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Research Paper

Integrated forest biorefineries: Recovery of acetic acid as a by-product from eucalyptus wood hemicellulosic hydrolysates by solvent extraction

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ABSTRACT

The biorefinery concept associated with pulp mills appears to be one of the best options for the valorisation of lignocellulosic biomass. Hemicelluloses can easily be pre-extracted from lignocellulosic biomass under mild operational conditions in order to obtain a hydrolysate that is rich in hemicelluloses, which can be used to produce bioethanol, as well as pretreated chips for further pulp production. However, the release of fermentable monosaccharides (mainly xylose) from the pre-extracted hemicellulose fraction is accompanied by the formation of decomposition products such as acetic acid, which inhibits fermentation by reducing conversion rates and yields. Due to the high level of acetyl groups in eucalyptus woods, acetic acid should be separated before the fermentation process in order to limit its inhibitory effect. Consequently, several studies have been conducted regarding the removal and recovery of acetic acid not only because of its inhibitory nature but also because it is a value-added compound in the chemical industry.

In this work, acetic acid recovery via liquid-liquid extraction from hemicellulosic hydrolysates of *Eucalyptus grandis* wood chips was evaluated. This study was carried out mainly because there are few reported data on the experimental recovery of acetic acid from pre-extracted hemicelluloses of eucalyptus wood, considering that the use of eucalyptus chips in a biorefinery platform is important due to the high commercial relevance of eucalyptus pulp over the last decades. Hemicellulose pre-extractions were carried out using green liquor with varying alkali charges (1–6% w/w), temperatures (100–160℃) and reaction times (30–150 min). The acetic acid extraction was performed using ethyl acetate at different pH values (2.0–4.0) for 36 min, in order to study the effects of the main experimental variables affecting the extraction process (hydrolysate-to-solvent volume ratio, pH and the coupling of the extraction stages). Under the best pH conditions, a single-stage extraction at an H/S of 1:4 achieved 82.0% removal of acetic acid, whereas by a three-stage extraction at an H/S of 1:2, up to 88.0% of the initial acetic acid was recovered. After a fractional distillation, an acetic acid yield of almost 30 L/t of dry eucalyptus wood chips was achieved, given the pre-extraction of hemicelluloses from *E. grandis* wood prior to the Kraft pulping process.

1. Introduction

The conversion of biomass into biofuels and chemicals has gained more and more interest because of the growing demand for energy, the limited supply of fossil fuels and growing concerns about the environmental impact of greenhouse gas emissions. At present, a pulp mill-based biorefinery has been proposed as a new concept where the production of wood pulp can be supplemented by the coproduction of high-value chemical products and biofuels. Considering the current process economics, these products should be derived from other components of the biomass and not from cellulose.

Lignocellulosic materials have been considered very attractive substrates for biofuels and biomaterials production because they are abundant, can grow in relatively poor soils, require little energy and few nutrients and do not compete with foodstuffs, as other matrices do (Kumar et al., 2009). However, wood products have additional advantages related to their high density, annual harvesting and low silica content as compared to other agricultural lignocellulosics (Van Heiningen et al., 2011). Wood is mainly composed of cellulose, lignin and hemicellulose. Hemicelluloses are a heterogeneous class of polymers that represent, in general, 15–35% of biomass. In the case of hardwood, xylans are the most relevant hemicelluloses and have

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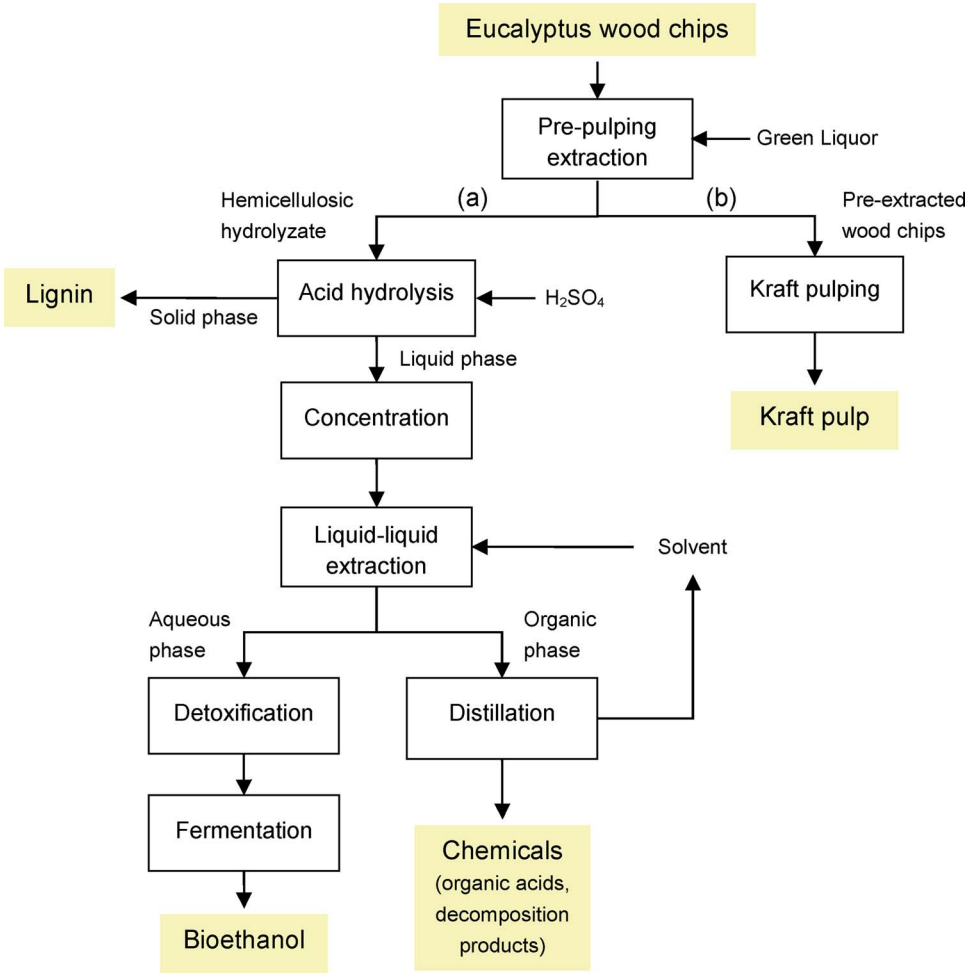

Fig. 1. Scheme representing the pre-pulping extraction process of *E. grandis* wood in an integrated biorefinery concept producing: (a) bioethanol and chemicals from hemicellulosic hydrolysate, and (b) cellulose pulp from pre-extracted wood chips. Note: acetic acid recovery by means of LLE is the focus of this work.

backbones that may contain a number of substituents, including arabinosyl units, acetyl groups and uronyl residues (Sjöström, 1993). In the pulp and paper industry, high-value-added products, such as biofuels, polymers and carbon fibres, can be derived from hemicelluloses or lignins. Hemicellulose is a byproduct which is not optimally used in a conventional Kraft process today, as they are partially degraded, dissolved in the black liquor and burned in the recovery boiler to produce steam and energy. Therefore, instead of burning the hemicelluloses, the pre-extraction of hemicelluloses prior to the Kraft pulping process could provide new opportunities for biomaterials and/or biofuels production, retaining the pulp properties and adding value to the global process (Van Heiningen, 2006).

Several pre-pulping extraction methods have been proposed for removing hemicelluloses from biomass, such as treatments with dilute acid, dissolution with organic solvents or alkali solutions, steam explosion, liquid hot water extraction (autohydrolysis). The hemicellulose pre-extraction process should remove hemicelluloses while preserving the quality of the pulp obtained, and these hemicelluloses can be hydrolysed into fermentable sugars, which can be converted to ethanol or used to derive other value-added product. It has been shown that carrying out pre-pulping extraction using green liquor as solvent allows the recovery of hemicelluloses without substantially affecting the pulp quality and yield of the mill (Cabrera et al., 2016; Walton et al., 2010).

During pre-pulping extraction, several compounds derived from sugar and lignin degradation (furfural, hydroxymethylfurfural, acetic acid, formic acid, phenols, etc.) are formed, which can negatively affect subsequent bioconversion of the solubilized sugars into desired products by reducing fermentation rates and conversion yields (Camesasca et al., 2015; Um et al., 2011; Palmqvist and Hahn-Hägerdal, 2000a). A variety of detoxification methods can be performed to remove these compounds from hemicellulosic hydrolysates in order to limit their effects, such as solvent extraction, neutralization and overliming, steam stripping, adsorption in activated charcoal and anion exchange (Palmqvist and Hahn-Hägerdal, 2000b). Acetic acid is one of the major inhibitory compounds released during pre-pulping extraction, and generated via the de-acetylation of the hemicellulose fraction when lignocellulosic biomass is hydrolysed. It represents a well-known fermentation inhibitor but, if separated and purified, it can be sold as a chemical product. It is one of the carboxylic acids widely used to produce various acetic esters such as vinyl acetate, which is used to prepare polyvynilacetate, and ethyl acetate. Industrially, acetic acid is obtained via the carbonylation of methanol or the oxidation of acetaldehyde; it is also obtained as a by-product of the production of cellulose acetate. Thus, several studies have been focused on the removal of acetic acid from lignocellulosic hydrolysates not only because of its fermentation-inhibitory character but also because it is of great interest given its status as a value-added chemical (Lenzing, n.d.).

The recovery of acetic acid from lignocellulosic hydrolysates prior to fermentation is industrially important, but current methods for the extraction from ethanol fermentation broths are time consuming and costly. Many technologies have been reported for the separation of organic acids from different solutions, such as distillation, adsorption using ion-exchange resin. The separation of acetic acid from aqueous solutions by simple distillation is very difficult and involves high running costs. However, previous studies have shown that liquid-liquid extraction can successfully separate acetic acid from aqueous solutions (Um et al., 2011), so many solvents have been studied to improve such recovery by means of liquid-liquid extraction. Several properties and