



Monosaccharide production in an acid sulfite process: Kinetic modeling



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ARTICLE INFO

Article history:

Received 23 December 2013
Received in revised form 2 May 2014
Accepted 5 May 2014
Available online 14 May 2014

Keywords:

Kinetic parameters
Monosaccharides
Spent sulfite liquor
Sugar
Inhibitors

ABSTRACT

Spent sulfite liquor is a lignocellulosic waste obtained after the sulfite pulping process. It is mainly formed by sugars and lignosulfonates which are isolated from the pulp during the cooking process. The current work investigates the kinetic modeling of the sulfite process from a biorefinery point of view since monosaccharides present in the spent liquor can be used as a raw material in further biorefinery processes to produce other value-added products. Kinetic parameters of carbohydrate degradation have been determined following sugar and inhibitors from wood to spent liquor, using laboratory scale reactors and different temperatures, 130, 140 and 150 °C. Three types of reaction schemes were developed. Kinetic parameters were obtained for each one using first and n order reactions, using Aspen Custom Modeler. Results show that the best temperature to be used in the process is 130 °C, giving the maximum sugar conversion, 33.91 mol% and obtaining 13.81 mol% of decomposition products.

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1. Introduction

Wood is a complex lignocellulosic feedstock. It consists of cellulose, hemicellulose, lignin and extractives. Cellulose is the most abundant cell wall polysaccharide in nature and is made of long chains $\beta(1\rightarrow4)$ linked glucose where the molecules fit together over long segments, regions of crystallinity, which are difficult to penetrate by solvents or reagents, are developed. However, the relatively more amorphous regions are readily penetrated and therefore more susceptible to hydrolysis reactions (Smook, 2002). By contrast to cellulose, the hemicellulose is a branched heteropolymer of pentoses (xylose and arabinose), hexoses (glucose, mannose and galactose) and sugar acids. Xylans are quantitatively the most important hemicelluloses of hardwood cell walls, whereas softwoods consist of glucomannan (Saha, 2003). The hemicellulose is more easily degraded and dissolved than cellulose. Lignin is a racemic heteropolymer composed of three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols. Lignin differs mainly in the proportion of the three alcohol units. Softwood lignin is made up mainly of coniferyl although it presents traces of sinapyl alcohols. In contrast, hardwood lignin is composed of coniferyl and sinapyl alcohols (Zahedifar, 1996). Extractives are the last group of the main components of wood. These are substances which can be

present in native fibers, depending on the plant source such as resin acids, waxes and fatty acids, terpenes, polyphenols and alcohols (Biermann, 1996).

Due to the fact that wood is a plentiful and cheap material with high carbon content and renewable potential; it looks like one of the main substitutes of oil-based products at the time of producing bioproducts within the biorefinery concept.

Biorefinery processes take advantage of the various components in biomass and their intermediaries, maximizing in this way the value of derivatives from biomass. For this, it uses a cross-disciplinary focus which involves physical and mechanical methods, chemical and biological conversions or catalysis, all of this to obtain a high efficiency process; with low cost and low power consumption (Ramaswamy, Huang, & Ramarao, 2013). In contrast to petroleum-based products, biorefinery products are usually non-toxic, biodegradable, reusable and recyclable. One of the most important types of biorefineries is the Integrated Forest Biorefinery (IFBR) where forest-based biomass such as wood and forestry residues can be processed into bioenergy and bioproducts (Christopher, 2013). The IFBR can be built around different platforms that are intermediaries between the feedstock and the end product. The main biorefinery platforms are cellulose, hemicellulose, lignin and extractives platforms. When wood as biomass is treated in a biorefinery, due to the association of the components of the wood, a pre-treatment is necessary to make the carbohydrates available for subsequent treatments such as detoxification or fermentation. For economic reasons, thermochemical methods are the most common pre-treatments, such as dilute acid hydrolysis

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and steam explosion which solubilize the hemicellulose components and increase cellulose accessibility (El-Zawawy, Ibrahim, Abdel-Fattah, Soliman, & Mahmoud, 2011; Tunc & van Heiningen, 2011).

The Pulp and Paper (P&P) industry has many assets to effectively integrate biorefinery processes adapting their traditional portfolio of pulp, paper or wood products; creating new bioproducts, energy and renewable materials. In this sense, the delignification process can be adapted not only to produce pulp but also other products with a very rich composition of sugar substrates which can be extracted and converted into biofuels or bioproducts following the mentioned pathways.

Among the obtained products in the P&P industry, dissolving pulp is a bleached wood pulp with a high content of cellulose. It has special properties and can be useful to manufacture several cellulose-derived products. To produce dissolving pulp, it is necessary to separate cellulose from the rest of components of wood. Two main chemical processes are used to manufacture dissolving pulp: (i) a modified kraft, called dissolving kraft process, which involves a pre-extraction step of the hemicelluloses previous to the cooking stage; and (ii) the acid sulfite process. The sulfite process is based on the digestion of wood by means of aqueous solutions at different concentrations of sulfur dioxide (SO_2) in the presence of bisulfite (HSO_3^-). The acid sulfite process is characterized by a pH in the range of 1.2–1.5 (Casey, 1990). Due to distinct disadvantages of the sulfite process over kraft technology, the share of sulfite pulps decreased from 60% in 1925 to 3.7% in 2000 (Sixta, 2006). No new sulfite mills have been built in North America since the 1960s. Nonetheless, sulfite pulping still exists, and process modifications have been proposed which would make the process more competitive. One of its main advantages is that the pulp is easier to bleach to full brightness, thus it produces higher yield of bleached pulp and gives some opportunities in cellulose fibers (Sixta et al., 2013; Smook, 2002). Regarding the pulp issues and also the biorefinery opportunities, existing sulfite mills have a chance to diversify their portfolio of products.

A usual sulfite process is as mentioned below. Wood and cooking liquor are introduced into the digester and unbleached pulp and weak spent liquor are obtained as products after applying specific temperature and pressure conditions. The pulp continues along the washing, bleaching and drying line to remove the remaining lignin and hemicelluloses up to the required dissolving pulp parameters. On the other hand, the spent liquor is concentrated and afterwards is processed to obtain other products. The global description of the process can be seen in schematic form in Fig. 1.

The spent liquor is rich in sugar (products of hydrolysis of cellulose and overall of hemicelluloses) and lignosulfonates (products of sulfonation of lignin). However, it also presents decomposition products of sugar as furfural or hydroxymethylfurfural (HMF) and derived products from acetyl groups present in wood. Thus, taking advantage of the sugar present in it, this byproduct can be converted into high value products such as ethanol, xylitol, polyhydroxybutyrates (PHB's), hydrogen and furfural (Rueda et al., 2011).

In previous studies on the spent liquor of the research group, it was demonstrated that it is not possible to depolymerize carbohydrates into monomers by means of acid hydrolysis after the acid sulfite cooking process under some conditions tested (Llano, Rueda, Quijorna, Blanco, & Coz, 2012). Because of that, it is necessary to modify some operation conditions during the process instead of treating the resulting spent liquor.

The objective of this work is to develop a kinetic study about the digestion process of wood regarding the sugar content present in the spent liquor and not in the obtained pulp, getting the knowledge for the prediction of the evolution of polysaccharides, monosaccharides and degradation products at different temperatures (130–150 °C) from a future biorefinery point of view by means of the sugar valorization to other high value-added products.

Modeling of the sulfite process regarding the produced pulp and following the cellulose, lignin content and sulfur compounds was developed a few decades ago and has been improved lately (Hagberg & Schöön, 1973, 1974a, 1974b; Masura, 1998; Richards & Van Heiningen, 2004; Sixta, 2006). These models have been used in this work to set the operation variables for modeling such as the liquor to wood ratio or the composition of the cooking acid. Results obtained by Hagberg and Schöön (1973) show that the rate of dissolution of hemicellulose is independent of the combined sulfur dioxide content; however, it is highly dependent on temperature. In general, these models explain the dissolution of the major components of wood, such as lignin and hemicellulose and do not enter in detail about specific sugars and decomposition products.

As the interest of this work is about the sugar content present after the hydrolysis of wood in the spent liquor and not about the pulp, other kinds of models have been taken into account. These models have been used to determine the kinetic parameters of different lignocellulosic materials such as potato peel, oil palm, corn stover, poplar wood chips, switchgrass sweet sorghum or hardwood (Kobayashi & Sakai, 1956; Lenihan et al., 2010; Liu, Lu, Ai, Yu, & Ji, 2012; Lu & Mosier, 2008; Lynd, Wyman, & Gerngross, 1999; Rahman, Choudhury, & Ahmad, 2006; Wyman, 2003) but not for this type of process and raw material.

2. Materials and methods

2.1. Raw material

Eucalyptus globulus wood from Cantabrian forests supplied by Sniace SA group (Torrelavega, Spain) has been chipped and classified for the cooking experiments. Chips with 15–30 mm length and 2–4 mm thickness were used.

Cooking liquor with a calcium base has been used. The parameters of the cooking liquor have to be as homogeneous as possible between the following values: total SO_2 (7.5–8.5 g/100 mL liquor), combined SO_2 (1.5–1.8 g/100 mL liquor), pH (1.1–1.5) and density (1050–1070 g/L).

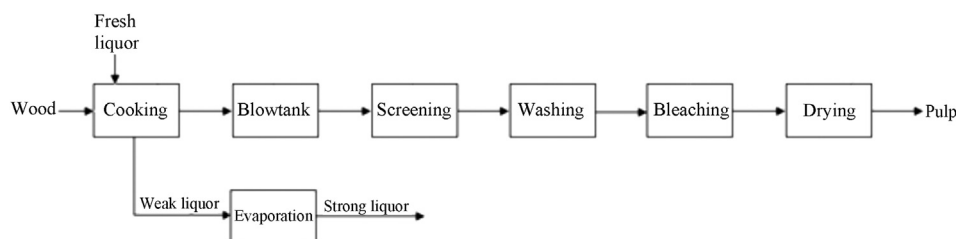


Fig. 1. Schematic representation of sulfite pulp mill.

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