Rapid liquefaction of giant miscanthus feedstock in ethanol–water system for production of biofuels

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A B S T R A C T

Energy issues nowadays are one of the critical priorities for the United States. There is a strong desire and tremendous efforts employed towards replacing fossil fuels with sustainable alternative sources of energy. In this study, hydrothermal liquefaction with ethanol and water as co-solvents was applied on giant miscanthus (*Miscanthus giganteus*) perennial biomass feedstock. Four temperatures and six ethanol ratios were chosen for the study. The optimum combination of temperature and water/ethanol ratio was 280 °C and 50%, respectively. The effect of time, biomass to solvent ratio and catalyst type was studied as well. The best liquefaction results without applying catalysts (53% oil yield and 8% solid residue) were obtained after 15 min. When zinc chloride was used as catalyst, more than 52% of oil yield with 1% solid residue was obtained after 5 min. The crude bio-oil chemical composition was identified by using gas chromatography/mass spectrometry (GC/MS).

1. Introduction

Energy issues in the United States are currently receiving a very high priority. There is a strong desire for alternative sources of energy since fuels prices are increasing dramatically. The price of crude barrel oil has more than tripled since 2003; it increased from around $30 to over $100 today. Also, the environmental and health impacts associated with fossil fuels necessitate seeking of new renewable energy sources [1]. Biomass is the fourth largest energy source worldwide, it is estimated to contribute 10–14% of the world's energy supply [2]. There is a wide range of biomass feedstocks (generally composed of cellulose, hemicellulose, and lignin) such as energy crops, perennial grasses, wood residues and industrial residues [3]. Their availability, costs of collection and transportation are often critical and vary widely. The southeast of the United States and many other parts of the Midwest are ideal regions for the production of high yield perennial grasses. Giant miscanthus is one of the best perennial grasses grown in the southern parts of US when compared to other biomass due to numerous of advantages. It can also yield up to 15 tons/acre/year and a height of up to 15 ft. [4,5].

There are many conversion technologies can convert biomass into other forms of energy; the three main methods are thermochemical, chemical, and biochemical. Thermochemical conversion processes employ elevated temperature to convert the biomass feedstock into liquid fuel. Thermochemical conversion technologies include pyrolysis, gasification, and direct liquefaction. The typical direct liquefaction process was conducted at temperature (300–500 °C). Under these conditions, the biomass converted into crude oil which subsequently upgraded into true hydrocarbon products. In the recent years, many developments were introduced in the direct liquefaction of biomass to overcome various problems associated with the process. One of these developments was the application of supercritical fluids such as water (hydrothermal liquefaction) to convert biomass materials into liquid fuels [6]. Hydrothermal liquefaction is generally performed at temperature 280–370 °C and between 10 and 25 MPa [7]. High temperatures and pressures are to be held at or below the critical temperature of water 374 °C, resulting in a pressure of 2500–3000 psi to successfully run the process. At these conditions, water has a range of exotic properties, for example, it is a poor solvent for electrolytes, however, it is a very good solvent for non-polar molecules, due to its low dielectric constant and poor hydrogen bonding, viscosity and dielectric both decrease at this point. For these reasons, water is an important reactant and catalyst, and thus the biomass can be directly converted without an energy consuming drying step, as in the case of pyrolysis [8]. Catalytic hydrothermal liquefaction was also investigated; a large number of catalysts were studied and successfully increased the yield of bio-oil [9–11].

Alcohol/water system (methanol, ethanol, propanol and butanol) showed more effectiveness and synergetic effect in the

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hydrothermal liquefaction of biomass [12,13]. One of the most important advantages of this system is the ability to evaporate, recycle and reuse solvent for several times [13]. The properties and mode of action of alcohol in the medium vary with the ratio of alcohol to water, and hence, the determination of the optimum ratio is necessary. The excess of water leads to a higher amount of solid residues via self-condensation reactions, whereas using alcohol as the only solvent for the liquefaction could lead to a reduction in free radical reactions due to its weak acidity [14]. In previous study, Yuan et al. [15] found that replacing till 50% water with alcohol during the liquefaction of rice straw was very efficient in increasing the bio-oil yield, but replacing more than 50% water with alcohol results in an adversely effect on the oil yield. Also, Cheng et al. found that replacement 50% water with ethanol has a significant effect in increasing the oil yield during the hydrothermal liquefaction of white pine wood [13]. Therefore, for this work, we designed our experiments to study the effect of water/ethanol ratio till 50%. It is also well known that replacing water with alcohol will lower the critical liquefaction temperature for the mixture than the critical temperature of water (374 °C). The critical temperature of any water/alcohol mixture depends mainly on the ratio of water to alcohol. Previous studies [15,16] indicated that replacing 50% water with ethanol will lower the critical temperature for ethanol/water mixture to 280 °C. Also, it was mentioned in the literatures that increasing the liquefaction temperature over 300 °C up to 350 °C reduce greatly the bio-oil yield due to char formation from side reactions and the formation of hydrocarbon gases through cracking reactions [13]. Due to the above reasons, 280 °C which represents the critical temperature for 50% water/ethanol system will be the maximum temperature used in this study.

Therefore, the aim of this study is to optimize the low-temperature hydrothermal liquefaction of giant miscanthus by adding ethanol as co-solvent. More specifically, the target was the optimization of parameters and conditions that affect the liquefaction process, the reduction of reaction time and energy inputs applied in the process, and characterization of the produced bio-oil chemically and physically.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were purchased from commercial resources and used without further purification. Ethanol, dichloromethane, zinc chloride, sodium carbonate, trifuloroacetic acid, formic acid and filter paper were purchased from Fisher Scientific. Sugar standards such as D(+)Glucose, D(+)Xylose, D(+)Galactose, L(+)Arabinose, D(+)Mannose and Dextran with different molecular weights (1000–80,000 Da) used for chemical composition analysis were purchased from Sigma Aldrich.

2.2. Raw material

Giant miscanthus biomass was obtained from the south farm in Mississippi. The biomass was first air dried then ground in a Wiley mill and sieved. The miscanthus powder of 40–60 mesh size was fractionated, kept in sealed plastic bag and used in this study. The biomass was extracted according to NREL/TP-510-42619 standard method. The results of elemental and component analysis are given in Table 1. Elemental analysis (C, H, N and O) was determined by Exeter Analytical Incorporation (EAI CE-440) elemental analyzer, the amount of oxygen was determined by difference. The higher heating value (HHV) for the biomass was calculated from the following Dulong equation [17].

Table 1
Chemical composition and elemental analysis of giant miscanthus biomass.

Analysis	Wt.%
Chemical composition	
Glucose	42.8
Xylose	20.7
Galactose	1.3
Arabinose	2.1
Mannose	2.1
Lignin	24.8
Ash	2.3
Elemental analysis (%)	
Carbon	46.0
Hydrogen	6.24
Nitrogen	0.18
Oxygen (by difference)	47.54
Heating value (MJ/kg)	16.97

$$HHV(MJ/kg) = 0.3383 * \% \text{ of carbon} + 1.422 * (\% \text{ of hydrogen} - \% \text{ of oxygen}/8)$$

The component analysis for giant miscanthus was determined by NREL/TP-510-42681 standard method [18].

2.3. Liquefaction of biomass

The liquefaction of giant miscanthus biomass (40–60 mesh) was performed in a 450 mL high pressure Parr reactor (5500 series) equipped with a stirrer (Fig. 1). The reactor was charged with the biomass and water or ethanol/water co-solvent. After charging the reactor with the biomass and liquefying agent, the reactor was sealed and the air inside the reactor was purged with high-purity nitrogen for 3–5 times. The reactor was subsequently pressurized with nitrogen to prevent the reactive material from boiling in the course of the heating process. The reactor was ramped up to the desired temperature at a heating rate of 15 °C/min. The temperature and water/ethanol ratio were studied simultaneously to examine the best combination of temperature and ethanol ratio, as they are considered the primary factors during the process of liquefaction. At the optimum conditions, different catalysts were added to improve the bio-oil yield, the weight of catalyst was 10% (w/w) based on the original dry weight of biomass. All experimental conditions used in this study such as biomass weight, biomass to solvent ratio, water to ethanol ratio, temperatures and catalysts are summarized in Table 2. Following the liquefaction, the reactor was rapidly cooled in ice-water to room temperature. After cooling, the liquid products and solid residue in the reactor were completely washed with excess ethanol, filtered under reduced pressure through a pre-weighed Whatman filter paper and dried in the oven at 105 °C for 6 h before weighing. The excess of ethanol in the filtrate was removed by rotary evaporator under
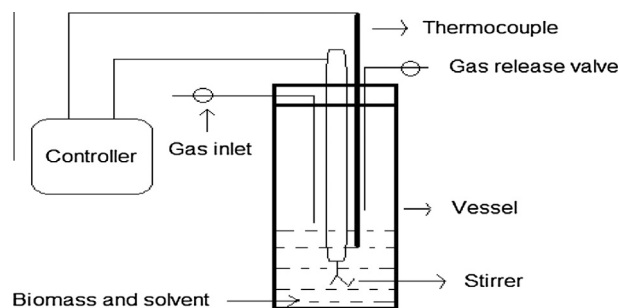

Fig. 1. Diagram for Parr reactor used in the liquefaction process.