Energy 76 (2014) 284–291

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Assessment of miscanthus biomass (*Miscanthus sacchariflorus*) for conversion and utilization of bio-oil by fluidized bed type fast pyrolysis

Jae-Young Kim [a], Shinyoung Oh [a], Hyewon Hwang [a], Youn-Ho Moon [b], Joon Weon Choi [a, *]

[a] *Department of Forest Sciences and Research Institute for Agriculture and Life Science, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-921, Republic of Korea*

[b] *Bioenergy Crop Research Center, Rural Development Administration, Muan 534-833, Republic of Korea*

ARTICLE INFO

Article history:
Received 21 April 2014
Received in revised form
2 July 2014
Accepted 3 August 2014
Available online 2 September 2014

Keywords:
Miscanthus sacchariflorus
Fast pyrolysis
Bio-oil
Inorganic constituent
Thermo-gravimetric analysis
GC/MS

ABSTRACT

Liquid bio-oils were produced from miscanthus (*Miscanthus sacchariflorus*) by fast pyrolysis at various temperature ranges (350–500 °C) with a short residence time and their physicochemical properties were determined to evaluate the potentials for biofuel utilization. Before operating fast pyrolysis, miscanthus was subjected to ICP-ES (inductively coupled plasma emission spectrometer) analysis and TGA (thermogravimetric analysis). It was learned that miscanthus was thermally unstable due to large amounts of inorganic constituents including potassium (5643.8 ppm), calcium (711.0 ppm) and magnesium (1403.1 ppm). With fast pyrolysis, the yield of bio-oil gradually decreased with increasing temperature and residence time. The maximum yield of bio-oil was ca. 58.9 wt% at 350 °C with a residence time of 1.9 s. The HHV (higher heating value) of bio-oil was determined up to 18.0 MJ/kg produced at 400 °C with a residence time of 1.9 s. The water content of bio-oil was ranged from 21.1 to 56.9 wt%. GC/MS (gas chromatography/mass spectrometry) analysis showed that bio-oil was mostly composed of carbohydrate derivatives and lignin derivatives. 1-(Acetyloxy)-2-butanone, furfural, dihydro-methy-furanone and levoglucosan were the predominant low molecular weight compounds that originated from carbohydrate and those from lignin were guaiacol 4-vinylphenol and syringol.

1. Introduction

Lignocellulosic biomass is an alternative carbon-based resource that can be converted to various products such as feed, energy, fuel and chemicals. In particular, renewable energy from lignocellulosic biomass has received growing interest due to the concerns over depletion of fossil fuel and increases in energy demand and costs [1]. For example, several kinds of bioenergy such as organic waste, wood pellet, and biogas have been used for district heating [2]. Moreover, lignocellulosic biomass contains a negligible amount of nitrogen and sulfur, which results in lower emission of environmentally harmful substances such as NOx and SOx [3]. Recently, miscanthus (*Miscanthus sacchariflorus*) has gained significant attention as a potential bio-energy crop because of its high growth rate as well as low nutritional requirements [4]. In addition, miscanthus, a genus of the C_4 perennial grasses, has additional advantages such as high biomass yield potential, high energy density, low water content, low establishment costs and low soil erosion compared to alternative biomass sources [5–7]. The harvested miscanthus can be used as crude fuel for the generation of heat or electric power as well as other advanced transport fuels or chemicals [8,9].

There are many biochemical and thermochemical technologies which can convert miscanthus to liquid fuel or chemicals [10]. Fast pyrolysis is one thermochemical conversion technology, which requires 350–550 °C in the absence of oxygen. Under this condition, organic materials are rapidly thermo-decomposed to volatile compounds, which are condensed to bio-oil (liquid) by passing through a quenching system. In addition, char (solid) and non-condensable gases (CH_4, H_2, CO and CO_2) are formed as by-products due to side reactions [11,12]. Bio-oil, the main product of fast pyrolysis, is supposed to substitute fossil fuel oils in household or industrial field including boilers, engines and turbine for energy generation. The utilization of bio-oil as alternative of heavy fuel oil has already been proven in several studies [13,14]. According to burner fuel standard (ASTM D 7544), caloric value (MJ/kg), water content (%), kinematic viscosity (cSt), pH and ash content (%) are

---

* Corresponding author. Tel.: +82 2 880 4788; fax: +82 2 873 2318.
E-mail address: cjw@snu.ac.kr (J.W. Choi).

http://dx.doi.org/10.1016/j.energy.2014.08.010
0360-5442/

important properties to determine bio-oil grade as burner fuel, and typical bio-oil produced from wood showed competent level as comparable with burner fuel grade D or G [15]. In the view of exhaust gas emission problems, nitrogen as well as sulfur content of bio-oil is another consideration because these elements yield substantial NOx and SOx emission problem and corrosion issue. It was well known that bio-oil had very low level of nitrogen (<0.4 wt%) and sulfur (<0.05 wt%) [12,15].

Previous studies have shown that the feedstock type, reactor design, pyrolysis temperature, residence time of volatiles, moisture content, particle size and inorganic content of feedstock were crucial parameters determining the yield as well as physicochemical properties of pyrolytic products [16–21]. In general, it is well known that maximum yields of bio-oil from woody biomass have been obtained at reaction temperatures around 500 °C and with short vapour residence times of less than 2 s [22]. In recent years, however, many researchers have found that the optimum condition for maximum bio-oil yield has been clearly dependent on the kinds of raw materials due to different chemical composition (cellulose, hemicelluloses, lignin, and extractives) and inorganic content [23–26]. Therefore, fundamental studies of characteristics of feedstock need to be established before fast pyrolysis is implemented on a broader scale.

In this study, miscanthus, a representative biomass energy crop, was pyrolyzed at various temperatures (350–500 °C) and residence times (1.2–3.8 s) to investigate the effect of each parameter on the distribution of pyrolytic products as well as various physicochemical properties of the resulting bio-oil. To investigate catalytic effects of inorganic constituents on thermal degradation properties of miscanthus, quantitative analyses of inorganic content (such as potassium, calcium and magnesium) as well as TGA (thermogravimetric analysis) of miscanthus and demineralized miscanthus (W-Miscanthus) were preliminary examined.

2. Experimental

2.1. Feedstock

Miscanthus was provided by Bioenergy Crop Research Center, National Institute of Crop Science, Rural Development Administration, Korea. Miscanthus were ground using a cutting mill pulverisette (FRITSCH, Germany) with a 0.75 mm screen. The moisture content was maintained at approximately 7% prior to fast pyrolysis. To remove inorganic constituents, miscanthus (20 g) were treated with distilled water at 90 °C for 2 h with stirring followed by freeze-drying until the moisture content was below 7% by dry weight [27]. The demineralized miscanthus is abbreviated as W-Miscanthus. These two samples were fundamentally analyzed to investigate catalytic effects of inorganic constituents on thermal degradation properties of miscanthus.

2.2. Characterization of feedstock

The chemical composition of miscanthus and W-Miscanthus were determined according to NREL (national renewable energy laboratory standard biomass analytical protocol and evaluated ash, extractive, holocellulose (cellulose and hemicellulose), monomeric sugar and lignin content. Furthermore, several inorganic constituent in samples were quantified using inductively (inductively coupled plasma emission spectrometer) analysis with an ICPS-1000IV instrument (Shimadzu, Japan) located in NICEM (National Instrumental Center for Environmental Management), Seoul National University. Before ICP-ES analysis, 0.5 g of samples (Miscanthus and W-Miscanthus) were digested with 10 ml of HNO_3: HCl: H_2O_2 (ratio 8:1:1 v/v) using a microwave system (Multiwave 3000, Anton Paar). Elemental composition (C, H, N and O) of samples were determined using an US/CHNS-932 (LECO Corp, USA). The thermal decomposition characteristics of samples were investigated in an inert atmosphere (N_2) using Q-5000 IR instrument (TA Instruments, USA) with constant heating rate of 10 °C/min up to 800 °C.

2.3. Fast pyrolysis

Fast pyrolysis of miscanthus was performed at 350 °C, 400 °C, 450 °C and 500 °C across residence times of 1.29 s, 1.93 s and 3.87 s using a fluidized bed type pyrolyzer (Fig. 1). The residence times were calculated based on the volume per inert gas flow rate (N_2) of the reactor; inert gas was purged prior to the pyrolysis run for 40 min to maintain a non-oxygen atmosphere in the pyrolysis system. The pyrolysis system consisted of a screw feeder, quartz thermo-heater, reactor, cyclone, char collector, two coolers, electrostatic precipitator and bio-oil collector, and 0.5 mm silica sand (140 g) was used as a heat carrier. The 400 mm (height) × 35 mm (diameter) reactor was made of stainless steel (SUS316). The bed height was 50 mm. The screw feeder maintained the feeding rate at 150 g/h (156 kg/m^2 h) and the temperatures of two coolers were maintained at −2 °C with ethanol during fast pyrolysis. The feeding period of each experimental run was 1 h. As pyrolytic products, bio-oil, char and non-condensable gas were formed, the yield of each pyrolytic product (bio-oil, char, and gas) was determined with the following equations [28]:

$$\text{The yield of bio}-\text{oil (wt\%)} = \frac{\text{bio}-\text{oil (g)}}{\text{raw material (g)}} \times 100 \tag{1}$$

$$\text{The yield of char (wt\%)} = \frac{\text{char (g)}}{\text{raw material (g)}} \times 100 \tag{2}$$

$$\begin{aligned}\text{The yield of gas (wt\%)} = 100 - (&\text{The yield of bio}-\text{oil} \\ &+ \text{The yield of char})\end{aligned} \tag{3}$$

These equations represent the weight conversion rate between biomass to each pyrolytic product. The yield of gas was calculated by the difference because it was not recovered. After fast pyrolysis, 0–6.9 g of char was accumulated with silica bed material in reactor. Thus, inside of the reactor was cleaned (char removal) and silica sand was also replaced to new one in every experimental run.

2.4. Physicochemical analyses of pyrolytic products

The water content of the bio-oil was determined by an automatic Karl–Fischer titrator (Daihan Scientific, Korea). The acidity of bio-oil was measured by pH meter (Thermo Fischer Scientific Inc., USA). The kinematic viscosity of the bio-oil ($cSt = mm^2/s = 10^{-6}\ m^2/s$) was measured at 40 °C using a capillary-type viscometer (Schott, Germany). The HHV (higher heating value) and elemental composition of bio-oil and char were measured using a Parr 6400 (Parr Instrument Co., USA) and US/CHNS-932 (LECO Corp, USA), respectively. GC/MS (gas chromatography/mass spectrometry) analysis of the bio-oil was carried out using an Agilent HP7890A GC equipped with an Agilent HP5975A MSD (mass selective detector). The GC column was a DB 5 (60 m × 0.25 mm × 0.25 μm). In sample preparation, 0.4 ml of bio-oil was diluted with 0.59 ml of acetone, followed by injection of 10 μl of internal standard (50 mg of fluoranthene/2 ml of acetone). The oven was programmed to hold at 50 °C for 5 min and then increase the temperature at 3 °C/min to 280 °C and then hold there for 20 min. The injector and detector temperature were 220 °C and 300 °C, respectively, and the injector split ratio was 10:1. Identification of