Fuel Processing Technology 174 (2018) 53–60

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Mechanical deconstruction of corn stover as an entry process to facilitate the microwave-assisted production of ethyl levulinate

Huan Liu, YuXuan Zhang, Tao Hou, Xueli Chen, Chongfeng Gao, Lujia Han, Weihua Xiao*

Biomass and Bioresource Utilization Laboratory, College of Engineering, China Agricultural University, Box 191, Beijing 100083, China

ARTICLE INFO

Keywords:
Corn stover
Mechanical ball milling
Physicochemical properties
Microwave-assisted heating
Ethyl levulinate

ABSTRACT

In this study, ball milling was applied as a pretreatment to promote the production of ethyl levulinate (EL) from corn stover under microwave irradiation. The experiments showed mechanical grinding significantly increased the EL yields by 31.23 and 23.31% at 160 and 170 °C, respectively. To further understand the influence of ultrafine grinding on alcoholysis process, we have presented a series of physicochemical and morphological analysis for the ball milled corn stover. The characterization indicated that ball milling sharply reduced the particle size to cellular scale and the intact, smooth surface changed to an open, porous structure during ball milling. It also resulted in the disruption of crystalline cellulose to amorphous state and the depolymerization of polysaccharides with an increase in reducing-ends. In general, mechanical processing approach could efficiently modify the corn stover and facilitate the EL production in the following three ways: firstly, the reduction in particle size with increased surface increased the reaction accessibility of cellulose; secondly, the destruction of compact cellulose crystal structure conduced to the reduction of alcoholysis energy barrier; moreover, the depolymerized polysaccharides resulted in the increase of the reaction sites, which further improved the reaction activity and promote EL conversion. The mechanical processing approach could well hold the key to a better use of the mechanical forces in the alcohol reaction system, providing an environment-friendly method into lignocellulosic biorefinery schemes.

1. Introduction

Ethyl levulinate (EL) is a versatile chemical that can be applied in the flavoring and fragrance industries [1] and as an additive in gasoline and diesel [2,3]. The direct production of EL from lignocellulosic biomass via acid-catalyzed with ethanol is considered to be an economic and attractive method [4]. Corn stover is an important lignocellulosic biomass resource because of its large-scale output across in China, however, most of them have not been efficiently utilized. To enhance the value of corn stover, the direct conversion of corn stover into EL might be a promising approach for the abundant cellulosic biomass.

It is well known that, degradation of cellulose from lignocellulosic material remains challenging due to biomass recalcitrance. The conversion efficiency of cellulose is greatly affected by cellulose accessibility and the highly ordered crystalline structure. Previous studies have reported the direct conversion of lignocellulosic biomass to EL need to be conducted at rigorous conditions. Specifically, Mao et al. [5] developed a unique process for the sulfuric-acid-catalyzed conversion of wood chips into EL, and their highest yield was 44.4%, which was achieved at 190 °C. Mascal and Nikitin [6] utilized dried conifer wood to produce EL in an autoclave at 200 °C for a total yield of 23%. Most of the reactions in these studies were conducted in a temperature range of 180–200 °C. A previous study by our team explored the alcoholysis temperature from 160 to 200 °C under microwave irradiation [7], and we found that excessively high temperature caused the formation of byproducts (such as humins), resulting in a decline of EL yield. Thus, we need to seek a practical pretreatment approach to further improve the alcoholysis conversion efficiency of lignocellulose biomass under relatively mild temperature.

In recent years, several methods have been applied to pretreat lignocellulosic biomass to improve its utilization, including physical, chemical, biological methods, as well as a combination of these methods. Mechanical ball milling (BM) has been found to be an effective pretreatment, which uses collision, friction, and shear to destroy the crystalline structure of cellulose and to improve its digestibility [8]. BM can directly rupture plant cell walls and dissociate tissues, thus effectively reducing the particle size and crystallinity of lignocellulosic substrates [9,10]. Mechanically reducing the size of lignocellulose particles is an important step in valuable chemical production processes. Furthermore, this pretreatment offers the advantages of

* Corresponding author at: China Agricultural University, East campus, Box 191, Beijing 100083, China.
E-mail address: xiaoweihua@cau.edu.cn (W. Xiao).

https://doi.org/10.1016/j.fuproc.2018.02.011
Received 13 October 2017; Received in revised form 29 December 2017; Accepted 11 February 2018
Available online 22 February 2018
0378-3820/

avoiding byproduct generation and being environmentally friendly [11].

A large number of lignocellulosic materials possess a great potential for the production of valuable chemicals and fuels after pretreatment. However, most researchers are focus on enhancing the products yields with ball-milled biomass in enzymatic hydrolysis. Ball milling to pretreat biomass combined with direct conversion to EL in alcohol has rarely been studied. For example, Licari et al. [12] compared 4 kinds of mechanical milling modes (ball mill, vibratory ball mill, centrifugal mill, jet mill) applied to bagasse in terms of energy efficiency, and the results indicated that VBM provided more effective enzymatic accessibility and sugar solubilization than the other methods. Ji et al. [13] reported mechanical fragmentation of corncob sample at the cellular scale (50–30 μm) significantly enhanced enzymatic digestibility. However, Boissou et al. [14] developed a system to use n-butanol as a solvent to produce butyl glycosides with ball-milled cellulose, the yield of butyl glycosides reached a maximum of 62% after a 2-h reaction. Compared with the enzymatic hydrolysis in water, reaction system in alcohols offers some advantages. For example, they can minimize wastewater discharge and provide higher-grade products that are easily isolated by extraction. The results inspired us to investigate the acid-catalyzed alcoholysis of ball-milled corn stover to EL in ethanol and with the hope of gaining insights into the mechanism of the ball-milling pretreatment on the effect of alcoholysis reaction.

Several studies have investigated the physicochemical changes occurring in lignocellulose during ultrafine grinding, such as cellulose crystallinity and the surface area [11,13,15]. However, mechanochemical effects initiated by ball milling, such as structure change in polysaccharides and depolymerization in polysaccharides, are still poorly understood. It should be noted that the structure change in polysaccharides and depolymerization of the cell wall polysaccharides in the lignocellulosic biomass during mechanical ball milling is vital to improve alcoholysis conversion efficiency because of the natural resistance of plant cell wall.

In addition, analyzing the current literature revealed that some milling factors such as the mass ratio of the ball to the material, the filling ratio, and ball-milling speed that could exert an effect on grinding efficiency [16]. Among these, milling time is considered the main factor. Moreover, since the milling process is not cost-effective, high energy consumption is the main drawback in industrial applications, thus it is necessary to discuss milling process to improve the ball milling efficiency. We used microwave heating instead of conventional heating in our study, the advantage of this method is that microwave uses the capability of direct interaction between the target object and an applied electromagnetic field. Microwave irradiation is an alternative method that can be used to reduce reaction times in organic synthesis [17]. Comparing conventional heating, our team previous study demonstrated that microwave treatment can be applied to significantly accelerate the alcoholysis reaction of lignocellulose biomass and enhance the product yields [18,19].

In this paper, the mechanical ball-milling pretreatment and alcoholysis of corn stover were carried out, and the material was characterized using physicochemical and morphological analyses. To the best of our knowledge, this is the first work in the literature combining a ball-milling pretreatment and alcoholysis techniques for a comprehensive approach to reveal physicochemical, morphological, and structural changes during ball milling.

2. Materials and methods

2.1. Materials

Corn stover was obtained from Henan Province, China, in 2016. The air-dried raw material was roughly cut using a cutting machine to the size < 2 cm.

Table 1
The compositions of raw materials expressed as % of dry matter.

Component	Content (%)
Moisture	4.73 ± 0.32
Cellulose	28.50 ± 0.17
Hemicellulose	20.93 ± 0.20
Lignin	14.68 ± 0.25
Ash	15.93 ± 0.57

Data are shown as their replicate mean ± standard deviation.

2.2. Vibration ball-milling pretreatment

The material coarsely milled by an RT-34 milling machine (Hong Quan Pharmaceutical Machinery Ltd., Hong Kong, China), with the final sample passing through a 1.00-mm screen. This coarsely milled material was defined as the un-ball-milled material and labeled UBM. Then, the UBM was placed in CJM-SY-B ultrafine vibration ball milling (Qinhuangdao Taiji Ring Nano Ltd., Hebei, China) and mixed with ZrO_2 balls (6–10 mm diameter) at a volume ratio of 1:2 for different times (5, 10, 20, 30, 60, 90, and 120 min). The samples ball milled for these times were labeled BM5, BM10, BM20, BM30, BM60, BM90, and BM120, respectively. The BM instrument temperature was controlled to remain below 30 °C.

2.3. Biochemical analysis

The carbohydrate and lignin composition of lignocellulose samples were measured by NREL methods [20]. All the measurements were performed in duplicate. The composition of the raw materials is shown in Table 1.

2.4. Physicochemical and morphological characterization

2.4.1. Particle size distribution

The particle size distribution of all samples was measured using a laser diffraction particle analyzer, Mastersizer 3000 (Malvern Co., United Kingdom), equipped with a dry sample delivery and measuring system, the particle size distribution was determined by the median diameter (D_{50}) and the span was calculated by $(D_{90} - D_{10}) / D_{50}$, where D_{10}, D_{50}, and D_{90} represent the 10th, 50th and 90th percentiles of the total volume [16].

2.4.2. Specific surface area analysis

The surface area was measured with a Multipurpose Micromeritics Tristar II Apparatus (ASAP 2020, Micrometrics Co., USA) and determined using the Brunauer–Emmett–Teller (BET) method based on nitrogen gas adsorption at 77 K. Prior to N_2 sorption, all samples were degassed at 50 °C overnight. The SAs were determined from the nitrogen adsorption/desorption isotherms at 100 °C.

2.4.3. Field-emission scanning electron microscopy

Field-emission scanning electron microscopy (FE-SEM, Hitachi, Co., Japan) was used to analyze micromorphological changes in the samples during ball milling. Samples were sputtered with Pt and then observed at an accelerating voltage of 5.0 kV. The micrographs were taken at 5.00 k magnification.

2.4.4. X-ray diffraction analysis

X-ray diffraction (XRD) patterns were recorded by an Analytical X-diffractometer (Persee XD3 Co., China) equipped with Cu-Kα radiation at 36 kV and 20 mA. The samples were detected in the range of 2θ = 5–40° at a scanning rate of 2°/min with a step interval of 0.2°. The degree of crystallinity can be expressed as the percentage crystallinity index, called the crystallinity index (CrI), which was calculated using