Carbohydrate Polymers 119 (2015) 8–17

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Structural changes of *Salix miyabeana* cellulose fibres during dilute-acid steam explosion: Impact of reaction temperature and retention time

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ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form
11 November 2014
Accepted 16 November 2014
Available online 20 November 2014

Keywords:
Salix miyabeana cellulose fibres
Dilute-acid steam explosion
Severity factor
Structural changes
Physical characterization

ABSTRACT

Dilute-acid steam explosion of *Salix miyabeana* has been carried out to understand the effect of processing conditions, expressed through a severity factors (SFT), on the changes in cellulose fibre structures in a perspective of using these in polymer composites. This thermo-chemico-mechanical extraction leads to the isolation of cellulose fibres as observed by SEM images. Fibre length as well as length to diameter aspect ratios decreased with the severity of the treatment. Likewise, fibre whiteness diminished with an increasing severity factor, which could be a tangible effect of physical degradation. Variations in crystallinity seemed to be dependent upon the reaction temperature, generally decreasing with regards to retention time. Above a severity threshold, a structural disorganization was observed. Overall, dilute-acid steam explosion was shown to be a valuable cellulose extraction process that can provide a variety of fibre structures.

1. Introduction

Cellulose fibres are generally produced from lignocellulosic feedstock (wood, straw, grass, etc.) and they can be extracted and/or purified depending on the final targeted application. Beside its large and well-known use in the pulp and paper industries, cellulose is increasingly being considered as a potential feedstock for biofuel production, implying its hydrolysis to glucose and fermentation to "cellulosic" ethanol (Beauchet et al., 2013). However, the crystalline fraction of the cellulose is the most resistant to acid-hydrolysis and thus may be found as a post-treatment residue. In the current work, in an effort to minimize chemical and energy requirements, it is envisioned that fermentable sugars could be produced out of the easily hydrolysable amorphous cellulose fractions. The crystalline residues could then be used in a second step as natural fibre reinforcement for polymer composites.

Various standard pulping methods are available at an industrial level including but not limited to mechanical, thermo-mechanical, chemical and chemico-mechanical pulping. Recent studies by Liu, Ju, Li, and Jiang (2014) and Wang, Li, Cao, and Tang (2011) investigated the use of ionic liquid extraction of cellulose from various sources and showed that up to 62% cellulose extraction could be obtained using these green solvents, which in addition can be recycled.

Among the less common techniques, steam processes as steam explosion, which were first introduced in 1926 by Mason (1926) is getting increasing attention in the field of biofuels. The technique is more challenging to scale to an industrial level than classical pulping process although it allows efficient separation of the different constitutive fraction of biomass (Lavoie, Capek-Menard, Gauvin, & Chornet, 2010). The process involves cooking water-impregnated lignocellulosic biomass under pressure at temperatures in the range of 160–260 °C. After a few minutes of reaction, the content is rapidly purged out of the pressurized vessel and undergoes a rapid decompression or "explosion". The process is environmentally friendly due to the low acid concentration and no organic solvents.

The hydrolytic power of the steam processes is often assessed through a *severity factor*, which is a valuable tool used to quantify the intensity of the hydrolytic conditions of the steam treatments. When using an acid catalyst, the role of the pH in the reaction is combined to the other hydrolytic parameters (temperature and residence time) generating a combined severity factor (Chum, Johnson, Black, & Overend, 1990). The versatility of the severity factor has been demonstrated by adapting it to lignin removal for a wide array of biomass and conversion processes including steam processes (Lee & Lavoie, 2013). Compared to other pre-treatment

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http://dx.doi.org/10.1016/j.carbpol.2014.11.031
0144-8617/

technologies, steam-explosion presents several advantages particularly for the biorefineries. These advantages are summarized in the work of Garrot, Domínguez, and Parajó (1999). They noted the high hemicellulose yield with by-products showing little degradation and disruption of the solid residues from bundles to individual fibres that occur during the explosion effect. Steam-explosion is generally performed without addition of any chemicals. When a dilute-acid (i.e. with acid concentration ranging between 1 and 5%) is used as a catalyst, it increase the hydrolysis rate of hemicellulose and thus further improves the process.

Many investigations reporting on the steam processes focused on the extractability of cellulose as a source for high yield fermentable sugars (Brownell, Yu, & Saddler, 1986; Mosier et al., 2005). However, fewer researchers considered the impact of the steam-process on the fibre structure and properties when used for others purposes as in pharmaceutical, biocomposites and biomaterials. The use of steam processes on lignocellulosic materials can lead to significant changes in their structure and properties, such as reduction of the fibre length, fibre degradation and modification of the crystalline structure. This process should be better optimized to better understand the parameter for the production of high quality natural fibres.

The utilization of natural fibres as reinforcing fillers for polymer composites has previously been investigated in the open literature. As an example, Petinakis, Yu, Simon, and Dean (2003) reviewed that using natural fibres compared with other reinforcing agents such as glass fibres, talc or carbon fibres for improving the performance of biodegradable polymers include the retention of the biodegradability of the composite, but generally also exhibit lower density, superior performance, and lower cost due to the abundance of cellulose fibres.

Han and Choi (2010) explained the role of surface areas especially with regards to the different mechanical properties of reinforced biocomposites. They showed as well that the surface morphology of cellulose fibres is a significant factor to consider for the composite interfacial adhesion. Other important fibre specifications include fibre strength, length to diameter ratio and surface area.

In this work, the physical modifications induced by a dilute-acid steam explosion treatment on *Salix miyabeana* (*willow tree*) cellulose fibres were investigated. In particular, the objective of the work was to determine how dilute-acid steam-explosion process modifies the fibre length, whiteness, thermal stability, crystallinity and degree of polymerization of cellulose. These results were correlated with the steam process conditions via the combined severity factor. The resulting equations generated from simple linear regressions allow an estimation of the properties of the cellulose fibres at a known severity factor. In addition, the dimensions of extracted fibres were compared with those of the existing commercial microcrystalline cellulose. The potential use of dilute-acid steam-explosion as a new route for microcrystalline cellulose isolation from biomass residues is discussed.

2. Materials and methods

2.1. Material

Salix miyabeana residues obtained from Le Saule Magique Inc. (Laval, Québec, Canada) were used as feedstock. Biomass was processed using an 800 g pilot-scale steam gun, which was extensively described by Beauchet et al. (2013), Lavoie et al. (2010) and Lavoie and Beauchet (2012). Sulfuric acid 98% and sodium chlorite (technical grade nominally 80%) were bought from Anachemia Canada Inc. Acetic acid glacial (99.8%) was purchased from VWR International LLC. All reagents were used as received.

2.2. Method

2.2.1. Steam explosion treatment

Prior to steam processes, the feedstock was grinded and screened to an average size of two (2) cm. The severity factor of the steam treatment was determined using an empirical equation developed by Overend and Chornet (1987), which correlates temperature and residence time:

$$\log(R_0) = \log[t \times e^{(T-T_{ref})/14.75}] \quad (1)$$

where $\log(R_0)$ is the severity factor, t is the residence time (min), T is the reaction temperature (°C), T_{ref} is the reference temperature arbitrarily settled at 100 °C assuming that the hydrolytic effect of water on cellulosic material is negligible below this temperature.

By including the effect of the pH on the reaction, Eq. (1) was further adapted to the experimental conditions for the determination of the combined severity factor (SFT), under an acidic catalysts (Chum et al., 1990):

$$\mathrm{SFT} = \log(R_0) - \mathrm{pH} \quad (2)$$

with $\log(R_0)$ obtained from Eq. (1).

Screened woodchips (200 g, dry basis) were initially impregnated in a solution of 3% (wt.%) sulphuric acid (ratio solid to liquid 1:10, m/v) for 10 min after which they were dewatered with a filter press. The acid concentration was fixed to 3% (wt.%) following preliminary investigation on the feedstock (not published). The acidic-wet biomass was then cooked in the steam gun at three different temperatures (190, 205 and 220 °C), which were maintained for a residence time arbitrarily fixed at 3, 5 and 10 min respectively. Following steam treatment, the resulting lignocellulosic material was washed using hot water and press filtered until neutral pH was attained. A laboratory filter press was used for dewatering the wet biomass after treatment. By applying a controlled pressure of 0.7 MPa, the water content was reduced to the minimum in order to facilitate the drying process. Fibres were then dried at room temperature in a convection oven for 72 h. The experimental uncertainty on the process temperature was around 2 °C. For the concentration measurement and residence time, the relative uncertainty is below 0.5%. Based on the above, the overall uncertainty on the calculated SFT was less than 1%.

2.2.2. Fibre delignification and bleaching

Following the steam explosion treatment, *Salix miyabeana* cellulose fibres were bleached using a slight modification of the chlorine dioxide method employed by Kumar, Mago, Balan, and Wyman (2009). Bleaching was performed during six hours at 75 °C, using distilled water (ratio solid to liquid 1:20 wt/v) sodium chlorite (0.6 g/g of dry matter) and acetic acid (0.2 ml/g of dry matter). The reaction was done in three stages of two hours in which an equal amount of sodium chlorite and acetic acid were added to the medium. Fibres were then repeatedly washed with hot and distilled water and dried at room temperature in an air-circulating oven for 72 h and then kept in a sealed plastic bag until analysis.

2.2.3. Fibres characterization

2.2.3.1. Fibre quality analysis. Length of the cellulose fibres as well as diameter and length to diameter aspect ratios were determined using a Fibre Quality Analyzer (FQA) (Optest Hires model, Hawkesbury, Canada).

2.2.3.2. X-ray diffraction analysis (XRD). The X-ray diffraction patterns were obtained using a Philips X'Pert diffractometer using copper radiation K_α (λ = 1.5418 Å), a voltage of 40 kV and an operation current of 50 mA. All scans were performed from $2\theta = 5°$ to $2\theta = 40°$. MDI Jade 10 software packages were used for pattern processing as well as for calculation of the degree of crystallinity