Biomass and Bioenergy 86 (2016) 36–42

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Direct acid-catalysed mechanical depolymerisation of fibre sludge to reducing sugars using planetary milling

Yue Dong [a, b], Laura Schneider [a, b], Tao Hu [a], Mari Jaakkola [c], Jana Holm [d], Jean Marc Leveque [e], Ulla Lassi [a, b, *]

[a] University of Oulu, Research Unit of Sustainable Chemistry, P.O.Box 3000, FI-90014 Oulu, Finland
[b] University of Jyvaskyla, Kokkola University Consortium Chydenius, FI-67100 Kokkola, Finland
[c] University of Oulu, CEMIS-Oulu, FI-87400, Kajaani, Finland
[d] Centria University of Applied Sciences, FI-67100, Kokkola, Finland
[e] LCME/CISM University of Savoie Mont-Blanc, F-73376, Le Bourget du Lac cedex, France

ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form
15 January 2016
Accepted 18 January 2016
Available online xxx

Keywords:
Fibre sludge
Mechanocatalytic depolymerisation
Ball mill
Hydrolysis

ABSTRACT

This study performed a direct solvent-free acid-catalysed mechanical depolymerisation of fibre sludge to reducing sugars which involves one step of acid milling in a planetary mill. The common reported 'solvent-free' mechanocatalytic depolymerisation of lignocellulose which includes 1) acid impregnation, 2) vacuum evaporation and 3) mechanocatalytic depolymerisation was also performed as a reference. The major converted monosaccharides were determined by capillary electrophoresis and the results of total reducing sugar (TRS) yields were carried out based on the 3,5-dinitrosalicylic acid (DNS) method. The results showed that the TRS conversion of direct acid-catalysed mechanical depolymerisation of biomass is 35%, whereas, the commonly reported method yields 31% under the same milling conditions. In addition, the direct acid-catalysed mechanical depolymerisation simplifies the reaction procedures to one step and shortens the total reaction time. Moreover, the present study indicates that the frequency of the transferred energy which is caused by the collisions, acid concentration, milling time and moisture content of the sample are the major factors in influencing yield of converted TRS in acid-catalysed mechanical depolymerisation of fibre sludge.

1. Introduction

Lignocellulose-based by-products and solid residuals from the forest industry as well as from pulp mill industry have recently been highlighted to be utilised as potential raw materials to generate revenue in biorefineries, such as alternative biomass-based fuels and chemicals [1,2].

Fibre sludge is the main solid residual material in process wastewater. It is generated from the chemical pulping processing of wood in a pulp mill. The form of produced fibre sludge is wood-derived virgin fibre which is rich in cellulose. In Finland the current method of handling fibre sludge depends on the pulp mill. Fibre sludge is either incinerated for energy production and/or disposed at landfills [3–5]. However, the rising cost of landfill disposal, in conformance with the EU Waste Framework Directive [6] and the Renewables Directive (2009/28/EC) [7] has accelerated a trend to reuse or recycle solid residuals in a more energy-efficient way. Furthermore, the Landfill of Waste Directive [8] mandates a maximum of 35% of biodegradable or organic biowaste by weight at landfills which comes into force in 2016 and further encourages the separate collection, sorting, recovery and recycling of these types of waste fractions.

Mechanical pulping processes have been used for over 100 years in pulp and paper mills. They focus on deconstructing the structural matrix of lignocellulose, such as fragmenting wood, shortening fibres and reducing fibre strength for further paper production [9–11].

The combination of mechanical depolymerisation of lignocellulose and catalysis has recently received increasing attention in the conversion of biomass into valuable sugars. Up to now, the most efficient 'solvent-free' approach to convert biomass to sugars is through acid-solvent impregnation of lignocellulose and vacuum evaporator drying followed by a milling process in a ball mill

* Corresponding author. University of Oulu, Research Unit of Sustainable Chemistry, P.O.Box 3000, FI-90014, Finland.
E-mail address: ulla.lassi@oulu.fi (U. Lassi).

http://dx.doi.org/10.1016/j.biombioe.2016.01.006
0961-9534/

[12–14]. Schüth et al. [11] have performed the depolymerisation of biomass based on the method mentioned above and found that water-insoluble lignocellulose-based materials become water-soluble with mainly C_5 (from hemicellulose) and C_6 (from cellulose) sugars and sugar oligomers [9,14,15].

The present study focused on the acid-mediated conversion of lignocellulose-based residual fibre sludge (from the pulping process) into reducing sugars through a direct depolymerisation. For that, different concentrations of sulphuric acid (H_2SO_4) were examined and the milling process was done with two different sizes of grinding balls. For comparison purpose, aforementioned acid-catalysed mechanical depolymerisation with a selected optimal concentration of acid impregnation was also performed. The amounts of total reducing sugars (TRS) were determined based on the DNS method. Certain specific sugars were analysed by capillary electrophoresis (CE). Finally, the obtained results from direct acid-catalysed mechanical and mechanocatalytic depolymerisation of fibre sludge were compared and discussed for a comprehensive understanding of mechanocatalytic depolymerisation for further studies.

2. Materials and characterisation

2.1. Fibre sludge

The fibre sludge used in this research was acquired from the waste stream of a Finnish pulp mill. It contains mixed species of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*), downy birch (*Betula pubescens*) and silver birch (*Betula pendula*). The original wet fibre sludge has an approximate mass fraction of only 4% before pressing and air drying. This corresponds to an average generated annual amount of 300,000 tonnes (calculated as dry mass) in the Finnish pulping industry.

The α-, β-, and γ-cellulose contents of the air dried fibre sludge sample were determined based on the TAPPI's official standard method T 203 cm-99 [16]. The FTIR spectrum of dried fibre sludge and α-cellulose have been presented in our previous study [3]. Both spectra displayed high similarities emphasising the high content of cellulose in the fibre sludge sample, which also confirmed when looking at the physical properties of dry fibre sludge shown in Table 1. According to the chemical analysis of total carbon materials, cellulose is predominant in fibre sludge with a mass fraction of approximately 72%, hemicelluloses and lignin with mass fractions of 11% and 14% respectively [17].

Table 1
Elemental analysis and some physical properties of air dried fibre sludge.

Fibre sludge	
α-cellulose, d.s.[a] (%)	72
β-cellulose, d.s.[a] (%)	3
γ-cellulose, d.s.[a] (%)	11
Klason lignin, d.s.[a] (%)	14
Carbon, d.s. (%)	41.9
Hydrogen, d.s. (%)	6.0
Oxygen, d.s. (%)	n.d.
Nitrogen, d.s. (%)	0.88
Sulphur, d.s. (%)	n.d.

d.s. (%): Mass fraction calculated from dry material (substance).
n.d.: Not determined.
[a] Calculated from the organic material in the sample.

3. Experiments

Mechanocatalytic depolymerisation of fibre sludge with (refers to impregnation mechanocatalytic depolymerisation) and without (refers to direct acid-catalysed mechanical depolymerisation) H_2SO_4 impregnation and vacuum evaporation were performed in this study. The sample fibre sludge was dried in an oven (static air) at 60 °C for 24 h prior to the mechanocatalytic treatment. Treatment procedures are shown in Fig. 1.

3.1. Direct acid-catalysed mechanical depolymerisation of fibre sludge

The depolymerisation with different H_2SO_4 (95–97%)/dry fibre sludge ratios (400 mmol kg^{-1}, 600 mmol kg^{-1} and 800 mmol kg^{-1}) was performed with a planetary micro mill (FRITSCH, planetary micro mill pulverisette 7 premium line).

In a 45 cm^3 stainless steel bowl, dry fibre sludge (approximately 15 cm^3 measured with measuring cylinder) and H_2SO_4 were premixed and milled at 13.3 Hz with two different sizes of grinding balls which are made of zirconium oxide: 46.8 g of 16 grinding balls with a diameter of 10 mm; and 46.2 g of grinding balls with a diameter of 3 mm, respectively (see Fig. 1a). The volume of the grinding balls is calculated based on the equation of sphere's volume (1). Since they are from the same material and have similar weight, the total volumes of these two grinding balls are similar, approximately 67 cm^3.

$$\textit{Total volume of the grinding ball } v = \frac{4}{3\pi r^3} \quad (1)$$

The milling was performed with a 10 min process in order to control the reaction temperature, followed by a 10 min pause. This milling/resting sequence was eventually repeated to match the desired processing time (20 min, 40 min, 60 min, 80 min and 100 min). The processed sample was then directly transferred and treated for further water-soluble product determination and hydrolysis (see Section 3.3).

3.2. Mechanocatalytic depolymerisation of fibre sludge with acid impregnation and vacuum evaporation

Based on the yields of TRS from direct mechanocatalytic treatment, acidic concentration of 600 mmol kg^{-1} was observed as an optimal concentration in acidic catalysed depolymerisation of fibre sludge. The impregnation mechanocatalytic depolymerisation of fibre sludge was performed according to the procedures described in Schüth et al. [11].

Dry fibre sludge was immersed in a diluted H_2SO_4 solution with an acid/fibre sludge ratio of 600 mmol kg^{-1} in diethyl ether and shaken in an incubator at 3.3 Hz and at room temperature for 1 h. The homogenised impregnated fibre sludge was then moved to vacuum evaporation for drying at approximately 5 kPa and 40 °C for 40 min. Directly after drying, the sample was transferred to the same milling bowl and reaction processed as in Section 3.1 with 10 mm grinding balls, in order to have a comparison with direct acid-catalysed mechanical treatment with 10 mm grinding balls (see Fig. 1b). After the depolymerisation reaction, the process followed the same procedures described in Section 3.1.

3.3. Determination of water-soluble products and acidic hydrolysis of the ground fibre sludge

After mechanocatalytic treatment, 500 mg of the processed sample was used to determine the percentage of water-soluble