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Effect of glycerol as co-solvent on yields of bio-oil from rice straw through hydrothermal liquefaction

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HIGHLIGHTS

- Glycerol was able to improve the hydrothermal degradation of rice straw.
- Under the optimal conditions, promising bio-oil yield (50.31 wt%) was obtained.
- The quality of the derived bio-oil was also significantly improved.
- Na_2CO_3 assisted glycerol in the HTL process of rice straw.

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ABSTRACT

This study examined the effect of glycerol used as a co-solvent on yields of bio-oil derived from rice straw through hydrothermal liquefaction (HTL). The reaction was conducted in a high-pressure batch reactor with different volume ratios of glycerol to water. The quality of the derived bio-oil was analyzed in terms of its elemental composition, heating value, water content, ash content, and acid number. Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry were conducted to analyze the chemical composition of the derived bio-oils. The following optimal conditions were obtained: 1:1 vol ratio of glycerol to water with 5 wt% of Na_2CO_3 at 260 °C for 1 h. Under these conditions, 50.31 wt% of bio-oil and 26.65 wt% of solid residue were produced. Therefore, glycerol can be used as a co-solvent in HTL of rice straw at moderate temperatures to obtain bio-oil with high yield and quality.

1. Introduction

Human beings currently face many issues regarding the future energy needs as a result of diminishing fossil fuel reserves, unsecured supplies, increasing in cost and environmental pollution. In order to address these issues, researchers should develop various alternative fuels, such as biofuels (Batan et al., 2016; Bauer et al., 2016; Razaghi et al., 2016; Tang et al., 2011; Thiruvenkadam et al., 2015; Zhou et al., 2010, 2012). Biomass is a potential source for chemical and fuel production because it is easily reproduced, versatile, and environmentally beneficial.

In current research, techniques such as fermentation, combustion, gasification, pyrolysis, and hydrothermal liquefaction (HTL) have been utilized to process biomass waste (Neveux et al., 2013). HTL is one of the thermochemical processing technologies that have been extensively investigated for bio-oil production (Tungal and Shende, 2014; Guo et al., 2012; Gan et al., 2012). HTL provides several advantages over other techniques. First, this process does not require prior thermal drying and thus results in a reduction of costs for wet materials (Yang et al., 2014). Second, hot pressurized water is used as a reaction medium and reactant. As such, other chemicals are unnecessary; and the whole process is versatile and environmentally friendly (Christensen et al., 2014; Gan and Yuan, 2014; Kinata et al., 2014). HTL is also less corrosive to equipment than other alternatives (Cybulska et al., 2010). Therefore, HTL is a unique approach to treat biomass resources. Prepared bio-oils can be used as fuels for burners, stationary diesel engines, and turbines or boilers. Bio-oils can also be further upgraded or converted to transportation fuels (diesel and gasoline) and products, including aromatics, polymers, asphalt, and lubricants (Guo et al., 2012; Ramos-Tercero et al., 2015).

Lignocellulosic materials (LCMs) are the most abundant renewable biomass. Approximately 1.3×10^{10} metric tons of LCMs were produced worldwide in 2015 (Zhang et al., 2016). LCMs are mainly composed of cellulose, hemicellulose, and lignin that can be utilized as renewable and cheap feedstock for various applications (Kang et al., 2013; Matson et al., 2011; Patil et al., 2010; Pham

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et al., 2013; Ruiz et al., 2013; Zhao et al., 2014). Typical LCMs include agricultural residues, such as rice, wheat, and corn straw, and these materials are abundant worldwide, especially in agricultural countries, such as China. LCMs provide promising beneficial effects on the economy and environment if such resources are utilized effectively. In China, about 200 million tons of rice straw was produced in 2013, but most of it was disposed of or burned after harvest. This ineffective utilization of LCMs has contributed to the exacerbation of waste and environmental pollution.

Research has shown that HTL has the potential to treat rice straw for liquid biofuel production. However, the yields of bio-oil from rice straw via HTL have been unsatisfactory to date. Minowa et al. (1998) investigated the bio-oil production from rice straw through its liquefaction in water (300 °C, 10 MPa). The bio-oil yield was 22.5 wt%. Yuan et al. (2007) reported that the maximum yield of bio-oil was 39.7 wt% for the 2-propanol:water volume ratio of 5:5 at 573 K. Li and Yuan (2009) reported that a bio-oil yield of 57.30 wt% can be obtained through rice straw liquefaction at 300 °C. However, they used 1,4-dioxane, which is carcinogenic and environmentally harmful, as a co-solvent. Therefore, further research should be performed to improve the yield of rice straw bio-oil by using environmentally friendly methods.

Glycerol is a viscous, odorless, colorless, simple polyol liquid that is highly soluble in water because it contains three hydroxyl groups. With advancements in the biodiesel industry, the production of glycerol, which is a major byproduct of biodiesel production, has increased (Grilc et al., 2015; Kim et al., 2015; Sun et al., 2015). Its supply will be six times more than the demand by 2020 (Christoph et al., 2000). Therefore, current glycerol surplus should be utilized to manufacture useful products (Fountoulakis and Manios, 2009; Silva et al., 2009).

Some researchers have reported that glycerol can be used as solvent/co-solvent to improve the liquefaction process for producing liquid fuel (Demirbas, 2008, 2010; Pedersen et al., 2015, 2016; Xiu et al., 2011; Ye et al., 2012). Demirbas (2008, 2010) reported the utilization of pure glycerol as the sole solvent in the HTL of wood biomass. Xiu et al. (2011) and Ye et al. (2012) focused on the liquefaction of animal wastes, such as swine manure at 340 °C. Rosendahl's group (Pedersen et al., 2015., 2016) focused on the conversion of wood biomass in crude glycerol at a relatively high temperature (about 400 °C). There is a paucity of technical data in the literature that investigates the utilization of glycerol as co-solvent in HTL process of agricultural residues at moderate temperature (<300 °C). The objectives of this work are (1) the evaluation of the effect of glycerol, used as a co-solvent, on the production of bio-oil during the HTL process of rice straw at moderate temperature, and (2) the proposal of the impact mechanisms of glycerol that lead to the improvement of the oil yield. In addition, the oil properties and compositions were analyzed.

2. Materials and methods

2.1. Materials

Rice straw was obtained from a farm in Henan in central China. The sample was initially dried in an oven at 104 °C for 8 h to determine moisture content in the feedstock. Before compositional analysis was performed, the fresh feedstock was prepared in accordance with NREL/TP-510-42620. The components of feedstock were determined in accordance with NREL/TP-510-42618. The detailed procedure was described in our previous work (Cao et al., 2016). The characteristics of the rice straw samples are given in Table S1 (Supporting information). Glycerol was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai) and all other chemicals were obtained from Aladdin Reagent Co., Ltd. (Shanghai). The main characteristics of glycerol are shown in Table S2 (Supporting information).

2.2. HTL and separation procedures

The HTL experiments were conducted in a 250 mL GSH-0.25 type autoclave (Fig. 1). In a typical experiment, 15 g of dried rice straw, 150 mL of solvent, and 0.75 g of Na_2CO_3 were mixed in the reactor. The reactants were agitated by using an internal magnetic stirrer at 180 rpm. The temperature was controlled by an electric furnace and was set at 260 °C. After the reaction was completed, the reactor was rapidly cooled down to room temperature by a cooling water system installed inside the reactor.

After the reaction, the gas was vented without further analysis. The other products were removed from the reactor by washing them with 100 mL of deionized water, and this procedure was repeated five times. After filtration, the liquefied mixture was separated into a liquid phase and a solid phase. Bio-oil was then extracted from the two phases using ethyl acetate (EA). Two EA solutions were separated from aqueous phase and solid phase by being treated with separatory funnel and filtrator, respectively. Excessive anhydrous sodium sulfate was then used to remove water and residual glycerol in the solutions, thus ensuring that there were no water and glycerol in the final bio-oil product. The oil derived from liquid phase and solid phase were designated as light oil (LO, 3.42 g) and heavy oil (HO, 4.13 g), respectively. The EA insoluble fractions were called water products (WP) and solid residue (SR, 4.00 g) after drying.

The yield of each fraction was calculated as follows:

$$\text{HO yield } (\%) = \frac{\text{weight of heavy oil}}{\text{weight of dry rice straw}} \times 100$$

$$\text{LO yield } (\%) = \frac{\text{weight of light oil}}{\text{weight of dry rice straw}} \times 100$$

$$\text{oil yield } (\%) = \frac{\text{weight of (heavy oil + light oil)}}{\text{weight of dry rice straw}} \times 100$$

$$\text{residue yield } (\%) = \frac{\text{weight of soild residue}}{\text{weight of dry rice straw}} \times 100$$

$$\text{gas + aqueous product yield } (\%) = \frac{\text{weight of (feedstock} - \text{oil} - \text{solid residue)}}{\text{weight of dry rice straw}} \times 100$$

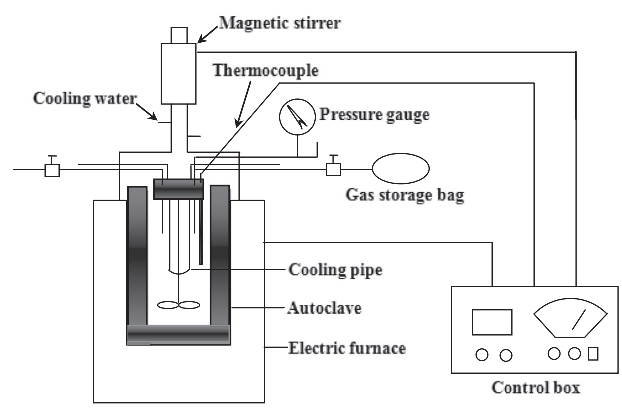

Fig. 1. Schematic diagram of the hydrothermal liquefaction system.