



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, FFAE, 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.

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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 ($d_p = 190 \mu\text{m}$, $\rho_s = 3210 \text{ kg/m}^3$) 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 N₂ gas was preheated in the air plenum to 440 °C. A

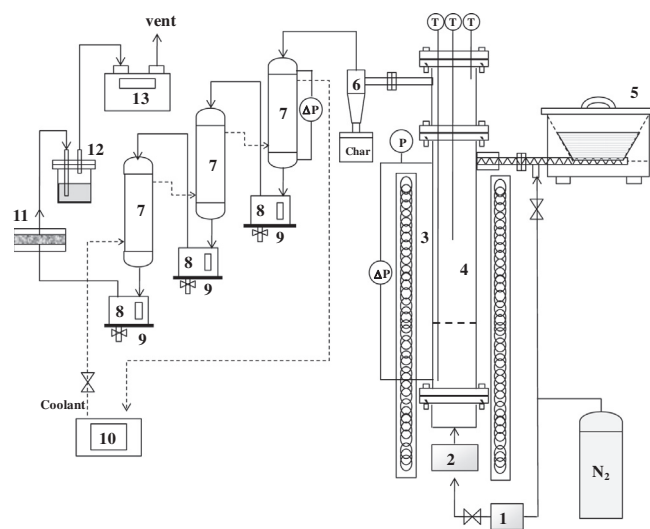


Fig. 1. The experimental apparatus. 1, mass flow meter; 2, preheater; 3, furnace (electric heater); 4, fluidized bed reactor (pyrolyzer); 5, screw feeder; 6, cyclone; 7, condenser; 8, sampling pot; 9, heating plate; 10, chiller; 11, oil filter; 12, water trap; 13, accumulated gas flowmeter; P, pressure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

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