Energy Conversion and Management 93 (2015) 23–30

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Effects of Chemical–Biological pretreatment of corn stalks on the bio-oils produced by hydrothermal liquefaction

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A R T I C L E I N F O

Article history:
Received 8 October 2014
Accepted 29 December 2014

Keywords:
Corn stalks
Chemical–Biological pretreatment
Liquefaction
Bio-oils

A B S T R A C T

The production of bio-oils by hydrothermal liquefaction of lignocellulose is an attractive prospect. However, bio-oils produced using traditional methods have multiple components and are low grade, which limit their application. In this study, a new method was proposed to improve the quality of bio-oils. Chemical–Biological pretreatment (CB-pretreatment) was performed on fresh corn stalks to separate a partial lignin and to convert hemicellulose, generating ethanol for hydrothermal liquefaction and improving the quality of the resulting bio-oils. Furthermore, the influence of CB-pretreatment on the components of lignocellulose in corn stalks and the pretreated samples was analyzed. And the materials and bio-oils were analyzed with TGA and GC–MS. The results showed that the relative content of lignin reduced from 13.25 ± 0.87% to 8.97 ± 0.77% in the alkaline treatment. And the relative content of hemicellulose in the alkaline-acid pretreated substrates decreased from 21.65 ± 0.74% to 10.06 ± 0.48%. After the whole pretreatment, the concentrations of ethanol and remaining reducing sugar in the fermented liquor were 2.88 ± 0.09 mg/mL and 3.59 ± 0.30 mg/mL, respectively. Moreover, the pretreated substrates had a lower degradation temperature and less ash content than the corn stalks. The heating value of the bio-oil was 32.21 MJ/kg. Moreover, the number of bio-oils components was obviously reduced. Toluene and 2,6-di-tert-butyl-4-methylphenol, which are respectively used as high octane additive and antioxidant in fuels increased significantly in quantity, with their total percentage of corresponding peak area reaching 30.77%.

1. Introduction

Shortage of traditional fossil fuels and problems such as environmental pollution and global warming [1] that arise as a result of fossil fuel consumption has become worldwide concerns. As a result, there is an urgent need for new liquid fuels [2,3]. Based on the characteristics of water under high temperature and pressure conditions, liquid bio-oils can be produced by hydrothermal liquefaction of biomass [4] through the destruction of the complex molecular structure of biomass and aggregating small molecules. This technology is regarded as the most promising bio-oils production technology to date [5,6]. The types of biomass used to produce bio-oils by hydrothermal liquefaction mainly consist of agricultural straw, wood waste, animal and vegetable oils, algae, animal waste, as well as municipal sludge. A number of studies [4,7,8] had shown that different types of biomass contain different components, such as lignocellulose, protein, and lipid, in varying amounts, and that the chemical compositions of the resulting bio-oils are also different, consisting of varying quantities of lipids, alcohols, phenols, ethers, ketones, acids and aromatic compounds. In general, lignocellulosic biomass contains cellulose, hemicellulose, lignin, extractives and ash [9]. Due to limited biomass resources, it is important to experiment with lignocellulosic biomass with relatively abundant reserves.

Factors that influence the bio-oils via hydrothermal liquefaction (HTL) include the type of raw materials, solvent, temperature, reaction time, and catalyst [10]. Raw materials and solvent determine the chemical composition of bio-oils, whereas reaction conditions mainly influence the quantity and pathway of bio-oils production. By investigating hydrothermal liquefaction of cellulose under acidic and neutral conditions, Yin et al. [11] found that the main products of hydrothermal liquefaction were furfural, as well as a small quantity of organic acids and dihydroxy acetone. Gosselink et al. [12] liquefied lignin in supercritical water to obtain phenolic and aromatic compounds. Peng et al. [13] studied hydrothermal liquefaction of corn stalks under CO atmosphere and found that the main products were aromatic compounds,

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http://dx.doi.org/10.1016/j.enconman.2014.12.089
0196-8904/

phenols and fatty chain compounds. Li et al. [7] converted brown algae to bio-oils by hydrothermal liquefaction and detected 132 chemical compounds. The studies listed above showed that the more complex the original biomass, the more complex the resulting bio-oils chemical compositions profile. This could be attributed to the varying lignocellulose content in different biomass. And differences in the physical structure and chemical bond energy of lignocellulose components which are influenced by the species or living environment of the biomass also result in varying bio-oils chemical compositions. Those indicated that the characteristics of the raw biomass materials are the decisive factors in the final chemical composition of bio-oils, and the type of reactant also has a profound effect on the yield and chemical profile of the resulting bio-oils. Organic alcohols such as methanol and ethanol [14,15] are sometimes adopted as reaction solvents to help improve bio-oils yield and to reduce the oxygen content. Ethanol is widely used as reaction solvent [16,17]. Chen et al. [18] showed that using ethanol as the reaction solvent during hydrothermal liquefaction, esterification reactions occurred between ethanol (about 5%) and the organic acids that were generated during biomass breakdown, suggesting that only a small amount of ethanol can act as the reactant. Using ethanol as solvent may accelerate the biomass to bio-oils conversion [19] and increase the reaction efficiency.

In summary, it is clear that raw materials characteristics significantly influence on the chemical composition of bio-oils. When it was used as solvent, ethanol plays a key role in optimizing the chemical composition profile of bio-oils and increasing the reaction efficiency. Therefore, an efficacious pretreatment process for raw materials that helps adjust the contents of the raw components can be a simple way to improve the chemical composition of bio-oils. However, there are only a few studies about pretreatment of raw materials during bio-oils production using hydrothermal liquefaction. Therefore, the technology used in the cellulosic ethanol industry was applied to this work [20,21]. Lignocellulose was pretreated using chemical treatments and biological fermentation. This pretreatment method was denoted as “Chemical–Biological pretreatment” (CB-pretreatment) throughout this paper, and the bio-oils production method was named the “Chemical–Biological pretreatment Hydrothermal Liquefaction method” (CB-HTL). To investigate the influence of Chemical–Biological pretreatment on bio-oils production, the components and thermo-physical properties of the treated materials were analyzed, and the variation in the chemical composition profiles of the bio-oils was further compared.

2. Materials and methods

2.1. Materials and reagent

Fresh corn stalks with a moisture content of 66.2% were collected from the city of Shenyang. The corn stalks were thoroughly washed, frozen, stored at −10 °C, and thawed at room temperature before use. They were minced into particles <5 mm in size. NaOH, concentrated sulphuric acid, 3,5-Dinitro salicylic acid (DNS), potassium dichromate, methylene chloride, and acetone were analytical grade. The saccharomycetes used for fermentation was commercial Angel yeast (alcohol active dry yeast, Angel).

2.2. Chemical–Biological pretreatment

NaOH solutions (w/v) with concentration of 2%, as well as H_2SO_4 solutions with concentration of 3% were prepared. 30.00 g of the minced stalks were weighed and placed in 250 mL Erlenmeyer flasks. Then, 150 mL of the NaOH solutions with differing concentrations was added to every flask and kept at 40 °C in water bath for 0.5 h. The solutions were filtered using single-layer medical gauze and the treated biomass was rinsed with deionized water until the pH was neutral. The Erlenmeyer flasks were tilted to remove any remaining water. When no remaining water dripped from the flask, dilute H_2SO_4 solutions of 3% were added to the Erlenmeyer flasks, and the biomass was hydrolyzed in a boiling water bath (97 °C) for 1 h. And then the Erlenmeyer flasks were cooled with running water to room temperature and appropriate quantities of NaOH solutions were added to reach neutral pH to generate fermentation slurries. Dry yeast was revived using the method of adding dry yeast into 2% glucose water and incubating for 15 min in a 35 °C water bath. The amount of yeast was calculated as follows:

$$\text{Amount} = \frac{\rho_{yeast} \times v_{add}}{30} \times 1000‰ \tag{1}$$

where ρ_{yeast} was the concentration of yeast in the yeast mixture, V_{add} was the added volume, 30 was the mass of fresh corn stalks. Different volumes of the yeast mixture were added to the prepared fermentation slurries, and allowed to ferment at 35 °C for several days. After fermentation, all of the remaining matter in the Erlenmeyer flasks was used as raw materials for hydrothermal liquefaction.

2.3. Hydrothermal liquefaction

After fermentation, the volume of the slurry was adjusted to 200 mL before being placed in the reactor (KCFD 05-30). The reaction temperature was set at 370 °C and the reaction time was 30 min. After the reaction, the reactor was cooled to 25 °C and the exhaust valve was opened to exhaust gas generated during the reaction. Because the gas generated was mainly CO_2, it was not collected for further analysis [22]. The liquefaction products were collected and separated according to the process shown in Fig. 1. As shown in Fig. 1, the liquefaction products included gas, solid and liquid (including aqueous products and bio-oils). The reactor was then opened, and 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). Since the bio-oils was adsorbed together with residue and they were sticked in the wall and coil of reactor, the bio-oils were mainly extracted by the wash solution in beaker B. Firstly, the content of Beaker A was vacuum filtered using an organic membrane (0.45 μm) to separate the aqueous products and solid residues (Solid 1). The Erlenmeyer flask of the vacuum filter device was replaced by a new one. And the aqueous products were extracted with methylene chloride to get the organic solution. The organic solution in Beaker B was filtered under the vacuum filter with new flask to separate solids and organic solution. Bio-oils were designated as the remaining liquid of all the organic solutions after removing methylene chloride and acetone with rotary evaporation. The bio-oils yield is the ratio of the mass of bio-oils to the mass of dried corn stalks. The yield of liquid, solid and gas products of CB-HTL were calculated as follows:

$$Yield_{solid} = \frac{M_{solid}}{M_{driedCS}} \times 100\% \tag{2}$$

$$Yield_{liquid} = \frac{\rho \times V}{M_{driedCS}} \times 100\% \tag{3}$$