



Comparative study on flash pyrolysis characteristics of microalgal and lignocellulosic biomass in entrained-flow reactor



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ABSTRACT

Entrained-flow fast pyrolysis of *Chlorella vulgaris* microalgae (MA) and palm kernel shell (PKS) was investigated in the temperature range of 600–900 °C. The effects of pyrolysis temperature and biomass type on the yields and composition of pyrolysis products were systematically investigated and the possible reaction pathways during MA and PKS biomass pyrolysis were discussed. The highest bio-oil yields of 60.22 wt% and 73.74 wt% were obtained during MA and PKS pyrolysis at 800 °C and 600 °C, respectively. The results showed that MA bio-oil was rich in hydrocarbons and nitrogen-containing compounds, while PKS bio-oil mostly contained phenols, esters, and hydrocarbons. High concentration of nitrogen-containing compounds in bio-oil from MA was attributed to its high-protein nature. Nitrogen-containing compounds such as indole, imidazole, and pyridine were formed as the result of primary decomposition of basic amino acids such as tryptophan and histidine in MA. The formation of single-ring aromatics (such as styrene) during MA pyrolysis was the result of phenylalanine amino acid decomposition. The higher content of phenols in PKS was attributed to decomposition of lignin in its structure. PAHs in PKS bio-oil were formed during secondary gas phase reactions as a result of direct combination of aromatic rings. The concentration of H₂ and CO in bio-gas generally increased with temperature, while CO₂ concentration showed an opposite trend. Bio-char analysis showed that at higher pyrolysis temperatures the concentration of functional groups decreased in bio-char, while the formation of large-size aromatic rings and amorphous carbon was enhanced. Scanning electronic microscopy (SEM) images showed that sphericity and surface smoothness of bio-chars increased with temperature, indicating softening of biomass particles under fast heating rates.

1. Introduction

Over the past decades, energy consumption has increased progressively as the global economy has developed. The conventional non-renewable fossil fuels have the highest share of energy sources worldwide. However, the environmental impact of fossil fuel utilization such as greenhouse gases emission and global warming has motivated scientists to evaluate renewable energy sources to meet the increasing power, heat, and transportation fuels demand [1–3]. Among the renewable energy sources, biomass is the only source of energy that can be used for production of renewable fine chemicals, liquid fuels, biogas, and bio-char [4]. Biofuels derived from plant material can reduce the carbon emissions of crude oil. Biomass attracts tremendous interest due to its abundance and can be divided into lignocellulosic biomass

[5], agricultural waste [6], macro- and microalgae [7,8], other plant residues [9], animal wastes [10,11], and sewage sludge [12]. Among the biomass conversion processes, fast pyrolysis at high heating rates, moderate temperatures and short resident time is a promising and efficient way of converting biomass to renewable fine chemicals and liquid fuels [13,14]. The main advantage of fast pyrolysis is short residence time of pyrolysis gas in the reaction zone that limits the secondary cracking reactions of products, thereby increasing the bio-oil yield [15].

Lignocellulosic biomass is mainly composed of hemicellulose, cellulose, and lignin. Cellulose forms 30–55 wt% [16] of biomass and is a crystalline polymer of glucose that decomposes in the temperature range of 240–350 °C to form anhydrocellulose and levoglucosan. Hemicellulose forms 15–40 wt% [16] of biomass and is an amorphous

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shorter polymer of various sugars that decomposes in the temperature range of 200–260 °C [17]. Lignin (10–40 wt% of biomass) [16] is an aromatic polymer that decomposes in the temperature range of 280–500 °C to form single ring aromatic compounds such as phenols [18]. During the pyrolysis of lignin, phenols and other small molecular weight compounds are released via the cleavage of interunit linkages followed by the decarbonylation, dehydration and reformation [19]. Phenols are used as precursor for synthesis of bio-plastics, phenol-formaldehyde resins or epoxy- and polyurethane materials [14]. Palm kernel shells (PKS), a by-product of palm oil industry is a promising and abundant biomass feedstock and because of its high lignin content (over 45 wt%), can be used for production of a phenolic-rich bio-oil [5,20].

Microalgae (MA) is known as a third generation renewable feedstock for biofuels production [21]. Microalgal species have a different chemical composition compared with lignocellulosic biomass. MA mainly contains proteins (35–40%), carbohydrates (10–25%), and lipids (40–50%) [22]. The unique properties of MA such as rapid production and high growth rate, low sulfur content, no requirement for arable land, simple cellular structure, high efficiency in CO₂ capture, and adjustable composition through growth medium makes this type of biomass very suitable for production of liquid fuels and fine chemicals [17,23–25].

The chemical structure of biomass determines the yield and composition of its pyrolysis products. Most available studies on biomass pyrolysis have focused on a single type of lignocellulosic or algal biomass. The number of studies comparing the pyrolysis characteristic of lignocellulosic or algal biomass is limited in the literature. Chiodo and co-workers [26] studied the bio-oil and bio-char formation during pyrolysis of wood chips, seaweed, and freshwater algae in a fixed-bed reactor. They reported that oxygen-containing organic compounds were detected in bio-oil derived from both woody and algal biomass. Maddi and co-workers [27] used a tubular reactor for pyrolysis of a number of lignocellulosic and algal biomass species and reported that bio-oil yields from algae and some lignocellulosic biomass were similar. They observed that algal bio-oils composition was different to that of lignocellulosic biomass and nitrogen-containing compounds were detected in algae bio-oil. Yuan et al. [23] used TGA and fixed-bed reactor to investigate the pyrolysis characteristics of four algal and lignocellulosic biomass samples and observed that bio-oil from lignocellulosic biomass was rich in phenolic compounds while bio-oil from *C. vulgaris* microalgae contained more nitrogen-containing compounds. Similar results were obtained by Wang et al. [17] who studied microwave pyrolysis characteristics of microalgae *Chlorella vulgaris* and peanut shell in a modified domestic microwave oven. The heating rates in TGA and fixed-bed reactors are usually lower than 30 °C/min and do not represent the heating conditions in industrial reactors. Furthermore, the longer volatiles residence times in TGA and fixed-bed reactors can cause secondary cracking of primary volatiles, decreasing bio-oil yield and quality [28]. More recently, Li et al. [19] compared the pyrolysis behavior of cornstalk and *Chlorella* microalgae using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) with heating rate of 20 °C/ms and reported that bio-oil from lignocellulosic biomass contained phenolic and carbonyl compounds, while algal biomass were rich in long-chain fatty acids and nitrogen-containing compounds. Trinh et al. [13] studied the fast pyrolysis of lignin, macroalgae, wood, and straw in a pyrolysis centrifugal reactor at 550 °C with a gas residence time of 0.5–2 s. They reported higher heating value (HHV), molecular mass distribution, viscosity, pH, density, thermal behaviors, elemental concentrations, phase separation, and aging of bio-oil but did not provide any comparison regarding compositional differences between bio-oil from lignocellulosic and algal biomass.

Entrained-flow reactor (EFR) in which particles are fed into preheated vertical tubular reactor, operate with the fuel feed and carrier gas in co-current flow. EFR can realize continuous feeding and offer implementation of high heating rates of about 10⁴–10⁵ °C/s, medium to high pyrolysis temperatures, and a short gas residence time of

milliseconds to seconds [29]. Therefore, in order to achieve full fuel conversion the fuel particle size should be much smaller, compared to other types of pyrolysis reactors such as fixed-bed, fluidized-bed, and spouted-bed. Entrained-flow reactor is capable of maintaining accurate control of the reaction conditions [30]. Biomass pyrolysis at high temperatures and short volatiles residence times results in higher yields of bio-oil [25]. Fast heating rate of fuel particles and short volatiles residence time in entrained-flow reactor allows detailed investigation of pyrolysis characteristics in conditions similar to that of industrial reactors and under single particle heating conditions. The amount of sample that can be tested in EFR is much larger than TGA, Py-GC/MS, and lab-scale fixed-bed reactors. To the authors' knowledge there are no reports on comparative pyrolysis behavior of lignocellulosic and algal biomass using entrained flow reactor in published literature.

Better understanding of the difference in pyrolysis characteristics of microalgal and lignocellulosic biomass is critical for development of efficient biomass pyrolysis technologies. Therefore, in this study an entrained-flow pyrolysis experimental setup was used for fast pyrolysis of palm kernel shell (PKS) and *Chlorella vulgaris* microalgae (MA), to allow a systematic and comparative characterization of pyrolysis behavior of lignocellulosic and microalgal biomass. The effects of pyrolysis temperature and biomass type on products yields and composition were studied systematically. The bio-oil and bio-gas were collected and characterized using gas chromatography-mass spectrometry (GC-MS) and gas chromatography (GC) techniques, respectively. Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and scanning electron microscopy (SEM) techniques were used for detailed investigation of morphology and structural changes in bio-char during pyrolysis.

2. Materials and methods

2.1. Sample preparation

Microalgae *Chlorella vulgaris* was purchased from Spirulina Bio-Engineering Co. Ltd., China in powder form (< 105 µm). Palm kernel shell (PKS) biomass from Malaysia was used to represent lignocellulosic biomass in this study. The PKS samples were grinded and sieved to obtain the particle size in the range of 75–125 µm. Samples were dried in oven at 105 °C for 24 h and then stored in a desiccator to avoid the moisture reabsorption. The volatile matter and ash contents of samples were measured using ASTM E872 and E1755 standard methods, respectively, and the fixed carbon content was calculated by difference. The ultimate analysis of biomass samples was carried out using Euro Vector Euro EA elemental analyzer. The proximate and ultimate analyses of raw biomass are shown in Table 1. The composition of PKS was determined based on the procedure described elsewhere [31]. PKS sample contained 33.04 wt% cellulose, 23.82 wt% hemicellulose, 45.59 wt% lignin, and 9.89 wt% extractives and was used as a representative of lignocellulosic biomass in this study. The protein

Table 1
Proximate and ultimate analyses of raw biomass samples.

Composition	Percentage	
	Raw microalgae	Raw PKS
Moisture content (wt%, ar)	10.21	13.65
Volatile matter (wt%, db)	80.41	75.32
Ash content (wt%, db)	5.54	3.87
Fixed carbon (wt%, db)	14.05	20.81
C (wt%, daf)	43.75	48.82
N (wt%, daf)	7.86	0.42
H (wt%, daf)	6.07	5.68
S (wt%, daf)	0.71	–
O (by difference) (wt%, daf)	41.61	45.08

ar: as received; db: dry basis; daf: dry ash free.

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