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A comparative study of bio-oils from pyrolysis of microalgae and oil seed waste in a fluidized bed

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HIGHLIGHTS

- Pyrolysis of *Scenedesmus* and *Jatropha* waste was compared under similar condition.
- Microalgae bio-oil was featured by higher H/C and O/C molar ratios compared to JSC.
- Microalgae bio-oil has high fractions of aliphatics, FAAE, alcohols and nitriles.
- Microalgae showed potentials for alternative feedstock for green fuel and chemicals.

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ABSTRACT

The pyrolysis of *Scenedesmus* sp. and *Jatropha* seedshell cake (JSC) was investigated under similar operating condition in a fluidized bed reactor for comparison of pyrolytic behaviors from different species of lipids-containing biomass. Microalgae showed a narrower main peak in differential thermogravimetric curve compared to JSC due to different constituents. Pyrolysis liquid yields were similar; liquid's oil proportion of microalgae is higher than JSC. Microalgae bio-oil was characterized by similar carbon and hydrogen contents and higher H/C and O/C molar ratios compared to JSC due to compositional difference. The pyrolytic oils from microalgae and JSC contained more oxygen and nitrogen and less sulfur than petroleum and palm oils. The pyrolytic oils showed high yields of fatty oxygenates and nitrogenous compounds. The microalgae bio-oil features in high concentrations of aliphatic compounds, fatty acid alkyl ester, alcohols and nitriles. Microalgae showed potentials for alternative feedstock for green diesel, and commodity and valuable chemicals.

1. Introduction

Pyrolysis is one of the most promising technologies of biomass utilization, which converts the biomass to bio-oil, char and gasses depending on the pyrolysis conditions (Bridgwater et al., 1999). The pyrolysis is a thermal degradation of materials in the absence of oxygen. The pyrolysis can be a promising option for lignocellulosic biomass conversion because bio-oils derived from biomass pyrolysis could act as feedstocks for producing hydrocarbons that may be readily integrated into the existing petroleum refineries or future bio-refineries (Kim et al., 2013a).

Much attention has focused on identifying suitable biomass species capable of high energy outputs to replace conventional fossil fuels. However, low conversion efficiency, availability and logistical constraints are major challenges to the large scale development of biomass-based facilities for the production of fuels and chemicals (Caputo et al., 2005). One of the most viable renewable energy sources is biomass from agricultural residues, because it is cheap, abundant and does not require significant effort to collect (Eom et al., 2013). The residue from fruit for oil production such as *Jatropha* seedshell cake or palm kernel shell has an additional benefit in terms of transportation because it can be utilized on the spot after oil processing. Especially, the residue is useful for liquid fuel production using the pyrolysis technology, because they are remnants from oil extraction and contain oil residue such as fatty acid in the shell cake (Kim et al., 2013a; Singh et al., 2014). However, the production amount of the residues is small because they are a part of the fruits, and the utilization of the residues could be limited in industrial energy production.

Microalgae have been suggested as very good candidates for production of renewable fuel because of their advantage of higher photosynthetic efficiency, higher biomass production and faster growth compared to the lignocellulosic materials (Miao et al.,

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2004; Peng et al., 2001). The microalgae can contain substantial amounts of lipids like fruit oil seed. In principle, bio-oil produced from pyrolysis of the microalgae might have improved properties (Harman-Ware et al., 2013). Hence, the use of microalgae as a feedstock for the production of biofuels offers many opportunities if challenges in large-scale cultivation, harvesting, dewatering of harvested algae and conversion to fuels can be overcome (Amin, 2009; Brennan and Owende, 2010). Many studies have previously reported on pyrolysis of microalgae. Several studies showed that different types of microalgae have their own optimal operating conditions for relatively high oil yields. However, most of the studies, which report results of pyrolysis of microalgae or other aquatic species, do not include comparisons of results with lignocellulosic biomass for which a much larger body of literature and economic feasibility studies are available (Wright et al., 2010; Maddi et al., 2011). A few studies compared the bio-oil properties with pyrolytic oil from lignocellulosic biomass data in literature (Miao et al., 2004). However, bio-oil yield and components vary with reactor type or geometry, because activation energy of decomposition and reaction path depend on the heating rate (Cao et al., 2004). In addition, pyrolytic oil yield and components are affected by the fluidizing conditions, such as gas velocity and static or expanded bed height in case of fluidized bed. Recently, Maddi et al. (2011) reported a comparison study of pyrolytic bio-oils from microalgae and lignocellulosic biomass under similar condition in fixed bed. The results are significant as feasibility study, but pyrolysis in the fixed bed is not much attractive for commercial application of liquid fuel production compared to that in fluidized bed due to high energy input relating with low heating rate of fixed bed (Miao et al., 2004).

In this study, microalgae and oil seedshell waste were pyrolyzed under similar reactor condition in a fluidized bed pyrolyzer for comparison of pyrolytic behaviors and pyrolytic oils from different species of lipids-containing biomass. The study has determined characteristics of pyrolytic bio-oil produced from *Scenedesmus*, a microalgae species with wide range of lipid contents suitable for biodiesel production and amenable for wastewater treatment (Vardon et al., 2012). The bio-oil was compared with pyrolytic bio-oil from *Jatropha* seedshell cake (JSC) as oil seedshell waste, which showed a potentiality for bio-fuel production due to higher containing of fatty acid compared to other lignocellulosic biomass (Kim et al., 2013a). The pyrolysis bio-oils from microalgae and JSC were also compared with petroleum fuel oils and feedstocks for bio-diesel production. Possible applications of the oils are discussed with respect to their practicalities in petrochemical refineries.

2. Methods

2.1. Raw material

The algae feedstock (*Scenedesmus* sp.) was provided by Korea Research Institute of Bioscience and Biotechnology at Daejeon, Korea. Sample of *Jatropha* (*Jatropha curcas* L.) seedshell cake (JSC) was acquired from an oil extraction plant in Indonesia.

Proximate analysis was carried out by an analyzer of model Thermostep (ELTRA) according to the ASTM 5142 standard test method. Elemental composition by ultimate analysis was obtained by an elemental analyzer of model EA 1108 (Fisons instruments) according to the ASTM D3176 standard procedures. The high heating values (HHVs) were obtained by an analyzer of model Parr-1261 (Parr Instrument).

For determination of the total lipid content in microalgae, the Bligh and Dyer method was used (Bligh and Dyer, 1959). The Kjeldahl method was used to determine protein content in microalgae (Makkar et al., 2008). Chemical composition for macrocomponents of JSC was determined according to the TAPPI (Technical Association of the Pulp and Paper Industry) method. For these determinations, first removal of soluble extractives was performed according to TAPPI T264 om-97. Then, lignin and cellulose in JSC were determined according to TAPPI T222 om-83 and TAPPI T203 os-74, respectively, and holocellulose according to Browning method (Browning, 1967). Hemicellulose concentration in JSC was calculated as the difference between holocellulose and cellulose.

To compare the properties of the pyrolytic oils with petroleum fuel oils, high sulfur diesel (HS diesel) and heavy fuel oil (HFO) samples with low and high sulfur content were acquired from SK Energy's Ulsan complex, Korea. Crude palm oil (CPO) and palm fatty acid distillate (PFAD) sample were also obtained from an oil mill in Pertamina, Indonesia.

2.2. Experiments

Microalgae sample was dried by freeze dryer. The dried algae clusters were then milled and sieved to 0.125–0.701 mm. JSC sample was ground and sieved to 0.125–1.40 mm using an electric mixer and standard sieves. The resulting particles were dried at 80 °C for 24 h until constant weight. Bed materials for the fluidized bed pyrolyzer were selected considering fluidity, stability and abrasion resistance: silicon carbide (d_p = 190 μm, ρ_s = 3210 kg/m^3) was used for both microalgae and JSC.

To confirm the thermal decomposition characteristics of microalgae and JSC as a preliminary to pyrolysis test, thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were performed using the TGA-1 (Mettler Toledo, Swiss). TG analysis of the samples (3.0 mg) was carried out at 30 °C/min at temperatures ranging from 40 to 800 °C. A carrier gas of purified nitrogen was flowed at a rate of 25 mL/min to maintain an inert atmosphere.

The pyrolysis system (Fig. 1) consisted of a mass flow controller (MFC), main column, screw feeder, cyclone, condensers, and accumulative flowmeter. The flow rate of nitrogen (99.9%) for fluidization was controlled by the MFC and the volume of product gas was measured by the accumulative flowmeter. Before entering the stainless steel fluidized bed reactor (0.102 m id. and 0.97 m high), the fluidizing N_2 gas was preheated in the air plenum to 440 °C. A

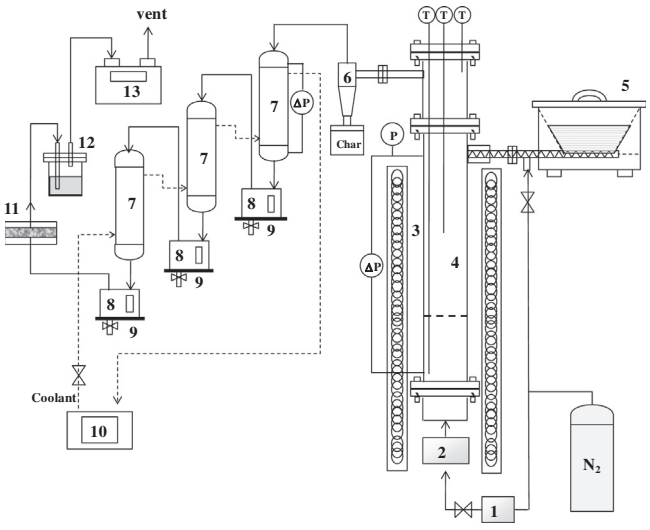

Fig. 1. The experimental apparatus. 1, mass flow meter; 2, preheater; 3, furnace (electric heater); 4, fluidized bed reactor(pyrolyzer); 5, screw feeder; 6, cyclone; 7, condenser; 8, sampling pot; 9, heating plate; 10, chiller; 11, oil filter; 12, water trap; 13, accumulated gas flowmeter; P, pressure gauge; ΔP, differential pressure gauge; T, thermowell.

distributor with 7 bubble caps, each with 4 orifices (holes of 1 mm), was fitted at the bottom of the reactor to allow even gas distribution. To prevent condensation of the pyrolysis vapor, the reactor's top and the pipe connecting the reactor to the 1st condenser were maintained at 400 °C. Refrigerant was circulated in the shell of the condensers by a chiller system. The gas was sampled by a gas sampler to analyze its composition.

A pyrolysis test condition, such as temperature and gas velocity, was determined based on authors previous study (Kim et al., 2013a), which found a condition to maximize pyrolytic liquid yield by balancing yield-increasing by much vigorous bubbling and bed mixing in fluidized bed reactor. The pyrolysis tests were conducted at 440 °C with N_2 flow rates of 33 L/min at 25 °C (superficial gas velocities of 0.067 m/s), corresponding to ca. 8.7 U_{mf} at 440 °C and bubbling fluidization regime. Static bed heights of 0.2 m were maintained in each test, giving residence times of the pyrolysis vapor out of the bed of *ca.* 3.8 s considering expansion of the fluidized bed. Biomass particles (average size = 0.42 mm for microalgae and 0.71 mm for JSC) were fed at approximately 1.0 kg/h. Pyrolysis liquid product was collected in the oil sampling pots. Aerosol from the condenser was trapped in an oil filter. After pyrolysis, the filter was washed with methanol. The amount of trapped pyrolysis oil was determined after evaporating the solvent.

2.3. Product analysis

The collected liquid was distilled at 100 °C to separate aqueous and oil phases using a set of 3 batch fractionators which simulate simple oil refining. To assess the oils' applicability as fuel, the oil phase products were characterized by the standard procedures used to assess conventional petroleum fuel. The following properties were determined: (a) specific gravity (ASTM D-4052), (b) calorific values (ASTM D-2222), (c) total acid number or TAN (ASTM D-664), (d) distillation curve (ASTM D-2887), (e) proximate analysis by thermogravity analyzer (Thermostep, ELTRA) and (f) elemental analysis by elemental analyzer (EA1110, CE instruments). The oil phase was characterized by GC/MS analysis (Gas chromatograph (GC: Agilent model 5972) equipped with mass spectroscopy detector (MS: Hewlett Packard model 5973)) to determine its qualitative and semi-quantitative composition. A HP-5MS UI (Hewlett Packard) capillary column (60 m × 0.25 mm × 0.25 μm film thickness) was used for the analyses. GC carrier gas was He (1.0 mL/min). The temperature program was as follows: constant temperature of 40 °C for 5 min followed by temperature ramp to 300 °C at 10 °C/min and finally a constant temperature of 300 °C for 10 min. Chemical compounds corresponding to each peak in chromatograms were identified by comparing the MS data with NIST and Wiley Libraries. Product selectivities were evaluated by area percentage (%) of each peak detectable in GC/MS. It should be noted that many higher boiling point compounds such as poly-aromatic hydrocarbons are not capable of being analyzed via GC–MS analysis.

3. Results and discussion

3.1. Feedstock characterization

Properties of microalgae and JSC, including proximate and elemental analyses, higher heating values (HHV) and chemical compositions are listed in Table 1. The proximate analysis showed volatiles (mainly organic), of 75.33 wt% in microalgae and 79.80 wt% in JSC. The elemental analysis showed that microalgae and JSC mainly consisted of carbon and oxygen. The HHVs of microalgae and JSC were *ca.* 21 MJ/kg, similar to that of typical lignocellulosic biomass. Nutrition analysis showed that the microalgae has higher content of protein (*ca.* 36 wt%) than JSC with *ca.* 26 wt% (Makkar et al., 2008), indicating a possibility of high contents of nitrogen-containing compounds in pyrolytic oil from the microalgae. Chemical composition analysis showed JSC to have higher lignin and lower hemicellulose contents than other oil seed wastes (Kim et al., 2013a,b).

Table 1
Characteristics of microalgae and JSC.

Biomass feedstock	Microalgae		JSC
Proximate analysis (wt%)			
Moisture	4.59		2.65
Volatiles	75.33		79.80
Fixed carbon	12.78		14.13
Ash	7.30		3.42
HHV (MJ/kg)	21.10		20.80
Elemental analysis (wt%)			
C	50.00		50.52
H	7.11		6.15
O	30.70		39.41
N	7.25		2.32
S	0.54		<0.1
Nutritional profile (wt%)		Component analysis (wt%)	
Protein	36.4	Cellulose	36.64
Lipid	19.5	Hemicellulose	4.82
Carbohydrate	29.3	Lignin	39.61
Others[a]	14.8	Others[a]	18.94

[a] The remainder from mass balance.

3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to obtain an a priori estimate of pyrolysis behavior of microalgae and JSC. Thermal degradation profiles show typical decomposition characteristics due to their chemical components. The microalgae exhibit three stages of decomposition, namely dehydration, devolatilization and decomposition of carbonaceous solids. The first weight loss was observed in the temperature range of 80–160 °C with weak peak in DTG curve, which corresponds to removal of physically adsorbed water in the sample. The second stage in the weight loss is very broad, from 170 to 410 °C with a weight decrease of *ca.* 68%, which corresponds to the main pyrolysis process or devolatilization. Lipid is initially removed at *ca.* 220 °C and then carbohydrates and proteins are mostly decomposed at *ca.* 320 °C in this stage, which are similar with results from thermal decomposition of *Chlorella* containing lipids (Babich et al., 2011). Remaining carbonaceous species are further decarboxylated and dehydrogenated above 410 °C. The weight decrease above 500 °C is related to the slow further decomposition of the solid residue. The total observed weight loss under pyrolysis condition is *ca.* 73 wt% and is related to the amount of volatile organics as shown in Table 1. For JSC, the thermal degradation profile showed similar pattern but much broad main peak in DTG curve compared to that of microalgae. The profile consists of one major derivative weight loss peak at 342 °C, preceded by a shoulder around 270 °C. The primary classes of thermally degradable biopolymers in lignocellulosic biomass are cellulose, hemicellulose and lignin. Hemicellulose is more thermally labile and decomposes first in the temperature range of 170–310 °C. Cellulose, more thermally stable due to its crystalline structure (Yang et al., 2006), decomposes at a higher temperature of 310–410 °C. Lignin is relatively heterogeneous polymer and decomposes over a much wider temperature window of 190–900 °C without showing a discernible peak in DTG curve (Maddi et al., 2011). The JSC contains oil residue, indicating it likely has another devolatilization process of the oil like microalgae, but different from other lignocellulosic biomass like wood. Overall, the devolatilization of the oil and the decomposition of

hemicellulose and cellulose in the JSC occur simultaneously with showing main peak on DTG, and a large portion of the thermal degradation temperature interval of lignin overlaps with the peak, which is a reason for the broader single peak of JSC on DTG curve than microalgae. The difference of chemical composition between biomass feedstocks makes main peak shapes and locations in the DTG curves different, indicating biomass pyrolytic behavior is affected by its chemical composition.

3.3. Characterization of the pyrolysis products from microalgae and JSC

Fig. 2 shows product distribution in pyrolysis of microalgae and JSC. Pyrolysis liquid yields of microalgae and JSC showed 46–52 wt% with no significant differences between them. The liquid yield of microalgae seems to be reasonable, compared with other fast pyrolysis studies (Miao and Wu, 2004; Maddi et al., 2011), although yields varied with reactor type or geometry and the fluidizing conditions, such as gas velocity and static or expanded fluidized bed height. However, the pyrolysis liquid's oil proportion of microalgae is much higher than JSC. The higher bio-oil yield from microalgae than JSC is consistent with results previously observed in pyrolysis of microalgae and lignocellulosic biomass in fixed bed (Maddi et al., 2011). The similar amount of char was obtained from microalgae and JSC. JSC might be expected to have higher char yield than microalgae, because cellulose and lignin contribute to char formation during pyrolysis (Kim et al., 2013a). However, high amounts of ash in microalgae (Table 1) led to large char formation since inorganic elements in the ash are known to catalyze char forming reaction during the pyrolysis (Cheng, 2010; Eom et al., 2013). The pyrolysis liquid's aqueous proportions did not vary greatly between microalgae and JSC. This is reasonable, given that it originated from dehydration reactions of organic compounds at similar pyrolysis condition considering free water in biomass. Microalgae showed lower gas yield than JSC. In composition of gas, carbon oxides (mainly CO_2) were dominant at *ca.* 94 wt%. CO_2 is produced by the primary pyrolysis of carbohydrates; CH_4 and CO are mainly produced by the secondary cracking of volatiles (Yanik et al., 2007). Methane was produced at *ca.* 3 wt% and hydrogen at *ca.* 0.2 wt% because the experimental conditions were chosen to maximize primary cracking. The composition of gas products did not vary greatly between microalgae and JSC, and these results agreed with previous works on fast pyrolysis (Maddi et al., 2011).

Fig. 3 shows boiling point distributions of pyrolytic oils and their comparison with petroleum fuel oils and palm fatty acid distillate (PFAD), which is a representative biodiesel feedstock, to provide basic information that the obtained oils correspond to

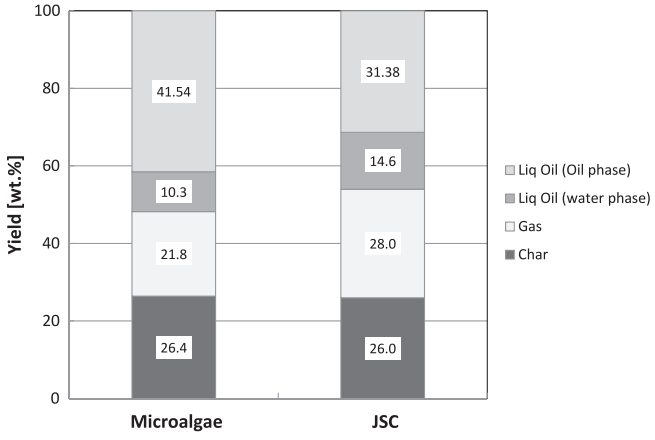

Fig. 2. Product distributions from the pyrolysis of microalgae and JSC.

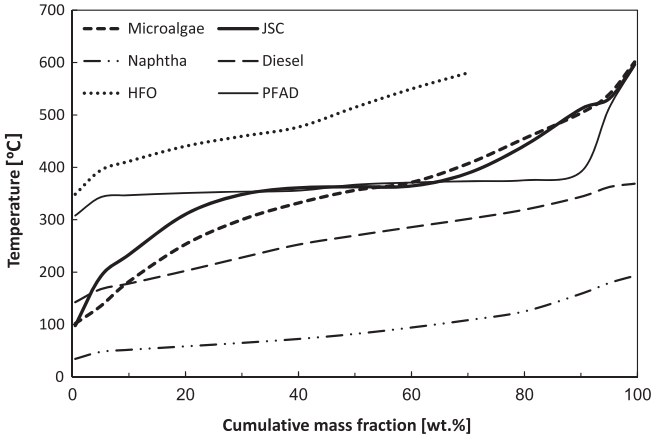

Fig. 3. Boiling point distributions of pyrolytic oils, petroleum fuel oils and palm oil.

which petroleum fuel application. Oils from microalgae and JSC showed wide distributions from 100 to 600 °C due to water phase removal. Microalgae showed almost a distribution curve with gentle slope in 290–370 °C. The distribution implies that various compounds with wide range of boiling points exist and compounds with boiling point of 290–370 °C are concentrated in the bio-oil; JSC showed plateau at *ca.* 360 °C, implying that several compounds were highly concentrated in the pyrolytic oil. In comparison with petroleum fuel oil, considerable part of the pyrolytic oils is in the range of diesel and heavy fuel oil. Major portion (*ca.* 75 wt%) of the microalgae and JSC oils is expected to be shifted possibly into the diesel range if they were deoxygenated for blending with petroleum fuel oil. In comparison with biodiesel feedstock, the major part of PFAD is in 350–370 °C range where JSC showed plateau regions. Microalgae and JSC showed boiling point distribution curves more similar to PFAD than that of petroleum fuel oil.

Table 2 lists the properties of the fractionated pyrolytic oils, petroleum fuel oils and palm oils. High-sulfur diesel and high and low sulfur fuel oils (Bunker-C oils) as petroleum fuel oils were chosen for comparison. The pyrolytic oils from microalgae and JSC showed similar specific gravities, but higher than those of the petroleum oils and palm oils because they had wide distributions of compounds and heavy long chain compounds similar to crude petroleum oil and possibly had small amount of char from nature of thermal decomposition (Kim et al., 2013a). Interestingly, the pyrolytic oils showed similar contents of carbon and hydrogen between microalgae and JSC even though they are from different species of biomass. The microalgae pyrolytic bio-oil has higher H/C and O/C molar ratios than JSC, implying the microalgae oil has less number of multiple bond and higher oxygen contents in hydrocarbon compounds than JSC. However, the pyrolytic oils from microalgae and JSC have higher H/C, lower O/C molar ratio and consequently higher HHVs than other lignocellulosic biomass such as wood with H/C = 1.38, O/C = 0.37 and HHV = 21 MJ/kg (Miao et al., 2004), implying the microalgae and JSC are much attractive for the production of transport fuels. The pyrolytic oils had higher oxygen contents than the petroleum oils and palm oils, and showed lower HHVs and higher TANs consequently. However, the properties gap between pyrolytic oils and palm oils were smaller than that with petroleum oils. The pyrolytic oils' TANs were much higher than that of CPO and slightly lower than that of PFAD, indicating that the pyrolytic oils and PFAD had higher amounts of carboxylic acid groups (possibly, fatty acids) than CPO. Another feature of the pyrolytic oils is relatively lower sulfur. Their low sulfur contents are a positive property for fuel application. However, the pyrolytic oils showed higher nitrogen contents than petroleum and palm oils, likely due to organically bonded nitrogen generated from the raw materials like proteins during pyrolysis. The high

Table 2
Properties of distilled pyrolytic oils, petroleum fuel oils and palm oils (dry basis, wt%).

Properties	Microalgae	JSC	HS diesel	HFO (0.3S B-C)	HFO (4.0S B-C)	CPO	PFAD
Specific gravity	1.09	1.08	0.87	0.94	0.98	0.91	0.90
Elemental composition (wt%)							
C	62.6	65.2	85.90	87.30	82.79	76.8	76.2
H	8.77	8.49	12.98	12.19	12.98	12	12.1
O	22.5	18.8	0.10	0.17	0.48	11.5	11.5
N	8.8	6.50	0.57	0.06	0.20	<0.1	<0.1
S	<0.1	0.14	0.46	0.28	3.55	<0.01	<0.01
H/C molar ratio	1.68	1.56	1.813	1.675	1.881	1.875	1.906
O/C molar ratio	0.27	0.22	<0.005	<0.005	<0.005	0.11	0.11
TAN (mg KOH/g)	162.6	112.5	0.25	0.451	N/A[a]	6.8	187.9
HHV (MJ/kg)	29.6	31.2	39.1	44.7	43.4	39.6	39.4

[a] N/A = not available.

nitrogen contents in the pyrolytic oils are not favorable due to causing NOx emission in fuel use and catalyst poisoning of deoxygenation step for further processing (Wildschut et al., 2010). The results imply that the pyrolytic oils should be denitrogenated before deoxygenation to improve their applicability as fuels (Hu et al., 2013).

Bio-oils produced from pyrolysis of feedstocks were analyzed based on peak area (%) obtained from GC–MS, and main components identified are listed in Table 3. (chromatograms are shown in Fig. S1 in Supplementary information). Pyrolysis of microalgae and JSC produces a significant amount of fatty oxygenates. These compounds are derived predominantly from devolatilization and pyrolysis of the fatty acids and triglycerides present in the algae and JSC. The chromatogram of microalgae (Fig. S1) is featured by existence of aliphatic compounds from C_{10} to C_{20}. The observation of aliphatic compounds in bio-oil from microalgae was reported in previous pyrolysis study with other microalgae species such as *Chlorella protothecoides, Microcystis aeruginosa* (Miao et al., 2004) and *microcystis* sp. (Hu et al., 2013). It is observed that the distribution of carbon number in majority of alkanes and alkenes are similar with range of major fatty oxygenates (Fig. S1(a)). This indicates that generation of the aliphatic compounds is related to the secondary reaction of fatty oxygenates during microalgae pyrolysis; Diels Alder reaction of olefinic fatty acid is a possible route (Harman-Ware et al., 2013), which is well agreed with occurrence of CO and CO_2 in product gas. However, major peaks of aliphatic compounds are not observed in JSC chromatogram even though many peaks of fatty oxygenates are shown (Table 3 and Fig. S1(b)). Lipid in microalgae is easily exposed to hot bed materials to lead the secondary reaction due to weaker cell wall structure than lignin of lignocellulosic biomass. Also, smaller feedstock size of microalgae than JSC is likely to allow much uniform spatial temperature distribution within the feed particle and following high reactivity (Lin et al., 2012; Kim et al., 2013b), implying more chance of secondary reaction of lipid in the particle than JSC. Chromatograms of microalgae and JSC also show that a large amount of nitrogenous products is created. The nitrogen-containing compounds are most likely derived from protein degradation. Interestingly, JSC has been identified as high quality feed source for ruminants because of high crude protein contents (Makkar et al., 2008). However, the protein degradation products from microalgae and JSC are different in compound species, as shown in peaks of chromatograms, suggesting that they are composed of different type of proteins.

Product types and compounds distributions in the pyrolytic bio oils based on peak identification and area (%) from GC–MS analysis

Table 3
Main compounds identified in the bio-oil by GC–MS analysis.

Microalgae				JSC			
No.	Residence time (min)	Compounds	Area (%)	No.	Residence time (min)	Compounds	Area (%)
1	2.85	2,3-Butanediol	2.34	1	2.45	Propanoic acid	0.20
2	3.79	Butanoic acid	5.27	2	2.81	Acetamide	0.27
3	8.52	Phenol	1.93	3	5.22	1,2,3-Propanetriol	0.84
4	11.39	4-Methyl-phenol	1.72	4	5.53	Phenol	0.53
5	17.27	Indole	1.52	5	7.12	2-Methoxy-phenol	1.01
6	19.80	3-Methyl-1H-indole	0.92	6	8.68	1,2-Benzenediol	1.58
7	22.66	Dodecanenitrile;	2.80	7	9.58	3-Methylpyrrolizidine	0.60
8	24.91	Dodecanoic acid	2.59	8	9.92	2-Methoxy-benzeneethanol	0.73
9	27.46	Tetradecanenitrile	1.46	9	10.71	2,6-Dimethoxy-phenol	0.78
10	29.23	Tetradecanoic acid	1.10	10	12.14	2-Methoxy-4-(1-propenyl)-phenol	1.69
11	31.16	Neophytadiene	5.16	11	15.02	2,6-Dimethoxy-4-(2-propenyl)-phenol	0.74
12	31.99	6,6-Dimethyl-cyclooct-4-enone	2.32	12	17.97	Hexadecanoic acid	10.22
13	32.52	1-Methylene-2-vinyl-cyclopentane	5.49	13	19.60	9,12-Octadecadienoic acid	25.06
14	33.31	Hexadecanoic acid	7.38	14	19.68	9-Octadecenoic acid	33.80
15	36.14	Phytol	3.96	15	19.85	Octadecanoic acid	6.37
16	36.45	Ethyl lenoleate	11.62	16	21.27	1-Acetoxy 9Z,12E-tetradecadiene	1.34
17	36.51	9-Octadecenoic acid	2.53	17	21.34	9-Octadecenamide	2.55
18	36.58	9-Octadecenoic acid	2.86	18	23.91	9-Octadecenoic acid	1.67
19	39.68	Cyclododecyne	1.08	19	28.30	4-Hydroxy-3-nitro-2H-1-benzopyran-2-one	0.41
20	42.65	1-Nonadecene	0.81				
21	45.29	Bicyclo[10.8.0]eicosane	1.44				
22	45.60	Z-5-Nonadecene	1.35				
23	53.24	Stigmasta-7,16-dien-3-ol	1.65				

Table 4
Distribution of product types generated from pyrolytic bio oils by GC–MS analysis (area%).

Compounds	Derivatives	Microalgae	JSC
Fatty oxygenate	Fatty acid	23.57	75.75
	Fatty acid alkyl ester	12.96	1.67
Aliphatic	Alkane	10.03	–
	Alkene	11.44	1.34
Phenol		4.56	10.53
Alcohol		12.03	1.35
N-containing compounds	Nitrile	6.80	–
	Amide	0.54	3.18
	Amine	0.89	1.06
	Imide	1.46	–
	Aromatics	3.82	1.43
Others	Oxygen-rich	3.34	0.41
	Unidentified	8.56	3.28

are shown in Table 4. Microalgae bio-oil has relatively lower concentrations of fatty oxygenates but higher alkene and alkane concentrations than JSC. Interestingly, high portion of fatty acid alkyl ester (mainly, ethyl linoleate of *ca.* 12%) appears in the bio-oil, which was occurred in previous study about pyrolysis of lipid derived microalgae such as *Chlorella vulgaris* (Kebelmann et al., 2013). Major components of fatty oxygenate in microalgae bio-oil are fatty acid such as palmitic acid (*ca.* 7.4%) and oleic acid (*ca.* 5.4%). In JSC bio-oil, oleic (*ca.* 33.8%) and linoleic (*ca.* 25%) acids are major, and several compounds are highly concentrated as in Table 5, which is well agreed with results of boiling point distribution of the oil (Fig. 3). Neophytadiene is observed as major alkane compound (*ca.* 5.2%) in microalgae bio-oil, which is possibly derived from fatty oxygenate or lipid. The amount of phenol derivative in microalgae bio-oil is less than that of JSC. The major compounds are phenol (*ca.* 1.9%) and methyl phenol (*ca.* 1.7%), which are likely derived from lipid fraction (Harman-Ware et al., 2013). In case of JSC, various and large amount of alkyl phenol derivatives such as methoxy prophenyl phenol (*ca.* 2%) and benzenediol (*ca.* 1.6%) are identified; the phenolic compounds were associated with high lignin contents. Another feature of the microalgae bio-oil is high yield of alcohol components than JSC. Major products identified are butanediol (*ca.* 4.8%) and phytol (*ca.* 4.0%). The phytol is likely formed from the phytol chain of chlorophyll (Kebelmann et al., 2013). The microalgae bio-oil shows a larger amount of nitrogen-containing compounds than JSC (Fig. S1) because microalgae have high portion of protein as ingredient. Distribution of nitrogenous compounds and their types are much broader than those in JSC bio-oil as in Table 3. The majority of these compounds in microalgae bio-oil appear to be nitriles such as dodecanenitrile (*ca.* 2.8%) and hexadecanenitrile (*ca.* 1.5%), which are derived from fatty oxygenates. Also, protein derived compounds such as indole and 1H-indole (*ca.* 2.5%) are observed.

Table 5
Major chemical compounds of fatty acid in pyrolytic oils by GC–MS analysis (area%).

Chemical compound	Microalgae	JSC
Fatty acid		
Butyric acid ($C_4H_8O_2$)	5.66	0.10
Caproic acid ($C_6H_{12}O_2$)	0.43	–
Caprylic acid ($C_8H_{16}O_2$)	0.15	–
Capric acid ($C_{10}H_{20}O_2$)	0.37	–
Lauric acid ($C_{12}H_{24}O_2$)	2.59	–
Myristic acid ($C_{14}H_{28}O_2$)	1.10	–
Palmitic acid ($C_{16}H_{32}O_2$)	7.38	10.22
Stearic acid ($C_{18}H_{36}O_2$)	0.50	6.37
Oleic acid ($C_{18}H_{34}O_2$)	5.39	33.8
Linoleic acid ($C_{18}H_{34}O_2$)	–	25.06

The indoles may be produced from decomposed tryptophan amino acids (Tsuge and Matsubara, 1985). In JSC bio-oil, majority of nitrogenous compounds is amide such as octadecenamide (*ca.* 2.6%) as shown in Table 4, which is also derived fatty acid and protein. Most of these nitrogenous compounds are not present in the pyrolytic bio-oils from lignocellulosic biomass. Nitriles were reported to form during pyrolysis from alkanoic acids and ammonia via dehydration of the amide intermediate at high temperature, as previously reported in a test with a shale as source for inorganic ammonia (Simoneit et al., 2003). From the results, the alkyl amides and alkyl nitriles in pyrolytic bio-oils are suggested to be due to reactions of carboxylic group in fatty acids with ammonium salts from amino acids, which is possibly from protein decomposition during pyrolysis. In comparison of the nitrogenous compounds between microalgae and JSC, microalgae bio-oil shows higher yield of nitriles than JSC as shown in Table 3, implying much easy exposure of lipids in small microalgae feedstock to hot fluidized bed materials and following secondary reaction of amide to nitrile by high reactivity.

3.4. Pyrolytic oils' applicability as fuel and chemicals

A recent alternative for green diesel production is based on hydrotreating, which can be used to convert not only plant-derived oils such as CPO, but also various types of non-edible oils. Its advantages over trans-esterification are its compatibility with current infrastructure, engine compatibility and feedstock flexibility (Kim et al., 2013a). Kim et al. (2013a) suggested a possibility of the pyrolytic oils from oil seed wastes like palm kernel shell and *Jatropha* seed waste as feedstocks for biodiesel based on a comparison between PFAD and the pyrolytic oils. Pyrolytic bio-oil from microalgae is possibly a candidate for the feedstock for green diesel because it contains high amount of fatty oxygenates. Also high concentrations of aliphatic compounds in the oil indicate an advantage for compatible fuel use over the pyrolytic oil from oil seed waste like JSC (Miao et al., 2004). Fig. 4 and Table 5 compare the oil's compounds distributions for detail analysis about possibility as green diesel feedstock. The microalgae bio-oil exhibits different fatty oxygenates profiles compared to JSC bio-oil and PFAD. While the majority of fatty acids in JSC bio-oil and PFAD have carbon chain length (C_{10}–C_{23}) within range of typical diesel fuel, the microalgae bio-oil has wide distribution of carbon length from C_4 to C_{20}. Decomposition of lipids during pyrolysis produces products with carbon number less than C_{10} such as butyric acid. However, high concentration of ethyl linoleate in fatty oxygenates and aliphatic compounds with carbon number from C_8 to C_{20} are positive for green diesel production. Also, high portion of nitriles as nitrogenous compounds in the microalgae bio-oil is a positive for process of fuel production compared to other compounds, because carbon

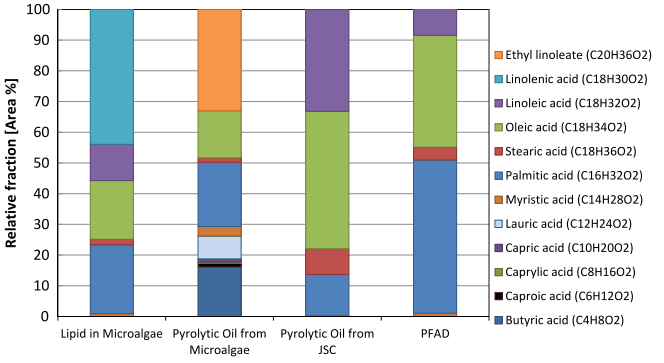

Fig. 4. Chemical compounds distributions of fatty oxygenates in pyrolytic oils and palm oil.

numbers (C_{12}–C_{16}) of major nitriles are within diesel range and nitrile group in nitrogenous compounds is easily removed in hydrotreating unit of existing petroleum refinery (Ahmad et al., 2011). These results suggest that the microalgae bio-oil could be used compatibly for bio diesel production in current refinery infrastructure, although fraction beyond the range of diesel should be separated and used for other application (Brennan and Owende, 2010). Additionally, the microalgae bio-oil could be a feedstock for chemical products like surfactants from nitriles and valuable chemicals like phytochemicals because the pyrolysis of microalgae generates a range of useful compounds as identified in GC–MS analysis (Amin, 2009). It is clear that the microalgae pyrolytic bio-oil would require an economical way for commercially efficient separation and refining for fuel and chemicals use (Czernik and Bridgwater, 2004). However, the greater potential of microalgae pyrolytic bio-oil, coupled with the advantages for algal farming over the use of arable land for food crops and its associated environmental impact, makes it an attractive alternative for further research and development including large-cultivation, harvesting and dewatering of microalgae and optimization of their water and nutrients consumption (Mata et al., 2010).

4. Conclusions

The microalgae bio-oil was characterized by higher H/C and O/C molar ratios compared to JSC due to compositional difference. The pyrolytic oils from microalgae and JSC contained more oxygen and nitrogen and less sulfur than petroleum fuel oils and palm oils. The pyrolytic oils showed high yield of fatty oxygenates and nitrogenous compounds due to high contents of lipids and proteins. The microalgae bio-oil features in high concentrations of aliphatic compounds, fatty acid alkyl ester, alcohols and nitriles. In assessment of the pyrolytic bio-oil's applicability, Microalgae showed potentials for alternative feedstock for green diesel, and commodity and valuable chemicals.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.03.136.

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