



Characteristics of the products of hydrothermal liquefaction combined with cellulosic bio-ethanol process



Rundong Li, Yinghui Xie, Tianhua Yang^{*}, Bingshuo Li, Yang Zhang, Xingping Kai

College of Energy and Environment, Shenyang Aerospace University, Key Laboratory of Clean Energy, Liaoning Province, No. 37 Daoyi South Avenue, Shenyang 110136, PR China

ARTICLE INFO

Article history:

Received 30 September 2014
Received in revised form
16 July 2016
Accepted 10 August 2016

Keywords:

Corn stalk
Fermentation residues
Hydrothermal liquefaction
Bio-oil

ABSTRACT

The integration utilization of fermentation residues from cellulosic bio-ethanol has attracted a great deal of attention to balance the total cost of bio-ethanol production while simultaneously dealing with bio-ethanol wastewater. A process of hydrothermal liquefaction (HTL) of intact materials from cellulosic bio-ethanol in a batch reactor was proposed. The effects of the reaction temperature and time on the liquefaction characteristics were examined. The optimum condition for liquefaction fermentation residues was 370 °C (21.25 MPa) and 30 min with a bio-oil yield of 40.79 wt%. GC-MS results indicated that the major chemical species in the bio-oil were phenols, ketones, long-chain hydrocarbons and fatty acids. Supercritical conditions (375 °C, 23.50 MPa) was favored for the low-molecular-weight species formation compared to subcritical conditions (370 °C, 21.25 MPa), as some long-chain species decreased. This work thus can provide a novel idea for bio-oil production from HTL of cellulosic bio-ethanol fermentation residues.

© 2016 Published by Elsevier Ltd.

1. Introduction

Biomass is one of the most abundant renewable resources and an important part of the renewable energy systems in the future. Over the last few decades, several ways of utilizing biomass for energy production in different forms, e.g., bio-ethanol, bio-gas and bio-oil, have attracted considerable attention [1]. Moreover, bio-ethanol and bio-oil can be further converted into liquid fuels, thus meeting the global renewable energy demand.

Recently, extensive research has been carried out on second-generation ethanol production from lignocellulosic biomass [2]. Not only is lignocellulosic material the most widespread and abundant biomass but also there is a need to deal with food security. Generally, lignocellulose consists of 40–50 wt% cellulose, 20–35 wt% hemicellulose, 20–40 wt% lignin [3] and other extractives depending on the origin. Cellulosic bio-ethanol production usually consists of pretreatment, enzymatic hydrolysis of polysaccharides, ethanol fermentation and product recovery four steps [4]. However, the high cost is still a barrier for the development of cellulosic ethanol production technology [5]. Additionally, amounts

of liquid and solid wastes throughout the process, including fermentation by-products, undecomposed lignocellulose and organic wastewater, are also needed for further harmless treatment. The solid wastes are mainly composed of cellulosic materials with a higher lignin content, which can be used for combustion, but it is uneconomic. As regards to liquid wastes, it was defined as the high COD concentration, high suspended solids and viscous organic wastewater [6], which was a serious threat to the environment. Therefore, it is difficult to treat compared to the disposal of solids, and it was traditionally used as feedstock for anaerobic digestion [7].

Recently, a new concept for enhancing energy recovery from cellulose bio-ethanol is through hydrothermal liquefaction (HTL), which is optimal for wet biomass conversion without the pre-treatment of feedstock drying [8]. Agricultural & forestry residues, herbaceous crops, aquatic and marine biomass, and wastes have been studied as feedstock for bio-oil production through HTL process [9–14]. Therefore, all wastes from bio-ethanol fermentation without drying may directly be used as materials for bio-oil production by HTL. Additionally, bio-oils from HTL also have lower oxygen contents and higher heating values in comparison to that from pyrolysis [15]. Toor et al. [16] studied the combination of enzymatic bio-ethanol production and catalytic liquefaction of wet distillers grains with soluble (WDGS, a byproduct from the bio-

^{*} Corresponding author.

E-mail address: thyang2013@163.com (T. Yang).

ethanol process), and results showed that WDGS could be converted to bio-oil with high yield.

In addition, ethanol obtained from fermentation is also a good reactant, which can be directly used in the HTL conversion process to improve some properties of the bio-oil. Zheng et al. [17] studied the depolymerization of the stalk cellulose in sub- and supercritical ethanol and found that ethyl ester was the main component. This result suggested that organic acids could be reduced through ethanol and acids reactions. Zhang et al. [18] investigated the direct liquefaction of *Dunaliella tertiolecta* in ethanol-water system with an ethanol volume of 0–100%. The highest bio-oil yield of 64.68 wt % was achieved when the volume of ethanol was 40%, suggesting that ethanol can enhance bio-oil yield. Liu et al. [19] also liquefied rice husk in an ethanol-water mixed solvent. Result showed that the highest bio-oil yield (21.15 wt%) was obtained at 260 °C at the ethanol/water (V/V) of 5/5. The above studies also suggested that mixed solvent shows synergistic effects on biomass hydrothermal degradation. Effects of various liquefaction conditions on the liquefaction of the bio-ethanol fermentation residues of reed- and corn stover in the presence of ethanol were also investigated by Lu et al. [20].

Both fermentation waste and ethanol can be used directly in HTL, indicating that all products from bio-ethanol production can be used as materials to produce bio-oils. Studying the liquefaction characteristics of products and byproducts from lignocelluloses bio-ethanol not only can solve the pollution of wastewater from bio-ethanol but also obtain potential bio-oils as well as improve the whole biomass utilization efficiency.

To our best knowledge, the lignocellulose bio-ethanol fermentation process followed by HTL conversion for bio-oil production has not been reported. In the present study, fresh corn stalks with 66.7 wt% moisture content were used as fermentation materials. All fermentation products including ethanol and byproducts were chosen as the raw material for HTL process. The aim of current work was to carry out an initial study of the conversion of lignocelluloses bio-ethanol products to bio-oil. Investigation focuses on the optimum treatment conditions of HTL process by using the following treatment variables: liquefaction temperature and liquefaction retention time. Bio-oil was characterized by Fourier transform infrared spectroscopy (FT-IR) and gas chromatography–mass spectrometry (GC-MS) aimed to realize the effects of sub- and supercritical conditions on the chemical compositions of the bio-oil.

2. Material and methods

2.1. Materials

Fresh corn stalks were collected from Shenyang, China. The stalks were thoroughly washed and stored at –10 °C to keep fresh for further use. The samples were thawed at room temperature, and they were manually minced into small particles, with size <5.0 mm before use. All other reagents used in this study were of analytical grade.

2.2. Bio-ethanol fermentation

The minced stalks (30.00 g) were weighed and placed in an Erlenmeyer flask (250 mL). Firstly, 150 mL of NaOH (20 mg/mL) solution was added into the flask, which was then placed in a water bath at 40 °C for 0.5 h. The solution was filtered using a single-layer medical gauze, and the treated sample was rinsed with deionized water until the pH was neutral. The Erlenmeyer flask was tilted to remove any remaining water. Secondly, 150 mL of dilute H₂SO₄ (0.03 mL/mL) solution was added into the flask. The flask was placed in a boiling water bath for 1 h and then cooled. Appropriate

quantities of NaOH were added to achieve a neutral pH and obtain fermentation slurry. Thirdly, about 4‰ of the yeast that corresponded with the sample (30.00 g) in the flask was added. The flask was then placed at 35 °C for 96 h. All the products obtained after fermentation were the new materials for HTL.

2.3. HTL and products separation procedures

HTL was performed in a 500 mL autoclave batch reactor made of stainless steel (SS316L) with a magnetic stirrer. The total volume of the new materials in each experiment was adjusted to 200 mL with distilled water before they were charged into the reactor. The reactor was heated with an external electric heater at a heating rate of 5.5 °C/min. Upon completion, the reactor was cooled to lower than 250 °C by fan and then to 25 °C with an internal cooling coil system. The volume of the gas was measured by displacement method, and the mass of the gas was estimated with CO₂ density. The aqueous products and some suspended solids were poured into a beaker (Beaker A). The reactor was washed with 100 mL of methylene chloride and 50 mL of acetone, and then the organic solutions and other solids were collected in a different beaker (Beaker B). The organic solution in Beaker B was filtered to separate the organic phase and the solids. The organic phase was evaporated to remove the solvents, and the resulting liquid was defined as bio-oil. All the solids were dried in an oven at 105 °C for 12 h and then weighted. The experimental errors were estimated as standard deviation and were represented as error bars placed in the graphs showing the results. Each run was conducted three times and the mean values were reported. The yield of liquefaction products and the conversion ratio were calculated as follows:

$$\text{Yield}_{\text{bio-oil}} = \frac{M_{\text{bio-oil}}}{M_{\text{CS}}} \times 100\% \quad (1)$$

$$\text{Yield}_{\text{solid}} = \frac{M_{\text{solid}}}{M_{\text{CS}}} \times 100\% \quad (2)$$

$$\text{Yield}_{\text{gas}} = \frac{V_{\text{gas}} \times \rho_{\text{CO}_2}}{M_{\text{CS}}} \times 100\% \quad (3)$$

$$\text{Yield}_{\text{aqueous}} = 100\% - \text{Yield}_{\text{bio-oil}} - \text{Yield}_{\text{solid}} - \text{Yield}_{\text{gas}} \quad (4)$$

where M_{CS} is the mass of the dry corn stalks, $M_{\text{bio-oil}}$ is the mass of the bio-oil, M_{solid} is the mass of the dry solid and ρ_{CO_2} is the density of CO₂ at atmospheric pressure.

2.4. Characterization

Cellulose, hemicellulose and acid insoluble lignin contents were determined by the Van Soest Cellulose Content Determination Method [21] with the FIWE6 fibrometer system. Functional groups of the bio-oils were examined using a Bruker Tensor TENSOR27 Model FT-IR with a spectral resolution of 4 cm⁻¹ at room temperature. Background-subtracted spectra were collected from 4000 to 400 cm⁻¹.

The chemical composition of bio-oils was analyzed by GC-MS (Agilent 6890N/5975). The carrier gas was He at a flow rate of 1.0 mL/min. An HP-5 column (30 m × 0.25 mm × 0.25 μm) was used for the separation. The heating process for the bio-oil analysis was as follows: an oven isothermal program was set at 60 °C for 3 min, followed by a heating rate of 10 °C/min to 280 °C for 20 min. The injected volume was 1 μL. MS was operated with the following conditions: transfer line 220 °C, ion source 220 °C and electron energy 70 eV. The compounds were identified by comparing with

Download English Version:

<https://daneshyari.com/en/article/8072892>

Download Persian Version:

<https://daneshyari.com/article/8072892>

[Daneshyari.com](https://daneshyari.com)