphatics. The types of microwave receptors seemed to have little influence on the total yield of nitrogen-containing compounds during pyrolysis. However, the addition of Fe₃O₄ increased the yields of both bio-oil and nitrogen-containing aliphatics, while AC seemed to have promoted the formation of nitrogen-containing aromatics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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List of Tables:**Table 1**

Proximate and ultimate analysis of microalgae samples.

	Chlorella	Spirulina
Proximate analysis (dry basis, wt. %)		
Moisture	1.0	0.9
Volatile matter	75.8	78.7
Ash	7.6	7.7
Fixed carbon	15.6	12.7
Elemental analysis (dry ash-free basis, wt. %)		
C	47.3	48.1
H	6.9	7.0
N	8.5	10.1
S	0.9	0.9
O ^a	36.4	33.9
Component analysis (dry basis, wt. %)		
Proteins	52.0	62.0
Lipids	12.4	8.2
Carbohydrates	17.3	15.1
Others ^a	18.3	14.7

^a Calculated by difference

Table 2

Main chemical compounds (area%) identified in bio-oil derived from microwave pyrolysis of *Spirulina* as a function of pyrolysis temperature.

Compounds	Spirulina : AC				Spirulina : Fe ₃ O ₄			
	350 °C	450 °C	550 °C	650 °C	350 °C	450 °C	550 °C	650 °C
Nitrogen-containing aliphatics								
Tridecanenitrile	1.79	1.97	2.02	1.76	-	-	-	-
Tetradecanenitrile	-	-	-	-	4.19	2.94	3.07	3.21
Dodecanamide	4.71	4.70	4.90	4.79	8.38	5.67	6.83	4.67
Nitrogen-containing aromatics								
Quinoline	-	1.01	0.96	-	-	0.83	0.80	0.94
Indole	4.19	5.44	5.27	7.55	4.30	5.58	5.02	5.02
1H-Indole,2-methyl-	1.64	1.86	1.99	2.98	1.91	1.85	2.10	2.93
Oxygen-containing aliphatics								
1-Dodecanol,3,7,11-trimethyl-	0.97	0.87	0.68	0.42	0.71	0.68	0.36	0.68
3,7,11,15-Tetramethyl-	4.93	4.81	5.45	5.07	11.68	9.44	8.73	8.08
2-hexadecen-1-ol								
Hexadecanoic acid	4.97	4.64	5.55	2.04	9.08	6.84	7.37	4.69
Oxygen-containing aromatics								
Phenol	5.76	5.65	5.41	5.71	3.24	3.79	4.32	5.16
Phenol, 3-methyl-	4.78	5.38	4.78	3.69	3.26	4.30	4.08	4.23
Butylated Hydroxytoluene	2.38	1.87	1.09	1.20	1.17	1.55	2.23	2.47
Aliphatic hydrocarbons								
Pentadecane	4.02	3.97	3.10	4.57	-	-	-	1.54
Aromatic hydrocarbons								
1H-Indene, 1-methylene-	1.75	2.30	2.78	3.18	0.52	2.01	1.82	2.16

Table 3

Main chemical compounds (area%) identified in bio-oil derived from microwave pyrolysis of *Chlorella* as a function of pyrolysis temperature.

Compounds	Chlorella : AC				Chlorella : Fe ₃ O ₄			
	350 °C	450 °C	550 °C	650 °C	350 °C	450 °C	550 °C	650 °C
Nitrogen-containing aliphatics								
3-Methyl-1,2-diazirine	5.58	2.77	1.90	-	1.08	2.97	2.12	-
Dodecanamide	1.58	2.24	1.31	0.89	2.66	3.37	2.01	2.03
Nitrogen-containing aromatics								
Indole	3.95	2.73	4.58	4.76	2.72	2.98	2.78	3.90
1H-Indole,7-methyl-	1.78	0.88	1.55	1.06	0.84	0.95	0.77	1.06
Oxygen-containing aliphatics								
1-Dodecanol,3,7,11-trimethyl-	1.53	1.93	1.87	0.18	0.81	0.90	0.58	0.53
3,7,11,15-Tetramethyl	19.9	17.27	15.96	7.76	22.15	23.24	20.55	25.48
-2-hexadecen-ol								
Hexadecanoic acid	9.74	10.09	9.65	9.74	9.51	8.53	10.32	10.08
Oxygen-containing aromatics								
Phenol	-	1.37	1.50	2.99	-	-	-	1.64
Phenol, 3-methyl-	3.40	3.24	3.73	4.87	2.90	3.76	2.90	4.23
Butylated Hydroxytoluene	0.78	0.39	0.79	1.63	-	-	0.14	0.20
Aliphatic hydrocarbons								
Pentadecane	2.69	6.10	4.46	4.73	1.08	1.36	2.07	3.37
Aromatic hydrocarbons								
1H-Indene, 1-methylene-	1.85	0.99	0.54	0.61	0.95	1.32	1.53	1.36

List of captions of figures:

Fig. 1. Microwave pyrolysis experimental setup: (1) microwave oven; (2) thermocouple; (3) reactor; (4) sample bed; (5) organic solvent; (6) condenser; (7) mass flow meter.

Fig. 2. Product yields from microwave pyrolysis of microalgae using AC and Fe_3O_4 as microwave receptor: (a) *Chlorella*, (b) *Spirulina*.

Fig. 3. Chemical composition of bio-oil derived from microwave pyrolysis of microalgae using AC and Fe_3O_4 as microwave receptor: (a) *Chlorella*, (b) *Spirulina*.

Fig. 4. Concentration of nitrogen-containing compounds in bio-oil as a function of temperature during microwave pyrolysis of microalgae using AC and Fe_3O_4 as microwave receptor: (a) *Chlorella*, (b) *Spirulina*.

Fig. 5. Nitrogen conversion during microwave pyrolysis of microalgae using AC and Fe_3O_4 as microwave receptor: (a) *Chlorella*, (b) *Spirulina*.

Highlights

- Bio-oil from microwave pyrolysis of microalgae was rich in N-containing compounds;
- The formation mechanism of N-containing compounds in bio-oil was proposed;
- Decarboxylation reaction by Fe_3O_4 led to formation of N-containing aliphatics;
- The research opens a way of producing high-value N-containing compounds from biomass.