



## Co-liquefaction of microalgae and synthetic polymer mixture in sub- and supercritical ethanol

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### ARTICLE INFO

#### Article history:

Received 8 May 2011

Received in revised form 30 August 2011

Accepted 9 September 2011

Available online xxxx

#### Keywords:

Co-liquefaction

Microalgae

Synergetic polymer

Sub- and supercritical ethanol

Synergetic effect

Bio-oil

### ABSTRACT

Co-liquefaction of microalgae (*Spirulina*) and synthetic polymer (HDPE, high-density polyethylene) in sub- and supercritical ethanol was investigated in a stainless steel autoclave (1000 mL) at different reaction temperatures ( $T$ ), *Spirulina*/HDPE ratio ( $R_1$ ), (*Spirulina* + HDPE)/ethanol ratio ( $R_2$ ) and solvent filling ratio ( $R_3$ ). Results showed that the addition of *Spirulina* to HDPE liquefaction could make the conversion conditions of HDPE milder. The yield of bio-oil obtained at 613 K with a 1/10  $R_2$  and a 2/10  $R_3$  was increased by 44.81 wt.% when the  $R_1$  was raised from 0/10 to 4/6. Meanwhile, the synergetic effects ( $SE$ ) between HDPE and *Spirulina* were increased from 0 to 30.39 wt.%. Further increasing  $R_1$  resulted in a decrease in  $SE$ . The yields of bio-oil increased with increasing  $R_2$  firstly and then declined. An opposite trend was observed for the yield of residue. The effect of  $R_3$  to the yields of liquefaction products was similar to that of  $R_2$ . The content of C and H in bio-oils reduced with increasing  $R_1$ , while the content of O increased. The bio-oil from pure *Spirulina* liquefaction runs mainly consisted of oxygen-containing compounds, such as carboxylic acids, esters and ketones. But the major components of bio-oil from co-liquefaction of *Spirulina* and HDPE mixture were similar to those of pure HDPE-derived bio-oil, in which aliphatic hydrocarbons dominated.

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### 1. Introduction

Generally, microalgae are well known as one of the main factors for water eutrophication. In the other hand, they are also considered to be a potential source of third generation biofuels with the advantages of higher photosynthetic efficiency, higher biomass production and faster growth than other biomasses [1]. Moreover, microalgae can be cultivated in either fresh water or saline environments avoiding the use of agricultural land [2]. Thermochemical conversion of microalgae into bio-oil has been widely studied in recent years [3–8]. The results of thermogravimetric analysis (TGA) of microalgae showed that the initial temperatures for *Spirulina* decomposition were 463–493 K and the final temperature was approximately 833 K [7]. Bio-oils obtained from microalgae liquefaction mainly consist of various complex organic chemicals, such as organic acids, esters, phenols, ketones, indoles, pyrrolidines and saturated or unsaturated hydrocarbons, etc. [3–5].

The rapid rate of plastic consumption throughout the world has led to the production of increasing amounts of waste with difficult disposal [9]. Now that land filling and incineration become more expensive and environmentally risky, the recycling of waste plastics is attracting more attention as an alternative to absorb vast amounts of post-consumer plastics

[10, 11]. Among various recovery processes of plastics, an option with great potential is recycling energy or chemicals through thermochemical conversion processes. These processes can reduce the potentially hazardous materials and simultaneously produce valuable chemical feedstock, such as liquid and gaseous hydrocarbons [9, 10, 12]. In particular, conversion of waste plastics to liquid fuels would be logical for its high heating value (about 40 MJ/kg) and high content of H and C [13]. Pyrolysis [14, 15] and liquefaction [16] of plastics have been studied by several authors. High temperatures were always required for thermal degradation of plastics due to their heat-resisting characteristics. The TGA results of HDPE indicated that HDPE began to decompose at a high temperature of 673 K [17–19]. Temperatures as high as 973–1173 K were essential to achieve decent product yields from plastic pyrolysis [20, 21].

Recently, co-processing of synthetic polymer with other materials has received more and more attentions [22–26]. Due to the high content of H in synthetic polymers, the effect of polymer as a hydrogen source in thermal co-processing has been observed, resulting in the improvement of yield and quality of obtained oil [24–26]. Furthermore, the degradation of polymer could be enhanced by blending with other materials [22, 23]. Jakob et al. demonstrated that charcoal issued biomass could shift the thermal decomposition of polypropylene to a lower temperature and enhance the formation of monomer and dimer [22]. Meanwhile, Yang et al. reported that the thermal stability of polymer decreased with the addition of lignocellulosic filler [23].

To the best of the 'authors' knowledge, to date, there are few studies focusing on the co-liquefaction characteristics of synthetic polymer and

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microalgae. In this paper, *Spirulina* (high-protein microalgae) and HDPE (a typical plastic) were chosen as the energy recovery sources. Ethanol was adopted as the solvent. In the present work, the effects of reaction temperature ( $T$ ), *Spirulina*/HDPE ratio ( $R_1$ ), (*Spirulina* + HDPE)/ethanol ratio ( $R_2$ ) and solvent filling ratio ( $R_3$ ) on the co-liquefaction of *Spirulina* and HDPE in sub- and supercritical ethanol were studied in 5.9–11.9 MPa, as shown in Table 1. In addition, the properties of the obtained oils were characterized by FT-IR, GC-MS and elemental analyses. The objectives of this study are, firstly, to discuss the possibility of co-liquefaction of *Spirulina* and HDPE and secondly, to investigate the influence of reaction parameters for the future commercial utilization.

## 2. Experimental

### 2.1. Materials

The feedstock materials used in this study were microalgae cells of *Spirulina* and HDPE. Microalgae cells of *Spirulina* were provided from Xigema Biological Technology Co., Ltd. (Fujian, China). Samples were prepared by pulverization in a mortar to <150  $\mu\text{m}$  and then stored in a desiccator. The amounts of dry solid and ash were detected as the drying residue at 378 K and the ignition residue at 973 K, respectively. The elemental composition of the organic matter was determined with an elemental analyzer. The amounts of crude protein, crude fat and crude fiber of *Spirulina* were determined through the Kjeldahl method [27], Soxhlet extraction and the improved Henneberg–Stohmann method [28], respectively. HDPE was commercially-available polymer obtained from Tianjin Petrochemical Company. The particle diameters of HDPE were in the range of 4–6 mm and its density was 0.95 g/mL. Analysis results of *Spirulina* and HDPE are tabulated in Table 2.

All chemical reagents used for the experiments were of analytic grade. Freshly prepared daily-diluted solutions were prepared using deionized water. All glassware and plastic containers were washed with 15% nitric acid solution and rinsed thoroughly with deionized water.

### 2.2. Experimental procedure and separation

The liquefaction experiments were conducted in a 1000 mL GSHA-1.0 type autoclave. In a typical liquefaction experiment run, the mixture of microalgae and plastic blended with ethanol were loaded into the reactor, and the temperature was raised up to the reaction temperature by an electrically heated furnace. Agitation was set at 60 rpm and kept constant for all the autoclave tests. After the reaction was completed, the autoclave was removed and cooled by fan and cool water to room temperature.

**Table 1**  
The final reaction pressures at different liquefaction runs (MPa).

Runs	Feedstock	$T$ (K)	$R_1$	$R_2$	$R_3$	Pressure (MPa)
1	<i>Spirulina</i> /HDPE	593	5/5	1/10	2/10	9.3
2	<i>Spirulina</i> /HDPE	613	5/5	1/10	2/10	9.7
3	<i>Spirulina</i> /HDPE	633	5/5	1/10	2/10	10.1
4	<i>Spirulina</i> /HDPE	653	5/5	1/10	2/10	11.4
5	<i>Spirulina</i> /HDPE	613	0/10	1/10	2/10	9.0
6	<i>Spirulina</i> /HDPE	613	2/8	1/10	2/10	9.1
7	<i>Spirulina</i> /HDPE	613	4/6	1/10	2/10	9.4
8	<i>Spirulina</i> /HDPE	613	6/4	1/10	2/10	9.5
9	<i>Spirulina</i> /HDPE	613	8/2	1/10	2/10	9.6
10	<i>Spirulina</i> /HDPE	613	10/0	1/10	2/10	9.6
11	<i>Spirulina</i> /HDPE	613	5/5	0.6/10	2/10	9.1
12	<i>Spirulina</i> /HDPE	613	5/5	0.8/10	2/10	9.2
13	<i>Spirulina</i> /HDPE	613	5/5	1.2/10	2/10	9.2
14	<i>Spirulina</i> /HDPE	613	5/5	1.4/10	2/10	9.4
15	<i>Spirulina</i> /HDPE	613	5/5	1/10	1.2/10	5.9
16	<i>Spirulina</i> /HDPE	613	5/5	1/10	1.6/10	8.5
17	<i>Spirulina</i> /HDPE	613	5/5	1/10	2.4/10	10.6
18	<i>Spirulina</i> /HDPE	613	5/5	1/10	2.8/10	11.9

Fig. 1 depicts the procedure for separating liquefaction products. The liquefaction products included gaseous, liquid, and solid phases. After the autoclave was cooled down, the gas products were vented without being further analyzed. The reaction mixture in the autoclave was collected in a beaker for separation. In addition, the autoclave was washed with 150 mL ethanol thrice. The ethanol extract was obtained by extraction followed by filtration from the reaction mixture. Ethanol was evaporated in a rotary evaporator at 343 K, after which the obtained product was weighed and labeled as Oil 1. The ethanol insoluble fraction was subsequently extracted with tetrahydrofuran (THF) to collect THF extract. After evaporating THF in a rotary evaporator, the obtained fraction was weighed and designed as Oil 2. The oil yield was represented by the combined mass of Oil 1 and Oil 2. The THF insoluble fraction remaining on the filter paper was dried at 378 K overnight to a constant weight, then weighed and designed as residue.

### 2.3. Product analysis

The bio-oil products obtained from liquefaction experiments at 613 K with different  $R_1$  (0/10, 5/5 and 10/0) were applied to analyses. The elemental compositions of the bio-oil were determined with a CHNOS Elemental Analyzer Vario EL III (Elementar Analysensysteme GmbH, Germany). The gross calorific values of the obtained oil product were determined by a KLSR-400 Bomb Calorimeter (Kesheng Instrument Manufacturing Co., Ltd., Changsha, China).

FT-IR spectra of the obtained bio-oils were recorded on a WQF-410 type FT-IR spectrometer to determine its functional groups. All samples were analyzed in the wave number range of 4000–500  $\text{cm}^{-1}$ .

GC-MS analyses were conducted on a Trace GC, Palaris Q GC-MS spectrometer (Thermo-Finnigan, USA) using carbon capillary column, DB-1 (film thickness, 0.25 mm; column dimensions, 30 m  $\times$  0.25 mm). Inject mode was set as splitless and splitless time was 1.0 min. As a carrier gas, helium was at a flow rate of 1 mL/min. The column temperature of GC used in this study was programmed from an initial temperature of 353 K up to 523 K by a heating rate of 5 K/min and finally held at 523 K for 30 min. The ionizing voltage was 70 eV, and mass ranged from 40 to 500 m/z. The identification of compounds was performed using electronic library search routines.

A scanning electron microscope (QUANTA 200, United FEI Corp.) was used to examine the morphology of obtained residues.

## 3. Results and discussion

The yield of each product was calculated as follows:

$$\text{Yield of bio-oil (wt.\%)} = \frac{\text{weight of (Oil1 + Oil2)}}{(\text{weight of feedstock})} \times 100\% \quad (1)$$

**Table 2**  
Characterization of *Spirulina* and HDPE.

Elemental analysis results of <i>Spirulina</i> and HDPE (wt.%) <sup>a</sup>						
Feedstock	C	H	O <sup>b</sup>	N	S	
<i>Spirulina</i>	42.9	8.5	39.2	8.9	0.5	
HDPE	85.5	14.2	- <sup>c</sup>	-	0.3	
Components and proximate analysis of <i>Spirulina</i>						
Proximate analysis (wt.%)			Component analysis (wt.%) <sup>a</sup>			
Volatile <sup>d</sup>	Ash <sup>d</sup>	Moisture	Crude protein	Crude fat	Crude fiber	Non-fibrous carbohydrate
89.2	10.8	4.3	69.4	8.2	3.3	19.1

<sup>a</sup> On an organic basis.

<sup>b</sup> Calculated by difference.

<sup>c</sup> Not contained.

<sup>d</sup> On a dry solid basis.

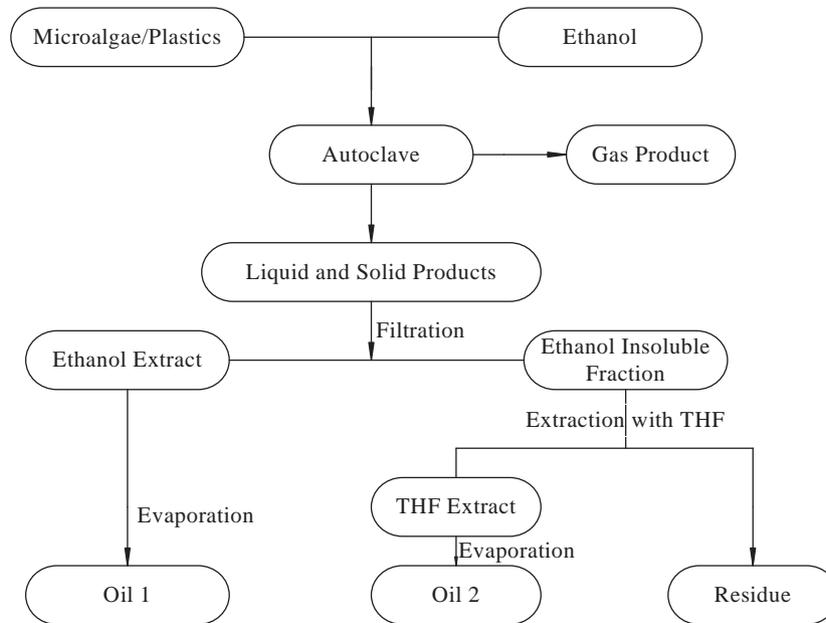


Fig. 1. Procedure for separation of products.

$$\text{Yield of residue (wt.\%)} = \frac{\text{weight of residue}}{\text{weight of feedstock}} \times 100\% \quad (2)$$

$$\text{Yield of liquefaction conversion (wt.\%)} = 100 - \text{yield of residue} \quad (3)$$

The value of synergetic effect (*SE*) of *Spirulina* and HDPE can be calculated as follows:

$$SE(\text{wt.\%}) = Y_c - (Y_0 \times Y_M + (1 - Y_0) \times Y_{HDPE}) \quad (4)$$

where  $Y_c$  (wt.%): the bio-oil yields obtained from co-liquefaction of *Spirulina* and HDPE;  $Y_M$  and  $Y_{HDPE}$  (wt.%): the bio-oil yields obtained from pure *Spirulina* and pure HDPE liquefaction in the same operational conditions, respectively;  $Y_0$  (wt.%): the weight percent of *Spirulina* in the liquefaction feedstock.

### 3.1. Effect of reaction temperature (*T*)

Fig. 2 shows the effect of reaction temperature (*T*) on the distribution of products (bio-oil and residue) during the co-liquefaction of *Spirulina*

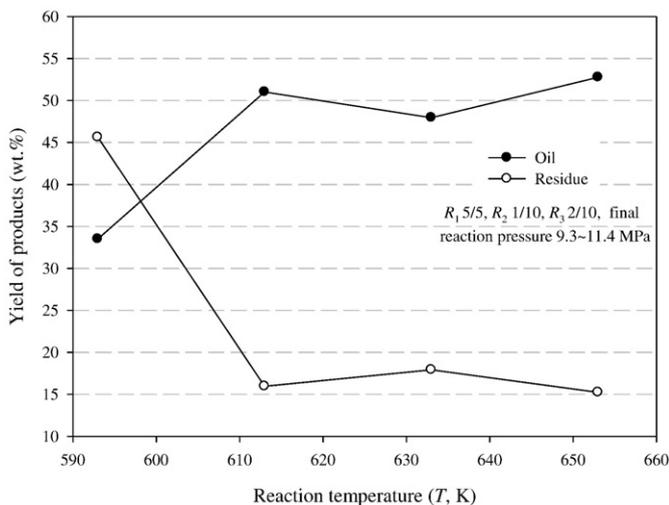


Fig. 2. Effect of reaction temperature (*T*) on the product yields.

and HDPE with fixed  $R_1$  (5/5),  $R_2$  (1/10) and  $R_3$  (2/10). As shown in the figure, the bio-oil yield increased markedly by 17.52 wt.% with the reaction temperature increasing from 593 K to 613 K. Accordingly, the yield of residue obviously declined by 29.67 wt.%. However, further increasing the reaction temperature had no obvious influence on the product yields.

It is well known that HDPE is difficult for thermal conversion because of its heat-resisting characteristics [12]. However, it was noteworthy that HDPE was successfully decomposed at a lower reaction temperature in this study. The yields of conversion obtained from co-liquefaction of *Spirulina* and HDPE at temperatures from 613 K to 653 K were all beyond 82 wt.%. This fact suggested that a large amount of HDPE had been decomposed under the given conditions. Jackab et al. [22] reported that the thermal decomposition of polypropylene could begin at a lower temperature with the addition of charcoal issued biomass. Furthermore, it was proposed that the solid products from wood decomposition influenced the depolymerization pathways of polypropylene [22]. Yang et al. put forward that the thermal stability of polymer would slightly decrease with the addition of lignocellulosic filler. The dispersion and interfacial adhesion between the lignocellulosic filler and thermoplastic polymer were important factors affecting the thermal stability of the composite system [23].

To identify the influence of *Spirulina* on the thermal stability of HDPE, the morphology of the liquefaction residues obtained from different liquefaction runs of pure HDPE and *Spirulina*/HDPE (5/5) was evaluated. Fig. 3 shows that the microfabric features of the liquefaction residue from the co-liquefaction process were markedly different from that from pure HDPE liquefaction. A bridge-like structure of the composite system was formed during co-liquefaction of *Spirulina* and HDPE (Fig. 3b). Moreover, significant pore spaces were found in the particle arrangements. The microfabric with pore spaces might create vulnerability to liquefaction of HDPE. In the other hand, during the co-liquefaction process with HDPE, *Spirulina* was decomposed and de-polymerized firstly, as expected due to a lower temperature required for *Spirulina* decomposition [7]. In summary, the decomposition of *Spirulina* could influence the thermal stability of HDPE, and finally accelerated the thermal degradation of HDPE at lower temperatures.

### 3.2. Effect of *Spirulina*/HDPE ratio ( $R_1$ )

Series of experiments varying *Spirulina*/HDPE ratio ( $R_1$ ) in the liquefaction feedstock were performed. The variations of products'

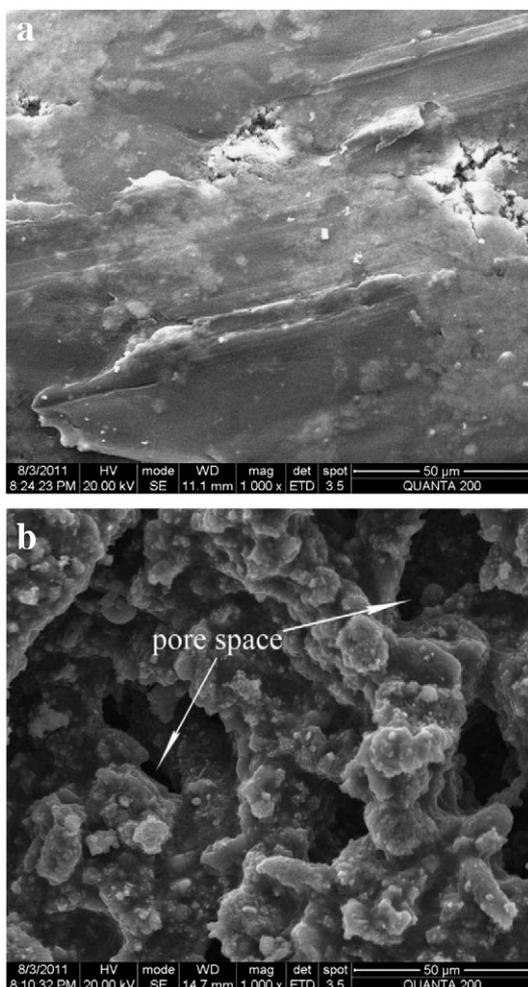


Fig. 3. SEM of liquefaction residues obtained at 613 K with different feedstock composition.

yields with different  $R_1$  at 613 K,  $R_2$  1/10 and  $R_3$  2/10 are presented in Fig. 4. Meanwhile, Fig. 5 depicts the variations of synergetic effects (SE) with different  $R_1$  for the bio-oil yields.

As shown in Fig. 4, addition of *Spirulina* had a great influence on the bio-oil yields. An almost linear increment of bio-oil yield can be observed when  $R_1$  was elevated from 0/10 to 4/6. However, further increasing  $R_1$  would lead to a decrease in bio-oil yield. The varying

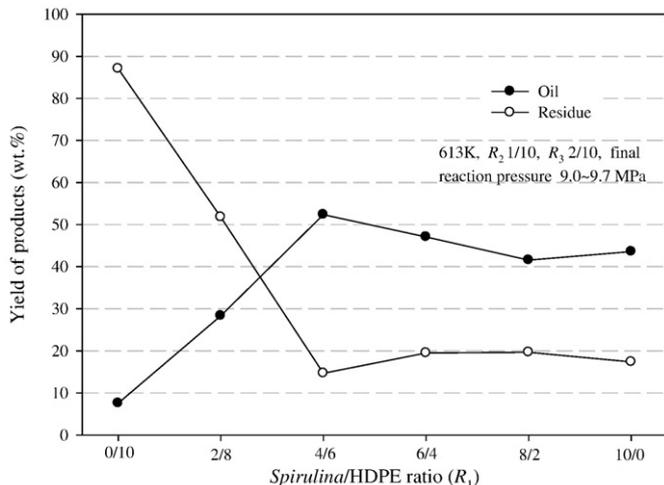


Fig. 4. Effect of *Spirulina*/HDPE ratio ( $R_1$ ) on the product yields.

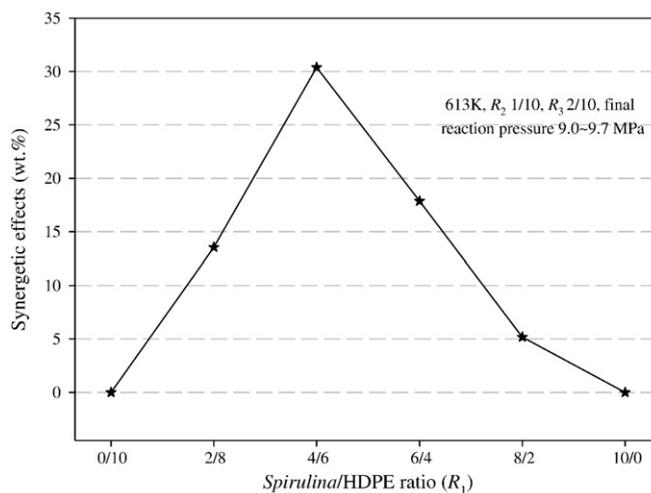


Fig. 5. Effect of *Spirulina*/HDPE ratio ( $R_1$ ) on the synergetic effects.

trend on the yield of residue was just opposite. According to Fig. 5, the synergetic effects during co-liquefaction of *Spirulina* and HDPE mixture were all positive, suggesting remarkable mutually enhancing effect. The synergetic effect increased significantly with  $R_1$  elevated from 0/10 to 4/6. When  $R_1$  was fixed at 4/6, the maximum synergetic effect was obtained (30.33 wt.%).

The point ( $R_1$  0/10) shows the experiment results of pure HDPE liquefaction. After the reaction was completed, sheet-like deposits of unconverted polymer were observed in the autoclave. The yield of bio-oil was only 7.55 wt.%. In other words, almost of HDPE were not decomposed. The point ( $R_1$  10/0) summarized the results of pure *Spirulina* liquefaction. The bio-oil yield was up to 43.59 wt.%, and the liquefaction conversion yield was as high as 82.64 wt.%, indicating that *Spirulina* was decomposed easily in the given experiment conditions. Therefore, during the co-liquefaction process, *Spirulina* would be decomposed prior to HDPE. Degradation products of *Spirulina* may play a role in promoting the decomposition of HDPE. However, the bio-oil yields and the synergetic effects decreased with further increasing  $R_1$ , implying that the rational  $R_1$  was about 4/6.

As mentioned in Section 3.1, the co-liquefaction process may be divided into two stages. In the first stage, *Spirulina* was decomposed firstly at the lower temperatures. Meanwhile, the thermal stability of HDPE was influenced by the degradation products of *Spirulina* and hence HDPE began to decompose. In the second phase, the amount of HDPE became to be the main factor influencing the co-liquefaction process. The possible reason for explaining this point may be that HDPE was a hydrogen donor during the co-liquefaction reactions. The active hydrogen could stabilize the free radicals formed during decomposition of *Spirulina* and hence prevent the condensation reactions of free radicals [24].

### 3.3. Effect of (*Spirulina* + HDPE)/ethanol ratio ( $R_2$ )

The effect of (*Spirulina* + HDPE)/ethanol ratio ( $R_2$ ) on the products' yields was investigated at 613 K with  $R_1$  5/5 and  $R_3$  2/10. Specific results are listed in Fig. 6. The oil yield increased from 32.56 to 51.20 wt.% when  $R_2$  was increased from 0.6/10 to 1/10. However, further increasing  $R_2$  to 1.4/10 led to a significant decrease in the bio-oil yield. An opposite trend was observed for the yield of residue.

The major functions of solvent during liquefaction process were decomposing raw feedstock materials and providing active hydrogen by hydride transfer of their  $\alpha$ -hydrogen through a so-called "hydrogen shuttling" mechanism [29]. Increasing  $R_2$  implied that the amount of liquefaction feedstock was increased. But the relative amount of liquefaction solvent was reduced. In other words, the

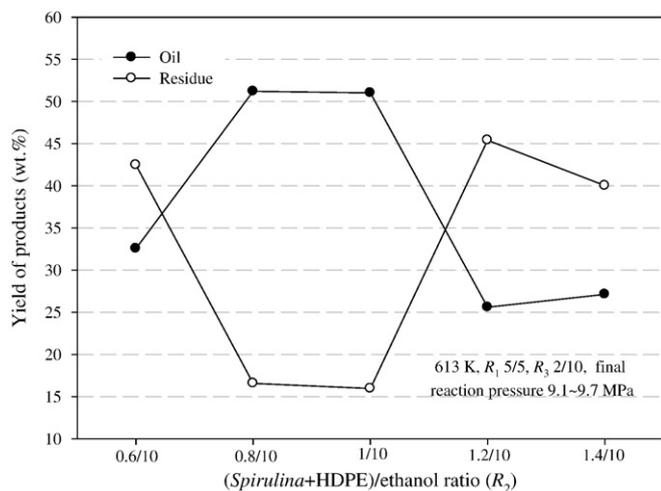


Fig. 6. Effect of  $(Spirulina + HDPE)/ethanol$  ratio ( $R_2$ ) on the product yields.

functions of solvent (dissolving and stabilization) were relatively weakened. Therefore, the yield of bio-oil would be reduced when  $R_2$  exceeded the optimum point. In the other hand, excessive solvent (at the lower  $R_2$ ) may serve to keep the decomposition intermediates from *Spirulina* and HDPE in proximity of each other for longer period of time and deactivate the thermally excited molecules through collisions [30]. Therefore, a lower yield of bio-oil was obtained at lower  $R_2$  below the critical value. Similar results have been also found by Bookcock et al. [31].

### 3.4. Effect of the solvent filling ratio ( $R_3$ )

The solvent filling ratio ( $R_3$ ) was defined as the ratio of the volume of ethanol solvent (mL) to that of the autoclave (1000 mL). The effect of  $R_3$  on the co-liquefaction characteristics of *Spirulina* and HDPE is depicted in Fig. 7. The data presented in this figure were obtained from the experimental runs at 613 K with  $R_1$  5/5,  $R_2$  1/10 and different  $R_3$ . According to Fig. 7, the yield of bio-oil was improved from 33.01 to 51.02 wt.% with  $R_3$  increasing from 1.2/10 to 2/10. After then, a declining trend was followed when  $R_3$  further increased from 2/10 to 2.8/10. As regard to the yield of residue, a decline trend was observed firstly, and then a rising phenomenon appeared. It was also found that  $R_3$  had a positive correlation with final reaction

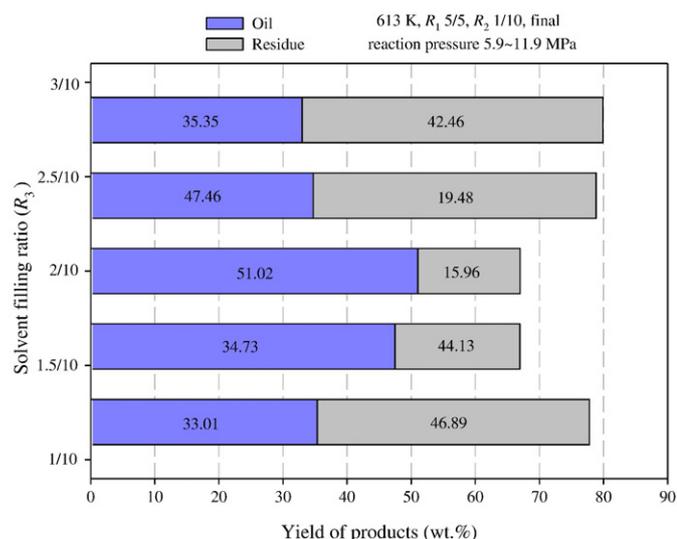


Fig. 7. Effect of solvent filling ratio ( $R_3$ ) on the product yields.

pressures. The final reaction pressures increased approximately two times when  $R_3$  was promoted from 1.2/10 to 2.8/10.

There were several reasons for explaining the fact that the yield of bio-oil increased with the increment of  $R_3$ . (1) The extraction activity between the decomposition materials and ethanol may also be enhanced with increasing reaction pressures [32]; (2) The prompting pressure in reaction system could reduce the condensation, cyclization and re-polymerization of the intermediates and liquid product [5]; (3) the higher the system pressure during liquefaction, the less liquid components would be gasified [33].

However, further increasing  $R_3$  from 2/10 to 2.8/10 led to a decrease in the bio-oil yield. Large amounts of deposits with a smooth surface were found in the experimental runs at higher  $R_3$  (2.4/10 and 2.8/10). Due to the high viscosity of HDPE, adhesion between *Spirulina* and HDPE might impede the heat and mass transfer during the co-liquefaction process. As clearly shown in Fig. 8, the morphology of the liquefaction residues obtained at 613 K with different  $R_3$  (1.2/10, 2.0/10 and 2.8/10) was obviously different. At a low  $R_3$  (1.2/10), the size of the liquefaction residue (Fig. 8a, b) was much smaller than that of the liquefaction residues at higher  $R_3$  (Fig. 8c–f). It indicated that the mixture of *Spirulina* and HDPE was cracked into small irregular fragments during liquefaction. As regards the liquefaction residue obtained at a higher  $R_3$  (2/10), a bridge-like structure bonding the small fragments was observed (Fig. 8c, d). Further increasing  $R_3$  to 2.8/10, HDPE adhered to the interface of *Spirulina* forming an almost continuous matrix. This compact structure with limited pore space significantly impeded heating and mass transfer. Therefore, a lower bio-oil yield was obtained with further increasing  $R_3$  to 2.8/10.

Attentions should also be paid to the fact that when  $R_3$  was 1.2/10, the final reaction pressure was 5.9 MPa. Therefore, the experiment was conducted under subcritical conditions (critical point of ethanol: temperature 516 K, pressure 6.37 MPa). The yield of bio-oil in subcritical condition was lower than those in supercritical conditions. This may be due to the advantage of super-critical fluids. Super-critical fluids not only possessed unique transport properties (gas-like diffusivity and liquid-like density), but also had complete miscibility with the liquid/vapor products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions [34].

### 3.5. Characterizations of liquid products (bio-oil)

#### 3.5.1. Elemental analysis

Table 3 presents the elemental compositions of bio-oils obtained from different liquefaction runs at 613 K with  $R_2$  1/10,  $R_3$  2/10 and different  $R_1$  (0/10, 5/5 and 10/0). As expected, the bio-oils obtained from pure plastic liquefaction runs ( $R_1 = 0/10$ ) were enriched in H and C, accompanied with a high calorific value (51.02 MJ/kg). In the *Spirulina*/HDPE co-liquefaction runs ( $R_1 = 5/5$ ), the bio-oils contained higher H content and lower O concentration in comparison to those in the pure *Spirulina* runs ( $R_1 = 10/0$ ). As shown in Table 2, the content of H in HDPE was high to 14.2 wt.%, while that in *Spirulina* was only 8.5 wt.%. Therefore, the higher H content in bio-oil from *Spirulina*/HDPE mixture may be due to hydrogen matching reactions between *Spirulina* and HDPE during co-liquefaction process.

Moreover, the O/C ratio decreased from 0.11 to 0.04 when HDPE was added to pure *Spirulina* liquefaction process. The greatly reduced oxygen content in the bio-oil could be mainly attributed to two reasons including (1) a hydrogen-donor process of the combination of oxygen in *Spirulina* with hydrogen in HDPE to produce water (2) formation of CO/CO<sub>2</sub> through decarboxylation reactions were promoted during the co-liquefaction process [32, 35]. Heating values of the obtained bio-oils were remarkably promoted with the percent of HDPE in the mixture increasing. In the case of co-liquefaction of *Spirulina* and HDPE, the heating value of the oil was 48.35 MJ/kg, significantly higher than that of pure *Spirulina*-derived bio-oil.

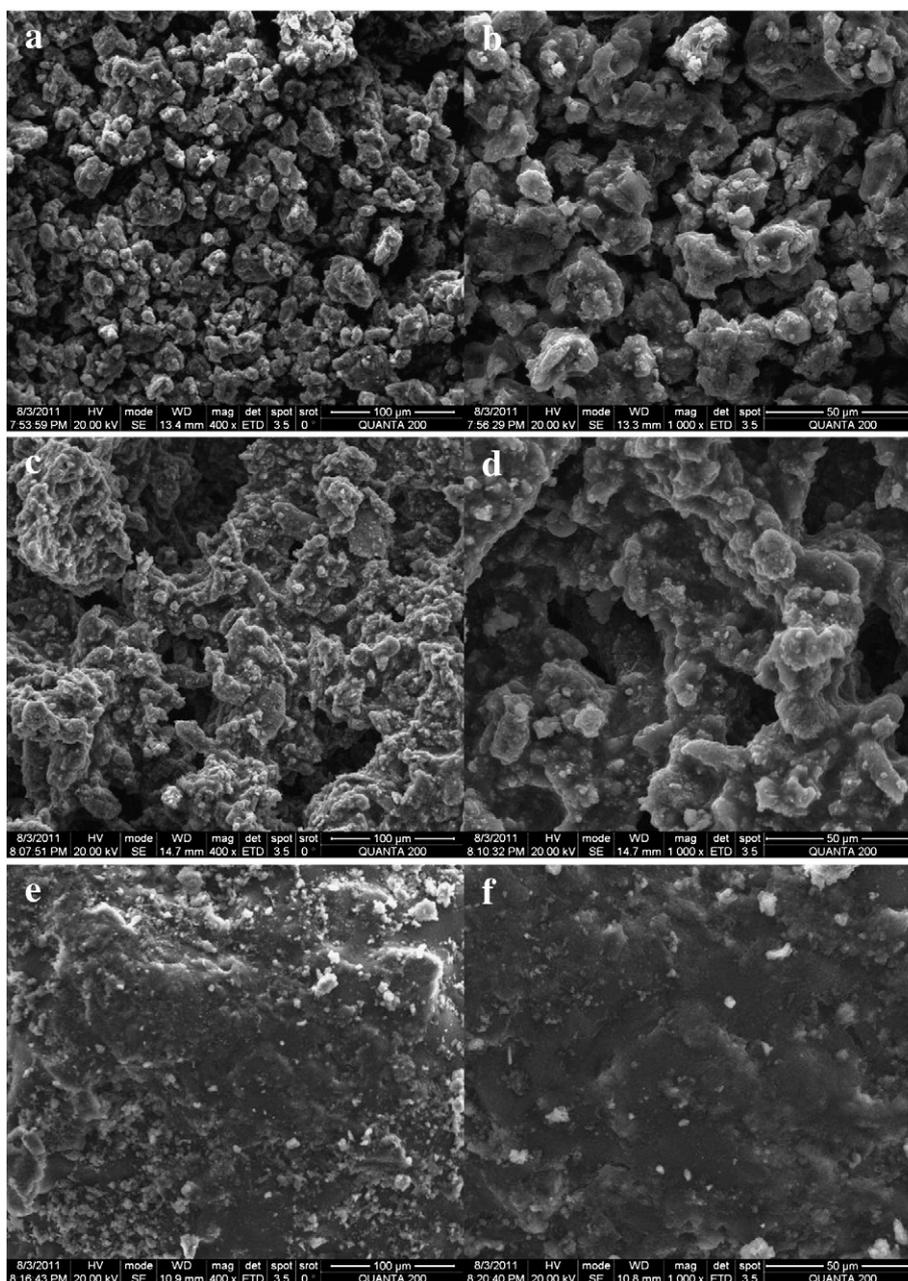


Fig. 8. SEM of liquefaction residues obtained at 613 K with different  $R_3$  (1.2/10, 2.0/10 and 2.8/10).

### 3.5.2. FT-IR analysis

The FT-IR spectra of bio-oils obtained from liquefaction of pure *Spirulina*, pure HDPE and *Spirulina*/HDPE mixture (5/5) are presented in Fig. 9 and the analysis results are summarized in Table 4. For the pure *Spirulina*-derived bio-oil, the broad vibration at around

Table 3

Elemental analyses and calorific values of bio-oils from liquefaction of pure *Spirulina* ( $R_1$  10/0), pure HDPE ( $R_1$  0/10) and *Spirulina*/HDPE mixture ( $R_1$  5/5) at 613 K with  $R_2$  1/10 and  $R_3$  2/10.

Sample	Weight fraction (wt.%)					O/C ratio	H/C ratio	Heating value (MJ/kg)
	C	H	O <sup>a</sup>	N	S			
Pure <i>Spirulina</i>	63.96	17.04	7.12	9.87	2.01	0.11	0.27	<b>35.69</b>
<i>Spirulina</i> /HDPE	67.97	20.20	3.04	7.16	1.64	0.04	0.30	<b>48.35</b>
Pure HDPE	72.25	26.07	0.66	0.17	0.86	0.01	0.36	<b>51.02</b>

<sup>a</sup> By difference.

3253  $\text{cm}^{-1}$  can be attributed to O–H stretching vibrations indicating the presence of phenols or alcohols. The strong signals observed at 1730–1700  $\text{cm}^{-1}$  were typical for the C=O stretching vibration. Their appearance may be connected with the presence of aliphatic carboxylic acids. Moreover, weak signals at 2950–2800  $\text{cm}^{-1}$  and 1460–1350  $\text{cm}^{-1}$  were assigned to alkyl groups. Meanwhile, strong signals were observed at 770–735  $\text{cm}^{-1}$ , corresponding to aromatic compounds and their substituted derivatives.

The mixing of HDPE and *Spirulina* intensely changed the spectra of bio-oils. Characteristic vibrational modes originated from alcohols disappeared. The distribution of functional groups in bio-oil from co-liquefaction of *Spirulina*/HDPE mixture was similar to that in bio-oil from pure HDPE liquefaction, in which a wide range of intensive signals corresponding to hydrocarbons was detected. The C–H stretching vibrations at 2950–2850  $\text{cm}^{-1}$  and 995–905  $\text{cm}^{-1}$ , the C–H bending vibrations at 1465–1375  $\text{cm}^{-1}$  and the CH<sub>2</sub> rocking vibrations at 720  $\text{cm}^{-1}$  were indicative for long aliphatic hydrocarbons.

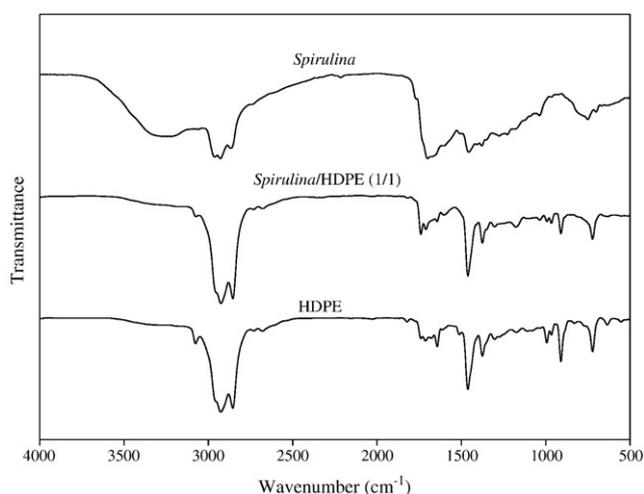


Fig. 9. FT-IR spectra of bio-oils.

Meanwhile, the absorption band between 1675 and 1575  $\text{cm}^{-1}$  and the weak band at around 3075  $\text{cm}^{-1}$ , representing the C=C and C=C–H stretching vibrations, respectively, were indicative for internal alkenes and aromatics [36]. Additionally, alkynes may exist in the bio-oil from pure HDPE liquefaction proved by the vibration at 650–600  $\text{cm}^{-1}$ .

### 3.5.3. GC-MS analysis

GC-MS analysis results of the bio-oils obtained from liquefaction of pure *Spirulina*, pure HDPE and *Spirulina*/HDPE mixture (5/5) based on peak areas are listed in Table 5. The total ion chromatograms of bio-oils are presented in Fig. 10. It was clearly shown that the composition of liquefaction feedstock obviously affected the components of bio-oils.

The bio-oil derived from pure *Spirulina* mainly consisted of oxygen containing compounds including fatty acids, fatty acid esters, and ketones etc. Octadecanoic acid (RT = 27.39 min) was the most abundant compound, according to the maximum peak area (41.23%). Meanwhile, nitriles and nitrogen heterocycles (for example, pyrroles and

Table 4

FT-IR analysis results of bio-oils from liquefaction of pure *Spirulina* ( $R_1$  10/0), pure HDPE ( $R_1$  0/10) and *Spirulina*/HDPE mixture ( $R_1$  5/5) at 613 K with  $R_2$  1/10 and  $R_3$  2/10.

Functional group	Wave number ( $\text{cm}^{-1}$ )	<i>Spirulina</i>	<i>Spirulina</i> /HDPE	HDPE
<i>Alkyl</i>				
C–H stretching	2950–2800	w	+	+
CH <sub>2</sub> bending	~1460	+	+	+
CH <sub>3</sub> bending	~1375	w	+	+
CH <sub>2</sub> bending (four or more)	~720	–	+	+
<i>Alkenyl</i>				
=C–H stretching	3100–3010	–	+	+
C=C stretching	1690–1630	–	+	+
C–H bending	~990, ~970, ~910	–	+	+
<i>Alkynyl</i>				
=C–H bending	650–600	–	–	+
<i>Aromatic</i>				
Substitution in aromatic ring	770–735	+	–	–
<i>Carboxylic acids</i>				
C=O stretching	1730–1700	+	–	–
<i>Alcohols, phenols</i>				
O–H stretching	3600–2400	b	–	–

b: broad signal.  
w: weak peak.

Table 5

Organic compounds identified in bio-oils from liquefaction of pure *Spirulina* ( $R_1$  10/0), pure HDPE ( $R_1$  0/10) and *Spirulina*/HDPE mixture ( $R_1$  5/5) at 613 K with  $R_2$  1/10 and  $R_3$  2/10.

No.	Compound	Samples		
		<i>Spirulina</i>	<i>Spirulina</i> /HDPE	HDPE
1	Pyrrole,3-ethyl-2,4,5-trimethyl-	○	△	△
2	Benzenepropanoic acid, ethyl ester	●	△	△
3	Pyrrolidine,1-(7-oxo-2,4,6-trimethylheptanoyl)-	○	△	△
4	Benzonitrile, 2,4,6-trimethyl-	○	△	△
5	Heneicosane	●	△	△
6	Hexadecanenitrile	●	△	△
7	Ethyl-9-hexadecenoate	●	△	△
8	Octadecanoic acid	●	●	△
9	Linoleic acid ethyl ester	●	△	△
10	Ethyl oleate	●	△	△
11	Heptadecanoic acid, 15-methyl-, ethyl ester	●	△	△
12	Androstan(A)-3-formoxy-11-ol-17-one	○	△	△
13	Phenol, 3-methyl-	△	○	△
14	4-(2,5-dihydro-3-methoxyphenyl)butylamine	△	○	△
15	Oleic acid	△	○	△
16	Geranyl isovalerate	△	●	△
17	1-Nonadecene	△	●	●
18	Docosane	△	●	●
19	Tetradecane, 2,6,10-trimethyl-	△	●	△
20	1-Eicosylene	△	●	△
21	Pentacosane	△	●	○
22	Pentadecane, 8-hexyl-	△	●	●
23	Heptacosane	△	●	○
24	1-Docosene	△	○	●
25	Nonacosane	△	●	○
26	Dotriacontane	△	●	○
27	Pentatriacontane	△	●	△
28	Cyclotridecane	△	△	○
29	Nonadecane	△	△	○
30	9-Nonadecene	△	△	●
31	Eicosane	△	△	●
32	10-Heneicosene	△	△	●
33	Tetracosane	△	△	●
34	9-Octadecyne	△	△	●
35	Phenol nonyl-	△	△	○
36	Octacosane	△	△	●
37	Z-1 2-pentacosene	△	△	○
38	1-docosanol	△	△	○
39	Heneicosane,11-(1-ethylpropyl)-	△	△	○
40	Erucic acid	△	△	○
41	17-pentatriacontene	△	△	○

● Peak area beyond 2% of total area.

○ Peak area between 1 and 2% of total area.

△ Peak area less than 1% of total area.

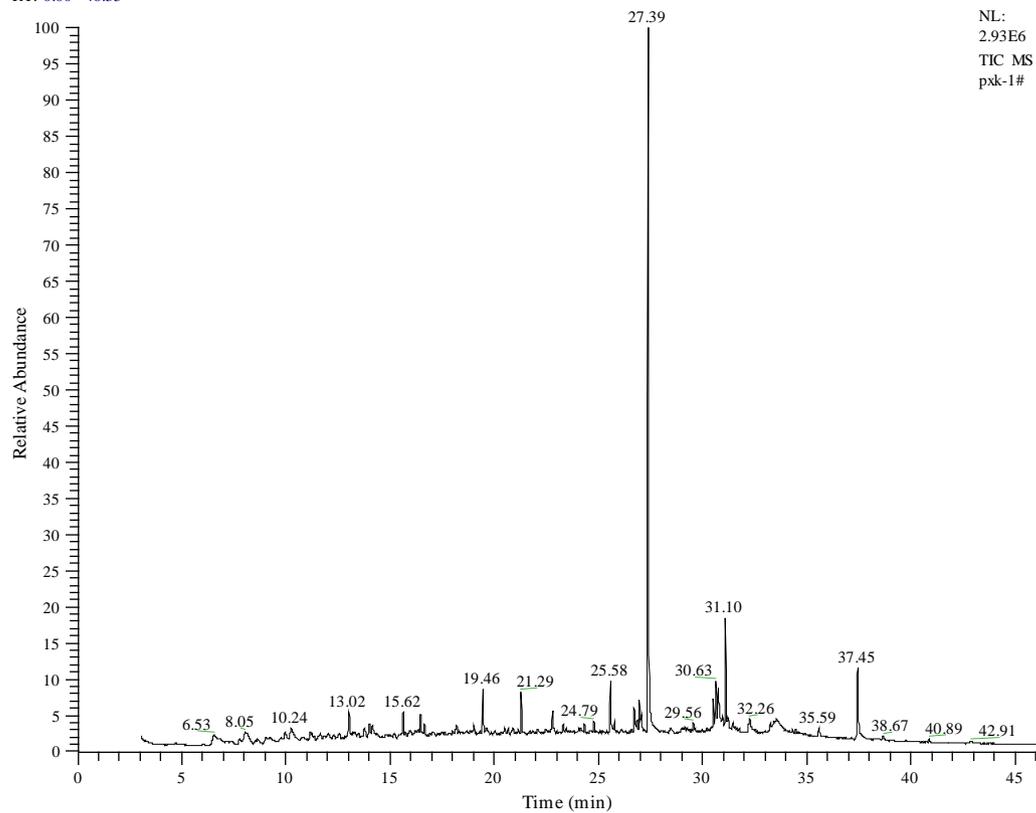
pyridines) had also been observed. The presence of a large amount of oxygen and nitrogen containing compounds may be ascribed to the decomposition of protein, the main component of *Spirulina* biomass, through decarboxylation and deamination reactions during liquefaction [37]. Lots of ethyl esters were produced mainly attributed to the esterification between organic acid and solvent ethanol.

As regards the bio-oil derived from HDPE, wide spectrum of hydrocarbon fragments was present, which included saturated and unsaturated aliphatic hydrocarbons. Now that all the C–C bonds in the HDPE chain were equivalent, HDPE was expected to show random bond scission along the chain, resulting in producing a distribution of aliphatic hydrocarbons of varying length [16, 30].

For the bio-oil from co-liquefaction of *Spirulina*/HDPE mixture, high content of aliphatic hydrocarbons was also detected. Compared with the bio-oil from pure microalgae, the amount of oxygen-containing compounds significantly decreased. The peak area belonging to octadecanoic acid declined to 11.76%. Moreover, the fatty acid esters disappeared when *Spirulina* was blended with HDPE. In other words, addition of HDPE could reduce the formation of oxygen-containing compounds, and favor the formation of hydrocarbons.

**(a) *Spirulina***

RT: 0.00 - 46.35

**(b) *Spirulina*/HDPE(5/5)**

RT: 0.00 - 45.15

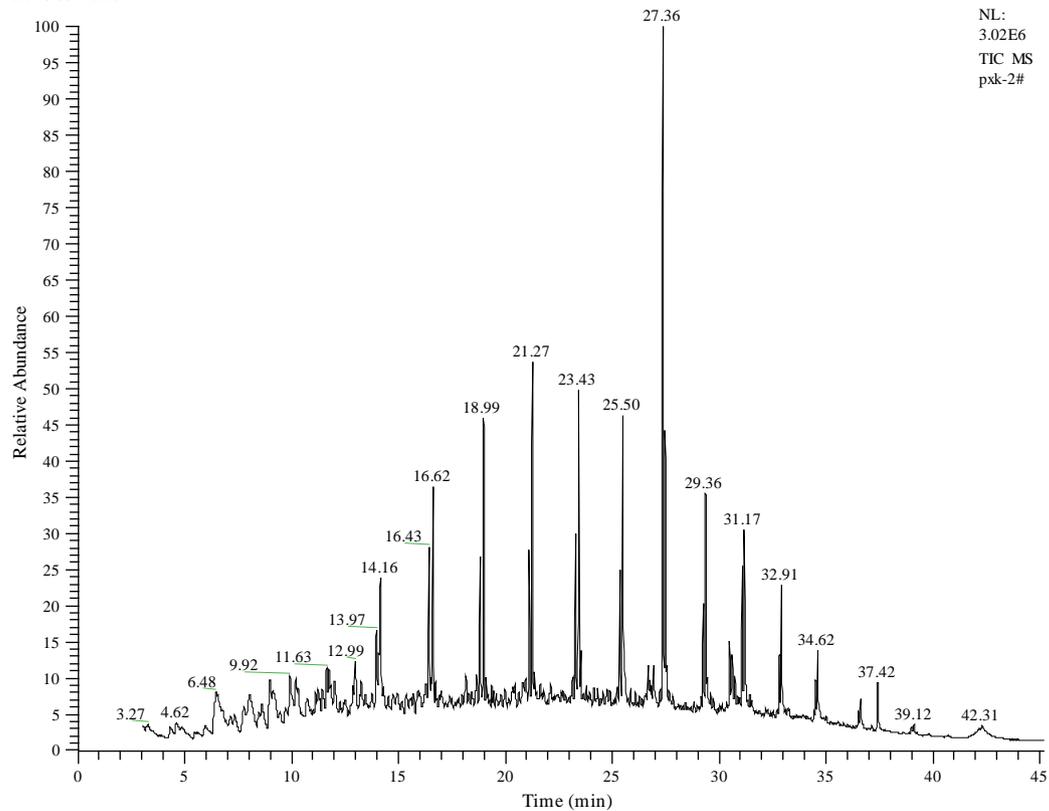


Fig. 10. Total ion chromatograms of bio-oils.

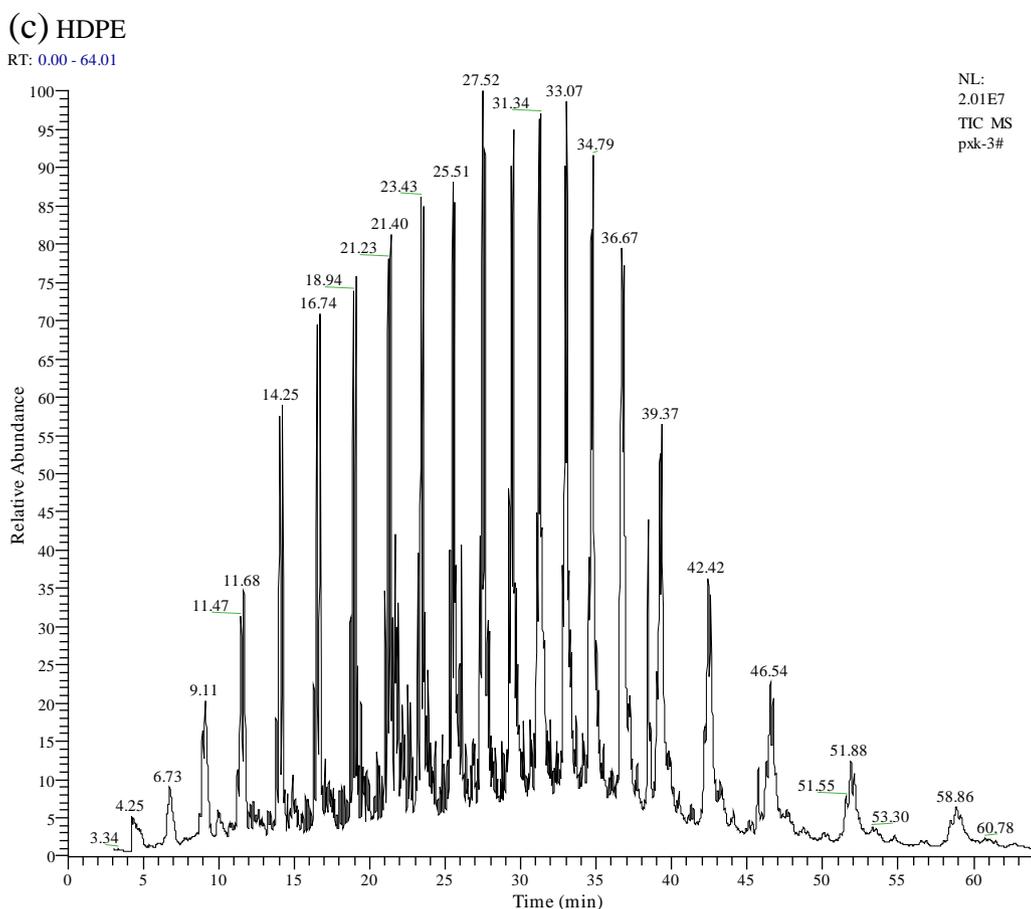


Fig. 10 (continued).

The chemical compositions of the bio-oil derived from *Spirulina*/HDPE co-liquefaction were similar to that from pure HDPE liquefaction, which indicated that a significant number of HDPE had been thermally decomposed with the addition of microalgae at 613 K. This supported the above hypothesis mentioned in Section 3.1 that the introduction of *Spirulina* could enhance the susceptibility toward thermal degradation of HDPE and lower the reaction temperature required for HDPE decomposition. Among the hydrocarbons detected in the bio-oil derived from co-liquefaction of *Spirulina*/HDPE mixture, a large proportion of saturated compounds were included. Meanwhile, higher content of unsaturated hydrocarbons was detected in the bio-oil from pure HDPE. It may be supposed that large amounts of unsaturated products from HDPE decomposition reacted with degradation products of *Spirulina* to the formation of saturated compounds. Moreover, there was a wide range of molecules present in the bio-oil from *Spirulina*/HDPE co-liquefaction. This indicated that some secondary reactions between the decomposing products took place during the co-liquefaction processes.

#### 4. Conclusions

During co-liquefaction process, the decompositions of *Spirulina* and HDPE were mutually enhanced. Firstly, the presence of *Spirulina* during the co-liquefaction process makes the degradation conditions of HDPE milder. At 613 K, large amounts of HDPE were converted. Secondly, the quality of the bio-oil derived from *Spirulina* could be improved for the high content of H in HDPE. The bio-oil from *Spirulina*/HDPE co-liquefaction had higher C and H content but a lower O content, resulting a higher calorific value (48.35 MJ/kg). In addition, the chemical compositions of the bio-oil from liquefaction of *Spirulina*/HDPE mixture were similar to that from pure HDPE liquefaction,

in which aliphatic hydrocarbons dominated. The microfabric features of liquefaction residues were likely to be influenced by the solvent filling ratio. At higher solvent filling ratio, the “compact” microfabric with limited pore space was formed, which may impede heating and mass transfer during the co-liquefaction process.

#### Acknowledgments

This research was supported by the Key Project for Science and Technology Research, Ministry of Education of China (No. 108100), the National Natural Science Foundation of China (No. 50978087), and Hunan Provincial Innovation Foundation for Postgraduate (CX2009B078).

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