Industrial Crops and Products 61 (2014) 160–168

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Optimization of sequential alkaline–acid fractionation of pine sawdust for a biorefinery

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ARTICLE INFO

Article history:
Received 21 February 2014
Received in revised form 12 June 2014
Accepted 23 June 2014
Available online 17 July 2014

Keywords:
Lignocellulosic material
Sawdust
Alkaline deresination
Acid treatment
Extractives
Hemicelluloses

ABSTRACT

The aim of this work was to apply an alkaline–acid sequence for the fractionation of slash pine sawdust, to obtain a solid lignocellulosic material (which can be subsequently delignified to obtain pure cellulose), and separate liquid fractions containing extractives and hemicelluloses. Processes were optimized using a central composite design of two variables for the alkaline extraction stage (NaOH concentration and temperature), and another of three variables for the acid treatment (H_2SO_4 concentration, time and temperature). Yield and contents of extractives, lignin, carbohydrates and degradation products, all by NREL Standards were determined. Maximum removal of extractives in the alkaline stage (90.7%) was reached using 5% NaOH (oven dry basis, od) at 90 °C for 1 h, and maximum hemicelluloses extraction in the acid stage (57%) was obtained using 7.5 g/L H_2SO_4 at 150 °C for 30 min The alkaline–acid sequence has shown to be effective for the sequential extraction of resin and hemicelluloses from slash pine sawdust, making possible its use for the production of high value products.

1. Introduction

The environmental care has become in a factor that adds value to industrial production, making it more competitive by the use of renewable resources and advanced technologies. Following the concept of oil refineries, the forest biorefinery consist of lignocellulosic biomass processing (wood debris, sawdust, shavings) to produce energy, chemicals and biomaterials. Pine sawdust is one of the main residues of the primary industrialization of wood in the Northeast of Argentine (NEA Region). About 50% of industrially processed wood is become in waste, generating 1.5 million of dry ton wood wastes per year, which are not properly exploited (Uasuf and Hilbert, 2012).

The chemical composition of *Pinus elliottii* grown in Misiones, Argentina, depending on soil type and climate, involves about 41–44% of cellulose, 28–31% of lignin, 27–33% of hemicelluloses, and 2–4% of extractives in dichloromethane (Area et al., 1992). This high resin content makes difficult the direct application of acid processes because of pitch formation. Considering that resin content in pine sawdust is usually higher than in solid wood, we seek to find a technological alternative to make possible the extraction of hemicelluloses, allowing the recovery of extractives, as well as the integral utilization of these wastes.

Chemical fractionation involves the separation of biomass components, so that each component can be industrialized. One important obstacle to overcome is to find efficient and cost effective methods of fractionation (FitzPatricka et al., 2010). Sawdust has the additional advantage of not requiring milling pretreatment.

Pretreatments of resinous softwoods have been not extensively researched mainly because this material presents high contents of crystalline cellulose, lignin and extractives. However, it is a very promising raw material due to its high content of hexoses and its wide availability (Bengoechea et al., 2012).

The extractives in organic solvents of pines are composed of resin acids (abietic and hydroabietic acids), fatty acids (oleic and linoleic acids) and a neutral fraction, often called unsaponifiables (phytosterols, fatty and wax alcohols, terpenes and hydrocarbons).

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http://dx.doi.org/10.1016/j.indcrop.2014.06.047
0926-6690/

Fatty and resin acids can be extracted in mild alkaline conditions, since they are dissolved forming sodium soaps. The concentration of the pulping solution (black liquor) prior of the inorganic pulping chemicals recovery allows the skimming of the insoluble soaps from the surface. Acidification of the skimmed soaps yields tall oil resin and fatty acids. Fatty acids can be recovered from tall oil by vacuum distillation. These tall oils by-products are a source of valuable chemicals which could improve the economic balance of the pulping industry (Demirbas, 2011). When liquors are very dilute and cannot be concentrated, the extractives can be removed by other techniques such as flotation, with removal efficiency of 80–90% of flocculated extractives (Tanase et al., 2010).

Fatty and resin acids are source of valuable chemicals as surfactants, detergents, adhesives, plastics, glues, inks, soaps, medicines, health promoting agents, and biodiesel (Hillis, 1962; Arshadi et al., 2013). It could also make more attractive the production of bioethanol from loblolly pine (Frederick et al., 2008). On the other hand, despite their small amount, they generate deposits and foam in production processes, and provide toxicity to the mill effluents (Foran, 1992).

Extractives removal prior to Kraft pulping (Baptista et al., 2006) sulfite pulping (Arrabajal and Cortijo, 1995) and bleaching (Sitholé et al., 2010) has also been studied to improve pulp properties.

Once the resinous material has been removed, fractionation must focus on the macromolecular components present in plant tissues. Dilute acid treatment with sulfuric acid has the advantage to be inexpensive, simple and effective to remove hemicelluloses, producing fewer amounts of degradation products than other processes (Wyman, 1994; Larsson et al., 1999; Frederick et al., 2008). The oligomers and monosaccharides extracted from hemicelluloses have multiples uses, as chemicals products, bioethanol, biopolymers and other applications (Hayes et al., 2006; Vallejos, 2012). The residual porous structure consisting mainly of cellulose and lignin can be subsequently delignified by an alkaline process to obtain cellulosic pulps, which can be used to produce bioethanol or dissolving pulp. Lignin in spent liquor can be precipitated and transformed into high-value products such as vanillin and other phenolic components (Stoffel et al., 2012).

The most studied pretreatments for softwood are steam explosion, which combines physical and chemical methods (Kim, 2005; Nguyen et al., 1998; Söderström et al., 2003) and treatment with dilute acid (Shuai et al., 2010; Marzialetti et al., 2008; Lim and Lee, 2013). However, no work applying alkaline deresination prior to the above mentioned treatments were found.

Despite the relevance of extractives components and their possible exploitation, no studies have been found about alkaline deresination of pine sawdust as part of neither wood fractionation nor antecedents concerning the dilute acid fractionation of slash pine.

The aim of this work was to study the fractionation of slash pine sawdust by a sequential alkaline–acid process. The influence of the main parameters of both processes (concentration, time and temperature) and their optimization were established by Central Composite Experimental Designs (CCD).

2. Materials and methods

2.1. Raw material

Slash pine sawdust was supplied by a local sawmill (Forestal Eldorado, Misiones). The sawdust was air-dried, screened and maintained in closed plastic bag. The fraction passing a 3 square mm^2 screen was used for the treatments.

2.2. Experimental design

Sawdust was subjected to alkaline and acid fractionation to sequentially extract the extractives and hemicelluloses. The experiments were arranged according to a Central Composite Design (Barker, 1985) in each case. The variables for the alkaline extraction were NaOH charge and temperature, and for the acid treatment, H_2SO_4 concentration, time and temperature.

The experimental designs for the alkaline and acid stages are shown in Fig. 1a and b, respectively. Each axis corresponds to a factor and each point on the cube represents an experimental combination of conditions. CCD consists of $2^k + 2k + m$ runs, where k is the number of factors, 2^k is the number of the factorial points at the corners of the square or cube, $2k$ is the number of the axial points on the axis of each design factor at a distance of $\pm\alpha$ ($\alpha = 2^{k/4}$) from the center of the square or cube and m is the number of the center points at the center of the square or cube. In this study, three replicas of the center point were performed to estimate the experimental error. Accordingly, the total number of experiments was $4 + 4 + 3 = 11$ for the alkaline stage and $8 + 6 + 3 = 17$ for the acid one. The experiments were performed randomly. Factors and levels of each treatment with coded and uncoded variables are shown in Fig. 1c.

The Desirability function is the most popular method for the solution of multiresponse optimization problems. This approach to simultaneously optimize multiple equations, translates the functions to a common scale ([0,1]), and combines them using the geometric mean and optimizing the overall metric.

Statistical analysis of results (ANOVA and optimization by the desirability function) was performed using Statgraphics Centurion XV software at 95% significance ($p < 0.05$).

2.3. Alkaline deresination

All reactions were performed in 250 mL glass vessels heated in a hot water bath for one hour. Ten grams (dry basis) of pine sawdust was used, with a liquid to dry wood ratio (v/w) of 10 in all tests. The vessels were closed with a plastic film and placed in the bath at the desired temperature. Sawdust and liquor were mixed manually before closing the vessels. Stirring was not necessary since the liquid to dry wood ratio was high, and heating promoted the movement of the solid in the liquid. After the reaction, the vessels were cooled down with ice, and the liquor was separated from the solid by filtration at reduced pressure.

In order to verify the representativeness of data obtained at laboratory scale, a scaling-up trial was performed, for which a point near the optimum was chosen. The selected experience was reproduced in a 7 L reactor (M/K Systems, Inc., Maryland) with liquor circulation, using 500 g of dry sawdust with 5 L of alkaline solution (liquor to wood ratio of 10, v/w). Once the reaction finished, the spent liquor was separated from the solid by centrifugation to approximately 40% of solids. Subsequently, the wood residue was exhaustively washed with water, it was filtered and air dried to measure the weight loss. A sample for chemical analysis was taken.

2.4. Dilute acid treatment

Acid stage with diluted sulfuric acid was conducted in 200 mL stainless steel reactors heated in a glycerin bath. The treatment was applied on the alkaline-pre-extracted sawdust and on the original sawdust, as control. The reactors were loaded with 15 g of dry sawdust and 150 mL of the acidic aqueous solution, at the concentration established by the experimental design (liquor to wood ratio of 10, v/w). As in the case of the alkaline treatment, sawdust and liquor were mixed manually before closing the vessels. Stirring was not necessary since the liquid to dry wood ratio was high, and