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A biorefinery approach based on fractionation with a cheap industrial by-product for getting value from an invasive woody species

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HIGHLIGHTS

- *Acacia dealbata* shows potential as a biomass to yield high sugar conversions.
- *A. dealbata* wood was successfully fractionated by glycerol treatment.
- High percentage of delignification was achieved, preserving the cellulose fraction.
- High enzymatic conversions and glucose concentrations (up to 85.4 g/L) were obtained.

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ABSTRACT

Acacia dealbata wood (an invasive species) was subjected to fractionation with glycerol (a cheap industrial by-product), and the resulting solid phase was used as a substrate for enzymatic hydrolysis. Glycerol fractionation allowed an extensive delignification while preserving cellulose in solid phase. The solids from the fractionation stage showed high susceptibility to enzymatic hydrolysis. Solids obtained under selected fractionation conditions (glycerol content of media, 80 wt%; duration, 1 h; liquid to solid ratio, 6 g/g; alkaline and neutral washing stages) were subjected to enzymatic saccharification to achieve glucose concentrations up to 85.40 g/L, with almost complete cellulose conversion into glucose. The results confirmed the potential of glycerol as a fractionation agent for biorefineries.

1. Introduction

The sustainable production of fuels and chemicals from lignocellulosic materials (LCM) can be carried out by fractionation (enabling the selective separation of the major components, including cellulose, hemicelluloses and lignin) and further transformation of the resulting fractions into marketable products (Romaní et al., 2011), according to the biorefinery approach.

Considered as a raw material for biorefineries, *A. dealbata* wood shows a high polysaccharide content (Yáñez et al., 2009 and Yáñez et al., 2014), and the interest on its utilization is boosted by environmental reasons: for example, its invasive character causes structural modifications in native ecosystems and threatens the native aboveground biodiversity (Lorenzo et al., 2010).

A typical approach for manufacturing chemicals and fuels from biomass involves the following major steps: (i) fractionation of LCM, (ii) saccharification of the cellulosic fraction into glucose, and (iii) fermentation of hydrolyzates into the desired products (Romaní et al., 2013).

The enzymatic hydrolysis (EH) of cellulose presents well-known advantages, including low capital costs, utilization of mild operational conditions and selectivity of the enzymatic reaction (Hundt et al., 2013a). However, as native LCM are poorly susceptible to cellulolytic enzymes, a treatment (improving the access of enzymes to cellulose by causing structural and chemical modification of substrates) must be performed.

Abbreviations: CCG, cellulose conversion into glucose; EH, enzymatic hydrolysis; EMIMAc, 1-ethyl-3-methylimidazolium acetate; ESR, enzyme to substrate ratio; FPU, filter paper units; IU, international units; KL, Klason lignin; LCM, lignocellulosic materials; LSR, liquor to solid ratio; PCR, percentage of cellulose recovery; PLR, percentage of Klason lignin removal; PXnR, percentage of xylan recovery; SY, solid yield; Xn, Xylan.

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Organosolv treatments are coherent with the biorefinery concept and yield substrates with improved accessibility to cellulases (Novo et al., 2011). They were first considered as alternative technologies to conventional pulping methods such as the *kraft* or sulfite processes (Barberà et al., 2011). In organosolv pulping, an aqueous solution of an organic solvent (with or without addition of mineral acid catalysts) is employed to remove lignin selectively, yielding a solid phase enriched in cellulose (Martín et al., 2011). Methanol, ethanol, acetone, ethylene glycol, glycerol and organic acids are typical solvents used for this purpose (Zhao et al., 2009). Organosolv treatments break down bonds such as α-aryl ether and arylglycerol-β-aryl ether in the lignin macromolecule (Zhao et al., 2009), causing lignin alteration, including increases in the contents of phenolic and methoxyl groups and decreases of the average molecular weight (Gilarranz et al., 2000). In organosolv processes, solvent and non-volatile components (lignin and polyols) can be easily separated by distillation, enabling the simultaneous recycling of solvents (Novo et al., 2011). Other remarkable advantages of organosolv technologies are: low environmental impact, high pulp yield, limited investment for new plants and recovery of sugars (Saberikhah et al., 2011). However, owing to other factors (for example, energy demand), the organosolv pretreatment can result in more expensive than traditional pretreatments, such as acid, alkali and hydrothermal treatments (Zhao et al., 2009).

Glycerol, a non-toxic organic solvent of high boiling point (290 °C), is available from the biodiesel industry as cheap by-product (da Silva et al., 2009), and can be an attractive alternative to reduce processing cost and environmental problems (Novo et al., 2011; Guragain et al., 2011). In particular, glycerol offers several advantages as a solvent for LCM fractionation, including: (i) low environmental impact; (ii) operation can be carried out at atmospheric pressure even at high temperatures; (iii) ability for penetrating into the fiber tissue, due to its highly polar polyol structure, and (iv) ability for creating an effective reaction medium for LCM delignification (Hundt et al., 2013a). Despite this, literature is scarce concerning the fractionation of LCM by autocatalytic glycerol-organosolv pretreatments (Novo et al., 2011; Martín et al., 2011; Sun and Chen, 2008a; Romaní et al., 2013).

This study provides an experimental evaluation of autocatalytic glycerol-water media for fractionating *A. dealbata* wood and enhancing the susceptibility of treated solids to enzymatic hydrolysis. The effects of the major operational variables (temperature, reaction time, glycerol content of media and liquor to solid ratio) on wood delignification were assessed. The enzymatic hydrolysis (EH) was optimized respect to the liquor to solid ratio (LSR) and enzyme to solid ratio (ESR).

2. Methods

2.1. Raw material

A. dealbata wood samples were collected locally, debarked and chipped. Air-dried samples were milled (using a Retsch SM1 74075 instrument, Germany) and sieved (Retsch AS200 Basic, Germany) to select the fraction of particles with size in the range 1–0.250 mm, which were accumulated in a single lot and homogenized by hand.

2.2. Processing of *A. dealbata* wood

In order to assess the effects of the selected parameters affecting the glycerol fractionation (temperature, reaction time, LSR, glycerol content of media and washing conditions), a set of 13 experiments were performed. Table 1 lists the operational

Table 1
Operational conditions considered in fractionation treatments, and results achieved for solid yield and chemical composition of pretreated solids.

	Operational conditions								Results			
Run	Temperature (°C)	Time (min)	So	Glycerol (%)	LSR (g/g)	Washing steps			SY (%)	Cellulose[b] (%)	Xn[b] (%)	KL[b] (%)
						Step 1[a]	Step 2	Step 3				
1	200	120	5.03	80	10	Glycerol 40%, 20 °C	Water, 60 °C	Water, 20 °C	63.5	60.7	6.50	21.4
2						Glycerol 40%, 60 °C	Water, 60 °C	Water, 20 °C	64.5	63.2	7.33	18.9
3						NaOH 1%, 20 °C	Water, 60 °C	Water, 20 °C	52.2	74.5	7.56	10.5
4	230	120	5.91	80	10	NaOH 1%, 20 °C	Water, 60 °C	Water, 20 °C	40.6	86.9	2.59	8.7
5		90	5.79						47.2	88.8	3.09	8.3
6		60	5.63						50.3	85.0	4.90	8.0
7		30	5.34						48.9	83.2	5.31	7.4
8	230	60	5.63	80	6	NaOH 1%, 20 °C	Water, 60 °C	Water, 20 °C	50.6	82.1	6.61	9.4
9		90	5.79						47.9	81.2	5.54	10.6
10	230	90	5.79	70	6	NaOH 1%, 20 °C	Water, 60 °C	Water, 20 °C	46.3	78.3	2.48	11.6
11				60					45.7	75.1	2.17	15.4
12				50					50.1	72.9	1.99	25.0
13				40					49.6	64.7	1.71	25.9

[a] Volume of washing solution/mass of delignified solid = 10 mL/g.
[b] Expressed as g/100 g oven-dry pretreated solid.