

Fiber modifications by organosolv catalyzed with H₂SO₄ improves the SSF of *Pinus radiata*



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ABSTRACT

Pinus radiata is an appropriate feedstock for the production of second-generation bioethanol through a biochemical platform due to its high content of fermentable sugars. However, because of this tree's recalcitrance, a suitable pretreatment is necessary. In this paper, the effect of the concentration of H₂SO₄ as a catalyst for the organosolv pretreatment for this raw material was studied. It was determined that a concentration of 1.1% of H₂SO₄ promotes structural and morphological changes, such as the formation of lignin droplets, which increase the digestibility of the pretreated material to achieve an efficient conversion of cellulose to glucose of 94% using the proper dosage of a last-generation cellulase complex. Because of the good digestibility of the pretreated material obtained, it was possible to obtain high concentrations of ethanol, reaching 85.01 g/L after 72 h of reaction, working with fed-batch simultaneous saccharification and fermentation at 40 °C at high substrate loadings using the thermotolerant strain of *Saccharomyces cerevisiae* IR2-9a. The importance of obtaining high concentrations of ethanol is that if the concentrations are above 4%, the cost of the distillation process is decreased.

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1. Introduction

Lignocellulosic biomass has become an important source of raw material for the production of second-generation bioethanol because it is the most abundant biopolymer on earth with a high content of fermentable sugars and does not compete with the food supply (Stephen et al., 2012). Thus, countries concerned to reduce their dependence on fossil-based fuel and to produce second-generation bioethanol have needed to look within their borders and seek a suitable raw material for its production. Chile is a forestry country with 2,300,154 ha of planted surface, and the first choice for bioethanol production is *Pinus radiata* (*P. radiata*), which constitutes 63.7% of the total wooded area in the country and features a high content of cellulose (~44%) and hemicelluloses, mainly composed of mannose, a hexose that can be fermented (Galbe and Zacchi, 2002). However, similar to all softwoods, *P. radiata* is recognized as being more recalcitrant than hardwoods and agricultural residues. This property is observed because softwoods have a more

rigid structure and contain more lignin. Furthermore, the content of acetyl groups in the hemicelluloses is considerably less than that in hardwoods; hence autohydrolysis reactions cannot occur to the same extent (Galbe and Zacchi, 2002).

A typical bioconversion of lignocellulose biomass into ethanol involves at least four major steps: (1) a pretreatment process to reduce substrate recalcitrance (to increase porosity and accessibility and to remove lignin and hemicelluloses completely or partially), (2) enzyme-catalyzed hydrolysis of cellulose and hemicellulose components into fermentable sugars, (3) the fermentation of these sugars into ethanol and (4) distillation (Ragauskas et al., 2006). Both enzymatic hydrolysis and fermentation can be sequentially performed in different vessels at their optimal conditions, a process known as separate hydrolysis and fermentation (SHF), or in a single reaction vessel that compromises conditions for optimal hydrolysis and fermentation, known as simultaneous saccharification and fermentation (SSF). The latter process is more efficient because it increases the product yield of ethanol and reduces the end product inhibition of the cellulase enzymatic complex (Anish and Rao, 2009; Sainz, 2009).

Organosolv pretreatment is one of several pretreatments investigated and used today for different varieties of lignocellulosic

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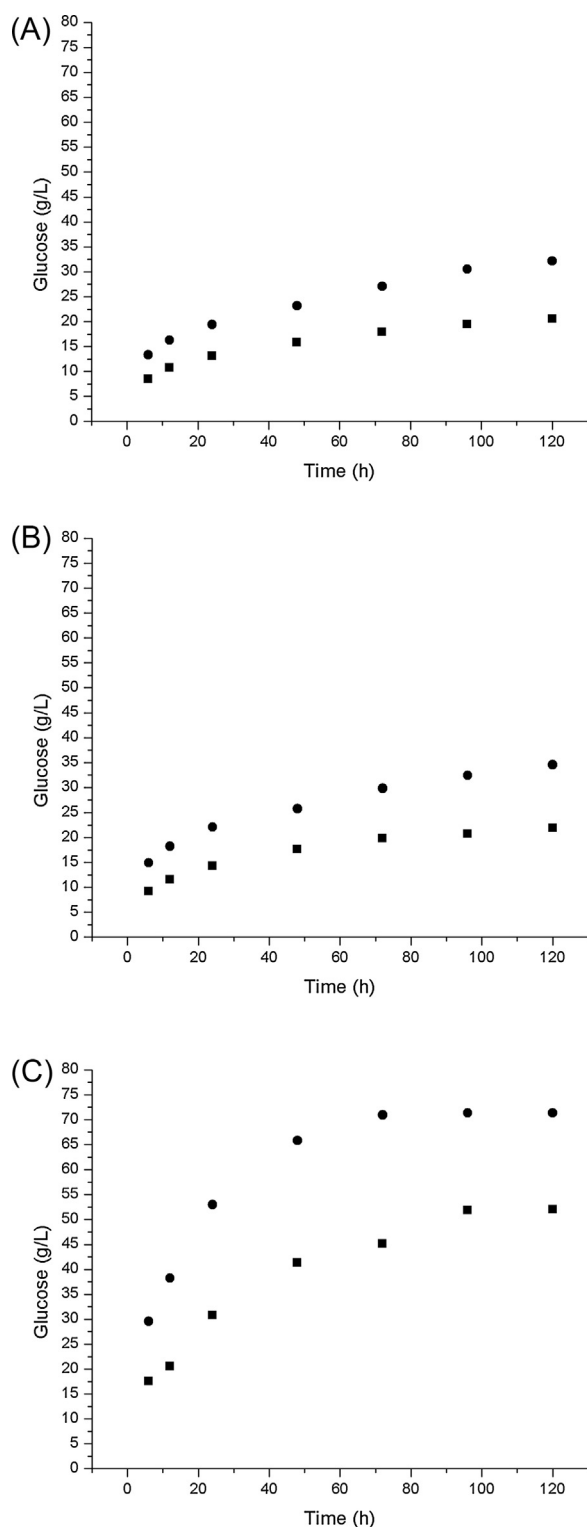


Fig. 1. Enzymatic hydrolysis profiles of pretreated material obtained by organosolv conditions (A) OSP1, (B) OSP2 and (C) OSP3; using enzyme dosages of (●) 0.044 and (■) 0.022 g of Cellic Ctec[®]3 enzyme complex per gram of dry, pretreated material. Reactions were performed with a dry-substrate loading of 10% (w/v) at 50 °C, pH 4.8 and 150 rpm.

biomass (Balat, 2011). This pretreatment employs organic solvents, mainly primary alcohols, or their aqueous solutions, which can be later recovered and reused to extract lignin from the biomass (Pan et al., 2005; Zhao et al., 2009). The development of the organosolv process can be traced to the University of Pennsyl-

vania and the General Electric Company in the 1970s to make a clean biofuel for turbine generators (Pan et al., 2005) and the earliest ethanol organosolv pretreatment process research demonstrated its effectiveness for the enzymatic hydrolysis of western cottonwood (Neilson et al., 1983). Commonly the organosolv pretreatment is conducted at high temperatures (185–210 °C) without need of the action of acid as catalyst because the acid released from the biomass acts as catalysts for the cleavage of the carbohydrate-lignin complex (Duff and Murray, 1996). The reactions associated with the alcohol organosolv process are the hydrolysis of internal bond in lignins as well as lignin-hemicelluloses bonds (ether and 4-O-methylglucuronic acid ester bonds to the α -carbons of the lignin units), hydrolysis of the glycosidic bond in hemicelluloses and into a smaller extent in cellulose and acid-catalyzed dehydration of monosaccharides into furfural and 5-hydroxymethyl furfural followed by the condensation reactions between lignin and these reactive aldehydes (Zhao et al., 2009). When mineral acids, such as sulfuric, hydrochloric and phosphoric acids, are used as catalyst for the organosolv pretreatment the delignification and degradation of hemicellulose is accelerated (Zhao et al., 2009). In the ethanol organosolv process catalyzed by H₂SO₄, the acid breaks down and modifies the lignin macromolecule until the resulting molecular fragments become small enough to dissolve in the aqueous alcohol solution. The primarily responsible for lignin breakdown is the cleavage of ether linkages (α and β aryl ether) is primarily responsible for lignin breakdown (McDonough, 1993; Sannigrahi et al., 2010b).

The organosolv process generates a solid fraction rich in cellulose that can be readily hydrolyzed for bioethanol production because enzymatic conversion increases through lignin or hemicellulose removal (Chang and Holtzapple, 2000; Lee et al., 1995; Ohgren et al., 2007; Zheng et al., 2013). The lignin fraction obtained in the liquid phase after the pretreatment can be used for the generation of co-products (Pan et al., 2005; Zakzeski et al., 2010) or thermal fuel (de la Torre et al., 2013). This pretreatment, as well as derivatives thereof, has been used on various materials, such as wheat straw (Wildschut et al., 2013), *Eucalyptus globulus* (Yanez-S et al., 2013), Loblolly pine (Sannigrahi et al., 2010a), *P. radiata* (Araque et al., 2008a; Monroy et al., 2010; Munoz et al., 2007), *Liriodendron tulipifera* (Koo et al., 2012), and *Pinus rigida* (Park et al., 2010), among many others, all of which have high yields of conversion of cellulose to glucose.

Today, there is great interest in the relationship between the chemical and structural characteristics of the pretreated material and enzymatic digestibility (Chandra et al., 2007). This work focused on the study of the structural changes that occur when *P. radiata* is pretreated with organosolv using different concentrations of H₂SO₄ as a catalyst and on how they affect the enzymatic digestibility and fermentability. For this, three concentrations of acid were tested, and the corresponding structural changes were evaluated by scanning electron microscopy (SEM) and confocal laser microscopy (CLM). The enzymatic digestibility of the pretreated material was assessed using two dosages of a last-generation cellulase complex, and finally, the best pretreated material was subjected to simultaneous saccharification and fermentation (SSF) in batch and fed-batch modes at high substrate loadings to obtain the highest possible ethanol concentration.

2. Materials and methods

2.1. Raw material

P. radiata wood chips were air-dried to a 10% w/w moisture content and then stored in plastic bags at 4 °C. The raw material was

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