Bioresource Technology 237 (2017) 11–19

Contents lists available at ScienceDirect

Bioresource Technology

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

Impact of ultrasounds and high voltage electrical discharges on physico-chemical properties of rapeseed straw's lignin and pulps

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HIGHLIGHTS

- Physical treatments were applied on rapeseed straw for delignification purposes.
- The US and HVED assisted fractionation was an effective delignification strategy.
- US induced hemicelluloses loss, while HVED impacted cellulose.
- Physico-chemical treatments improved the enzymatic digestibility.

ARTICLE INFO

Article history:
Received 6 December 2016
Received in revised form 30 March 2017
Accepted 1 April 2017
Available online 2 April 2017

Keywords:
Ultrasound
High voltage electrical discharges
Soda
Organosolv
Delignification

ABSTRACT

In this study, ultrasound (US) and high voltage electrical discharges (HVED) were combined with chemical treatments (soda or organosolv) for rapeseed straw delignification.

Delignification was improved by both physical pretreatments. US increased the extractability of hemicelluloses and HVED induced a partial degradation of cellulose. Best synergies were observed for HVED-soda and US-organosolv treatments. The obtained lignin fractions were characterized with ^{13}C NMR and 2D ^{1}H–^{13}C HSQC. It was observed that the physical treatments affected the syringyl/guaiacyl (S/G) ratios. The values of S/G were ≈1.19, 1.31 and 1.75 for organosolv, HVED-organosolv and US-organosolv processes, suggesting recondensation reactions. The lignin fractions obtained from HVED-organosolv treatment contained less quantity of p-coumaric acid and ferulic acid as compared to those extracted by US-organosolv. Thermogravimetric analysis (TGA) revealed a better heat resistance of physically extracted lignins as compared to the control. The enzymatic digestibility increased by 24.92% when applying HVED to mild organosolv treatment.

1. Introduction

Lignocellulosic feedstocks such as wood residues and agricultural co-products are important resources for biorefineries for the production of biofuels, chemicals and polymers. Nowadays, cellulosic ethanol is considered as one of the credible alternatives to mitigate fossil fuel dependence. Nevertheless, the conversion of biomass to bioethanol is hindered by the naturally low accessibility of polysaccharides. The inherent resistance of the biomass to deconstruction contributes to the recalcitrance of biomass processing. The recalcitrance of lignocellulosic materials can be overcome during the pretreatment which is one of the key steps in a biomass to bioethanol process. The goal of the pretreatment is to break the physical and chemical barriers due to the lignin-carbohydrate complex and to increase the sugars accessibility to enzyme degradation. Alkaline treatment (soda) and organosolv processes are two promising pretreatment technologies to fractionate the lignocellulose and to increase the sugars accessibility. However, these two pretreatment technologies have been considered as expensive compared to dilute acid hydrolysis or steam explosion. In this context the optimization of the pretreatment parameters in order to

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http://dx.doi.org/10.1016/j.biortech.2017.04.003
0960-8524/

increase the sugars yield and to decrease the processing cost of soda and organosolv pretreatments constitutes major issues for a cost effective and large scale bioethanol and lignin production. Moreover, regarding both technologies, the relevant utilization of the lignin fractions produced is important for the economic viability of the whole processes.

Lignin represents many challenges for the biorefinery. Chemically it differs from sugars by a complex aromatic substructure. Unlike cellulose with its linear substructure of glucose subunits, lignin has a high degree of structure variability, which depends on the biomass source. The valorization of lignin within the lignocellulose biorefinery is a particularly important topic. Indeed, lignin is the main renewable raw material composed of aromatic units. As a biobased polymer, lignin is characterized by the heterogeneity of its composition and the lack of a defined primary structure. This polymer is most often valued by combustion. However, biorefineries generate more lignin than needed to power the energy facility. Thus, efforts are underway to transform lignin into value-added products (e.g. aromatic compounds of low molecular weight, carbon fibers, polymers and resins).

Until now rapeseed straws have been mostly dedicated to animal feed and combustion while it could be of great interest for the production of fermentable sugars (Jeong and Oh, 2011) and lignin. Several pretreatments and different conditions were applied in previous studies for the treatment of rapeseed straw. The chemical pretreatment of rapeseed straw with sodium hydroxide (soda) and aqueous ammonia was studied by Kang et al. (2012a,b) for the production of bioethanol and biobutanol. Castro et al. (2011) studied the influence of acid pretreatment at different temperatures (140–200 °C) on the production of fermentable sugars from rapeseed straw. Thermochemical pretreatment of rapeseed straw have been investigated by Díaz et al. (2010) et Pińkowska et al. (2013). These authors intended hydrothermal depolymerization of the polysaccharide fractions of rapeseed straw and in a batch reactor using subcritical water. The influence of the main pretreatment variables was evaluated. Arvaniti et al. (2012) have optimized wet oxidation pretreatment of rapeseed straw.

Recently, we described the coupling of physical and chemical pretreatments for the extraction of phytomelanins from rapeseed hulls (Brahim et al., 2016a). Among studied treatments, US and HVED have shown their efficiency. These physical treatments have been described to cause cell damage, increasing the permeability of cell membranes and the accessibility of biomass components. However, the mode of action of US and HVED treatments is still unclear.

The aims of the present work are (1) to study the combination of physical (US, DEHT) and chemical (soda, organosolv) pretreatments in order to reduce the recalcitrance of rapeseed straw in a biomass to ethanol process, (2) to evaluate the impact of studied physical treatments on the biopolymers (lignin and polysaccharides) recovery, (3) to characterize the lignin fractions for future applications.

2. Methods

2.1. Raw material

Rapeseed straws are provided by SEGAGRI (France) and stored at room temperature until use and then dried in an oven at 70 °C before its fractionation. The average moisture content of the raw material was 17% w/w.

2.2. Enzymes

Cellulase from *Trichoderma reesei* (EC 3.2.1.4) were supplied by Sigma-Aldrich (Steinheim, Germany) and present a specific activity of 5 U/mg; one unit liberates 1.0 μmol of glucose from cellulose in 1 h at pH 5.0 at 37 °C (2 h of incubation).

2.3. Pretreatment processes

In this study, a two-step process was adopted (Fig. 1). The first step was a physical treatment either ultrasounds or high voltage electrical discharges followed by a second step corresponding to the chemical treatment either alkali (soda) or organosolv performed at different parameters range (mild (−)/harsh (+)). Control experiments are performed at a same contact time between water and raw material that physical treatment.

2.3.1. Physical pretreatment

2.3.1.1. Ultrasounds pretreatment (US). The ultrasounds treatment chamber contains a titanium ultrasounds probe with a length of 100 mm and a diameter of 14 mm connected to the US generator (Hieldscher GmbH, Stuttgar, Germany). In this study, the power and frequency of US generator were fixed to 400 W and 12 kHz respectively.

A mixture containing 6 or 15 g of rapeseed straw (depending of the following chemical treatment) was introduced to the US treatment chamber. Water was added at the temperature 60 or 80 °C respecting liquid to solid ratio L/S = 30.

The energy of US treatment E (kJ/kg) was calculated as follows:

$$E = P_{US} * t_{US}/m \qquad (1)$$

where E is the specific energy input (kJ/kg), P_{US} is the generator power (400 W) and m is the mass of rapeseed straw suspension (kg).

In this study optimal US treatment energies (1600 kJ/kg and 3200 kJ/kg) were chosen according to preliminary results.

2.3.1.2. High voltage electrical discharges (HVED) pretreatment. The apparatus is composed of a pulsed high voltage power supply (Tomsk Polytechnic University, Tomsk, Russia) and a treatment chamber with a 1 L capacity (inner diameter = 10 cm, wall thickness = 2.5 cm), and equipped with needle plate geometry electrodes. The distance between the electrodes was 0.5 cm. A positive pulse voltage was applied to the needle electrode.

For the application of HVED, 5 g of rapeseed straw and 150 g of water (60 or 80 °C) were introduced in the treatment chamber to respect the liquid to solid ratio L/S = 30. The HVED generate electrical breakdown in liquid. The energy input of HVED treatment was 800 kJ/kg (124 kJ/155 g) which revealed to be an optimal energy for rapeseed delignification in previous study (Brahim et al., 2016b).

The time of HVED application (t_{HVED}, s) was calculated as the product of the average pulse width (t_i, s) and the number of pulses (n_{HVED}):

$$t_{HVED} = n_{HVED} * t_i \qquad (2)$$

However, the total time of solid–liquid contact during the HVED treatment (t_{tot}) was longer and corresponds to:

$$t_{tot} = n_{HVED}/f \qquad (3)$$

where f = 0.5 Hz is the pulse frequency.

In this study, the effective HVED application duration and the corresponding total solid-liquid contact time were 7.75 ms and 39 min, respectively.

2.3.2. Chemical pretreatment

2.3.2.1. Soda: alkali extraction. Soda extraction was carried out in a 500 ml glass beaker. 15 g of rapeseed straw were used for the control experiments (without physical pretreatment) and after the US pretreatment. 5 g of rapeseed straw were used for experiments